Book of Abstracts

6th Spring Meeting of the International Society of Electrochemistry

Foz do Iguaçu, Brazil
16-19 March, 2008
Organising Committee

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São Carlos Federal University, Brazil

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Artur de Jesus Motheo
University of São Paulo at São Carlos
Romeu C. Rocha-Filho
São Carlos Federal University
Social Program

Sunday 16 March - PM

Welcome Reception
20:00 to 22:00
Room: Átrio Cataratas

Tuesday 18 March - PM

Special Dinner
20:30 to 22:30
Room: Brasserie Portinari

Wednesday 19 March - PM

Farewell Barbecue
20:30 to 22:30
Room: Carmen Miranda Café

Thursday 20 March - AM

Optional Tours
8:30 to 11:00
Brazilian Falls

8:00 to 11:00
Itaipu Hydroelectric Dam – Special Tour
Welcome to the
6th ISE Spring Meeting
Electrochemistry for a Healthy Planet

On behalf of the Executive Committee of ISE, the Organising Committee and the Local Organising Committee, we warmly welcome your participation in “Electrochemistry for a Healthy Planet”, the 6th Spring Meeting of the ISE, March 16 to 19, 2008. This is the second time in this decade that an ISE meeting is held in Brazil, and it is the third ISE meeting held in South America (the 1992 Annual Meeting was held in Córdoba, Argentina). In 2003, the ISE Annual Meeting was convened in Águas de São Pedro, in the state of São Paulo. This time, Foz do Iguaçu was chosen because of its proximity to the Iguassu National Park, where the magnificent Iguassu Falls (shared between Brazil and Argentina) are located. A visit to the park allows several panoramic views of the falls and of the tropical forest that is home to many different animals. Foz do Iguaçu is also the site of the world’s largest hydroelectric power station, Itaipu Binational, an international joint venture developed by Brazil and Paraguay in the Paraná River, with an installed power of 14.0 GW, with 20 generating units of 0.7 GW each. A visit to this man-made technological wonder is certainly worthwhile.

The theme of the meeting (Electrochemistry for a Healthy Planet) is very much in line with that of the 2003 ISE Annual Meeting (The Role of Electrochemistry in the Sustained Development of Modern Societies). Concepts, developments and applications of electrochemistry (detection, prevention and remediation of environmental pollution) that can contribute to keep Planet Earth healthy are being explored in depth in this meeting. Highlights of some the latest contributions will be presented in 4 keynote lectures, 10 invited lectures, 58 oral and 149 poster presentations, from scientists from many different countries – 35 to be exact. So there will be many opportunities for participation, discussion, and exchange of ideas. This will be facilitated by the fact that most participants are lodged in the venue hotel, the Mabu Thermas & Resort, which also offers many amenities and relaxation opportunities.

We hope you will enjoy your 6th ISE Spring Meeting.

Romeu C. Rocha-Filho
Meeting Chairman

Christopher M.A. Brett
President of ISE
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Program of Oral Presentations
Sunday 16 March - PM
Welcome Session
18:30 to 22:00
Room: Atlântico

Opening Ceremony
18:30 to 19:00
Chair: Romeu C. Rocha-Filho

Welcome Lecture
19:00 to 20:00
Chair: Luis A. Avaca (Univ. of São Paulo, Brazil)
Christos Comninellis (Faculty of Basic Science EPFL, Lausanne, Switzerland)
The importance of electrode material in environmental electrochemistry

Welcome Reception
20:00 to 22:00
Room: Átrio Cataratas
Monday 17 March - AM
Keynote Lecture 1

Environmental electrochemical engineering: protecting the planet

Room: Atlântico
Chair: Maria Valnice Boldrin (S. Paulo State Univ., Brazil)

09:00 to 10:00
Krishnan Rajeshwar (The University of Texas at Arlington, Center for Renewable Energy Science & Technology, Arlington, USA)
  Electrodeposition and Combustion Synthesis of Oxide Semiconductors for Solar Photocatalysis Applications
Monday 17 March - AM
Oral Sessions 1 and 2

Environmental analytical electrochemistry: monitoring the planet

Room: Santiago
Chairs: Yoshitaka Gushikem (Campinas State Univ., Brazil) and Joseph Wang (Arizona State Univ., USA)

10:10 to 10:40 — INVITED LECTURE
Joseph Wang (Biodesign Institute, Arizona State University, Tempe, USA)
New concepts for in-situ environmental electroanalysis

10:40 to 11:00 Coffee Break, Room: Pacífico

11:00 to 11:20
Karel Vytras (Analytical Chemistry Department, University of Pardubice, Pardubice, Czech Republic), Ivan Svancara
Recent Applications of Carbon Paste Electrodes in Electrochemical Analysis

11:20 to 11:40
Jacqueline Arguello (Instituto de Quimica, UNICAMP, Campinas, Brazil), Richard Landers, Yoshitaka Gushikem, Hérica Magosso
Electrocatalytic application of a sol–gel derived carbon ceramic electrode based on cobalt(II) tetrasulfonated phthalocyanine

11:40 to 12:00
Toshiyuki Usagawa (Advanced Research Laboratory, Hitachi Ltd., Kokubunji, Japan), Youta Kikuchi, Sadaki Nakano, and Koichi Yokosawa
Reliable Low Power Si-MOSFET Hydrogen Gas Sensors

12:00 to 12:20
Tavo Romann (Institute of Chemistry, University of Tartu, Tartu, Estonia), Enn Lust
Renewable Surface Microelectrode System for Research and Electroanalysis
Environmental electrochemical engineering:
protecting the planet

Room: Atlântico
Chairs: Nerilso Bocchi (S. Carlos Federal Univ., Brazil) and Guohua Chen (Hong Kong Univ. Sci. Tech., China)

10:10 to 10:40 — INVITED LECTURE
Guohua Chen (Department of Chemical Engineering, The Hong Kong University of Science and Technology, Hong Kong, China)
Hot-Filament Chemical Vapor Deposition Method to Fabricate Stable Diamond Film Electrodes for Wastewater Treatment

10:40 to 11:00 Coffee Break, Room: Pacífico

11:00 to 11:20
Yuri Pleskov (Frumkin Institute of Physical Chemistry and Electrochemistry, Moscow, Russian Federation)
Synthetic Diamond, Diamond-based, and Diamond-like Electrodes: the Dependence of Their Electrochemical Activity on the Resistivity

11:20 to 11:40
Sachio Yoshihara (Department of Energy and Environmental Science, Graduate School of Engineering, Utsunomiya University, Utsunomiya, Japan), Muthu Muruganantham
 Decomposition of Various Endocrine-Disrupting Chemicals at Boron Doped Diamond Electrode

11:40 to 12:00
Romeu C. Rocha-Filho (São Carlos Federal University, São Carlos, Brazil), Leonardo Santos Andrade, Nerilso Bocchi, Diogo Lima da Silva, Sonia Regina Biaggio, Thiago Teixeira Tasso
On the performances of lead dioxide and boron-doped diamond electrodes in the anodic oxidation of a simulated wastewater containing the Orange Reactive 16 dye

12:00 to 12:20
José L. Nava (Universidad Autónoma Metropolitana-Iztapalapa, Chemical Department, Mexico D.F., Mexico), Edgar Butron, Ignacio González
The role of the filter-press-type FM01-LC electrochemical reactor using BDD electrodes for the incineration of cresols, indigo textile dye and
Environmental electrochemical engineering: protecting the planet

Room: Atlântico
Chairs: Ernesto Calvo (Univ. of Buenos Aires, Argentina) and Edson Ticianelli (Univ. of S. Paulo, Brazil)

14:10 to 14:40 — INVITED LECTURE
Edson A. Ticianelli (Instituto de Química de São Carlos - USP, São Carlos, Brazil), Amanda C. Garcia, Valdecir A. Paganin, Luis G. S. Pereira
Catalyst and Electrode Designs for CO-tolerant PEM Fuel Cell Anodes

14:40 to 15:00
Vincenzo Baglio (CNR-ITAE, Messina, Italy), Vincenzo Antonucci, Antonino Arico, Alessandra Di Blasi, Fabio Matera, Alessandro Stassi
Investigation of a Passive DMFC Mini-Stack Operating at Ambient Temperature

15:00 to 15:20
Wolfgang Schuhmann (Analytische Chemie - Elektroanalytik & Sensorik, Ruhr-Universität Bochum, Bochum, Germany), Michael Bron, Xingxing Chen, Kathrin Eckhard, Artjom Maljusch, Andrea Puschof, Leonard Stoica
Local visualization of catalyst activity as a prerequisite for optimization of fuel cells and industrial electrolysis processes

15:20 to 15:40
Akimitsu Ishihara (Chemical Energy Laboratory/Yokohama National University, Yokohama, Japan), Shigenori Mitsushima, Ken-ichiro Ota
Partially Oxidized Group 4 and 5 Transition Metal Carbonitrides as New Non-Platinum Cathodes for PEFC

15:40 to 16:00
Rafael Eduard Szamocki (INQUIMAE-DQIAyQF, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Buenos Aires, Argentina), Ernesto Julio Calvo, Victoria Flexer
Laccase-modified electrodes by layer-by-layer self assembly for the use as fuel cell cathodes
16:00 to 16:20  Coffee Break, Room: Pacífico

16:20 to 16:40
Beatriz Antoniassi (Universidade Estadual Paulista (UNESP)/Faculdade de Ciências/Departamento de Química/Grupo de Eletrocatalise e Reações Superficiais, Bauru, Brazil), Antonio Carlos Dias Ângelo, Gessie Mércedes Brisard, Roberto Batista de Lima, Patrick Dubé, Tatiane Pereira Scachetti
DMS and FTIR Studies of Ethanol and Methanol Oxidation on Ordered Intermetallic Platinum Phases

16:40 to 17:00
Janaína Souza-Garcia (Instituto de Química de São Carlos/USP, São Carlos, Brazil), Juan Feliu, Edson Ticianelli
Nitrate Reduction on Pt Single Crystals with Pd Multilayer

Monday 17 March - PM
Oral Session 4

Environmental electrochemical engineering: protecting the planet

Room: Santiago
Chairs: Luis F.P. Dick (Rio Grande do Sul Federal Univ., Brazil) and Lo Gorton (Lund Univ., Sweden)

14:40 to 15:00
Lo Gorton (Department of Analytical Chemistry, Lund University, Lund, Sweden), Andreas Christenson, Nicolas Mano, Tautgirdas Ruzgas, Sergey Shleev, Alexander Yaropolov, Adam Heller
Direct Electron Transfer between Multicopper Blue Oxidases and Carbon

15:00 to 15:20
Adrian Hightower (Physics Department, Occidental College, Los Angeles, USA), William Cheuh, Marc Sells, Sossina Haile
Ceria Supported Rh3Pt2Sn Nanoparticles as Low Temperature Ethanol Steam Reforming Catalysts
15:20 to 15:40
Arnaldo Visintin (Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, La Plata, Argentina), Gustavo Andreasen, Ana Arenillas, Peter Barath, Marie Sedlá Iková, Jorge Thomas, Jiri Vondrak, L. Zubizarreta
Effect of Carbon Support on the Kinetic Behaviour of a Metal Hydride Electrode

15:40 to 16:00
Luis Frederico P. Dick (Depto de Metalurgia-UFRGS, Porto Alegre, Brazil), Daniel A. Dalla Corte
The hydrogen evolution reaction on surface modified nitinol (Ti-Ni)

16:00 to 16:20 Coffee Break, Room: Pacífico

16:20 to 16:40
Antoine Allanore (ArcelorMittal R&D Industrial Operations-Sustainability, Maizières-lès-Metz, France), Jean-Pierre Birat, François Lapicque, Hervé Lavelaine, Gérard Valentin
Iron electrowinning in alkaline media: Producing iron by electrolysis of an iron oxide suspension?

16:40 to 17:00
Sverre Rolseth (SINTEF Materials and Chemistry, Trondheim, Norway), Henrik Gudbrandsen, Geir Martin Haarberg, Eirin Kvalheim, Tsuyoshi Murakami
Production of iron with low CO2 emissions. Electrowinning from molten salts
Tuesday 18 March - AM
Keynote Lecture 2

Environmental electrochemical engineering: protecting the planet

Room: Atlântico
Chair: Mauro Bertotti (Univ. of S. Paulo, Brazil)

09:00 to 10:00
Derek Pletcher (School of Chemistry, University of Southampton, Southampton, United Kingdom)
   Electrochemical Technologies for a Healthy Planet – Promises or Achievement?
Tuesday 18 March - AM
Oral Sessions 5 and 6

Environmental analytical electrochemistry: monitoring the planet

Room: Santiago
Chairs: Tony Breton (Univ. d’Angers, France) and Greg M. Swain (Michigan State Univ., USA)

10:10 to 10:40 — INVITED LECTURE

Greg Swain (Department of Chemistry, Michigan State University, East Lansing, USA)
Addressing Environmental Challenges Electrochemically Using Diamond Electrodes

10:40 to 11:00  Coffee Break, Room: Pacifico

11:00 to 11:20
Huimin Zhao (School of Environmental and Biological Science and Technology, Dalian, China), Hongbin Yu, Hua Wang, Shuo Chen
Chemical Oxygen Demand Sensor Based on a Boron–Doped Diamond (BDD) Electrode

11:20 to 11:40
Pawel Kulesza (Department of Chemistry, University of Warsaw, Warsaw, Poland), Katarzyna Karnicka, Barbara Kowalewska, Krzysztof Miecznikowski, Iwona Rutkowska, Magdalena Skunik
Development of Novel Nanostructured Electrode Materials for Electrocatalytic and Bioelectrocatalytic Analytical Determinations

11:40 to 12:00
Tony Breton (University of Angers, Angers, France), I. Tapsoba, M. Pontié
Development of bi-layer modified carbon fiber ultramicroelectrodes (UME) for a selective analysis of methyl-parathion and its metabolites

12:00 to 12:20
Carmel Breslin (Department of Chemistry, National University of Ireland, Maynooth, Ireland), Valeria Annibaldi, Sinead McDermott, Denise Rooney
Polypyrrole Modified with Supramolecular Cages: Applications in the Electrochemical Sensing of Herbicides
Environmental electrochemical engineering: protecting the planet

Room: Atlântico
Chairs: Erik G. Soegaard (Aalborg Univ., Denmark) and Sibel Pamukcu (Lehigh Univ., USA)

10:10 to 10:40 — INVITED LECTURE  page 57
Sibel Pamukcu (Department of Civil and Environmental Engineering, Lehigh University, Bethlehem, USA)
Electrically Enhanced Transformations on Clay Surfaces

10:40 to 11:00 Coffee Break, Room: Pacifico  page 112

11:00 to 11:20
Erik Soegaard (Aalborg University, Esbjerg Institute of Technology, Esbjerg, Denmark), Christian Damsgaard, Rasmus Erichsen, Jens Muff
Electrochemical Degradation of Pollutants of Drainage Water from a Depot of Organophosphates (Insecticides) buried as Waste in a Sand Dune

11:20 to 11:40  page 97
Yoshihiro Kitatsuji (Nuclear Science and Engineering Directorate, Japan Atomic Energy Agency, Ibaraki, Japan), Sorin Kihara, Takaumi Kimura
Electrolytic Control of Oxidation State and Removal of Neptunium Ion based on Reduction and Adsorption on the Carbon Fiber Electrode

11:40 to 12:00  page 91
Jorge Frade (Ceramics and Glass Engineering Dep., University of Aveiro, Aveiro, Portugal), Vladislav Kharton, Syargei Poznyak, E. Naumovich
Enhanced Performance of Ni-Based Anodes in Aqueous Hematite Suspensions.

12:00 to 12:20  page 117
Bart van Limpt (Wetsus, Centre for Sustainable Water Technology, Leeuwarden, Netherlands), Harry Bruning, Wim Rulkens, Michel Saakes
Prediction of Capacitive Deionization performance by BET surface area measurements
Tuesday 18 March - PM
Oral Sessions 7 and 8

Environmental analytical electrochemistry: monitoring the planet

Room: Santiago
Chairs: Johan Bobacka (Åbo Akademi Univ., Finland) and Jiri Barek (Charles Univ., Czech Republic)

14:10 to 14:40 — INVITED LECTURE — page 52
Jiri Barek (UNESCO Lab. of Environmental Electrochemistry, Dept. of Analytical Chemistry, Charles University, Prague, Czech Republic), Josino C. Moreira, Karolina Peckova, Jiri Zima
New electrode materials and arrangements for analysis of environmental carcinogens

14:40 to 15:00 — page 65
Johan Bobacka (Åbo Akademi University, Process Chemistry Centre, Laboratory of Analytical Chemistry, Åbo-Turku, Finland), Andrzej Lewenstam, Ulriika Mattinen
A New Type of Polymer-Based Solid-State Reference Electrode

15:00 to 15:20 — page 77
Gabriela Valdés (Univ. Autón. Metropolitana - Iztapalapa, México / Univ. Perpignan, Perpignan, France), Didier Fournier, Ma. Teresa Ramírez Silva, Jean-Loius Marty
Amperometric biosensors to quantify Dichlorvos and their application in real samples.

15:20 to 15:40 — page 75
Gustavo Urbano Reyes (Univ. Autó. del Estado de Hidalgo, Pachuca, Mexico), Ignacio González, Victor Reyes-Cruz, María Aurora Veloz
Electrochemical Characterization of Some Stages of the Acid Rock Drainages (ARD)

15:40 to 16:00 — page 68
Magdalena Gebala (Analytische Chemie - Elektroanalytik & Sensorik; Ruhr-Universität Bochum, Bochum, Germany), Sebastian Neugebauer, Wolfgang Schuhmann, Leonard Stoica
Electrochemical strategies for detection of Salmonellosis

16:00 to 16:20 — page 71
Grzegorz Milczarek (Institute of Chemistry and Technical Electrochemistry, Poznan University of Technology, Poznan, Poland)
Lignin and its derivatives as multifunctional electrocatalysts
Environmental electrochemical engineering: protecting the planet

Room: Atlântico
Chairs: Carlos A. Martinez-Huitl (Univ. of Milan, Italy) and Onofrio Scialdone (Univ. of Palermo, Italy)

14:10 to 14:40 — INVITED LECTURE
Onofrio Scialdone (Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, University of Palermo, Palermo, Italy), Giuseppe Filardo, Alessandro Galia, Chiara Guarisco, Serena Randazzo, Giuseppe Silvestri
Influence of operative parameters on the electrochemical incineration of oxalic acid

14:40 to 15:00
Carlos Alberto Martinez-Huitl (Department of Chemistry, University of Ferrara, Ferrara, Italy), Achille De Battisti, Martina Donatoni, Sergio Ferro
Electrooxidation of oxalic acid at different electrode materials

15:00 to 15:20
Sidney Aquino Neto (Departamento de Química, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, Universidade de São Paulo, Ribeirão Preto, Brazil), Adalgisa De Andrade
Electrodegradation of glyphosate herbicide at DSA® electrodes: pH, current density and concentration effects

15:20 to 15:40
Stéphane Fierro (Group of Electrochemical Engineering - Swiss Inst. of Techn., Lausanne, Switzerland) Helmut Baltruschat, Christos Comninellis
Investigation of oxygen evolution and formic acid oxidation on Ti/IrO₂ electrodes using isotope labelling and on-line mass spectrometry

15:40 to 16:00
Osugi Marly (Departamento de Química Analítica - Instituto de Química - UNESP, Araraquara, Brazil) C. R. Chanthamarakshan, N. R. Tacconi, G. A. Woldemariam, S. S. Mandal, M. V. B. Zanoni, K. Rajeshwar
Photoelectrocatalytic Oxidation of Disperse Dyes on Nanotubes Ti/TiO₂ Electrodes

16:00 to 16:20
Lucia G. Alvarado (Inst. de Metalurgia / Univ. Autonoma de San Luis Potosi, San Luis Potosi, Mexico), Israel Rodriguez, Armando I. Vazquez
Electrodeionization process applied to hexavalent chromium removal from synthetic solutions at pH 5

16:20 to 16:40  Coffee Break, Room: Pacífico
Wednesday 19 March - AM

Keynote Lecture 3

Environmental analytical electrochemistry: monitoring the planet

Room: Santiago
Chair: Artur de Jesus Motheo (Univ. of S. Paulo, Brazil)

09:00 to 10:00

Christopher Brett (Departamento de Química Fac. Ciências e Tecnologia, Universidade de Coimbra, Coimbra, Portugal)

Advances in electrochemical sensors and biosensors for monitoring environmental pollution
Wednesday 19 March - AM
Oral Sessions 9 and 10

Environmental analytical electrochemistry: monitoring the planet

Room: Santiago
Chairs: Ana Maria Oliveira-Brett (Univ. Coimbra, Portugal) and Damien Arrigan (Tyndall Nat. Inst., Ireland)

10:10 to 10:40 — INVITED LECTURE

Damien Arrigan (Tyndall National Institute, Lee Maltings, University College, Cork, Ireland)

Miniaturised Sensors and Devices for Environment and Health

10:40 to 11:00 Coffee Break, Room: Pacífico

11:00 to 11:20

Omotayo Arotiba (SensorLab, Department of Chemistry, University of Western Cape, Cape Town, South Africa), Amir Al-Ahmed, Priscilla Baker, Emmanuel Iwuoha, Joseph Owino, Tesfaye Waryo

An Electrochemical DNA Biosensor Developed on a Polypropylene Imine Dendrimer-Gold Nanocomposite

11:20 to 11:40

Judith Rishpon (Department of Molecular Microbiology and Biotechnology, Tel-Aviv University, Tel-Aviv, Israel), Tova Neufeld, Rachela Popovtzer, Yosi Shacham-Diamand

Electrochemical Monitoring of Biological Reactions Using a Novel Nano-Bio-Chip Array

11:40 to 12:00

Ana Maria Oliveira-Brett (Departamento de Química, Universidade de Coimbra, Coimbra, Portugal), Severino C. B. Oliveira, Oana Corduneanu, Victor C. Diculescu, Ana-Maria Chiorcea-Paquim

In situ Evaluation of Hazard Compounds-DNA Interactions Using an Electrochemical DNA-Biosensor

12:00 to 12:20

Nicolette Hendricks (SensorLab, Department of Chemistry, University of the Western Cape, Cape Town, South Africa), Amir Al-Ahmed, Priscilla Baker, Emmanuel Iwuoha, Tesfaye Waryo

Microsomal CYP3A4 Nanobiosensor for the Determination of 2,4-dichlorophenol - an Endocrine Disruptor Compound
Environmental electrochemical engineering: protecting the planet

Room: Atlântico
Chairs: Kaido Tammeveski (Univ. of Tartu, Estonia) and Rodnei Bertazzoli (Campinas State Univ., Brazil)

10:10 to 10:40 — INVITED LECTURE
Rodnei Bertazzoli (The State University of Campinas, Campinas, Brazil), Leticia Ferreira, Juliane Forti, Robson Rocha
Reduction and oxidation based electrochemical synthesis on gas diffusion electrodes

10:40 to 11:00 Coffee Break, Room: Pacífico

11:00 to 11:20
Kazuhiro Kaneda (Human Ecology Research Center/Sanyo Electric Company Ltd., Ora, Japan), Mineo Ikematsu, Masahiro Iseki, Katsura Kawata, Kenta Kitsuka
Electrochemical Ozone Generation by a Zirconium Oxide Electrode Fabricated by Sputtering

11:20 to 11:40
Christiane de Arruda Rodrigues (Departamento de Ciências Exatas e da Terra, Universidade Federal de São Paulo, Diadema, Brazil), Rodnei Bertazzoli, Raul Figueiredo
Investigation on the Performance of Gas Diffusion Electrode for Electrolysis in Chlor-Alkali Cell

11:40 to 12:00
Kaido Tammeveski (Institute of Chemistry, University of Tartu, Tartu, Estonia), Marko Kullapere, Uno Mäeorg, Gilberto Maia, Fernando Cesar Maschion, David J. Schiffrin, Jaanika-Maria Seinberg
Modification of glassy carbon surface with anthraquinone from the solutions of its diazonium derivatives: An oxygen reduction study

12:00 to 12:20
Ernesto Pereira (Depto. Química, Universidade Federal de São Carlos, São Carlos, Brazil), Ettore Antunes, Renato Freitas
Preparation and Characterization of Nanostructured Metallic Billayers of Pt/Ir/Pt for CO and Methanol Electrooxidation
Wednesday 19 March - PM
Oral Session 11

Environmental electrochemical engineering: protecting the planet

Room: Atlântico
Chairs: Luiz Henrique Dall’Antonia (Londrina State Univ., Brazil) and Enric Chairs: Brillas (Univ. Barcelona, Spain)

14:10 to 14:40 — INVITED LECTURE — page 54
Enric Brillas (Química Física/Universitat de Barcelona, Barcelona, Spain)

14:40 to 15:00 — page 121
Maria Valnice Boldrin Zanoni Zanoni (Institute of Chemistry, UNESP, Araraquara, Brazil), Luciano Fraga, Maria Beatriz, Fabiana Paschoal, Luciane Romão, Jeosadaque Sene, Marc Anderson
- Photoelectrochemical Generation of Chlorine and Oxidation of Organics in Superficial Water

15:00 to 15:20 — page 86
M.E. Henry Bergmann (Anhalt University, Koethen/Anh., Germany), Johanna Rollin
- The perchlorate problem in drinking water electrolysis

15:20 to 15:40 — page 99
Geoffroy R.P. Malpass (IQSC/USP, São Carlos, Brazil), Claudomiro P. Barbosa, Artur J. Motheo
- Electro-removal of Cu(II) in the presence of Humic Acid

15:40 to 16:00 — page 111
Woonsup Shin (Department of Chemistry and Interdisciplinary Program of Integrated Biotechnology, Sogang University, Seoul, Korea), Jieun Song, Chang Hwan Kim, Zhen Yu Hong
- Screening of Microbes for Searching for the Effective Catalysts in Electrochemical Activation of Carbon Dioxide

16:00 to 16:20 Coffee Break, Room: Pacifico
16:20 to 16:40
Paulo Olivi (Dep. Química, FFCLRP - USP, Ribeirão Preto, Brazil), Carla Regina Costa
Electrochemical treatment of tannery wastewater

16:40 to 17:00
Geir Martin Haarberg (Department of Materials Technology, Norwegian University of Science and Technology, Trondheim, Norway), Marte Bjørnsdotter, Torbjørn Engebretsen, Ole Edvard Kongstein
The Supply of Dissolved Oxygen by Electrolysis in Lake Biwa

Wednesday 19 March - PM
Oral Session 12

Environmental electrochemical engineering: protecting the planet

Room: Santiago
Chairs: Pawel J. Kulesza (Univ. of Warsaw, Poland) and Florian Mansfeld (Univ. of Southern California, USA)

14:40 to 15:00
Florian Mansfeld (Corrosion and Environmental Effects Laboratory, Mork Family Dep. of Chemical Eng. and Materials Science, University of Southern California, Los Angeles, USA), Orianna Bretschger, David Harrington, Aswin Karthik Manohar, Kenneth Nealson
An Evaluation of the Performance of a Mediator-less Microbial Fuel Cell

15:00 to 15:20
Elisabeth Lojou (Bioénergétique et Ingenierie des Protéines - CNRS, Marseille, France), Myriam Brugna, Sébastien Demantin, Marie-Thérèse Giudici-Orticoni, Marc Rousset
Hydrogenases as biocatalysts for biofuel cells: efficient H\textsubscript{2} oxidation at electrodes modified by carbon nanotubes
15:20 to 15:40
Federico Tasca (Analytical Chemistry Department, Lund University, Lund, Sweden), Gilbert Nöll, Wolfgang Harreither, Roland Ludwig, Dietmar Haltrich, Jindrich Volc, Lo Gorton
Immobilization of Pyranose Dehydrogenase on Graphite Electrodes Modified with Length Fractionated Single Wall Carbon Nanotube and Low Potential Osmium Polymer for Biofuel Cell Applications

15:40 to 16:00
Susan Boland (School of Chemistry, National University of Ireland, Galway, Ireland), Kevin Foster, Paul Kavanagh, Dónal Leech
Integration of Enzymes, Redox Mediators and Structured Materials to Provide Bioelectrochemical Fuel Cells

16:00 to 16:20 Coffee Break, Room: Pacífico

16:20 to 16:40
Yvonne Ackermann (Analytische Chemie - Elektroanalytik & Sensorik, Ruhr-Universität Bochum, Bochum, Germany), Nina Dimcheva, Lo Gorton, Dmitrii Guschin, Katarzyna Karnicka, Pawel J. Kulesza, Wolfgang Schuhmann, Leonard Stoica
Tunable redox polymer matrices for the development of membraneless biofuel cells using a laccase cathode and cellobiose dehydrogenase anode

16:40 to 17:00
Gilbert Nöll (Department of Analytical Chemistry Lund University, Lund, Sweden), Federico Tasca, Vasile Coman, Lo Gorton, Wolfgang Harreither, Roland Ludwig, Dietmar Haltrich
Direct Electron Transfer at Anodes for Biofuel Cells Constructed by Coadsorption of Cellobiose Dehydrogenase and Length Separated Single-Walled Carbon Nanotubes
Program of Poster Presentations
Room: Pacífico

Monday 17 March
17:00 to 19:00 (Open bar from 18:00)

s1-P-001; s1-P-003; s1-P-005; s1-P-007; s1-P-008; s1-P-012; s1-P-015; s1-P-017; s1-P-020; s1-P-024; s1-P-026; s1-P-028; s1-P-031; s1-P-034; s1-P-037; s1-P-039; s1-P-042; s1-P-045; s1-P-049; s1-P-052

s2-P-001; s2-P-005; s2-P-007; s2-P-009; s2-P-013; s2-P-016; s2-P-019; s2-P-022; s2-P-026; s2-P-028; s2-P-031; s2-P-034; s2-P-036; s2-P-039; s2-P-042; s2-P-045; s2-P-048; s2-P-051; s2-P-054; s2-P-057; s2-P-060; s2-P-063; s2-P-066; s2-P-068; s2-P-071; s2-P-074; s2-P-077; s2-P-081; s2-P-084; s2-P-088

Tuesday 18 March
16:40 to 18:40 (Open bar from 17:40)

s1-P-002; s1-P-004; s1-P-006; s1-P-009; s1-P-010; s1-P-013; s1-P-018; s1-P-021; s1-P-025; s1-P-029; s1-P-032; s1-P-035; s1-P-041; s1-P-043; s1-P-048; s1-P-050; s1-P-053; s1-P-055; s1-P-057

s2-P-002; s2-P-003; s2-P-008; s2-P-011; s2-P-014; s2-P-017; s2-P-020; s2-P-023; s2-P-025; s2-P-027; s2-P-029; s2-P-030; s2-P-035; s2-P-041; s2-P-044; s2-P-046; s2-P-049; s2-P-052; s2-P-055; s2-P-058; s2-P-061; s2-P-064; s2-P-067; s2-P-070; s2-P-073; s2-P-076; s2-P-079; s2-P-082; s2-P-085; s2-P-087

Wednesday 19 March
17:00 to 19:00 (Open bar from 18:00)

s1-P-011; s1-P-014; s1-P-016; s1-P-019; s1-P-022; s1-P-023; s1-P-027; s1-P-030; s1-P-033; s1-P-036; s1-P-038; s1-P-040; s1-P-044; s1-P-046; s1-P-047; s1-P-051; s1-P-054; s1-P-056; s1-P-058; s1-P-059

s2-P-004; s2-P-006; s2-P-010; s2-P-012; s2-P-015; s2-P-018; s2-P-021; s2-P-024; s2-P-032; s2-P-033; s2-P-037; s2-P-038; s2-P-040; s2-P-043; s2-P-047; s2-P-050; s2-P-055; s2-P-056; s2-P-059; s2-P-062; s2-P-065; s2-P-069; s2-P-072; s2-P-075; s2-P-078; s2-P-080; s2-P-083; s2-P-086; s2-P-089; s2-P-090
Environmental analytical electrochemistry: monitoring the planet

s1-P-001
Enrico Andreoli (Department of Chemistry, National University of Ireland, Maynooth, Ireland), Carmel Breslin, Denise Rooney
Modification of polypyrrole composites with metal nanoparticles: A new material for environmental applications

s1-P-002
Valeria Annibaldi (Department of Chemistry, National University of Ireland, Maynooth, Ireland), Carmel Breslin, Denise Rooney
Conducting Polypyrrole Matrix Modified with Sulfated α-Cyclodextrin and its Ability to Sense Viologens

s1-P-003
Patricia Alexandra Antunes (Universidad de Valladolid, Valladolid, Spain / UNOESTE, Presidente Prudente, Brazil), Marystela Ferreira, Osvaldo Novais Oliveira Jr., Maria Luz Rodriguez-Mendez, Jose Antonio S. Saja
Preparation and Characterization of Nanostructured Films Formed by Poly(allylamine), Albumin and Nickel Phthalocyanine. Sensing Properties Towards Biological Amines

s1-P-004
Verónica Arancibia (Chemistry Faculty, Santiago, Chile), Cesar Gonzalez, Edgar Nagles, Manuel Zúñiga
Determination of Chromium (VI) by Adsorptive Stripping Voltammetry with Morin

s1-P-005
Maurício Ribeiro Baldan (Instituto Nacional de Pesquisas Espaciais, São José dos Campos, Brazil), Neidenêi Gomes Ferreira, Jorge Tadao Matsushima, Leide L. G. Silva
Influence of nitrogen on boron doped diamond electrodes in the nitrate electrochemical response

s1-P-006
Talita Barcellos (Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto - USP, Ribeirão Preto, Brazil)
Electrochemical oxidation of maleic acid an import by-product in the phenolic compounds degradation route
s1-P-007
Jiri Barek (Analytical Chemistry, Charles University in Prague, Prague, Czech Republic), Miroslav Fojta, Tomas Navratil, Bogdan Yosypchuk
Multisensor for Electrochemical Determinations

s1-P-008
Jiri Barek (Analytical Chemistry, Charles University in Prague, Prague, Czech Republic), Ales Danhel, Vlastimil Vyskocil, Bogdan Yosypchuk
New Silver Solid Amalgam Paste Electrode for Environmental Application

s1-P-009
Jiri Barek (Analytical Chemistry, Charles University in Prague, Prague, Czech Republic), Ivan Jiranek, Zuzana Kralova, Josino Moreira, Karolina Peckova
The Use of Solid Amalgam Electrodes as Electroanalytical Sensors for the Determination of Nitroquinolines

s1-P-010
Jiri Barek (Analytical Chemistry, Charles University in Prague, Prague, Czech Republic), Dana Deylova, Karolina Peckova, Vlastimil Vyskocil
Voltammetric Determination of Submicromolar Concentrations of Genotoxic 5-Nitrobenzimidazole at Hanging Mercury Drop Electrode and Carbon Paste Electrode

s1-P-011
Jiri Barek (Analytical Chemistry, Charles University in Prague, Prague, Czech Republic), Hana Dejmkova, Zuzana Jemelkova, Monika Kocourkova, Josino Moreira, Jiri Zima
Voltammetric Determination of Benserazide Using Carbon Paste Electrodes

s1-P-012
Georgeta Burtica (Politehnica University of Timisoara, Department of Applied Chemistry and Engineering of Inorganic Compounds and Environment, Timisoara, Romania), Adriana Bebeselea, Florica Manea, Aniela Pop, Ciprian Radovan, Joop Schoonman, Carmen Teodosiu
Anodic Determination of Oxalic Acid in the Presence of 4-Chlorophenol using Expanded Graphite-Epoxy Composite and Boron-Doped Diamond Electrodes

s1-P-013
José Miguel Campiña (Chemistry Department, Porto University, Porto, Portugal), Ana Maria Martins, Fernando Silva
Effect of pH, Electrolyte Anion, and Temperature in the Permeation of SAMs by Electroactive Probes
s1-P-014
Ivani Carlos (DQ/UFSCar, São Carlos, Brazil), Joana Luiza Pires Siqueira
Development of Environmentally Non-Aggressive Pb-Sn Deposition
Baths: New Alternatives to Fluoborate Baths.

s1-P-015
Ivana Cesarino (Instituto de Química de São Carlos - USP, São Carlos, Brazil)
Thiol-functionalised Silica Film Modified Glassy Carbon Electrode in the
Determination of Mercury Ions

s1-P-016
Lucia Coelho (Universidade de São Paulo, São Paulo, Brazil), Ivano Gutz
Comparison between two electroanalytical techniques for atmospheric
formaldehyde determination

s1-P-017
Tiago Francisco da Silva (Departamento de Química Analítica - Instituto
de Química de Araraquara - UNESP, Araraquara, Brazil), Nelson Ramos
Stradiotto
Determination of Heavy Metals in Waters of Guarani Aquifer by
Voltammetric Methods Using Solid Amalgam Electrode

s1-P-018
Acelino de Sá (Departamento de Física e Química - UNESP, Ilha
Solteira, Brazil), Devaney do Carmo
Voltammetric behavior of a modified silica with copper nitroprusside

s1-P-019
Rodrigo Del Rio (Departamento de Quimica Inorganica, Facultad de
Quimica, Pontificia Universidad Catolica de Chile, Santiago, Chile),
Andrea Amaro, Ricardo Schrebler
Gold Nanowires Electrodeposition Using Block Copolymers Films as
Templates

s1-P-020
Devaney do Carmo (Departamento de Física e Química – Unesp - Ilha
Solteira, Ilha Solteira, Brazil), Urquisa Bicalho, Newton Dias Filho
Electrochemical properties of a new nanostructured azido copper (II)
octa (3-aminopropyl) octasilsesquioxane using graphite paste electrode

s1-P-021
Lukáš Fojt (Institute of Biophysics ASCR, Brno, Czech Republic), Jíří
Vanek, Vladimír Vetterl
Adsorption and two-dimensional condensation of nucleic acid
components
s1-P-022
Mariano Fonticelli (Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Facultad de Ciencias, Exactas, Universidad Nacional de La Plata – CONICET, La Plata, Argentina), Guillermo A. Benitez, Gaston Corthey, Lisandro Giovanetti, Felix Requejo, Roberto C. Salvarezza, Young S. Shon, Carolina Vericat
A Novel Electrochemical Strategy for the Production of Bimetallic Nanoparticles

s1-P-023
Catherine Fox (Department of Chemistry, National of University of Ireland Maynooth, Maynooth, Ireland)
An Application of Silver Nanoparticles in Environmental Chemistry: Sensing of Nitrates

s1-P-024
Cristiane X. Galhardo (Instituto de Química e Biotecnologia - UFAL, Maceió, Brazil)
Evaluation of Lead Concentration in Mussel Mytella charruana in the Mundaú Estuarine Lagoon, Maceió, Brazil

s1-P-025
Eric de Souza Gil (Faculdade de Farmácia - Universidade Federal de Goiás, Goiânia, Brazil), Sérgio Antonio Spinola Machado, Fernando Cruz Moraes, Aline Oliveira, Juliana Chaves Santana, Eduardo Queija Siqueira
Development of a Modified Biosensor by a Crude Extract of Guariroba (Syagrus oleracea) for the Analysis of Phenolic Compounds in Environmental Samples

s1-P-026
Karolina Haberska (Department of Analytical Chemistry/Lund University, Lund, Sweden), Thomas Arnebrant, Liselott Lindh, Tautgirdas Ruzgas, Sergey Shleev, Olof Svensson
Lactoperoxidase Activity at Gold Surfaces: Amperometric Response to Hydrogen Peroxide

s1-P-027
Lauro Kubota (Instituto de Química, Universidade Estadual de Campinas, Campinas, Brazil)
Monitoring the electrochemical oxidation of a mixture of phenol compounds on boron-doped diamond electrode using fluorescence and multiway methods
s1-P-028

**Lauro Kubota (Unicamp, Campinas, Brazil), Vitor Baranauskas, Helder Ceragioli, Marcia Ferreira, Alfredo Peterlevitz, Reinaldo F. Teófilo**

Use of Fluorescence Intensity for Aromaticity Monitoring of Phenolic Compounds during the Electrochemical Oxidation on Boron-Doped Diamond Electrode

s1-P-029

**Cecilia Lete (Institute of Physical Chemistry, Bucharest, Romania)**

Electrochemical monitoring of some phenol derivatives at modified electrodes

s1-P-030

**Maria Luisa Lozano (Universidad Autonóma Metropolitana-Iztapalapa, México, Mexico)**

Incorporation of Fe(III) into a poly (5-Amino 1,10 phenanthroline) matrix.

s1-P-031

**Florica Manea (Politehnica University of Timisoara, Department of Applied Chemistry and Engineering of Inorganic Compounds and Environment, Timisoara, Romania), Adriana Bebeselea, Georgeta Burtica, Dan Cinghita, Monica Ibos, Cristina Proca, Ciprian Radovan**

The Availability of Boron-Doped Diamond Electrode for Anodic Determination of Nonylphenols Etoxylates

s1-P-032

**Glimaldo Marino (Instituto de Química de São Carlos - USP, São Carlos, Brazil), Ivana Cesarino**

Evaluation of a Carbon Paste Electrode Modified with Oganofunctionalised Amorphous Silica in the Simultaneous Determination of Lead, Copper and Mercury Ions in Natural Water

s1-P-033

**Jorge Tadao Matsushima (Instituto Nacional de Pesquisas Espaciais - INPE, São José dos Campos, Brazil), Mauricio Baldan, Neidenêi Gomes Ferreira, William Melo Silva**

The correlation between boron content and surface modifications on the nitrate reduction for Boron-Doped Diamond Electrodes

s1-P-034

**Sinead Mc Dermott (Department of Chemistry, National University of Ireland, Maynooth, Ireland), Carmel Breslin, Denise Rooney**

Conducting Polymers modified with Cyclodextrins and their ability to detect the Pollutant Paraquat
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<td>Determination of 4-Nitrophenol in natural waters using a multi-wall carbon nanotubes sensor</td>
<td>Fernando Cruz Moraes (Departamento de Química / Universidade Federal de São Carlos, São Carlos, Brazil), Sérgio Antonio Spínola Machado, Lúcia Helena Mascaro, Sonia T Tanimoto</td>
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<td>Octyl dimethyl PABA Detection in Natural and Artificial Aquatic Systems based on a PANI/FeTSPc Sensor</td>
<td>Luis Moreira (Laboratório de Pesquisas em Eletroquímica e Eletroanalítica, Universidade São Francisco, Bragança Paulista, Brazil), Marcos Lanza, Maria Sotomayor, Auro Tanaka</td>
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<td>Carolina Muñoz (Departamento de Química Inorgánica I, Facultad de Química/ Pontificia Universidad Católica de Chile, Santiago, Chile), Verónica Arancibia, Manuel Zúñiga</td>
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<td>s1-P-038</td>
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Levent Özcan (Anadolu University, Department of Chemistry, Eskisehir, Turkey)
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s1-P-043
Thiago Paixão (Instituto de Química - Universidade de São Paulo, São Paulo, Brazil), Mauro Bertotti
Glassy carbon electrode modified with ruthenium oxide hexacyanoferrate as an electrochemical sensor for hydrogen peroxide determination in rainwater

s1-P-044
Rosalina Pérez García (Centro de Graduados e Investigación del Instituto Tecnológico de Tijuana, Tijuana, Mexico), Mercedes Oropeza Guzmán
Electroflotation as an alternative treatment for water containing suspended solids and emulsions

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Fábio Ruiz Simões (NANOFAEL - LIEC - Chemistry Department - Federal University of São Carlos, São Carlos, Brazil), Ernesto Chaves Pereira, Leandro Pocrifka
Study of the Electrochemical Behavior of Self-Assembled Films Used in Environmental Applications

s1-P-046
Silvana Saidman (INIEC - Departamento de Ingeniería Química - Universidad Nacional del Sur, Bahía Blanca, Argentina), Ivana Lehr, Oscar Quinzani
Comparative study of polypyrrole films electrosynthesized in alkaline and acid solutions

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Electrochemical processes for the treatment of dichloroethane in water solutions
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Vernon Somerset (Natural Resources and the Environment, CSIR, Stellenbosch, South Africa), Emmanuel Iwuoha, Joy Leaner, Robert Mason, Chantel Petersen, Chavon Williams
Stripping Voltammetric Determination of Inorganic Mercury Using a Polyaniline, Polyaniline-poly(vinylsulfonate) and Polyaniline-poly(methylene blue) Coated Glassy Carbon Electrode

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Gustavo Stoppa Garbellini (Departamento de Química e Física Molecular - Instituto de Química de São Carlos - USP, São Carlos, Brazil), Luis Alberto Avaca, Giancarlo R. Salazar-Banda, Robson T. S. Oliveira
On The Use of Ultrasound-Assisted Electrochemical Methods for The Determination and Removal of Model Pollutants

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Ludek Strašák (Institute of Biophysics - ASCR, Brno, Czech Republic), Fojt Lukáš, Hason Stanislav
Adsorption of microorganisms on mercury surface

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Characterization of soil samples from a heavy metals contaminated site and the possibility of using in-situ electrokinetic remediation

s1-P-052
Boland Susan (School of Chemistry, National University of Ireland, Galway, Ireland), Kevin Foster, Joanna Hajdukiewicz, Peter Jenkins, Paul Kavanagh, Dónal Leech
Mediated Enzyme Reactions: From Biosensors to Biopower

s1-P-053
Marcos F. S. Teixeira (Faculdade de Ciências e Tecnologia - Departamento de Física, Química e Biologia - UNESP, Presidente Prudente, Brazil), Fernando H. Cincotto
Electrocatalytic Oxidation of Peroxide by Ruthenium-Pyridil Complex Confined In a Polymer Perfluorinated Membrane

s1-P-054
Marcos F. S. Teixeira (Faculdade de Ciências e Tecnologia - Departamento de Física, Química e Biologia - UNESP, Presidente Prudente, Brazil), Tony R. L. Dadamos
Electrochemical Sensor for Sulfite Determination Based on Copper-Salen Film Modified Electrode
**s1-P-055**
María Soledad Ureta-Zañartu (Depto. Ciencias del Ambiente, Facultad de Química y Biología, USACH, Santiago, Chile), Roxana Arce, Cristhian Berrios, Claudio Gutiérrez

Oxidation of 2,4,6-trichlorophenol at a GC Electrode Modified with Metal Phthalocyanines

**s1-P-056**
María Aurora Veloz Rodríguez (Universidad Autónoma del Estado de Hidalgo, ICBI-AAMyM, Pachuca, Mexico), Ignacio González Martínez, Victor Esteban Reyes Cruz, Gustavo Urbano Reyes

Electrochemistry Applied to Detect Potentially Toxic Elements (PTE’s) in Contaminated Soils by Mining Residues

**s1-P-057**
Jarmila Vytrasova (Department of Biological and Biochemical Sciences, University of Pardubice, Pardubice, Czech Republic), Libor Cervenka, Michal Hrubes, Iva Peskova, Karel Vytras

Electroimmunoassay for Detection of Bacterial Cells

**s1-P-058**
Maria Valnice Boldrin Zanoni (Institute of Chemistry, UNESP, Araraquara, Brazil)

Simultaneous Photoelectrochemistry Reduction of Cr(VI) and Dye Oxidation in a Leather Effluent

**s1-P-059**
Jorge Omar Zerbino (INIFTA, La Plata, Argentina)

Voltammetric and ellipsometric study of platinum electrodes in acid solutions containing sulphur dioxide
Environmental electrochemical engineering: protecting the planet

s2-P-001
Sergey Alferov (Analytical Chemistry, Lund University, Lund, Sweden), Vasile Coman, Lo Gorton, Tobias Gustavsson, Cecilia Hägerhäll
Wiring of Escherichia coli With Different Electron Transport Mediators

s2-P-002
Patrícia A. Alves (Institute of Chemistry of São Carlos – University of São Paulo, São Carlos, Brazil), Geoffroy R. P. Malpass, Douglas W. Miwa, Artur J. Motheo
Electrochemical and Photo-Assisted Electrochemical Degradation of Real Textile Effluent

s2-P-003
Leonardo Santos Andrade (Chemistry Dep./UFSCar, São Carlos, Brazil), Nerilso Bocchi, Romeu Cardozo Rocha-Filho, Kallyni Irikura, Sonia Regina Biaggio
Electrochemical degradation of the Blue Reactive 19 dye in a filter-press reactor using a carbon-fiber/PbO₂ anode in the presence or absence of chloride

s2-P-004
José Mario Aquino (Chemistry Department/UFSCar, São Carlos, Brazil), Leonardo S. Andrade, Sonia R. Biaggio, Nerilso Bocchi, Romeu C. Rocha-Filho
Electrochemical Degradation of the Reactive Red 141 Dye on Ti-Pt/β-PbO2 and DSA Anodes

s2-P-005
Vincenzo Baglio (CNR-ITAE, Messina, Italy), Vincenzo Antonucci, Irene Gatto, Ester Modica, Ruben Ornelas, Enza Passalacqua, Alessandro Stassi
Electrochemical and Physico-Chemical Investigation of Polymer Electrolyte Fuel Cell Catalysts for High Temperature Operation

s2-P-006
Peter Barath (Department of Electrical and Electronic Technology/The Faculty of Electrical Engineering and Communication Brno, University of Technology, Brno, Czech Republic), Jiri Kazelle, Marie Sedlarikova, Petr Spicak, Arnaldo Visintin, Jiri Vondrak
Metal hydride electrodes studied by QCM technique
s2-P-007
Katlin Ivon Barrios Eguiluz (Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos, Brazil), Luis Alberto Avaca, Giancarlo Richard Salazar Banda
Effect of the catalyst composition in the Pt(Ru–Ir)$_x$/C system on the electro-oxidation of methanol in acid media

s2-P-008
Henry Bergmann (Anhalt University of Applied Sciences, Koethen/Anh, Germany), Karsten Kresse, Johanna Rollin
Bromate formation on BDD anodes

s2-P-009
Henry Bergmann (Anhalt University of Applied Sciences, Koethen/Anh, Germany), Tatiana Iourtchouk
The study of anion exchange materials for electrodionization

s2-P-010
José M. Bisang (PRELINE/Facultad de Ingeniería Química/Universidad Nacional del Litoral, Santa Fe, Argentina), Javier M. Grau
Development of a Bipolar Electrochemical Reactor with Rotating Cylinder Electrodes of Woven-Wire Meshes for Effluent Treatment

s2-P-011
José M. Bisang (PRELINE/Facultad de Ingeniería Química/Universidad Nacional del Litoral, Santa Fe, Argentina)
Comparative Study of Concentration-Time Relationships in Recirculating Electrochemical Reactor Systems

s2-P-012
Nilson Tadeu Camarinho de Oliveira (IQ-UNESP-Araraquara, Araraquara, Brazil), Antonio Carlos Guastaldi
Corrosion Resistance And Stability Of Ti-Mo Alloys For Biomedical Applications

s2-P-013
Nilson Tadeu Camarinho de Oliveira (IQ-UNESP-Araraquara, Araraquara, Brazil), Antonio Carlos Guastaldi, Salvatore Piazza, Carmelo Sunseri
Photoelectrochemical and Impedance Studies of Passive Films on Different Ti-Mo Alloys

s2-P-014
Carlos Carlesi Jara (Escuela de Ingeniería Química/Pontificia Universidad Católica de Valparaíso, Valparaíso, Chile)
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Beatriz Castro (INIFTA, Universidad Nacional de La Plata, La Plata, Argentina), R.H. Milocco, E. B. Castro, D. J. Cuscuetu, A.A. Ghilarducci, Sandra Rojas, H. R. Salva, A. Visintín
Model Validation of Ni-MH Batteries Under Constant Discharge Current

s2-P-016
Élida Beatriz Castro (Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas - Facultad de Ciencias Exactas - U.N.L.P., La Plata, Argentina), Mariela Ortiz, Silvia Graciela Real
Dynamic Monitoring of Structural Changes in Porous Nickel Hydroxide Electrodes Employed in Batteries

s2-P-017
Marisela Choy de Martínez (Chemistry Dep., Univ. de Los Andes, Mérida, Venezuela), María González, José Miguel Ortega, Zogehil Puentes
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Alejandro N. Colli (PRELINE/Facultad de Ingeniería Química/Universidad Nacional del Litoral, Santa Fe, Argentina), José M. Bisang
An Experimental Study of the Morphological Characteristics of Copper Electrodeposits in Three-Dimensional Electrodes

s2-P-019
Luiz Henrique Dall’Antonia (Departamento de Química/Universidade Estadual de Londrina, Londrina, Brazil), Samira Castellari, Luiz Henrique Dall’Antonia, Paulo Olivi, Demetrius Profeti, Maria C Solci
Electro-Fenton method for removal of hormones in an electrochemical system using Ti/Sn$_{0.99}$Ir$_{0.01}$O$_2$ as cathode

s2-P-020
Ken Darcovich (National Research Council of Canada, Institute for Chemical Process and Environmental Technology, Ottawa, Canada), Teddy Caroni, Isobel Davidson
Charge-Discharge Simulation of Lithium Ion Batteries in a Cogeneration Load-Leveling Context

s2-P-021
Martín Davila (Universidad Autonoma de Puebla, Puebla, Mexico), Maria Elizalde, Ana Mendez, Rigoberto Tovar
Electrochemical and Photocatalytic Degradation of Azo and Methine Dyes in Water
s2-P-022
Gildiberto M. de Oliveira (Chemistry Dep./Federal University of São Carlos, São Carlos, Brazil), Ivani A. Carlos
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s2-P-023
Alessandra Di Blasi (CNR-ITAE, Messina, Italy)
Investigation of Pt-M/C Tolerance in Presence of Ethanol Acid Solution for the Oxygen Reduction Reaction

s2-P-024
Paula Drob (Electrochemistry and Corrosion/Institute of Physical Chemistry, Bucharest, Romania), Silviu Iulian Drob, Mihai Vasile Popa, Julia Claudia Rosca, Ecaterina Vasilescu, Cora Vasilescu
Electrochemical Deposition Technology of Organic Coating to Protect the Environment

s2-P-025
Pablo Sebastián Fernández (Instituto de Investigaciones Fisicoquimicas Teóricas y Aplicadas - Facultad de Ciencias Exactas - U.N.L.P., La Plata, Argentina), Élida Beatriz Castro, María Elisa Martins, Silvia Graciela Real
Towards the Mechanism of Electrochemical Hydrogen Storage in Nanostructured Carbon Materials

s2-P-026
Violetta Ferri (Department of Chemistry, University of Ferrara, Ferrara, Italy), Achille De Battisti, Sergio Ferro, Carlos Alberto Martinez-Huitle
Electrokinetic extraction of surfactants and heavy metals from a municipal wastewater sludge

s2-P-027
Juliane Forti (Universidade Estadual de Campinas - UNICAMP, Campinas, Brazil), André Beati, Rodnei Bertazzoli, Fabiana Fisnack, Vânia Prado
Chloramphenicol oxidation via electro-fenton reagent on a flow reactor using modified gas diffusion electrodes

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Manuel Gacitúa (Laboratorio de Electroquímica de Polímeros, Facultad de Química, Pontificia Universidad Católica de Chile, Santiago, Chile), Luis Canales, María Angélica del Valle, Giovanny Soto
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A.R. Pierna (Chemical Engineering and Environment Dep./University of Basque Country, San Sebastian, Spain), J. Barranco, J. Barroso, B. Carton, F. Lopez, A. Lorenzo, F.F. Marzo, A. Perez
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Felipe J. Rodríguez NIeto (INIFTA, Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, La Plata, Argentina), Maite Elissalde, Miguel A. Pasquale
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Daniel Salinas (INIEC - Instituto de Ing. Electroquímica y Corrosión - Depto. de Ing. Química - Universidad Nacional del Sur, Bahía Blanca, Argentina), Silvana Garcia, Lorena Meier
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Csaba Visy (Institute of Physical Chemistry, University of Szeged, Szeged, Hungary), Gábor Bencsik, Csaba Janáky, Emese Kriván
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Jens Muff (Chemical Engineering Department, Esbjerg Institute of Technology, Aalborg University, Esbjerg, Denmark)
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S. G. García (INIEC - Inst. de Ing. Electroquímica y Corrosión - Universidad Nacional del Sur, Bahía Blanca, Argentina), M. C. del Barrio, D. R. Salinas
Formation of Ultrathin Films on Au(111) used as Electrocatalysts for Nitrate Reduction

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M.A. Dresch (Instituto de Pesquisas Energéticas e Nucleares – IPEN/CNEN-SP, São Paulo, Brazil), R.A. Isidoro, F. C. Fonseca, M. Linardi, E. I. Santiago
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Diego Barsellini (Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas, Facultad de Ciencias Exactas, UNLP, La Plata, Argentina)
Facetted Platinum Catalysts with Preferential Crystal Orientation for Low Temperature Fuel Cells

s2-P-090
Valderi Pacheco Santos (Universidade Estadual do Oeste do Paraná / Coordenação de Química, Toledo, Brazil), Germano Tremiliosi Filho
FTIRS Comparative Studies of the Ethanol Electrooxidation on Pt(100) and Pt(111) after Osmium Spontaneous Depositions
Oral Presentations
The importance of electrode material in environmental electrochemistry

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Oxidative electrochemical processes promising versatility, environmental compatibility and cost effectiveness have a continuously growing importance both in selective organic synthesis and in the electrochemical incineration (ECI) of organic pollutants in aqueous media. In case of organic electrosynthesis selectivity is to be enhanced and in the ECI process the aim is the mineralization of the toxic and non-biocompatible pollutants with high current efficiency. Anodic oxidation of organics may proceed by several mechanisms including direct and indirect oxidation.

In direct electrochemical oxidation, electron exchange occurs between the organic species and the electrocatalytic electrode surface. A typical example is the oxidation of organic compounds on platinum anodes at low anodic potentials. The main problem with electrocatalytic anodes of platinum group metals is the decrease of the catalytic activity during use when proceeding oxidation of organics at a fixed anodic potential, before oxygen evolution. This is mainly due to the adsorption of reaction intermediates (mainly CO) at the anode surface, commonly called poisoning effect.

In indirect electrochemical oxidation, the organics do not exchange with the surface directly but through intermediation of some electroactive species. This process may be homogeneous or heterogeneous.

In this work the electrochemical oxidation of organics at DSA® type electrodes based on synthetic boron-doped diamond (BDD) and metal oxide anodes in acid medium are presented. Both the direct and indirect electron transfer reaction are discussed.

In case of facile outer-sphere electrode reactions, both BDD and oxide electrodes behave similarly to that of noble metal electrodes.

In oxidation reactions of more complex mechanism, these anodes show no activity below the potential of oxygen evolution and electrochemical oxygen transfer reactions (EO-transfer) can take place only in the potential region of water discharge.

A simplified mechanism of EO-transfer reactions catalyzed by intermediates of oxygen evolution has been proposed distinguishing between two limiting electrode behaviors:

(i) At ‘non-active’ anodes (typically BDD and fully oxidized metal oxides) EO-transfer occurs at a high anode potential through physisorbed hydroxyl radicals.
(ii) At ‘active’ electrodes (IrO$_2$, RuO$_2$) the reaction takes place at lower potentials characteristic of the metal oxide and results in an EO-transfer reactions through the higher oxidized metal oxide surface sites.
Advances in electrochemical sensors and biosensors for monitoring environmental pollution

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Electrochemical sensors have an important role to play in the monitoring of environmental pollution, enabling in situ measurements and diagnostic of the existence of toxic trace species [1]. This can often be done without pre-treatment or digestion of samples, reaching towards the ideal of real-time monitoring. They possess unique capabilities for speciation investigations and for probing the chemically labile free fraction of potentially toxic species, i.e. that which can lead to toxicity. Nevertheless, the complexity of the matrices investigated, particularly outside the laboratory, can compromise their use. It is therefore necessary to develop strategies to overcome the difficulties posed by the chemical and biological components in natural matrices, which include minimising the contact between electrode and sample, protecting the electrode surface, carrying out in situ sample pre-treatment and using disposable sensor electrodes.

The development and application of these strategies will be surveyed, with particular emphasis on novel types of polymer-modified glassy carbon, carbon film and bismuth-modified carbon electrode sensors, e.g. [2], together with injection techniques to minimise the contact with the sensing electrode. Voltammetric, electrochemical impedance spectroscopic and surface morphological characterisation of polymer-modified electrodes prepared for this purpose has been carried out. Requirements for successful sensors will be considered as well as their integration into on-line and injection systems. Examples of application will be given to trace metals in environmental and ecotoxicological test media and in the monitoring of pesticides.

Another approach using electrochemical enzyme inhibition sensors will also be described. The advantages and limitations of this strategy will be discussed together with recent results for inhibition of invertase and glucose oxidase by trace heavy metal ions.

Electrochemical Technologies for a Healthy Planet – Promises or Achievement?

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Electrochemical technology has a long and distinguished history in meeting the diverse demands of mankind whether in the chemical industry, for energy supplies, for corrosion protection, for metal fabrication, for analytical devices etc. Moreover, looking to the future, there is every reason to believe that electrochemical technology can contribute to combating global warming and the pollution of atmospheres and oceans as well as providing clean water and secure energy supplies.

In general, however, electrochemists remain very dissatisfied with the view of electrochemical technology taken by the outside world and especially the rate at which new technology is exploited. To what degree are these problems the fault of electrochemists? How can we better bridge the gap between academic aspirations and commercial success and thereby improve the take-up of electrochemical processes? I believe that there are two critical factors in answering these questions. Firstly, the academic world needs to be more aware of the real problems facing a technology. Secondly, and more importantly, the academic world needs to avoid raising unreasonable expectations. Particular damaging is a great weight of literature that misleads the reader as to the applicability of a technology or concept.

In this lecture, I would like to discuss some of the electrochemical technology with which I have been involved. But, while highlighting the successes, I would also like to illustrate the pitfalls and give some examples where I believe that I and others are guilty of over-enthusiastic selling! The systems to be discussed will include:

- A portable electrochemical sensor for the determination of CO$_2$ levels in atmospheres based on some very simple aqueous chemistry of Cu(II).
- A number of effluent treatment processes – the removal of heavy and transition metal ions using three-dimensional electrodes, systems based on the cathodic generation of hydrogen peroxide for the removal of organics, hypochlorite generators for disinfection.
- The electrosynthesis of organic compounds – why has books of 1500 pages and an extensive literature over many years led only to a handful of commercial processes?
- Energy storage devices, especially redox flow batteries, for load levelling in conjunction with renewable energy generation.

In principle, electrochemical technology has much to offer the fight for a clean environment and a sustainable lifestyle. We need to be clearer about the goals of our work, the limitations of our approaches and the real bottlenecks to exploitation.
Electrodeposition and Combustion Synthesis of Oxide Semiconductors for Solar Photocatalysis Applications

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Inorganic semiconductors are generally prepared by high temperature methods or by the use of vapor phase and ultra-high vacuum environments. Milder temperatures coupled with the use of condensed media, using water or other solvents (organic compounds or ionic liquids) represent interesting and economic alternatives for the growth of semiconductors in either bulk or thin film form. Electrodeposition is one such preparative methodology in this category, which already has seen widespread acceptance in the metallurgical and microelectronics sectors. This method is attractive from both fundamental and practical perspectives in terms of applicability to large and irregular device areas and the ability to prepare composite (e.g., metal/semiconductor) structures and unique semiconductor morphologies (e.g., nanotubes, nanodots). Anodic and cathodic electrosynthesis of metal oxide films and nanoporous/nanotubular morphologies will be briefly reviewed in terms of the underlying chemistry/electrochemistry and the mechanistic aspects. A double-template approach based on the use of polystyrene spheres and a polypyrrole secondary template will be presented for the preparation of ZnO nanodot arrays. A new pulse anodization approach will be described along with data on titanium dioxide and tungsten trioxide nanotube and nanoporous films. The photoelectrochemical behavior of these novel materials will be discussed.

Another attractive method for the preparation of oxide semiconductors is combustion synthesis. This method offers an energy-efficient alternative to the high-temperature, energy intensive routes that are popular in the ceramics community. One attractive feature of this approach is the possibility it offers of in situ doping of oxide semiconductor hosts by simply tuning the precursor chemistry. New data on Nb-, Cr- and S-doped titanium dioxide will be presented as well as results on the enhanced visible light response of these materials relative to benchmark titania samples (e.g., Degussa P-25).

Finally, the use of these novel materials for solar or visible-light photocatalysis will be illustrated with examples drawn from organic and inorganic pollutants. In the former category, dye pollutants (e.g., azo dyes, methylene blue) will be considered. In the inorganic category, data on pollutants such as Cr (VI) will be presented. Specifically, the nanotubular oxide semiconductor morphology will be compared to the nanostructured (sol-gel derived) morphology and commercial benchmark photocatalysts in terms of their relative efficacy to degrade the above pollutants.
Miniaturised Sensors and Devices for Environment and Health

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The state of the natural environment is a matter of universal concern. The monitoring of water body quality has become more and more important in the last 30 years. One of the most widely used water quality indices is the trophic state. This refers to the aging process occurring in the water. This process normally takes thousands of years but human intervention, e.g. by loading the water body with excess nutrients (mainly nitrogen and phosphorous), can accelerate it considerably. This can be the result of runoff from agricultural land, urban lawns or golf courses, or of untreated or partially treated domestic and farm sewage. As a result of the excess nutrients, algal blooms can occur leading to oxygen depletion and resulting in fish kills and in some cases to the proliferation of toxic algae. Reliable measurements of nutrients in environmental waters would greatly benefit environmental resource management.

To be environmentally useful, a chemical detection method must be able to detect inorganic phosphate at sub-parts per million levels. For example, an Irish Environmental Quality Standard (EQS) concentration of 0.05 ppm (ca. 5 x 10^{-7} M) for river water quality at the good/moderate quality boundary was recommended [1]. Recent experiments in our laboratory have demonstrated that ca. 10^{-5} M phosphate can be detected quite easily in solution using traditional ion-selective electrode potentiometry at polymer membranes [2]. This presentation will describe our studies towards development of an environmental sensor for phosphate which can be integrated with autonomous system platforms from the electrical engineering domain. In particular, emphasis will be placed on alternative transduction methods, micro-interfaces for enhanced sensitivity [3] and ionophore design. Also, results on how the same platforms may be used for biochemical detection will be summarized, as a healthy planet implies also healthy people.

References:
New electrode materials and arrangements for analysis of environmental carcinogens

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There is an ever increasing demand for sensitive, selective, and inexpensive methods for the determination of trace amounts of various environmental carcinogens in various environmental matrices. Modern voltammetric and amperometric methods are suitable for these purposes, the biggest problem being the passivation of the used electrode. Therefore, there is continuous search for new electrode materials with broader potential window, lower noise, better mechanical stability and above all high resistivity towards passivation which is the biggest obstacle preventing more frequent practical applications of voltammetry and amperometry. In this contribution we will present our recent results regarding the application of non-traditional electrode materials and arrangements in batch and flow analysis of chemical carcinogens [1, 2]. It will be shown that solid and paste amalgam electrodes can be easily prepared in any laboratory and their simple electrochemical or mechanical pretreatment in many cases eliminates problems with their passivation. Glassy carbon paste electrodes based on glassy carbon microbeads and a suitable organic pasting liquid, are very suitable sensors for oxidizable chemical carcinogens. Carbon ink film electrodes with easily renewable surface present an inexpensive alternative to screen printed carbon electrodes. Relatively broad anodic potential window together with easy renewal of their surface (simply by wipping off the film) makes them suitable sensors for many oxidizable chemical carcinogens. Diamond film electrodes characterized by very low noise and broad potential window are applicable for the determination of both oxidizable and reducible chemical carcinogens. The problems with passivation are practically eliminated by aliphatic character of their surface suppressing adsorption of most organic substances.

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Reduction and oxidation based electrochemical synthesis on gas diffusion electrodes

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This communication reports the results obtained in a set of going on studies for the electrosynthesis of a number of products from gaseous reactants using gas diffusion electrodes. Graphyte gas diffusion cathodes have been used for the reductive synthesis of methanol and formic acid from carbon dioxide and of hydrogen peroxide from oxygen. TiO$_2$/RuO$_2$ powder has also been used to produce gas diffusion anodes over which natural methane has been oxidized to methanol. The synthesis of hydrogen peroxide has been carried out from the reduction of oxygen using a modified O$_2$ fed graphite/PTFE electrodes in which redox catalysts were incorporated into the graphitic mass. The organic redox catalysts chosen for the modification were 2-ethylanthraquinone, 2-terc-butylanthraquinone and azobenzene. H$_2$O$_2$ electrogeneration rate was optimized relative to cell potential and catalyst concentration. Hydrogen peroxide formation rate on oxygen fed graphite/PTFE was greatly improved by the presence of the organic redox catalysts and the potential for oxygen reduction was shifted more positive. Formic acid and methanol were synthesized in similar CO$_2$ fed graphite/PTFE electrodes. Improved selectivity for methanol have been reached by selecting suitable potential values and by the deposition of 1 mg cm$^{-2}$ of copper or ruthenium on the electrode surface. Oxidative electrosynthesis on gas diffusion electrodes is also a powerful synthesis tool since an appropriate electrode material is selected. Methane fed (TiO$_2$/RuO$_2$)/PTFE anodes have been used for the synthesis of methanol with simultaneous oxygen evolution. Once more, selectivity for methanol over formic acid is a function of applied potential.

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This lecture presents the fundamentals and some interesting applications of the solar photoelectro-Fenton (SPEF) method for the destruction of organics in wastewaters. This electrochemical advanced oxidation method is an environmentally friendly technique where hydrogen peroxide is continuously supplied to an acidic contaminated solution from the two-electron reduction of oxygen injected to a gas-diffusion cathode:

\[ \text{O}_2(g) + 2 \text{H}^+ + 2 e^- \rightarrow \text{H}_2\text{O}_2 \]  

(1)

The oxidizing power of electrogenerated \( \text{H}_2\text{O}_2 \) is then strongly enhanced by adding a small quantity of \( \text{Fe}^{2+} \) catalyst to the solution to give \( \text{Fe}^{3+} \) and hydroxyl radical (\( \cdot \text{OH} \)) by the well-known Fenton’s reaction:

\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot \text{OH} + \text{OH}^- \]  

(2)

An undivided cell is used to oxidize the pollutants by both, \( \cdot \text{OH} \) formed from reaction (2) and \( \text{M}(\cdot \text{OH}) \) produced from water oxidation at a high \( \text{O}_2 \)-overvoltage anode by reaction (3):

\[ \text{M}(\text{H}_2\text{O}) \rightarrow \text{M}(\cdot \text{OH}) + \text{H}^+ + e^- \]  

(3)

The SPEF process also involves the additional irradiation of the treated solution with sunlight to favor: (i) the photoreduction of \( \text{Fe(OH)}^{2+} \), which is the predominant \( \text{Fe}^{3+} \) species in acid medium, to \( \text{Fe}^{2+} \) and more \( \cdot \text{OH} \) by photo-Fenton reaction (4), and (ii) the photolysis of complexes formed between \( \text{Fe(III)} \) and final carboxylic acids such as shown for oxalic acid via reaction (5):

\[ \text{Fe(OH)}^{2+} + h\nu \rightarrow \text{Fe}^{2+} + \cdot \text{OH} \]  

(4)

\[ \text{Fe(C}_2\text{O}_4)_{n}^{(3-2n)} + h\nu \rightarrow 2 \text{Fe}^{2+} + (2n-1) \text{C}_2\text{O}_4^{2-} + 2 \text{CO}_2 \]  

(5)

Oxalic acid is formed during the oxidation of most aromatics and the fast photodecarboxylation of \( \text{Fe(III)} \)-oxalate complexes (\( \text{Fe(C}_2\text{O}_4)^+ \), \( \text{Fe(C}_2\text{O}_4)_2^- \) and \( \text{Fe(C}_2\text{O}_4)_3^{3-} \)) favors their decontamination.

Exemples on the good oxidation ability of SPEF are presented for solutions of: (i) salicylic acid and the aminoacid \( \alpha \)-methylphenylglycine using small electrolytic cells with a Pt or boron-doped diamond (BDD) anode and and \( \text{O}_2 \)-diffusion cathode, all them of 3 cm² area, and (ii) the herbicide mecoprop and \( o-, m-, \) and \( p \)- cresols using a flow plant of 2.5 l with a filter-press cell containing BDD and \( \text{O}_2 \)-diffusion electrodes of 20 cm² area, coupled to a solar photoreactor with 600 ml of irradiation volume. Treated solutions were prepared with 0.05 M \( \text{Na}_2\text{SO}_4 \) and 0.25-1.0 mM \( \text{Fe}^{2+} \) at pH 3.0 and
electrolyses were carried out by applying a constant current density between 25 and 150 mA cm\(^{-2}\). Comparative trials with electro-Fenton (EF) in the dark were also made to confirm the synergistic effect of sunlight during the SPEF process. While in the EF method a slow, but complete mineralization of all contaminants is found using a BDD anode due to the efficient oxidizing action of homogeneous \(^{\bullet}\)OH and BDD(\(^{\bullet}\)OH), the SPEF treatment yields a much faster decontamination with a Pt or BDD anode because of the efficient photodecomposition of Fe(III) complexes with UVA irradiation supplied by solar light. The efficiency of all degradation processes increases strongly with rising pollutant concentration and decreasing current density. The decay kinetics for all initial pollutants and the evolution of their aromatic by-products were followed by reversed-phase HPLC chromatography, whereas generated carboxylic acids were identified and quantified by ion-exclusion HPLC chromatography. Detection of reaction intermediates allows the proposal of a plausible sequence for the mineralization of each initial pollutant. In all cases the ultimate product is oxalic acid, which forms Fe(III)-oxalate complexes that can be destroyed with BDD(\(^{\bullet}\)OH) in EF, but much more rapidly photolyzed to CO\(_2\) in SPEF. Other final acids like acetic or oxamic are also formed, undergoing slower destruction. The treatment of 128 mg l\(^{-1}\) of all cresols with 0.5 mM Fe\(^{2+}\) by SPEF in the flow plant leads to an energy cost for total mineralization as low as 6.6 kWh m\(^{-3}\) at 25 mA cm\(^{-2}\), showing the viability of this procedure for its possible application to wastewater remediation at industrial scale.
Hot-Filament Chemical Vapor Deposition Method to Fabricate Stable Diamond Film Electrodes for Wastewater Treatment

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Growing diamond film on a titanium substrate is a challenge. The major problem is the stability of the diamond film form. Since titanium metal is an ideal material for electrode fabrication, especially for DSA type electrodes, the research on the improvement of working life of boron-doped diamond film on titanium (Ti/BDD) remains a hot topic.

By using proper pretreatment and a suitable combination of precursor gases, my research laboratory has been able to fabricate Ti/BDD electrodes using hot-filament chemical vapor deposition method with accelerated working life over 260 hours (measured under conditions of 10,000A/m² in 3M H₂SO₄). The accelerated service life was further improved to 320 hours by deposition a layer of silicon between Ti and BDD layers.

A recent innovation by having staged substrate temperatures lead to the producing of the Ti/BDD electrode with an accelerated service life over 800 hours. This great improvement was found to be attributed to the formation of a TiC layer at lower substrate temperature during the first stage of deposition, followed with a high quality BDD layer deposited at the latter stage at higher substrate temperature.

The Ti/BDD electrodes can be utilized as electrochemical sensors of measuring pollutants, or work as anodic electrode in electro-oxidation of various pollutants such as acetic acid, maleic acid, dyes, phenols, etc.
Electrically Enhanced Transformations on Clay Surfaces

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At electrochemical surfaces, such as that of a colloid or clay particle, double layer charging, electrochemical reactions, and surface conduction can take place simultaneously (Kortum and Bockris, 1951). Clay particles can be thought of as micro-electrodes possessing a compact Stern layer and a diffuse layer, which mediates Faradaic reactions. As the donated (or accepted) electrons pass across the electrical double layer into and out of the bulk fluid, species in the solution are transformed via oxidation-reduction reactions. This effect may become significant for polarizable surfaces due to strong sorption of exchangeable species by the double layer, as in the case of contaminated sediments.

When an external electric field is applied to water saturated clay of high ion concentration in the pore fluid, given the incompatibility between the conductivity of two conducting layers in the mixture: (1) the DDL of clay particles with low conductivity, and (2) the surrounding electrolyte solution (pore fluid) with high conductivity, a large electrical potential is induced across the DDL. This results in compression of the DDL, hence rendering the interface a capacitor (Bard and Faulkner, 1980). The compression of DDL occurs in the diffused section, resulting in higher charge density, and an increase the intensity of the electric field in the Stern layer. As the potential of the clay surface, acting as a “micro-electrode” is swept from its initial value to a new one, if a species is present in the DDL whose formal potential for redox lies between those values, electrochemical transformation of the species will be observed. This observation can be measured as a shift in the formal potential with respect to the solution potential.

Considering the overall conversion with the Nernst equation, the externally applied potential difference, $\Phi_{\text{applied}}$ necessary to drive the redox reaction at the polarizable surfaces of clay particles can be written as:

$$\Phi_{\text{applied}} = \Phi_r + \left[ \frac{q}{C} \right] + (\Phi_d \pm \eta)$$

where $\Phi_r$ is the Ohmic potential in the pore fluid. An equivalent electrical circuit can be used to model the soil electrolyte system described by the equation above.

Influence of operative parameters on the electrochemical incineration of oxalic acid

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Recent researches have demonstrated that electrochemical methods offer an attractive alternative to traditional routes for treating wastewaters containing toxic or/and refractory organic pollutants [1,2]. The effectiveness of the electrochemical treatment depends on many factors including the electrodic material. Synthetic boron diamond (BDD), with its high anodic stability and wide potential window, is considered to be a promising material for the direct combustion of organics in wastewater [3]. Hence, the electrochemical incineration of several compounds at BDD electrodes has been investigated by many researchers. It has been shown that carboxylic acids, common intermediates of the oxidative degradation of several compounds, and particularly the oxalic acid (OA), are rather stable [4-7] and are often mineralized at longer times with respect to the starting substrates [8-9]. Hence, the investigation of the electrochemical incineration of these compounds at BDD has attracted recently a certain interest. In the present work, the anodic incineration of OA at BDD has been investigated, both under potentiostatic and amperostatic alimentation, with the aim of studying in a systematic way the influence of numerous parameters, such as the working potential (in potentiostatic electrolyses), the current density (in amperostatic ones), the flow rate, the OA concentration, the nature of the supporting electrolyte, the presence and the concentration of NaCl and the pH on the performances of the process and to individuate the optimal operative conditions. Furthermore, for a comparison, many experiments were performed also at other anodes.

Addressing Environmental Challenges
Electrochemically Using Diamond Electrodes

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Electrically conducting diamond thin films, both the microcrystalline and nanocrystalline forms, have been successfully used as dimensionally stable anodes for the electrochemical destruction of organic and inorganic chemical waste, and as electrodes for water quality monitoring. The use of diamond as an electrochemical electrode dates back to the late 1980’s but it has only been within the last 5-10 years that much of the seminal research has been conducted with this unique and enabling material. Boron-doped, polycrystalline diamond is “complex” in terms of its physical, chemical and electrical properties. Several factors influence the electrical conductivity of diamond and, hence, the charge transfer kinetics at the solid-liquid interface. For example, electron-transfer kinetics at boron-doped diamond are controlled by the (i) potential-dependent density of electronic states, (ii) surface chemistry, (iii) morphology and microstructure, (iv) defect density, (v) nondiamond carbon impurity content and (vi) the structure of the electric double layer that forms at the electrified electrode-solution interface. The extent to which any of these factors affects the electrochemical response very much depends on the reaction mechanism for the particular redox system. This presentation will review some of the key accomplishments with diamond electrodes over the past two decades in terms of their use electrochemically to address environmental challenges. The focus will be on applications in remediation and water quality monitoring. The last part of the presentation will explore what is known about how the physicochemical properties of the material
Catalyst and Electrode Designs for CO-tolerant PEM Fuel Cell Anodes

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Proton exchange membrane fuel cells (PEMFC) are efficient and non polluting electrical power sources based on the oxidation of a fuel (hydrogen, small organic molecules) in the anode and the reduction of oxygen in the cathode. However, there are still significant challenges for their complete development, and one of them is the large potential loss in the conventional Pt anode caused by low levels of carbon monoxide, when reformed hydrogen is used as the anode reactant. In this work, the performance of H₂/O₂ proton exchange membrane fuel cells (PEMFC) fed with CO-contaminated hydrogen is discussed for anodes with M/C materials (where M = Mo, Cu, Fe e W) in the gas diffusion layer and Pt/C, PtRu/C, PtFe/C, PtMo/C, PtW/C, PdPt/C, and PdPtRu/C in the catalyst layer. Materials have been characterized by XRD (X-ray diffraction) and in situ XANES (X-ray absorption near edge structure) and EXAFS (extended X-ray absorption fine structure) measurements. Electrochemical investigations have been made with cyclic voltammetry and steady state single cell polarization measurements with the catalysts forming gas diffusion electrodes and the system supplied with pure oxygen in the cathode and hydrogen, without and with 100 ppm CO, in the anode. DEMS (Differential electrochemical mass spectrometry) has been employed to verify the formation of CO₂ at the PEMFC anode outlet.

The CO tolerance of the alloyed materials is discussed in terms of the so called bifunctional or electronic mechanisms, and the possibility of occurrence of the water gas shift process [1]. For most bimetallic electrocatalysts (PtRu/C, PtFe/C, PtMo/C, PdPt/C, and PdPtRu/C), which presented high CO tolerance, DEMS results have shown that the production of CO₂ starts at lower hydrogen electrode overpotentials as compared to Pt/C, confirming the occurrence of the bifunctional mechanism. On the other hand, XANES results indicate an increase in the Pt 5d-band vacancy for the bimetallic catalysts, particularly for PtFe/C, this leading to a weakening of the Pt-CO bond, helping to increase the CO tolerance (the electronic effect). For PtMo/C and PtRu/C, the formation of CO₂ is observed even when the cell is at open circuit, confirming some elimination of CO by a chemical process, most probably the water gas shift reaction. For the PdPt/C catalysts, no CO₂ formation is seen at the PEMFC anode outlet, indicating that the CO tolerance is improved due to the existence of more free surface sites for H₂ electrooxidation, probably due to a lower Pd-CO interaction compared to pure Pd or Pt. Finally, it is seen that the diffusion layers formed by Mo/C e W/C introduce good CO-tolerance, and this was attributed to the CO removal by parallel occurrence of the water-gas shift reaction and the bifunctional mechanism.

Reference
New concepts for in-situ environmental electroanalysis

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This talk will review new concepts for in-situ environmental analysis based on no electrochemical sensing strategies. Several new strategies are covered, including use of remotely deployed sensors, submersible analyzers, and adaptive (on-demand) systems. These devices offer a fast return of the chemical information in a safe and timely manner. The new concepts will be discussed in connection to the in-situ monitoring of priority inorganic and organic contaminants. The challenges facing development of such reliable in-situ electrochemical sensors and potential solutions will be discussed. An adaptive network of such widely distributed in-situ sensors should have an enormous impact upon pollution control and prevention, as they should lead to a substantially more effective and economic monitoring of priority pollutants.
Electrocatalytic application of a sol–gel derived carbon ceramic electrode based on cobalt(II) tetrasulfonated phthalocyanine

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A new carbon-ceramic electrode was prepared by dispersing cobalt (II) tetrasulfonated phthalocyanine (CoPcTs–4) absorbed on 3-n-propylpyridinium chloride silsesquioxane in a stannic/silica/C-graphite sol-gel matrix. The composition of the resulted material, determined by X-ray fluorescence, is as follow: 6.8 % SnO2, 39 % SiO2 and 0.5 % of CoPcTs–4. The BET surface area was found to be 104 m2 g–1, with a pore diameter of 26 Å. The electrode is prepared by pressing finely divided powdered SiO2/SnO2/C-graphite/(SiPy)+CoPcTs–4 in a format disk and glued to a glass tube as shown in figure 1A. A surface characterization was carried out using SEM-EDS and AFM (see the micrographs in figures 1B and 1C).

Figure 1. A) Picture of the electrode SiO2/SnO2/C-graphite/(SiPy)+CoPcTs–4, B) SEM image, C) AFM micrograph.

The electrocatalytic activity for the oxidation of oxalic acid and nitrite was tested. Figure 2 exhibits the cyclic voltammograms after successive additions of sodium nitrite to 1 mol L–1 KCl in 0.1 mol L–1 in phosphate buffer solution (pH = 7). Similar behavior was observed for oxalic acid; in both cases, the limit of detection and sensitivity were determined. The electrode shows a renewal surface, the variation coefficient (VC) for ten successive polishing steps is 2.5%.

Figure 2. Cyclic voltammograms at different concentrations of sodium nitrite (4.0 x 10–5 – 1.7 x 10–3 molL–1) in 1 mol L–1 KCl (0.1 mol L–1 in phosphate buffer solution, pH = 7), scan rate: 20 mV s–1.
An Electrochemical DNA Biosensor Developed on a Polypropylene Imine Dendrimer-Gold Nanocomposite

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Electrochemical DNA biosensors (EDB) exploit DNA’s versatile chemical and biochemical reactions and specificity towards its complementary strand to generate measurable electrical signals. EDBs therefore have promising applications for environmental monitoring, disease screening, toxin detection in agricultural products, water and biomedical samples. In the quest for suitable immobilization layer for better sensor performance, we have developed a polypropylene imine (PPI) dendrimer and gold nanoparticle (AuNP) nanocomposite platform for the immobilisation of a thiolated 21-base single strand probe DNA on glassy carbon electrode (GCE) as a biosensor for the detection of target DNA in samples. The PPI/AuNP nanocomposite platform was electrodeposited on GCE from a ratio mixture of 5 mM PPI and 3 mM HAuCl₄ in saline solution by cyclic voltammetry from -0.35 V to 0.1 V. To develop the EDB, 15 µL of 2 µM probe DNA in phosphate buffer solution (PBS) pH 7.2 was immobilized on the nanocomposite platform by drop coating for 2 hr at room temperature. The EDB was used to sense DNA targets in 1 mL saline PBS solution under hybridisation condition of 40 °C for 30 min. The nanocomposite, biosensor and its responses to DNA targets were characterised by voltammetry, electrochemical impedance spectroscopy (EIS) in Fe(CN)₆³⁻/⁴⁻ solution, transmission electron microscope, subtractively normalized interfacial FTIR, and UV spectrophotometry. Results showed that AuNP (ca 10 nm) was electrodeposited simultaneously with the PPI. The PPI capped the AuNP and adsorbed very strongly on the GCE surface via C-NH₂ chemistry. The PPI/AuNP platform demonstrated good conductivity and a reversible electrochemistry (E = 0.039 V) due to the dendrimer with formal potential E° = 0.23 V in PBS and also catalysed Fe(CN)₆³⁻/⁴⁻ redox chemistry. Voltammetric current was largely increased as the probe DNA was immobilised and adsorbed on the platform through Au-S linkage and was stable when kept in PBS at 4 °C. The EIS raw data was validated by Kramers-Kronig transform and fitted using complex non-linear regression least-squares method from a circuit model. Significant increase in current and charge transfer resistant (Rct) were observed after each hybridisation step and a plot of Rct against log of target DNA concentrations showed linearity in the range 10 pM (10⁻¹¹ M) to 5 nM with correlation of 0.9899, depicting the biosensor’s very high sensitivity. The biosensor was stable and selective toward non complementary and mismatch bases DNA targets. The platform’s reversibility and conductivity also allowed voltammetric determination in PBS giving the sensor a dual probe advantage.

References:
A New Type of Polymer-Based Solid-State Reference Electrode

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A new type of polymer-based solid-state reference electrode is proposed. The reference electrode is constructed by electrodeposition of poly(3,4-ethylenedioxythiophene) (PEDOT) on a glassy carbon disk electrode and by further coating the PEDOT film by a plasticized PVC membrane containing a moderately lipophilic salt, such as tetrabutylammonium tetrabutylborate (TBATBB). The construction thus resembles that of a solid-contact ISE, except for the composition of the plasticized PVC membrane. Our hypothesis is that the moderately lipophilic cations (TBA⁺) and anions (TBB⁻) with similar size and mobilities are slowly released from the plasticized PVC membrane, which prevents hydrophilic anions and cations in the aqueous sample solution from entering the PVC membrane. This means that the electrode potential is mainly determined by the activity of TBA⁺ and TBB⁻ close to the PVC/solution interface. This results in an electrode potential that is relatively independent of the composition of the aqueous sample solution. The role of PEDOT is to act as ion-to-electron transducer between the ionically conducting plasticized PVC membrane and the electronically conducting glassy carbon substrate.

The hypothesis was critically tested by measuring the equilibrium (open circuit) potential of the solid-state reference electrode vs. a conventional Ag/AgCl/KCl(3 M) electrode in sample solutions containing ions with different concentrations, mobilities and lipophilicities. The polymer-based solid-state reference electrodes tested so far show relatively stable potentials, and further optimization of the membrane composition is in progress.

The construction of the solid-state reference electrode is cost-effective and highly compatible with that of solid-contact ISEs. The new type of solid-state reference electrode may therefore be useful in such applications where the main goal is to determine approximate activities of ions in the area of environmental analysis.
Polypyrrole Modified with Supramolecular Cages: Applications in the Electrochemical Sensing of Herbicides

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In recent years there has been considerable interest in the development of new environmental technologies for both the monitoring of environmental pollutants and the remediation, or removal, of such pollutants from the environment. Herbicides are an example of one family of well-known pollutants that can be found in the environment. Paraquat, in particular, is a broad-spectrum herbicide that continues to be used in some countries for the control of weeds and grasses, but it is also highly toxic. A number of chemical approaches have been used to determine the concentration of paraquat. These include spectrophotometric [1], chromatographic [2] and the use of various electrode surfaces [3]. These latter electrochemical approaches offer considerable advantage in terms of simplicity and sample preparation.

In this paper, we show that cyclodextrin-doped polypyrrole films can be used for both the electrochemical sensing and trapping of paraquat and other viologen compounds. The cyclodextrins can be readily incorporated within polypyrrole during the electropolymerization of the pyrrole monomer to give a simple and cheap sensor. The presence of the cyclodextrin was confirmed using differential scanning calorimetry (DSC), while cyclic voltammetry and electrochemical quartz microbalance measurements showed that the material behaved as a cation exchanger. The large cyclodextrin was immobile and was permanently incorporated within the polymer matrix.

Paraquat (methyl viologen), ethyl viologen and benzyl viologen were detected at the modified electrodes using cyclic voltammetry, differential pulse voltammetry and square wave voltammetry. Evidence for the formation of an inclusion complex between the cyclodextrin and paraquat was obtained using cyclic voltammetry. The interactions between the cyclodextrin and the benzylviologen were more complex and our data suggest the formation of a strong adsorbed layer of the reduced viologen at the modified electrode.

In addition to the sensing of paraquat, the cyclodextrin-doped polypyrrole was observed to trap the paraquat, opening up the possibility of using these materials for the remediation and removal of paraquat from the environment.

References
Synthesis of bi-layer modified carbon ultramicroelectrodes for the analysis of methyl-parathion and its metabolites

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The development of electrochemical systems for the quantification of entropic organic pollutants has been the subject of intense research effort over the last ten years. The electrode surface modifications tend to increase the sensitivity and selectivity of the oxido-reduction reactions of some pesticides families as organophosphorous [1], carbamates [2], phenols [3], and thiourea [4]. As catalytic systems under electropolymerized form, metallophthalocyanines are well adapted to the electrochemical analysis allowing, in most of the cases, the amplification of the amperometric signal [5]. In that way, the improvement of the molecular activation mediated by metal based complexes led us to investigate their properties in the field of analysis in environmental matrices of organophosphorous compounds [6].

This work led to the setting up of two microsensors judiciously combining electroformation of nickel phtalocyanine (NiTSPc) and electropolymerization of para-phenylenediamine (p-PD) for the quantitative analysis of methyl-parathion (MPT) and para-nitrophénol (p-NP). The analysis of p-NP is essential because of the short livetime of organophosphorous compounds. The control of the film deposition conditions on our home made ultra-micro-electrodes (UME) allows to selectively quantify both MPT and p-NP. Hydrophobic-hydrophilic interactions between the p-PD film covering the electrode and MPT prevents electronic transfer even when high concentration of MPT is used. Moreover, the bilayer covering seems also to be a key factor to preconcentrate the pollutants before analysis. This observation could be explained by the increase of the electrode surface during the deposition of p-PD as characterised by AFM analysis.

The coupling of those modified electrodes with Square Wave Voltammetry acquisition mode lowers the detection limit of this family compound to 40 µg.L⁻¹ (150 nM). The final aim is the setting up of transportable tools for the monitoring of entropic pollutants concentration in aquatic media.

Références

Electrochemical strategies for detection of Salmonellosis

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Salmonellosis is one of the most hazardous foodborne illnesses which is caused by the *Salmonella* bacteria. It causes severe public health problem all over the world, thus, a comprehensive farm-to-table approach to food safety is necessary. Due to the expected global warming the probability for Salmonellosis will rise, and hence fast and reliable methods for the control of the overall food chain become important.

We propose two strategies for detection of DNA which is specific for *Salmonella* bacteria. The first method is based on monitoring hybridization via a DNA-attached enzyme, while in the second approach intercalation of compounds into double-stranded DNA is used for monitoring complementary hybridization.

Labelling the target-DNA with biotin is offering the possibility to further couple a streptavidine/alkaline phosphatase conjugate to the hybridized DNA [1]. By enzymatic cleavage of p-aminophenylphosphate electrochemically active p-aminophenol is generated, which is detected in an amplified redox cycling architecture by means of scanning electrochemical microscopy (SECM). For this, a DNA-modified ultramicroelectrode is approached into close proximity to an electrode surface for substrate recycling. Results concerning the assay architecture and amplification strategies will be demonstrated.

Furthermore, label-free and highly sensitive detection of DNA hybridization is very attractive for the development of DNA chips potentially avoiding initial PCR amplification, which has to be performed in the case of labelled DNA. Here, interactions between suitable intercalators (Actinomycin D, proflavine) and single as well as double stranded DNA was studied by means of electrochemical impedance spectroscopy (EIS). For this purpose, monolayers of thiol-modified ss-DNA were assembled on a gold electrode. The influence of the modified surface on the electron-transfer properties of suitable reversible redox mediators such as Fe(CN)$_6^{3-/4-}$ or Ru(NH$_3$)$_6^{2+/3+}$ was investigated. Changes in physical properties of DNA upon hybridization and subsequently intercalation were observed by means of EIS and can be used as a basis for a highly sensitive DNA assay. Results concerning assay architecture will be presented.

References:

Microsomal CYP3A4 Nanobiosensor for the Determination of 2,4-dichlorophenol - an Endocrine Disruptor Compound

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The pivotal role of cytochromes P450 (CYP450s) in detoxification of bioactive compounds and hydrophobic xenobiotics, (medicines, drugs, environmental pollutants, food supplements, steroids, etc) cannot be over-emphasized. In this study we present the development of cytochromal biosensor for the determination of endocrine disruptors and antiretroviral drugs. As a class II microsomal b-type heme enzyme, CYP3A4 requires the obligatory presence of electron transfer donor redox protein, NAD(P)H, and cytochrome b5 for its physiologic functions. Optimal reconstitution assays preferably involves vesicle forming phospholipids, detergents and specialized reducing agents. Biosensor offers the possibility of observing direct electron transfer reaction of CYP3A4 without the enzyme requiring its co-factors for its redox catalytic activity. In this study, a nanobiosensor based on the immobilization of CYP3A4 in supported lipid/protein membranes was developed. Optimum electron transfer was ensured by monolayer assemblies of interfacial enhancers consisting of conductive polypyrrole and derivatized metal nanoparticles. Monomeric enzyme configuration consisted of 1:1:1 mixture of L-α-dilaoroyl-, L-α-dioleyl-glycero-3-phosphocholines and phosphatidyl serine lipid bilayer. An electrochemically synthesized conducting polypyrrole-gold nanoparticle on glassy carbon electrode (GCE) surface was used as base conductive-support for the assembly of the consecutive layers. This was followed by the deposition of polyelectrolyte-gold nanoparticle layers. The polyelectrolyte was either lysine or mercaptosuccinic acid. Mixed lipid vesicles were then spontaneously fused onto the polyelectrolyte-Au nanoparticle surface with or without the presence of calcium ions. Purified human recombinant cDNA-expressed CYP3A4 was assembled on modified GCE by cross-linking with glutaraldehyde. The incorporation of CYP3A4 in lipid vesicle was done before or after the polyelectrolyte-gold nanoparticle fusion. Electron transfer characteristics of the bioelectrode was elucidated by anaerobic and aerobic cyclic (or square wave) voltammetry. The polyelectrolyte-stabilised gold nanoparticle was calculated to be 10Å. The sensor and was applied in the determination of 2,4-dichlorophenol (an endocrine disruptor and hepatocarcinogen) and indinavir (an antiretroviral drug.
Development of novel nanostructured electrode materials for electrocatalytic and bioelectrocatalytic analytical determinations

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Monolayers of alkanethiolates are capable of passivating gold nanoparticles and producing alkanethiolate monolayer protected clusters of gold. We have explored the ability of polyoxometallates (phosphotungstate, phosphomolybdate) to form analogous self-assembled monolayers on metal (e.g. Pt or Au) nanoparticles (ca. 2-7 nm) or carbon nanotubes. Such polyoxometallate modified nanostructures can be linked together by ultra thin conducting polymer (polyaniline, polypyrrole, PEDOT) bridges. The network films composed of polyoxometallates, ultra-thin conducting polymer layers and platinum or carbon nanostructures can produce interfaces with specific electrocatalytic properties towards reduction of such inert reactants as oxygen, hydrogen peroxide or bromate.

Electrocatalytic systems that would be useful in biological media, or the systems utilizing biocatalysts (enzymes), have to operate in neutral solutions. Recently, there has been growing interest in the fabrication of stable highly effective bio-electrocatalytic systems for oxygen reduction, particularly with respect to potential applications in biofuel cells. Unless highly specific and expensive enzymes belonging to a group of proteins with the copper active centers, such as bilirubin oxidase or laccase, are considered, the reduction of oxygen in neutral media is a two-step process suffering from the formation of hydrogen peroxide as undesirable intermediate product. Although the above enzymes are capable of the effective four electron reduction of oxygen to water in neutral media, and significant progress have recently been made in their practical utilization, there is a need to look for alternate bio-electrocatalytic systems. To facilitate electron transfers between the electrode surface and the redox protein centers, the concept of co-deposition of multi-walled carbon nanotubes (CNTs) within the bio-electrocatalytic film has been recently proposed. Good electronic conductivity of CNTs, together with their mechanical stability, have made them attractive for potential applications in electrochemistry and bio-electrochemistry. Representative examples include cases of electrocatalytic reductions of hydrogen peroxide and oxygen. To stabilize composite films, we utilize multi-walled carbon nanotubes, that have been modified with ultra-thin layers of organic (e.g. 4-(pyrrole-1-yl) benzoic acid or ABTS) and inorganic metal oxo compounds. We expect here attractive interactions between anionic adsorbates and positively charged domains of the enzymatic sites. The other important issues are stability and mediating capabilities of adsorbates.
Lignin and its derivatives as multifunctional electrocatalysts

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Lignin which is after cellulose the second most abundant biopolymer in the environment is generally thought to be a statistic copolymer formed upon the oxidation/dehydrogenation of three lignin precursors i.e. coumaryl, coniferyl and sinapyl alcohols. Thus formed copolymer consists of substituted C₉ units (6 aromatic and 3 propene carbons) interconnected by C-O (Scheme I) [1].

Although lignin was found to undergo variety of electrochemical reactions both during oxidation [2] and reduction [3] it found only limited application in practical or electroanalytical electrochemistry [4].

In this communication, the chemical and electrochemical properties of different commercially available lignins will be briefly discussed. Next, the possible applications of lignins as the modifiers of electrodic surfaces will be presented and discussed in more details. These applications include the electrocatalytic oxidation of ascorbic acid, NADH and electroreduction of different oxoanions. The discussion will be supported by the author’s data published so far [5]. Finally, possibilities of further chemical modification of lignins immobilized on the electrode surface using various strategies will be discuss on the basis of their chemical character. Some preliminary experimental data will be presented as well.

In conclusion, it will be shown that lignin (a byproduct from wood industry) appears to be cheap and valuable modifier of electrodic surfaces and probably will find wider applications in the design of chemically modified electrodes for electroanalytical purposes owing to low cost materials, easy of preparation and valuable properties.

In situ Evaluation of Hazard Compounds-DNA Interactions Using an Electrochemical DNA-Biosensor

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The need for the analysis of gene sequences, oxidative damage to DNA and the understanding of DNA interactions with molecules or ions has led to the development of electrochemical DNA-biosensors. The detection of hazard chemical compounds that cause irreversible damage to DNA is very important, as they may lead to hereditary or carcinogenic diseases. The electrochemical DNA-biosensor is a complementary tool for the study of biomolecular interaction mechanisms of hazard compounds with DNA, enabling the screening and evaluation of the effect caused to DNA by health hazardous compounds and oxidising substances.

A critical issue in the development of an electrochemical DNA-biosensor is the sensor material and the degree of surface coverage. AFM was used to characterize the process of adsorption of DNA on a highly oriented pyrolytic graphite (HOPG) electrode surface using different concentrations of DNA and adsorption procedures [1].

A dsDNA electrochemical biosensor, employing differential pulse voltammetry, was used for the in situ electrochemical evaluation of Pd^{2+}, Pb^{2+}, Cd^{2+} and Ni^{2+} interaction with dsDNA, recognized as changes in the oxidation peaks of guanosine and adenosine bases [2]. Heavy metal ions, lead, cadmium and nickel, are well known carcinogens with different natural origins and their direct mode of action is still not fully understood.

The results confirm that Pd^{2+}, Pb^{2+}, Cd^{2+} and Ni^{2+} bind to dsDNA, and that this interaction leads to different modifications in the dsDNA structure. The different interaction of Pb^{2+} with dsDNA, leading to oxidative damage, compared with Pd^{2+}, Ni^{2+} and Cd^{2+}, which only causes conformation structural changes, will be shown.

Using homopolynucleotides of guanine and adenine it has been proved that the interaction between Pb^{2+} and DNA causes oxidative damage and preferentially takes place at adenine-containing segments, with the formation of 2,8-dihydroxyadenine, the oxidation product of adenine residues and a biomarker of DNA oxidative damage. The Pb^{2+} bound to dsDNA can still undergo oxidation.

While no oxidative damage to dsDNA by Pd^{2+}, Cd^{2+} and Ni^{2+} was observed, the results indicate that these metal ions also affect the double helix structure of dsDNA, causing conformational changes, destabilizing the double helix, and opening the way to initiation of the action of other oxidative agents.

The sensitivity of the multilayer dsDNA electrochemical biosensor also offers the possibility to follow the interaction of carcinogenic compounds and pesticides with DNA under different conditions [1].

Electrochemical Monitoring of Biological Reactions Using a Novel Nano-Bio-Chip Array

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We developed an innovative electrochemical ‘lab on a chip’ system that contains an array of nano volume electrochemical cells on a silicon chip. Each of the electrochemical cells can be monitored simultaneously and independently, and each cell contains three embedded electrodes, which enable performance of all types of electrochemical measurements. In order to show the wide range of applications that can be beneficial from this device, biological components including chemicals, enzymes, bacteria and bio-films were integrated within the nano-chambers for various applications. The miniaturized device was designed in two parts to enable multiple measurements: a disposable silicon chip containing an array of nano-volume electrochemical cells that are housing the biological material, and a reusable unit that includes a multiplexer and a potentiostat connects to a pocket PC for sensing and data analysis.

This electrochemical 'lab on a chip' was evaluated by measuring various biological reactions including the microbial current response to toxic chemicals. These bacteria were genetically engineered to respond to toxic chemicals by activating cascade of mechanisms, which leads to the generation of electrical current. During the measurement period the bacteria remained active, enabling cellular gene expression and enzymatic activity to be monitored on line. A measurable current signal, well above the noise level, was produced within 5 minutes of exposure to heavy metals, or organic toxicants, such as phenol or hydrazine.

The same system was applied in a rapid, sensitive and high-throughput detection of colon cancer cells response to differentiation therapy. Differentiation inducing agents such as butyric acid and its derivatives were introduced to a miniature colon cancer samples. The efficacy of each of the differentiation inducing agents was evaluated through electrochemical detection of the cellular enzymatic activity level, while reappearance of normal enzymatic activity denotes effective therapy. The results demonstrate the ability to evaluate simultaneously multiplex drugs effect on miniature tumor sample (~15 cells) rapidly (5 min) and sensitively, with quantitative correlation between the cancer cell number and the induced current. Utilizing nano-volume analytical device is of special interest in clinically relevant samples since it requires less tissue for diagnostics, and enables high-throughput analysis and comparison of various drugs effect on one small tumor sample, while keeping uniform biological and environmental conditions.

In Summary, we demonstrate sensitive measurements on extremely small samples without special cell treatment prior to the insertion into the chip.
Renewable Surface Microelectrode System for Research and Electroanalysis

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In this work, a design and preparation of the renewable cleaved surface microelectrode and the measurement system have been worked out, suitable for replacement of the dropping mercury electrode. Non-toxic metal bismuth has been used as a working electrode in this system, but other materials can be used also. For the bismuth cleaved capillary electrode (BiCCE) system, the surface renewal has been generated by breaking quickly a small cylinder on a top of a bismuth filled glass capillary with the help of a simple mechanism, causing the cleave of brittle bismuth at room temperature. This process can be done repeatedly as the 50 micrometer diameter electrode is several centimetres long. For example, the very pure surface formed enables to measure the zero charge potential values at the moment of the electrode cleavage. The electrochemical response of the BiCCE has been characterized using cyclic voltammetry, electrochemical impedance and chronocoulometry methods, recorded in selected electrolytes. Some examples of electrochemical detection with the BiCCE are shown like trace metal stripping (similarly to bismuth film electrodes deposited on carbon [1,2]) and flow-injection analysis. The AFM images of the cleaved surfaces of these microelectrodes are similar to the cleaved Bi(111) massive electrode [3].

References
Electrochemical Characterization of Some Stages of the Acid Rock Drainages (ARD)

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Metal recovery is one of the main activities in the world; however, it generally ends with mining solid residues. This kind of residues is exposed to the open air, having the pyrite and arsenopyrite as the main components in some cases. Thus, the oxidation or dissolution of these sulfide minerals are responsible for the generation of acid rock drainage (ARD) during weathering [1-3]; here the importance of electrochemistry and surface chemistry of arsenopyrite and pyrite minerals for understanding the mineral behavior and, with this information, the possibility of proposing technological alternatives in the treatment of this residues. On the other hand, the electrochemical characterization using cyclic voltammetry with carbon paste electrodes containing mineral particles (CPE-Mineral) has been an effective tool to demonstrate the overall reactivity (i.e. dissolution factibility) of the minerals, at the last decade. In this work, a comparative voltammetric study has been performed on a high purity pyrite mineral (98.8%) and arsenopyrite mineral (content of 86.95% arsenopyrite, 11.84% pyrite), in order to identify the stages where the ARD is generated due to the oxidation processes of the pyrite and arsenopyrite and the repercussion on their reactivity. Results of this work showed that the anodic behavior of the pyrite was according to literature [3]; however in arsenopyrite mineral the voltammetric studies showed the oxidation stages where the ARD is generated, also some of the products of the arsenopyrite oxidation were identified. In a first stage the oxidation was to Fe\textsuperscript{2+}, realgar (As\textsubscript{4}S\textsubscript{4}), H\textsubscript{2}AsO\textsubscript{3}, S\textsuperscript{0} and H\textsubscript{2}AsO\textsuperscript{4} \textsuperscript{-} [4]. In a second stage the arsenopyrite and pyrite were oxidized to FeOOH\textsubscript{3}, and S\textsuperscript{0}, followed by oxidation of S\textsuperscript{0} to SO\textsuperscript{4} \textsuperscript{2-} and scorodite (FeSO\textsubscript{4}.2H\textsubscript{2}O) formation.

The analysis by SEM and EDS to surfaces of the electrodes with the mineral (CPE) modified by cronoamperometry, was carried out to support the reaction mechanisms. Meanwhile, to more negative potentials the recombination of FeAsS and the reduction to elemental arsenic [5] does not occur due to the formation of scorodite (FeSO\textsubscript{4}.2H\textsubscript{2}O) by a chemical reaction. On the other hand, the results indicate that the electrochemical reactivity of pyrite in the arsenopyrite mineral was delayed and displaced to more positive potentials with respect to the electrochemical response of high purity pyrite mineral, due to a galvanic effect, catalyzing the generation of the ARD.

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Reliable Low Power Si-MOSFET Hydrogen Gas Sensors

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In order to cope with global warming and environmental pollution problems, much research and developments for hydrogen energy technology have been done for the past several years as possible candidates for clean energy to keep our planet healthy. In this paper we have developed hydrogen gas sensor chips of Si-MOSFETs, which respond linearly with wide range of 100ppm~10%, and show high selectivity more than 20 times against interference gases of methane and ethane with low power dissipation of 100mW. The sensor chips are fabricated in industrial 0.8μm CMOS technology including Pt-gate’s lift-off process developed by GaAs electron devices. In order to establish a uniform distribution of threshold voltage, Vth, Pt-gate metal was formed by electron beam evaporation technique. Two FETs for differential operations, Si-doped Al wiring heater, and PN-junction diode as thermometer are integrated in 2mm×2mm Si chip area (Fig.1). Spatial variation of design parameters such as Vth, heater resistance, R, foward voltage of diodes, Vf, show very good uniformity; 3σ (Vth)=280mV@0.8V, 3σ (R)=9.3Ω @182Ω (room temperature), 3σ (Vf)=17.7mV@110°C.

Developed FETs kept in laboratory show good stability for seven months. Relative sensitivity variations show high reproducibility within 30% in Fig2. The control unit for sensor chips is also fabricated in Fig3. In this paper we will discuss experimental results for several reliability experiments and their physical origin of life times. We will also report the analysis about field tests for developed hydrogen gas sensors.

Fig1 Hydrogen Sensor Chip  Fig2 Sensitivity variations for 7months  Fig3 Sensor control unit

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Amperometric biosensors to quantify Dichlorvos and their application in real samples.

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Organophosphorous pesticides (OPs) are toxic-hazardous compounds that have been used for decades in agriculture, industry and, as chemical warfare agents in military applications. OPs toxicity is based on their ability to modify irreversibly the catalytic serine residue in acetylcholinesterase enzyme (AChE) [1]. Thus their presence in natural waters and foodstuffs is a major concern for public health [2]. Therefore rapid, simple and sensitive field methods are required to quantify the presence of these compounds [3-6]. In this way, biosensors are considered as an alternative analytical tool for pesticides quantification, due their good selectivity, fast response, miniature size, and reproducible results [4-6]. Amperometric AChE biosensors based on enzymatic inhibition by pesticides have been shown satisfactory results for water samples analysis [4,6], nevertheless when organic solvents are used in order to quantify pesticides from real samples, the enzyme activity decrease hindering the quantification [5]. Thus in this research sensitive detection and quantification of dichlorvos (OPs pesticide) in presence of acetonitrile is done. The strategy had been used biosensors based on AChE enzyme. Three AChEs from different sources were tested and compared: AChEs from Electric eel (Ee) and genetically engineered (B394) and wild type (B1) from Drosophila melanogaster (Dm). The enzymes were immobilized by entrapment in an azide-unit pendant water-soluble photopolymer (AWP) onto screen printing graphite electrode which working electrode is covered with cobalt phthalocyanine ink. The pesticide was measured in the presence of 5% acetonitrile without loss of enzyme activity. The best sensitivity was achieved with the Dm engineered B394 with a detection limit of 7x10^{-11}M as compared to 1x10^{-8}M with Dm B1 and 6x10^{-7}M with the Ee. The B394 biosensor was used to quantify dichlorvos in a sample of skin apple after extraction with acetonitrile, the results obtained with the apple sample show a 63% inhibition which is in good agreement with the reference sample which inhibition percentage was 65%.

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References
Recent Applications of Carbon Paste Electrodes in Electrochemical Analysis

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Carbon paste electrodes (CPEs) belong among promising electrochemical sensors of a wide applicability and presently, they represent one of the most frequent type of working electrodes [1,2]. The overwhelming number of CPEs used worldwide belongs to pastes with insulating liquids (paraffin oil, silicon oil, bromonaphthalene, tricresylphosphate, or others). The basic requirements for a pasting liquid are its practical insolubility in the measurement solution, low vapor pressure to ensure both mechanical stability and long lifetime, in case of voltammetric and amperometric applications further its electrochemical inactivity in the potential window of interest. In contrast to relatively complicated modifications of solid substrates, carbon pastes can simply be modified to obtain qualitatively new sensors with desired, often predefined properties.

An overview is given to show recent trends and advances in the electrochemistry with both unmodified and modified CPEs. Construction of ion-selective carbon paste-based potentiometric sensors is mentioned as well as of those used in electrochemical stripping techniques. Present day knowledge of their basic physico-chemical properties is surveyed. Special attention is paid to the possibilities of CPEs in electrochemical investigations and in electroanalysis, and numerous examples are presented, especially those based on the authors’ contributions.

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References
Chemical Oxygen Demand Sensor Based on a Boron–Doped Diamond (BDD) Electrode

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As an important environmental quality index, chemical oxygen demand (COD) is defined as the amount of a specified oxidant expressed in terms of oxygen equivalent that is necessary for the chemical oxidation of the sample [1]. Whereas the conventional dichromate method for COD test suffers from several severe constrains, such as the time consuming process, invalid determination for volatile organic compound, and consumption of expensive (Ag$_2$SO$_4$) and toxic (Cr and Hg) chemicals. Among the approaches to improve the COD measurements, electrochemical method has been developed in recent years [2]. The basic principle is that, at a proper constant potential, physiosorbed hydroxyl radicals are produced on the surface of anodic electrode, and the current on anode is proportional to the concentration of organic matter or COD.

In our previous work, a new COD sensor based on a boron–doped diamond (BDD) electrode was developed [3]. Here, we reviewed this BDD electrode on its performance in the COD test. It’s usually believed that the BDD material owned many advantages that could facilitate electroanalysis, for instance, wide working potential window, low and stable voltammetric background current, high mechanical strength and corrosion resistance. Under the optimized testing conditions such as pH and applied bias potential, the BDD electrode could be successfully employed to detect the COD of artificial wastewater samples (glucose and potassium hydrogen phthalate, etc.) and real wastewater from chemical manufacture and pharmaceutical factory. The COD values determined by this COD sensor and the conventional chromium method agreed well with each other. Moreover, the COD test for one sample could be completed simply in a short analysis period of 2-3 min with no requirement of complicated sample treatment like extraction and digestion. Consequently, the operation cost and the time consumed could be saved markedly. As compared with the conventional chromium method, the COD sensor based on the BDD electrode was more convenient and environmentally friendly.

References
Tunable redox polymer matrices for the development of membraneless biofuel cells using a laccase cathode and cellobiose dehydrogenase anode

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The development of alternative sources of energy become more and more important. In an ideal case of power production, environmental friendly fuels such as hydrogen, organic acids, alcohol, sugars, oxygen or hydrogen peroxide should be used. Biofuel cells fulfill these ultimate environmental requirements by applying the mentioned fuels as substrates together with biocomponents, such as enzymes, microbial or whole cells for catalyzing the reactions at the anode and/or cathode.

By customizing membraneless biofuel cells power losses at the membrane between anode and cathode can be minimized and the fabrication of the cell architecture can be simplified. Therefore, the biocomponents need to be immobilized on the electrodes. Specifically, entrapment in Os-complex modified redox polymers leads to i) design of optimized electron-transfer pathways between electrode and biocomponent; ii) increasing of possible loading of the biocomponent at the electrode and consequently to higher immobilized catalytic activity; and iii) improvement of the operational stability of the modified electrode. The chemical structure of the redox polymers will ultimately define the biofuel cell characteristics. By changing the coordination of the Os redox center the properties of the derived redox polymers can be tuned, and especially their formal potential can be adapted to those of the immobilized biocomponent.

![Fig.1. Dependence of the biofuel cell current on the addition and exclusion of substrates.](image)

The present research is focused on the development of a membraneless biofuel cells consisting of a cellobiose dehydrogenase-Os redox polymer anode and a laccase-redox polymer cathode, using lactose/cellobiose as fuel and oxygen as substrate for anode and cathode, respectively. Both anode and cathode have been optimized and its power characteristics and operational parameters will be presented.
Iron electrowinning in alkaline media: Producing iron by electrolysis of an iron oxide suspension?

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The Ultra Low CarbonDiOxide in Steelmaking (ULCOS) program aims at developing breakthrough steelmaking routes that match at least a 50% reduction target compared to a benchmarked coal-based integrated route. One of the possible techniques is the electrolysis of iron oxide particles in alkaline solution, a totally new route for steel production.

The reaction of direct electrolysis of iron oxide - hematite in the present case - results in two products and no waste: iron metal and oxygen gas:

$$\text{Fe}_2\text{O}_3(s) \rightarrow 2\text{Fe}(s) + \frac{3}{2}\text{O}_2(g)$$

The process consists in the electrolysis of a concentrated suspension of finely ground iron oxide particles. Such a conversion process of solid reactants is unusual for electrochemical processes and requires a better description of its mechanism. The electrochemical reduction of hematite has therefore been investigated on small scale pilots with various designs, focusing on the production of iron metal. This leads to the assessment of the electrochemical and metallurgical features of the reduction process. Large samples of iron (Figure 1a) have been produced with these cells, and conditions have been identified to produce low porosity deposits as shown in Figure 1b, as thick as 5mm.

![Figure 1: a- 1.5 kg metal deposit. b- Cross-section.](image)

The high metallurgical properties of the deposits together with the promising results of chemical balance and energy requirements, confirm the interest of such route for larger scale development. Thanks to the various flow configurations studied, cell design elements are discussed to achieve an efficient electrolysis configuration. This paper highlights the interest of the electrolytic route for iron making at low temperature, and evaluates the key engineering issues linked to scaling up.
Electrodeionization process applied to hexavalent chromium removal from synthetic solutions at pH 5

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Electrodeionization process (EDI) and its technologies base were studied to hexavalent chromium removal from synthetic solutions at pH 5. Chromium removal through ion exchange using IRA-67 resin was approximately of 45% in 30 minutes. From polarization curves, the current limit was determined for ED process at 12 mL min⁻¹. Applying a current of 7.14 mA, the decreasing of chromium concentration by Electrodeionization (ED) reached a value of 97% in 7 hours, using Neosepta CM-I and AFN membranes. Combining ED and ion exchange (Electrodeionization) and using a current of 8.6 mA, the kinetics of chromium elimination was lower than ED until 3 hours. After this time, the EDI rate increased and 95% of Cr(VI) removal was obtained in 5 hours. The power consumption was similar in both cases.

Figure 1. Comparison between EDI, ED and ion exchange for hexavalent chromium removal at pH 5

Figure 2. Power consumption over time for EDI and ED processes for Cr(VI) removal
DhEMS and FTIR Studies of Ethanol and Methanol Oxidation on Ordered Intermetallic Platinum Phases

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The Direct Methanol and Ethanol Fuel Cells are one of the most promising environment friendly devices for energy production from biomass derivatives. These alcohols became attractive fuel options because they can be produced from natural gas or from biomass renewable sources. However, the wide use of the corresponding fuel cells is still limited by the development of more efficient electrocatalysts and also by the improvement of the cell membranes to minimize the cross-over effect that decreases in a great deal the efficiency of the system. Platinum ordered intermetallic phases (OIP’s) have been recently proposed as a well-succeeded tool to develop anode materials for membrane fuel cells as well as to improve the electrocatalysis theory [1,2]. This class of materials joins the well-ordered crystallographic structure characteristic of the material and enhanced physical-chemical stability necessary for application in real systems. The encouraging good performance of some OIP has been attributed to a possible synergetic effect of enhancement of surface adsorption characteristics and the bifunctional action that minimizes the poisoning effect of CO. In the present work the electrochemical experiments were performed in C2H5OH or CH3OH 0.15 mol L−1 + H2SO4 0.15 mol L−1 solution. Differential Electrochemical Mass Spectrometry (DEMS) detection of intermediates/products involved in the electrochemical oxidation reactions has been proposed as a very important tool to perform small molecules mechanistic studies and, the experimental set up adopted in this work has been proved to be very useful for use with massive electrodes. From the results obtained the dual path mechanism was proposed to occur for the reactant molecule oxidation at Pt and some intermetallic surfaces. The intermetallic surfaces have always shown a better performance than Pt with a consequent higher efficiency of the reactant molecule conversion to CO2. In situ Fourier Transformed Infrared Spectroscopy experiments (FTIR) were carried out on PtSb, PtSn and polycrystalline platinum to detect soluble products of the ethanol oxidation reaction. On PtSb electrode it was clearly detected the production of CO2, acetic acid and acetaldehyde. On the other hand, on PtSn electrode, it was not detected the acetaldehyde, suggesting the preferential oxidation route that produces CO2. The suitable electronic configuration of the surface towards the electrode reaction was proposed as a possible cause of the improved performance. However, the bifunctional effect of the surface is also taking into account in the discussion of the results.

Electrodegradation of glyphosate herbicide at DSA® electrodes: pH, current density and concentration effects

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Metallic oxide electrodes containing RuO₂ and IrO₂ have been used widely in environmental electrochemistry due to their catalytic activity, selectivity and mechanical resistance. The electrode composition may play a key step to determine the material performance towards organic pollutant. A feature of the present work was to investigate the performance of a set of RuO₂ and IrO₂ electrodes on the electrodegradation of glyphosate herbicide (GH). This herbicide being is highly used in Brazil and worldwide to control many types of broadleaf weeds and the concern towards the use of this compound is due its toxicity towards aquatic organisms. The present work aims to investigate the performance of DSA-electrodes in the complete degradation of the toxic compound or to lower the toxic levels of the byproducts formed. The Ru₇₀Ta₃₀Oₓ, Ru₃₀Ti₇₀O₂, Ru₃₀Sn₇₀O₂, Ru₃₀Pb₇₀O₂ and Ir₃₀Sn₇₀O₂ electrodes were prepared as described elsewhere. The electrochemical characterization shows that under the conditions investigated GH is not electroactive (fig. 1). The efficiency of the electrochemical degradation was performed changing the current density (∆i < 100 mA cm⁻²) GH concentration (50 < C₇₀GH < 1000 ppm) and pH. As can be seen (fig. 2) the electrode composition has a marked effect in the GH degradation rate. The mineralization rate was evaluated following the total organic carbon (TOC) analysis, total amount of liberated phosphate ions and colorimetric analysis after derivatization of the GH.

Changes in the current density and total electrolysis time increases proportionally the GH degradation rate. Changes in the pH medium and the herbicide concentration are currently under investigation and will be presented. GH is very recalcitrant and shows lower degradation rate (65 %) even at the strongest electrochemical condition used. The main reason for this low performance is due to the competition between the oxygen evolution reaction and the oxidation of pollutant. The Ti/Ir₀.₃Sn₀.₇O₂ electrodic composition showed the greatest degradation power among the compositions investigated. This composition also shows a good mechanical resistance compared with ruthenium oxide counterpart.

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Investigation of a Passive DMFC Mini-Stack Operating at Ambient Temperature

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In the next years, electric power generation by fuel cells (FCs) is expected to play an important role in both stationary and portable systems [1]. The potential market for portable fuel cell systems deals with remote and micro-distributed electrical energy generation including mobile phones, lap-top computers, energy supply for weather stations, medical devices, etc. Direct methanol fuel cells (DMFCs) are promising candidates for these applications [2, 3]. The main advantages of such systems rely on the high energy density of liquid fuels such as methanol and ethanol, long-life-time, easy recycle and low emission of pollutants in the environment. Initially, DMFC stacks have been developed for assisted power units (APUs) purpose or for electrotraction. These stacks used a classical configuration where single cells are stacked in series through bipolar plates. More recently, the attention has been focused on portable applications and various stack configurations have been proposed. Moreover, in order to be commercially viable, it is necessary to eliminate power losses from auxiliaries, i.e. the pump and the fan that are usually used to feed methanol and air into the stack. To this scope, the concept of passive-feed DMFCs has been proposed. Under this configuration, DMFCs operate without any external devices for feeding methanol and blowing air into the cells. Oxygen can diffuse into the cathode from the ambient due to an air-breathing action of the cell (partial pressure gradient), whereas methanol can reach the catalytic layer from a reservoir driven by a concentration gradient between the electrode and the reservoir and through capillary force action of electrode pores.

In the present paper, an optimization of properties and operating parameters, such as methanol concentration and catalyst loading, of a passive direct methanol fuel cell monopolar mini-stack is presented. The influence of Pt loading, already investigated in a conventional forced-flow DMFC [4], was analysed taking into account the mass transfer constrains caused by high catalyst loading under passive operation.

References
The perchlorate problem in drinking water electrolysis
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The generation of disinfecting species by direct electrochemical treatment is a well-known and efficient method. Active chlorine compounds obtained by chloride ion oxidation are mostly responsible for the water disinfection. Several electrode materials are used in technical cell constructions. Unfortunately, little is known about the by-product formation potential during and after electrolysis. Theoretical consideration let us conclude that higher-oxidized oxychlorine species have to be expected if anodes are used able to generate radicals. Boron-doped diamond electrodes (BDD) may form *OH radicals. Consecutive products are hydrogen peroxide and ozone. Formation of sulfate radicals and others is discussed. Under these conditions, the fast chemical formation of chlorate and perchlorate in drinking water should be possible as known for higher concentration levels [1]. To prove this, experiments in discontinuous laboratory cells using rotating BDD anodes and parallel plate electrodes were carried out. Additionally, continuous flow-through cells of technical size using natural water matrices were tested. Firstly, the presence of perchlorate ions in drinking water systems was reported in [2,3]. The corresponding results were obtained by ion chromatography equipment working in the ppm range of perchlorate concentration. It could be shown that perchlorate is a final product - independent from the starting form of [Cl] component in the water such as chloride, hypochlorite, chlorite and chlorate. Thus, a consecutive and coupled mechanism is probable when waters containing chloride ions are electrolyzed. New experiments were performed using HPLC devices, which allowed analyzing perchlorate down to 0.2 ppb. Fig. 1 shows a corresponding chromatogram. It could be found that the electrode polarization is the main parameter influencing on the perchlorate formation rate.

Fig. 1 Chromatogram showing perchlorate concentration in ppb range obtained in a sample taken from a flow-through electrolyzer using natural drinking water (42 ppm [Cl-]).

Higher flow rates reduced both the disinfection product and the by-product concentration levels. Nevertheless perchlorate may accumulate in batch-wise operating. The results demonstrate that electrolysis conditions must be carefully controlled to avoid the formation of perchlorate that is highly dangerous for health.

References

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Integration of Enzymes, Redox Mediators and Structured Materials to Provide Bioelectrochemical Fuel Cells

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The main theme of our research is the integration of enzymes, redox mediators and high surface area materials to provide bioelectrochemical platforms capable of efficiently transferring electrons between chemicals and electrodes for application as biosensors and biofuel cells. These bioelectrochemical reactions are enabled by designing efficient mediated electron transfer processes between selected enzymes and electrode materials\textsuperscript{1,2}.

To advance our understanding of integrating immobilization and function (electron transfer efficiency) we have commenced synthesis of a library of osmium/ruthenium-based redox mediator complexes possessing a range of redox potentials. These mediators are designed to possess the dual function of mediation and amenability to covalent immobilization at electrode surfaces.

In addition to designing inbuilt immobilization strategies for the mediators, we have also commenced research on anchoring redox systems, and enzymes, onto electrodes. This anchoring chemistry can improve the stability of the enzyme/mediator layer and offer improved mediated bioelectrochemical systems for applications such as biosensors and biofuel cells.

The use of structured electrodes allows for an increase in surface area that is amenable to covalent attachment of mediator complexes and enzymes.

We will present recent development in integrating these strategies to provide a biofuel cell\textsuperscript{3} consisting of a glucose oxidase-based anode and a laccase-based cathode using osmium/ruthenium-based redox complexes as electron transfer mediators\textsuperscript{1,2} on structured electrodes.

Investigation on the Performance of Gas Diffusion Electrode for Electrolysis in Chlor-Alkali Cell

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The chlor-alkali industry consumes large amounts of energy. For energy saving, new cathodes consisting of gas diffusion electrodes (GDEs) have been studied. The lower voltage obtained for this type of electrolysis cell contributes to mitigate of millions of tons of CO₂, associated with electric power generation from fossil fuels.

The gas diffusion electrodes consisted of a mixture of graphite/PTFE mass and a current distributor, compressed and sintered at 340°C. A limited amount of different metals (such as Cu, Ag and Fe) was also incorporated into the graphitic mass of the electrode and the results in the voltage cell were examined.

The electrolysis was carried out in a divided cell with a dimensionally stable anode (DSA) and GDE cathode. The cell performances were investigated at about 70°C and a constant current load of 300 mA/cm². The results showed that by replacing the high voltage consuming hydrogen-evolving reaction as cathode materials, energy saving of more than 20% could be realized.

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The hydrogen evolution reaction on surface modified nitinol (Ti-Ni)

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For the production of hydrogen for energy storage purposes, standard water electrolysis on Ni electrodes may be used, based on a good corrosion resistance and catalytic properties of this metal [1]. However, the Ni-electrode performance usually decreases with service time [2]. It was shown, that the catalytic properties and stability of Ni can be increased by alloying it to other metals [3, 4]. Panek et al reported for codeposited Ni and Ti enhancement of the hydrogen evolution reaction (her) in alkaline solutions [4]. The authors attributed the increase of to the formation of the intermetallic Ni-Ti and formation of nonstoichiometric oxides on the electrode surface [4]. In this work, her was studied on surface modified bulk Ni-Ti alloy (48.05 wt% Ni) in 1M NaOH. The surface modifications were carried out by anodic polarization at potentials up to 3V in different electrolytes as 1M H₃PO₄ and 1M Na₂SO₄, which produced different grades of dealloying and oxide thickening, as determined by Rutherford backscattering spectrometry and µ-Raman spectrometry. Much higher her is observed on Ni-Ti compared to pure Ni or Ti (Fig.1). Previous polarizations of Ni-Ti (2h, 3V SHE) in 1M H₃PO₄ or Na₂SO₄ increase further the observed i. After 15h polarization in 1M NaOH strong R_p decrease 1/Cdl increase are observed by EIS(ig.2) due to surface increase by acicular hydride formation.

Fig. 1 left: her in 1M NaOH on Ni, Ti, untreated Ni-Ti, and Ni-Ti previously polarized in 1M H₃PO₄ or Na₂SO₄. Right: EIS and simulation (line) of Ni-Ti treated in 1M Na₂SO₄ before and after 15h cathodic polarization 1M NaOH at -1 V.

REFERENCES:
Investigation of Oxygen Evolution and Formic Acid Oxidation on Ti/IrO₂ Electrodes Using Isotope Labelling and On-Line Mass Spectrometry

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Oxygen evolution and formic acid oxidation on Ti/IrO₂ anodes have been studied in 1M HClO₄ electrolyte using ¹⁸O labelling together with differential electrochemical mass spectrometry (DEMS) measurements. It has been shown that during successive cyclic voltammetric measurements in H₂¹⁸O containing electrolyte the amount of ¹⁶O₂ (m/z=32) decreases, with a concomitant increase of ¹⁸O₁⁶O (m/z=34) after each cycle before reaching a steady state after four cycles. The obtained higher ¹⁶O₂ concentration in the evolved oxygen during the first scans is because ¹⁶O from the IrO₂ film contribute in the oxygen evolution reaction.

Other experiments performed have demonstrated that oxygen evolution on Ir¹⁶O₂ in H₂¹⁸O containing electrolyte result in the formation of Ir¹⁸O₂. This was verified in a second series of experiments, where an IrO₂ electrode that was labelled with ¹⁸O (formation of Ir¹⁶O¹⁸O) by treatment in H¹⁸O was used for the electrochemical oxidation of formic acid using cyclic voltammetry. The amount of C¹⁶O₂ and C¹⁸O¹⁶O formed during potential scan has been followed by on-line mass spectrometry. The presence of C¹⁸O¹⁶O (m/z=46) during the anodic scan proves clearly that the IrO₂ coating indeed participated in the oxidation of the formic acid as it was the only source of carbon in the electrolyte and it reacted with the marked oxygen atom present in the labelled IrO₂ lattice. Analysis of the experimental data have shown that the amount of lattice oxygen, which is involved in oxygen evolution and in the oxidation of the adsorbed formic acid, is in the order of 1% of the total IrO₂ loading. This is an indication that only the outer surface of the oxide electrode participates in the oxygen evolution reaction and in the oxidation of organics.

Consequently, we can conclude that at least a few monolayers of the IrO₂ coating participate in the oxygen evolution reaction in acid media as well as in the exchange of oxygen between electro-generated labelled IrO₃ (Ir¹⁶O¹⁶O¹⁸O) and formic acid (HC¹⁶O¹⁶OH) producing labelled carbon dioxide (C¹⁶O¹⁸O) and Ir¹⁶O₂.
Enhanced Performance of Ni-Based Anodes in Aqueous Hematite Suspensions.

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Optimization of oxygen evolution is essential for a variety of electrolytic processes with a potential to become environment friendly technologies such as hydrogen production, electro-winning of metals, etc. Ni-based anodes were selected for this study, taking advantage of the electrocatalytic activity and high stability of Ni under alkaline conditions. One studied the effects of different factors such as previous surface modifications of Ni-anodes, which contribute to enhance the electrode performance. In addition, one studied the kinetics of oxygen evolution of those anodes in NaOH solutions with and without suspensions of hematite, and found remarkable enhancement of performance on adding the hematite suspension. Addition of hematite particles lowers the overpotential by about 0.2V, at typical current density of 0.1 A/cm², in aqueous NaOH electrolytes. The Tafel slope also increases from about \( \frac{d\ln j}{d\eta} = 25 V^{-1} \) to \( \approx 38 V^{-1} \) on adding the hematite suspension. These effects are clearly distinguished from other factors contributing to enhanced electrode performance, including surface modifications by nanostructured \( \text{Fe(OH)}_3 \), or mixed \( \text{Ni(OH)}_2 + \text{Fe(OH)}_3 \) hydroxide scales. Contrary to hydroxide scales, which tend to become less effective at high NaOH concentrations and/or relatively high temperatures, hematite suspensions still contribute to enhance the electrode performance under those extreme conditions.
Direct Electron Transfer between Multicopper Blue Oxidases and Carbon.

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In the last decade much work has been focused on biofuel cells. For the cathode reaction the ultimate reaction would be to be able to reduce oxygen directly to water close to the redox potential of this reaction. One way to accomplished this is to catalyse this reaction on the electrode surface using a multicopper blue oxidase [1], either in a mediated or in a direct electron transfer mode. Direct (mediatorless) electrochemistry between graphite and gold electrodes and laccases from a number of high potential laccases from basidiomycetes [1], two bilirubin oxidases [2] as well as a bacterial laccase has been studied using cyclic voltammetry, square wave voltammetry as well as potentiometry. For all enzymes direct electron transfer (DET) was registered at spectrographic graphite and highly ordered pyrolytic graphite electrodes. The characteristics of DET reactions of the enzymes were analysed under aerobic and anaerobic conditions. It is shown that the T1 site of the enzyme is the primary electron acceptor, both in solution (homogenous case) and at the surface of the graphite electrode (heterogeneous case). A mechanism of ET for the electroreduction of oxygen at the enzyme-modified graphite electrodes is proposed and the similarity of this heterogeneous process to the enzyme catalysed oxygen reduction homogeneous reaction is concluded and will be discussed.

Direct electron transfer between copper containing proteins and electrodes.
Redox potentials of the copper sites of bilirubin oxidases.
The Supply of Dissolved Oxygen by Electrolysis in Lake Biwa

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Lake Biwa is located in Shiga Prefecture near the cities of Kyoto, Kobe and Osaka in Japan. It is the largest lake in Japan, and it is one of the oldest lakes in the world containing some unique plants and organisms. Pollution from the surroundings has caused the lake to suffer from eutrophication. A serious condition is the lack of oxygen in the deeper layers of the lake.

This study is related to a larger project where the aim is to develop a sustainable energy system for supplying dissolved oxygen to Lake Biwa by deep water electrolysis. The concept of a sustainable energy system is based on the production of electricity by using solar cells floating on top of the lake. In addition hydrogen produced cathodically will be captured and used in fuel cells to produce additional energy for the electrolysis. Electrochemical studies of the kinetics of oxygen formation and electrolysis experiments to produce dissolved oxygen were carried out under controlled laboratory conditions. Anodes of nickel, graphite and DSA were tested in an electrolyte having similar electrical conductivity as Lake Biwa, the specific electrical conductivity being about 135 µS/cm. A small laboratory cell was constructed for the precise measurement of the dissolved oxygen during electrolysis. Preliminary experiments showed that electrolysis using a titanium based DSA type anode is very efficient with respect to the formation of dissolved oxygen. It was found that the efficiency of supplying dissolved oxygen was about 85 % in the laboratory cell. The kinetics of the oxygen formation reaction were also studied by recording steady state current versus potential relationships. Recent experiments showed that electrolysis at low current densities is more efficient than bubbling oxygen or air at comparable rates. This could be due to the possibility for direct formation of dissolved oxygen at the anode during electrolysis.

A physical model of part of Lake Biwa was built to demonstrate the concept of oxygen generation by electrolysis and also to illustrate the sustainable energy system.
Ceria Supported Rh₃Pt₂Sn Nanoparticles as Low Temperature Ethanol Steam Reforming Catalysts

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The implementation of a hydrogen-based economy requires the capability of deriving hydrogen from a variety of renewable sources including solar, wind and biomass, particularly ethanol. Recent studies on ethanol reformation have focused on higher temperature systems (T>400°C) employing single or bimetallic catalysts composed of Co, Cu, Ni, Ru, Rh & Pd supported on Al₂O₃, ZnO, ZrO₂, SiO₂, and CeO₂ [1-3]. However, these systems are not suitable as internal pre-reforming catalysts for low-temperature solid acid or PEM fuel cell systems.

To address this need, ternary Pt-Rh-Sn catalysts for low temperature (T<400°C) ethanol steam reforming were characterized by a series of gas phase studies. The design of the proposed ternary Pt-Rh-Sn catalysts is guided by a hypothesis of “trifunctional mechanism” by which each catalyst component plays a coordinated role in the reforming of ethanol [4]. Trimetallic Pt-Rh-Sn nanoparticles were produced by a modified reverse micelles synthesis. TEM measurements confirm uniform size distributions of ranging from 3-5 nm. Stochioometry of trimetallic nanoparticles was confirmed by EDX and XPS. Broadening Pt 4d3/2 peak suggest charge transfer from Pt to Sn, while chemical shifts of Sn 3d and O 1s suggest SnOₓ. The (Rh₃Pt₂Sn)₅%/CeO₂ catalyst showed higher ethanol conversion than platinum. The mechanism for hydrogen production over (Rh₃Pt₂Sn)₅%/CeO₂ by dehydrogenation of ethanol to acetaldehyde is consistent with the literature results M/CeO₂ (M=Pd, Rh, Pt) [5]. However, the lack of CO₂ and CH₄ species is curious and does not support the hypothesis of a “trifunctional mechanism” for this reaction. The deactivation of the ternary catalyst at higher temperatures is likely caused by the presence of Sn and warrants further study.

Partially Oxidized Group 4 and 5 Transition Metal Carbonitrides as New Non-Platinum Cathodes for PEFC

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Polymer electrolyte fuel cells (PEFCs) are expected as power sources for residential and transportation applications due to their high theoretical efficiency of energy conversion, high power density, and low operating temperature. However, considering an application to FC vehicles, the natural resource of Pt is insufficient. Therefore, the development of a stable non-platinum catalyst is strongly required.

We have reported that group 4 and 5 transition metal oxide-based compounds were stable in an acid solution and had a definite catalytic activity for the ORR [1-2]. However, their activities were insufficient, and the factor which affected the catalytic activity has not yet been clarified.

In this study, partially oxidized tantalum carbonitride (TaC$_{0.58}$N$_{0.42}$) was evaluated as a new cathode for PEFC without platinum. The TaC$_{0.58}$N$_{0.42}$ powders were heat-treated at 1200°C for 10 h under different flowing rate of the 2%-H$_2$/N$_2$ gas containing 0.25% oxygen to obtain powder specimens with different oxidation state. In order to quantify the degree of oxidation of the TaC$_{0.58}$N$_{0.42}$, the XRD peak intensity at 2$\theta$ = 35° of TaC$_x$N$_y$ (1 0 0), which was expressed as I (TaC$_x$N$_y$), and the XRD peak intensity at 2$\theta$ = 28.3° of Ta$_2$O$_5$ orthorhombic (1 11 0), which was expressed as I (Ta$_2$O$_5$), were utilized to calculate the ratio, I (Ta$_2$O$_5$)/{I (TaC$_x$N$_y$)+ I (Ta$_2$O$_5$)}. The ratio, I (Ta$_2$O$_5$)/{I (TaC$_x$N$_y$)+ I (Ta$_2$O$_5$)}, was designated the degree of the oxidation of the TaC$_{0.58}$N$_{0.42}$ and expressed as DOO (Degree Of Oxidation).

Figure 1 shows the relationship between the DOO and the onset potential for the ORR. The onset potential abruptly increased with the increasing DOO up to 0.2. The onset potential had high value over 0.85 V above the DOO of 0.3. This result revealed that a certain oxidation was necessary to have a clear catalytic activity.

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References

Electrochemical Ozone Generation by a Zirconium Oxide Electrode Fabricated by Sputtering

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Ozone is a strong oxidizing agent with a high oxidation-reduction potential and it is used for the oxidation of many materials. We have focused on ozone generation by electrolysis\(^1\) and examined tantalum oxide (TaOx) electrode for the purpose\(^2,3\). In this paper, the characteristics of a zirconium oxide (ZrOx) electrode fabricated by sputtering are described.

A zirconium oxide electrode was prepared as follows. Firstly a titanium (Ti) film was deposited on a silicon (Si) wafer by sputtering followed by thermal oxidation. Secondly a platinum (Pt) film was deposited on the titanium oxide (TiOx) layer by sputtering. Finally a zirconium (Zr) was deposited on the Pt layer by sputtering followed by thermal oxidation. The oxidation temperature was 300, 400, 500 and 600 °C. Model tap water was used as an electrolyte solution\(^2\). Constant current electrolysis was performed for 1 min with ca. 20 mA/cm\(^2\). The ozone concentration in the solution was measured by indigo method. The crystallinity of the surface layer was evaluated by X-ray diffraction (XRD). The composition and the binding energy of the surface layer were measured by X-ray photoelectron spectroscopy (XPS).

According to a chemical shift of zirconium 3d, the surface of the electrode consisted only of oxide. Oxygen (O)/Zr ratio of surface was nearly identical irrespective of oxidation temperature. Surprisingly, the XRD peak intensity originating from ZrO\(_2\) was independent of the oxidation temperature except for 300 °C. Figure 1 shows the dependency of a current efficiency of ozone generation and half width of the XRD peak of ZrO\(_2\) (~28 °) on oxidation temperature. As shown here, the current efficiency seems related to half width of the peak rather than peak height. This may be due to a temperature-dependent decrease in grain boundaries because the current flowing through them is considered not contributing to ozone generation.


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Fig. 1. The dependency of current efficiency and half width of the peak originating from ZrO\(_2\) on oxidation temperature.
Electrolytic Control of Oxidation State and Removal of Neptunium Ion based on Reduction and Adsorption on the Carbon Fiber Electrode

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Actinide (An) elements which are of long-life radioactive and of α-emitters have significant hazard to environment and human health. Development of efficient and simple removal method of these ions from radioactive waste water is a major concern. The U, Np and Pu ions in acid or neutral aqueous solution exist as An(III)-An(VI) ions, and the oxidation state of the ions affects chemical phenomena such as complex formation and distribution between liquid/liquid or liquid/solid phases. Especially, pentavalent Np (NpO2⁺) which is most stable oxidation state for Np has so weak interaction with ligands or adsorbents that removal of Np from water is difficult.

The authors have developed rapid and quantitative electrolysis method for An ions by using column electrode. Here, the column electrode is a working electrode comprising a bundle of very thin glassy carbon (GC) fibers packed tightly in a cylindrical electrolytic diaphragm cell of porous glass, and the electrolysis is performed by passing the electrolyte solution containing the ions of interest through the narrow paths among GC fibers. Previously[1], the quantitative electrolysis with column electrode have been demonstrated even if the electrode reaction is completely irreversible as in the reduction of NpO2⁺ to Np3⁺ which is difficult to observe the reduction wave by conventional voltammetry with a platinum, glassy carbon or mercury electrode.

In this study, it is elucidated from bulk electrolysis method that the reduction of NpO2⁺ proceeds by a mediator of Np3⁺/Np4⁺ redox couple. In addition, authors found that electrolytic pretreatment of GC fiber resulting in an adsorption of An ions in weak acid solution on the GC surface. For example, concentration of An(III), An(V) and An(VI) ions in effluent solution of pH 3 through column electrode after pretreatment was decreased to about 0, 30 and 0 %, respectively. These results show that Np(V) is hardly expected to be removed completely without control the oxidation state. However, the Np can be removed by flowing through the column electrode of pretreated GC fiber with applying potential at -0.25V vs SSE to reduce to Np(III) as shown in Fig. 1. The developed method is very simply and high efficiently and no need the addition of some chemical reagent.


Fig. 1. Effect of electrolysis on removal of Np from a solution of pH 3 by column electrode. Initial concentration of Np: 10 µM. Flow rate : 1mL/min.
Hydrogenases as biocatalysts for biofuel cells: efficient H₂ oxidation at electrodes modified by carbon nanotubes

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In a forthcoming hydrogen economy, fuel cells are very promising in substitution of carbon-based fossil fuels and decrease of carbon dioxide emissions. Innovatory technology based on the use of biocatalysts in fuel cells emerges as a valuable alternative to platinum. Hydrogenases are abundant enzymes in the microbial world that catalyze with high turn-over the cleavage of hydrogen into protons and electrons or the evolution of H₂ from H⁺ reduction. They constitute renewable and clean catalysts, moreover resistant to impurities present in H₂ (CO, H₂S…). They are able to produce pure H₂, thus offering the concept of a futurist “biobatterie”, with no need of the highly cost H₂ purification steps.

Succeeding in the stability of the enzyme in extreme environments (presence of O₂, high T°…) can be achieved via genetic manipulation or by the use of intrinsically resistant hydrogenases from extremophilic bacteria [1]. But efficient immobilization of the enzymes onto electrode supports has to be developed as a key step. Research for highly developed surface area electrodes while increasing electrons transfer rate to hydrogenase, leads us to examine the advantages of using carbon nanotubes (CN) [2-3]. CN-modified electrodes have been examined in the last 5 years for biological systems [3-4]. We report in this work simple use of various commercially available CN for modification of electrodes in view of hydrogen evolution/consumption catalyzed by a bacterial [Ni-Fe] hydrogenase. Covalent attachment of hydrogenase through controlled architecture of CN at gold electrode, and adsorption of hydrogenase at carbon nanotubes-modified pyrolytic graphite electrodes are investigated. After characterizing the various CN-modified electrodes using AFM and electrochemistry, performances of the electrodes and kinetic data for H₂ uptake and evolution reactions will be compared and discussed.

References:
Electro-removal of Cu(II) in the presence of Humic Acid

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Humic acid (HA) is one of the principal components of humic matter, which is the major constituent of the organic content of soil. HA presents a complex structure and its presence in water destined for treatment is of considerable concern, complicating treatment procedures and even leading to the formation of carcinogenic degradation by-products (DBPs). In addition, HA presents a strong coloration and is known to complex with metal ions and liberation of toxic metal species is also a matter for concern. This paper presents the study of the removal of Cu²⁺ (10 mg/L) complexed with commercial HA (100 mg/L). Cu²⁺ removal was performed at different current densities (30 – 80 mA cm⁻²) using a filter-press cell with a Ti/Ru₂o₅Ti₀.₇O₂ anode and a stainless steel cathode. All galvanostatic electrolyses were performed at pH = 5 and NaCl (0.05 M) was used as the supporting electrolyte. Constant current electrolyses were performed with and without a membrane (anionic and cationic) separating the cathodic and anodic compartments of the cell. The degree of Cu²⁺ removal was determined by atomic absorption spectroscopy (AAS) and the extent of HA removal was monitored by UV-vis spectroscopy. Initial CV investigations of the Cu-HA system were performed using a Pt electrode. Cyclic voltammetry investigations indicate that the Cu²⁺ in solution is rapidly complexed with the addition of AH to the electrolyte. The rate of removal of the Cu²⁺ in solution is dependent on the nature of the type of membrane used. When no membrane is used, Cu²⁺ removals of up to 58 % are observed (30 mA cm⁻²). However, the separation of the cell using a cationic membrane results in 100 % Cu²⁺ removal in 3h of electrolysis at 30 mA cm⁻². On the other hand, removal using an anionic membrane gives removals of only ~30%. The electrochemical process is capable of removing the dark coloration of AH-containing solutions in all instances and solid residue formation was not observed. With the aim of shedding light on the possibility of either electrostatic interaction or the break-up HA being a key to the removal of Cu²⁺ complexed with the organic material, it was decided to study the effect of combining the oxidation/reduction processes. This was achieved by performing (Exp. A) oxidation (90 min) followed by inverting the cell and performing reduction (90 min) and (Exp. B) reduction (90 min) followed by oxidation (90 min). Cu²⁺ removal for Exp. A is slow during the oxidation step, but much fast during the reduction step (approx. 10 times). During Exp. B similar behavior to that observed for Exp. A is observed. During the reduction step, rapid Cu²⁺ removal is observed, approximately 7 times faster than for Exp. A. The results obtained stimulate the question: For the removal of Cu²⁺ from HA complexes which is more important destruction of HA and liberation of Cu²⁺ or electrostatic interaction (overcoming of metal-functional group interactions)? The results of this study indicate that both considerations are important. When the removal of Cu²⁺ is aided with the initial anodic break-up of the HA structure, efficiencies tend to be much greater.

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An Evaluation of the Performance of a Mediator-less Microbial Fuel Cell

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The properties of the anode and the cathode of a mediator-less microbial fuel cell (MFC) and the power output of the MFC have been evaluated using different electrochemical techniques. In the MFC under investigation the biocatalyst - Shewanella oneidensis MR-1 - oxidizes the fuel – lactate – and transfers the electrons directly into the anode which consists of graphite felt. Oxygen is reduced at the cathode which consists of Pt-plated graphite felt. A proton exchange membrane separates the anode and the cathode compartments. Ag/AgCl reference electrodes have been placed into both compartments.

Electrochemical impedance spectroscopy (EIS) carried out at the open-circuit potential (OCP) has been used to determine the electrochemical properties of the anode and the cathode as a function of time and experimental conditions. Potential sweeps have been employed to record the cell voltage (V) – current (I) curves for the MFC. From these V – I curves the cell voltage Vmax at which the power output of the MFC has a maximum value Pmax has been determined. Power (P) – time (t) curves have been measured at Vmax for 12 h periods. Cyclic voltammetry (CV) and potentiodynamic polarization curves have been used to evaluate the anodic and cathodic reaction kinetics in a wide potential range.

The internal resistance Rint of the MFC has been determined as a function of V using EIS. It has been found that Rint depends on V. A theoretical analysis shows that Rint = Rex at Vmax, where Rex is the resistance that has to be placed between the anode and the cathode to obtain Vmax. Additionally, Rint equals the slope of the V–I curve. A comparison of the results of these theoretical calculations and the experimental data shows very good agreement of the two sets of data.

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Photoelectrocatalytic Oxidation of Disperse Dyes on Nanotubes Ti/TiO₂ Electrodes


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Titania (TiO₂) nanotubes have been the subject of many recent studies because of their unusual electronic transport and mechanical strength characteristics that improved properties compared to any other form of titania for many applications¹. Photoelectrocatalytic oxidation has been investigated as an attractive approach to dye treatment, combining electrochemical and photochemical technologies. Interestingly neither of these latter techniques could effectively destroy and remove totally some of these dyes. The present work evaluates the performance of nanotubes Ti/TiO₂ electrodes prepared by anodization in the degradation of disperse azo dyes. These are a class of hydrophobic and non-ionic compounds heavily employed for dyeing synthetic fabrics that presents high toxicity and mutagenic property. They are applied in a form of stable aqueous dispersions containing surfactants, that in effluents can be easily transported and bioaccumulated in sediments, soils and others. Disperse Orange 1, Disperse Red 1 and Disperse Red 13 were studied as model compound of this class of dye. The results were compared with nanoporous Ti/TiO₂ electrode, prepared by sol-gel². The kinetic parameters have been evaluated by following solution discoloration to assess the effectiveness of this method. Preliminary results showed that discoloration of dyes in Na₂SO₄ and Emulsogen surfactant occurs practically after 60 min of photoelectrocatalytic treatment at 1.0 V on both, nanoporous and nanotubes TiO₂ films. Nanotubes TiO₂ performed better for the photoelectrocatalytic removal of azo dyes compared to their sol-gel derived counterparts. The degradation of surfactant was also observed during photoelectrocatalysis. Electrolysis of the azo dyes at 1.0 V practically did not degrade the dye whereas photocatalysis was found to be less efficient for the azo dye degradation. Solutions of dyes, Disperse Red 1, Disperse Red 13 and Disperse Orange 1, and surfactant Emulsogen, obtained after 3 hours of photoelectrocatalysis showed approximately 70% of TOC reduction. Photoelectrocatalytic oxidized solution of Emulsogen presented an increase in the acute toxicity for 293F cells lines compared with original solution.

References

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Electrooxidation of oxalic acid at different electrode materials

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Oxalic acid is one of the proposed metabolites of the anodic oxidation of more complex organic molecules. In spite of its simple structure, its mineralization strongly depends on the nature of the electrode material at which the process is carried out. Sargisyan and Vasil’ev [Elektrokhimiya, 18 (1982) 845] pointed out such dependence, investigating the kinetic behavior of OA at different metal (Rh, Pd, Os, Ir, Pt and Au), at dimensionally stable anodes (RuO$_2$-TiO$_2$) and at glassy carbon (GC) electrodes. Their conclusions highlighted the important role played by the organic anion adsorption step, claiming that OA is oxidized with increasing difficulty at electrode materials having higher oxygen affinity. More recently, these assumptions have been supported by data on OA oxidation at high anodic potentials [Electrochimica Acta, 49 (2004) 4027]. To further enrich the picture, in the present paper, kinetic investigations were carried out at different mixed-oxides, Pt, glassy carbon and highly conductive, boron-doped diamond electrodes, with either oxygen or fluorine at their surface.

A) Tafel plot for the OA electroxidation at different electrodes; [OA] = 750mM.
(a) Ti/IrO$_2$-2SnO$_2$; (b) Ti/Ir$_{0.67}$Ru$_{0.33}$O$_2$-2SnO$_2$; (c) Ti/RuO$_2$-2SnO$_2$; (d) Ti/IrO$_2$-Ta$_2$O$_5$; (e) GC; (f) Pt; (g) mildly ox BDD; (h) strongly ox BDD; (i) F-BDD.
B) Anodic potential required to measure a current density of 1 mA cm$^{-2}$, at the different electrodes investigated.
The role of the filter-press-type FM01-LC electrochemical reactor using BDD electrodes for the incineration of cresols, indigo textile dye and vinasses contained in industrial wastewater

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Electrochemical incineration was performed on different waste wastes containing recalcitrant organic matter, such as $p$- and $o$-cresol, indigo textile dye and vinasses in a filter-press-type FM01-LC cell, using boron doped diamond (BDD) electrodes. A strategy for the electrochemical incineration of organics is showed. The limits of current density, where the electrochemical incineration occurred via hydroxyl radicals ($\text{OH}^\cdot$), formed by water oxidation in the BDD-$\text{H}_2\text{O}$-media interface takes place, were determined by microelectrolysis tests through Tafel analysis. Based on these data, the electrochemical incineration at different Reynolds and current densities in the filtrpress-type FM01-LC electrochemical cell was characterized.

Electrolyses of $p$- and $o$-cresol were performed for different Reynolds numbers ($27,100 \leq \text{Re} \leq 42,600$) and $J = 10 \text{ mA cm}^{-2}$ in an undivided FM01-LC reactor. The rate of degradation of both cresols was slow, however it increased slightly as a function of the Re, indicating that the oxidation involves a complex pathway. Current efficiency also rises as a function of the Re. For $p$-cresol, the mineralization at $\text{Re} = 42,600$ reached 90% with 71% current efficiency, whereas $o$-cresol was mineralized to 84%, with 67% current efficiency [1].

Electrochemical incineration of indigo dye in the FM01-LC was accomplished via hydroxyl radicals ($\text{OH}^\cdot$) formed by water oxidation on the BDD surface, instead of active chlorine as usually occurs by using DSA. The experimental set up achieved 100% efficiency in color removal, indigo mineralization and current efficiency. Moreover, experimental data revealed that hydrodynamic conditions do not influence either the indigo degradation rate or the current efficiencies, presumably because indigo degradation involves a complex mechanism [2].

Electrolyses of a vinasse in the FM01-LC achieved 97% efficiency in vinasse mineralization and 100% current efficiency. Experimental data revealed that hydrodynamic conditions slightly influence the vinasse degradation rate, but not the current efficiencies. Therefore, vinasse degradation involves a complex mechanism.

The efficient performance of the FM01-LC, equiped with BDD electrodes, for the electrochemical incineration of organics qualifies this type of cell as a test electrolizer for these purposes.

References
Direct Electron Transfer at Anodes for Biofuel Cells
Constructed by Coadsorption of Cellobiose
Dehydrogenase and Length Separated Single-Walled Carbon Nanotubes

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Cellobiose dehydrogenases (CDHs) contain a larger flavin-associated (dehydrogenase) domain and a smaller heme-binding (cytochrome) domain. CDHs oxidize cellobiose, cellodextrins, and lactose at the flavin domain. Depending on their origin they may also oxidize monosaccharids to the corresponding lactones. A wide spectrum of different electron acceptors can be reduced by CDH either at the flavin or at the heme domain. Especially CDH from the ascomycete Myriococcum thermophilum is of major interest for the construction of anodes in biofuel cells because it exhibits a high electrocatalytical turnover rate combined with low substrate specificity. Different types of electrodes have been modified with CDH and compared with respect to the efficiency of their electron transfer (ET) properties. Intramolecular electron transfer may occur between flavin and heme and thereby enable electron transfer (ET) between the flavin domain and the electrode. When electrodes are immobilized with redox-active enzymes, direct or mediated ET can occur depending on the nature of the surface modification. By co-immobilization of CDH with length separated single-walled carbon nanotubes on graphite electrodes we could increase the rate of direct ET significantly. The reduction of the flavin and the heme subdomain could be detected by cyclic voltammetry and square wave voltammetry. Different methods for CDH immobilization are examined to achieve direct ET. The resulting electrode architectures are compared with CDH embedded in redox polymer hydrogels leading to excellent electrocatalytical properties via mediated ET. Depending on their stability CDH modified anodes (for oxidation of various organic substrates) will be combined in biofuel cells with enzyme modified cathodes for oxygen reduction.
Electrochemical treatment of tannery wastewater

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The leather industry is a major producer of wastewaters and solid wastes containing potential water and soil contaminants. Considering the large amount and variety of chemical agents used in skin processing, the wastewaters generated by tanneries are very complex. In this work we studied the electrochemical treatment of tannery wastewater using dimensionally stable anodes (DSA®) prepared by the Pechini method with compositions Ti/Ir0.01Sn0.99O2, Ti/Ir0.10Sn0.90O2, Ti/Ru0.10Sn0.90O2, Ti/Ru0.30Ti0.70O2, Ti/Ir0.15Ru0.15Sn0.70O2, and Ti/Ir0.30Ti0.30Sn0.40O2 [1].

Firstly, the electrolyses were performed to treat a real wastewater, which was collected from the equalization tank of a finishing tannery [1]. The treatment of this wastewater was performed in a 50 mL one-compartment batch cell, at room temperature (ca. 25 °C) and under magnetic stirring. The effects of the oxide composition and current density were investigated. Results showed that all the studied electrodes led to a decrease in the content of both total phenolic compounds and Total Organic Carbon (TOC), as well as lower absorbance in the UV-Vis region. At 20 mA cm-2, the best performance was obtained with the Ti/Ru0.30Ti0.70O2 electrode (TOC removal = 14.3% and phenol removal = 82.6%, after 5 h) and the Ti/Ir0.15Ru0.15Sn0.70O2 electrode (TOC removal = 14.2% and phenol removal = 80.4%, after 5 h). The Ti/Ru0.30Ti0.70O2 electrode was the most efficient for color removal at 440 nm, and the Ti/Ir0.15Ru0.15Sn0.70O2 electrode was the best for degradation of organic compounds with unsaturated bonds absorbing at 228 nm. Electrolyses performed at 50 and 100 mA cm-2 were more efficient for organic compound removal. Phenol removals were 78.5% at 50 mA cm-2 and 83.9% at 100 mA cm-2 and, TOC removals were 31.3% at 50 mA cm-2, and 40.5% at 100 mA cm-2, after 5 h of electrolysis with the Ti/Ru0.30Ti0.70O2 electrode. We also performed experiments using a synthetic wastewater prepared with 30 compounds used in skin processing. The treatment of this wastewater was carried out in a 145 mL flow cell, at a 152 mL min-1 flow rate, 20 mA cm-2 current density, room temperature (ca. 25 °C) and under magnetic stirring. A mixture of Na2SO4 0.1 mol L-1 and NaCl at different concentrations were added to evaluate the effect of chloride concentration on TOC and phenol removal. Results show that TOC removal is independent of the chloride concentration, but phenol removal depends on the concentration of this anion. The higher chloride concentration, the faster is the phenol removal rate.

The use of DSA® type electrodes in the electrochemical treatment of tannery wastewater proved to be useful since it can promote a decrease in total phenolic compounds, TOC, absorbance, and toxicity.

References

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Preparation and Characterization of Nanostructured Metallic Bilayers of Pt/Ir/Pt for CO and Methanol Electrooxidation

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Bimetallic catalysts comprise of Pt and Ir (PtIr) has been one of the most studied compositions and are suitable for technological applications. The used most electrodes are composed by alloys. Recently, Fert received the Nobel Prize due to its work on the unexpected properties of nanostructured multilayers of metals [1]. Using Fert ideas, our group observed distinct electrocatalytic properties in multilayers for the electrooxidation of small organic molecules compared to bulk platinum or its alloys [2]. The objective of this work is study the effect of the intermediate metallic layer thickness, from 0.6 up to 9.8 monolayers, MM, of Ir using CO electrooxidation as probe reaction.

Figure 1 shows the voltammetric profile for Pt, Ir/Pt and Pt/Ir/Pt in 0.1M HClO₄. Adsorption/desorption of H ads, double layer, formation and reduction of PtO can be observed for Pt and Pt/Ir/Pt electrodes. The voltammetric overlap of the H adsorption to Pt and Pt/Ir/Pt agree with the no change in the surface area meaning that the roughness factor did not change.

![Figure 1 - a) Voltammetric profile of Pt electrode, Pt/Ir and Pt/Ir/Pt multilayer and b) Stripping CO Inset: Methanol electrooxidation. The electrolyte was 0.1 M HClO₄, v = 50 mV s⁻¹. T = 25 °C. In Figure 1b, can be observed the CO electrooxidation. We observed that the potential peak was displaced 140 and 180 mV for more negative potential compared to Pt₅bulk for 40 and 1000 s of Ir electrodeposition, where was obtained 0.6 and 9.8 MM. The inset shows the methanol electrooxidation and can be observed the increase of 166.5% for Pt/Ir/Pt compared to Pt₅bulk showing that the thickness of this intermediate MM can modulate the activity of the Pt monolayer.

References
Synthetic Diamond, Diamond-based, and Diamond-like Electrodes: the Dependence of Their Electrochemical Activity on the Resistivity

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Synthetic diamond is a novel electrode material combining high corrosion resistance with reasonable conductivity and electrochemical activity. It is perspective for water purification, electroanalytical purposes, electrosynthesis of strong oxidants, and other environment-friendly applications. Nanocrystalline diamond and diamond-like carbon are somewhat inferior to crystalline diamond, as electrode materials, in their corrosion resistance; yet, they have some advantages, e.g., lower cost and technological effectiveness. The materials’ conductivity is controlled by “impurities”: by doping the semiconductor diamond with boron (an acceptor); by nitrogenation of the nanocrystalline diamond or diamond-like carbon; and by adding diamond-like carbon with metals.

In this work we aimed at optimizing the electrical properties of these electrode materials. We showed that the electrochemical activity of the electrodes increased with the increasing of the materials’ conductivity. The electrochemical activity was characterized by the measuring of either the Faradaic (charge-transfer) resistance or the cathodic and anodic current peak separation in cyclic voltammograms taken in the redox solutions ([Fe(CN)₆]³⁻/⁴⁻) with the varied Red/Ox concentration ratio. From the cyclic voltammograms or Nyquist impedance-spectra plots, the transfer coefficients for the electrochemical reaction were calculated. All three material types (diamond [1], nanocrystalline diamond [2], diamond-like carbon heavily added with N [3], Ti [4], W, or Pt) demonstrated gradual increase in the reaction rate, with the increasing of their conductivity, and eventually show reversible electrode behavior: the transfer coefficients approach ~0.5; the peak separation, ~60 mV.

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On the performances of lead dioxide and boron-doped diamond electrodes in the anodic oxidation of a simulated wastewater containing the Orange Reactive 16 dye

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The interest on the elimination of organic toxic compounds present in several kinds of industrial effluents has increased significantly in the last years. Dyes are one type of organic compound commonly present in industrial effluents, mainly from textile plants. Frequently, lead dioxide and, more recently, boron-doped diamond (BDD) anodes have been used for the electrochemical oxidation of organic compounds. In this work, the electrochemical performances of Ti-Pt/PbO$_2$ and Si/BDD electrodes in the oxidation of simulated wastewaters containing the Orange Reactive 16 dye (OR-16), using a filter-press reactor, were investigated. The β-PbO$_2$ electrode was electrodeposited on a Ti-Pt substrate using a one-compartment cell, applying 20 mA/cm$^2$. The amount of deposited oxide was equal to 50 mg/cm$^2$. The following magnetically stirred aqueous solution was used as electrodeposition bath: 100 mM Pb(NO$_3$)$_2$ + 0.5 g/L sodium lauryl sulfate, in 0.1 M HNO$_3$, at 65 °C. The BDD electrode, with a final boron content of 8000 ppm, was prepared at the Centre Suisse de Electronique et de Microtechnique SA (CSEM), Neuchatel, Switzerland, on silicon wafers using the hot filament chemical vapor deposition (HF-CVD) technique. In order to investigate the effects of operating parameters on the OR-16 dye oxidation (85 mg/L in 0.1 M Na$_2$SO$_4$), electrolyses were carried out at different flow rates (2-7 L/min), current densities (25-100 mA/cm$^2$) and in the presence (or not) of different chloride concentrations (10-70 mM). In the absence of chloride the performance of the BDD electrode in the dye decolorization was better than that of the β-PbO$_2$ electrode, achieving 100% decolorization by applying a total charge ($Q_f$) of only 1.0 A h/L and 2.0 A h/L, respectively. For both electrodes, the color removal was affected by the hydrodynamic conditions and the best results were achieved when a high flow rate (7 L/min) was used, indicating that the oxidation on the electrodes is a mass-transfer controlled process. On the other hand, in the presence of chloride the color removal rates were increased the higher the chloride concentration. For example, in the electrolyses carried out by adding 50 mM of chloride in the support electrolyte (at 50 mA/cm$^2$ and 7 L/min) the color removal rates were increased about tenfold ($Q_f$ = 0.1 A h/L – BDD, and $Q_f$ = 0.2 A h/L – β-PbO$_2$). The improvement of the electrodes performances was assumed to be due to electrogenerated hypochlorite ions (indirect oxidation); on the other hand, the color intensity (absorbance) decreased linearly with $Q_f$, indicating the occurrence of charge-transfer controlled processes. The energy consumption per unit mass of the OR-16 dye in the simulated wastewater for the electrolyses using the Ti-Pt/β-PbO$_2$ and Si/BDD electrodes were only about 8 kW h/kg and 5 kW h/kg, respectively; hence, both electrodes might be excellent options for the electrochemical treatment of dye wastewaters.

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Production of iron with low CO₂ emissions. Electrowinning from molten salts.

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With a long time perspective in mind the objective of these experiments were to investigate alternative steelmaking processes where the total carbon dioxide emission can be reduced substantially. Electrolysis experiments were conducted in iron oxide-fluoride/chloride mixtures in laboratory scale where solid iron was deposited on a steel cathode. Another objective of these tests was to find materials that could serve as oxygen-evolving anodes in the molten salt mixtures.

Electrolysis experiments were run for 4 to 6 hours at constant currents up to 10 A. The experimental set-up is shown in Figure 1. A rotating steel cylinder served as the cathode. Electrolysis was interrupted for short periods when the cathode was taken out for cleaning and removal of the deposit. The deposit was easily scraped off while it was still red hot as shown in Figure 2.

The deposited iron was very dendritic, causing substantial electrolyte entrainment. By a method of water treatment and magnetic separation the iron could be cleaned and separated as a fine powder. The structure varied with the experimental conditions, especially current density and the cathode’s rate of rotation.

The work on finding an “inert” oxygen-evolving anode was concentrated on materials where iron oxide was the main component. Most electrolysis experiments were carried out with magnetite and magnetite-iron cermets as anodes, as any wear of these would cause no contamination in the electrolyte and the deposited iron. Negligible wear was observed in these 4 – 6 hours experiments.

Local visualization of catalyst activity
as a prerequisite for optimization of fuel cells and industrial electrolysis processes

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CO₂ emission due to high energy consumption is of major concern due to its impact on the greenhouse effect and global warming. Hence, reduction of energy or replacement of fuels may significantly contribute to improvements of ecologically safe production processes of energy and basic chemicals.

Optimization of gas diffusion electrodes (GDE) for fuel cells and electrolysis applications requires an in-depth understanding of a variety of processes occurring in these devices. These include mass transfer of educts and products, the catalytic reaction as well as conductivity. The quality of a GDE thus depends on many interconnected parameters. Usually, however, optimization is carried out in a way, that either an isolated component like the catalyst itself is investigated, or a macroscopic quantity like current-voltage behavior is measured after one production parameter of the GDE is changed. Both approaches, despite indispensable in a certain stage of research, do not provide a microscopic picture of the processes in the GDE.

In order to obtain a microscopic picture of catalytic processes at surfaces, we use the scanning electrochemical microscope (SECM) for the local visualization of catalytic activity. Our current focus lies on cathode processes for fuel cells and NaCl as well as HCl electrolysis for chlorine production using odc (oxygen depolarized cathodes). We have recently introduced the redox-competition mode to investigate oxygen reduction at a variety of surfaces [1], which, in its extension, is also able to visualize the H₂O₂ production [2]. Thus, activity and selectivity of an electrode surface towards oxygen reduction can be obtained with high lateral resolution in a single experiment. This redox competition mode has been applied to investigate small catalyst libraries which have been prepared by either depositing small amounts of powder catalysts from suspension on a glassy carbon surface or by electrodeposition using a droplet cell for the electrochemical induced formation of small catalyst spots. The SECM thus allows for a fast screening of catalysts samples under identical conditions. To go a step further, we are currently applying the knowledge obtained in these experiments to the investigation of GDEs under relevant conditions. This includes measurements at high temperatures in alkaline environment as well as investigations in the presence of chloride and chlorine. Results concerning the local investigation of catalyst libraries and GDEs will be presented.

Screening of Microbes for Searching for the Effective Catalysts in Electrochemical Activation of Carbon Dioxide

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Our lab focuses on electrocatalysis which is useful for the effective conversion of carbon dioxide to useful organic compounds. *Moorella thermoacetica* (or *Clostridium thermoaceticum*) is an acetate-producing anaerobic bacteria which can grow under CO$_2$/H$_2$ or CO. Carbon Monoxide Dehydrogenase (CODH) is a key enzyme in this organism. We showed that the enzyme can convert CO$_2$ to CO selectively with almost no overvoltage by electrochemical reduction$^{[1]}$ and *Moorella thermoacetica* itself also can convert carbon dioxide to formate effectively with high current efficiency.$^{[2]}$ Currently we are trying to find useful microbial catalysts for the electrochemical reduction of CO$_2$ to organic acids among the group of *Clostria* and other formate dehydrogenase containing microbes. We tested *Clostridium thermoaceticum*, *Clostridium pasteuranum*, *Clostridium formicoaceticum*, *Clostridium acetobutyricum*, *Paracoccus sp.*, *Pseudomonas sp.*, *Saccharomyces cerevisiae*, etc. and found that the main product is formate and the production yield varies a lot depending on the kind of microbe. The immobilization of the microbes on the electrode was successful by using viologen redox polymer.

Electrochemical Degradation of Pollutants of Drainage Water from a Depot of Organophosphates (Insecticides) buried as Waste in a Sand Dune

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One of the most famous pollution sites in Denmark is Hoefte 42 at Harboore Tange in the west coast of Jutland where a local producer of insecticides during several years in the fifties and sixties was allowed to let out and bury several tons of raw wastewater, solid waste and pesticides in an sand dune. After a storm in 1971 and the escape of substantial amounts of waste the authorities became interested in the problem. Solid waste was removed from the depot in 1971 and again in 1981 but several tons of liquid chemicals was left in the sand dune. In 2006 a solid iron wall was established to isolate and control the remaining part of the waste and drainage water from the isolated area is now let to an absorbent system based on activated carbon.

By help of an electrochemical oxidation method with aqueous sodium chloride and a reactor with anode material of platinated titanium it was tried to decrease the amount of organophosphates in the drainage water and to investigate the treated water for degradation products. It was found that the principal pollutant components, methylparathion, parathion and malathion all were degraded to below the detection limit of 0.01 mg/L of the HPLC-chemical analytical method within short time. However, some degradation compounds turned up. Of these only o,o,o-triethyl phosphate could not be degraded. The electrochemical oxidation method could keep this compound at a rather low but still unacceptable steady state level. All other known components were degraded together with a number of unknown components as it could be seen from the HPLC-spectra of samples taken before and after the electrochemical treatment. These results looks promising with respect to purifying the drainage water from the polluted site. Before this method several methods has been tried for the purpose of degradation of the present pollutants. This still ongoing R&D-project is expected also to solve the problem with the recalcitrant ester that turns up and stays during the time of electrochemical treatment.
Nitrate Reduction on Pt Single Crystals with Pd Multilayer

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The increasing interest in the electro reduction of nitrate ions is related to the growing environmental problems caused by nitrate contamination of the water [1]. Platinum is the most studied catalyst to this reaction [1], but palladium containing catalysts present higher selectivity to N₂ [2], and for environmental purposes is the most interest metal to be investigated. The aim of this work was to study the nitrate electro reduction on Pt single crystals with basal orientations, modified or not by the adsorption of a Pd multilayer (about 2-5 Pd layers deposited on the platinum single crystal substrate).

Figure 1 shows some representative results. In H₂SO₄ 0,1M + KNO₃ 0,1M the reduction occurs at low potentials (E<0,3V vs RHE) in all cases, different from what happens with Pt single crystals, where nitrate reduction occurs in potentials with little or no hydrogen or sulfate adsorption, presenting structure sensitivity dependence[1].

The reduction rate increases following the order: Pt(110)/Pd < Pt(111)/Pd < Pt(100)/Pd. In Pt(110)/Pd nitrate reduction is only observed at scan rates lower than 10 mVs⁻¹, thus showing a severe kinetic dependence. After some cycles, all the electrodes become blocked and the same happens at high nitrate concentration. This is probably due to the effect of some adsorbed intermediate which is not completely reduced and accumulates on the electrode. This specie can be NO₃⁻. This species reduces at the same potential range as nitrate and is not fully stripped until E = 0.06V [3].

Figure 1: Voltamograms of Pt with Pd multilayers in 0,1M H₂SO₄ without (dotted lines) and with KNO₃ 0,1M (2nd cycle solid lines and 6th cycle dashed lines): a) (111), b) (100) and c)(110). Starting potential 0.7V. Nitrate reduction was recorded at 10mVs⁻¹ and the blanks at 50mVs⁻¹. The blank currents are divided by 5 to compare with nitrate reduction.

References
Laccase-modified electrodes by layer-by-layer self assembly for the use as fuel cell cathodes

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In the last decade the discussion about a replacement of classical fossil fuels as petrol, gas and coal has been getting more and more important. Not only a replacement of the fuels but also the efficiency of the combustion and the energy conversion are important aspects for the global ecology. For both of these problems the electrochemical „combustion“ in fuel cells present a very promising way to reach these goals. That is because these kind of cells have very high efficiencies and use ecologically friendly fuels like hydrogen, methanol or glucose and in addition they are miniaturizable, mobile and continuously usable by refilling the fuel. But one problem of these systems represent the catalyst, usually noble metals or their alloys, that are expensive, non selective and very sensitive to poisoning. Therefore in the last years more and more groups use enzymes as catalysts instead of inorganic catalysts e.g. Pt/Ru. The mostly used enzymes are Glucose Oxidase (glucose oxidation), Bilirubidium Oxidase and Laccase (both for oxygen reduction) and the design of so called biofuel cells have been reported on several occasions [1-3].

In this presentation we report the preparation of *Trametes togii* (arg.) Laccase modified electrodes using the layer-by-layer self assembly technique (lbl) with Os-redox polymers as polycation with integrated redox mediator and the enzyme as polyanion. The main advantage of this approach over other methods [3-6] is that almost all important film properties (thickness, concentration of enzyme and mediator, permeability etc.) can be controlled by the choice of the number of layers and the deposition pH. The dependence of the catalytic current on the oxygen partial pressure, the pH during the lbl deposition and during the electrochemical measurement was studied. We also have studied the tolerance of these cathodes to methanol.

Modification of glassy carbon surface with anthraquinone from the solutions of its diazonium derivatives: An oxygen reduction study

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The electrocatalytic reduction of oxygen on quinone-modified carbon electrodes is of great importance since it allows the fast electrochemical production of hydrogen peroxide. Quinones were grafted by the reduction of diazonium salts on carbon electrode surfaces. These electrodes exhibited good electrocatalytic properties for oxygen reduction, yielding hydrogen peroxide quantitatively [1-3].

In the work presented here we report for the first time the spontaneous grafting of anthraquinone (AQ) to glassy carbon (GC) from the solutions of its diazonium derivative. Surface modification was performed in acetonitrile and in aqueous solutions of various pHs. A strong bonding between AQ and GC surface is in evidence as the modified electrodes withstand long-term sonication in acetonitrile. The effect of immersion time on the cyclic voltammetric response of the AQ-modified GC electrodes was tested. These experiments revealed the quasi-reversible redox-behaviour of the spontaneously attached AQ in 0.1 M KOH. Rotating disk electrode voltammetry was used to characterise the electrocatalytic properties of the electrodes for O₂ reduction. The kinetic parameters for oxygen reduction were determined using a surface redox-catalytic cycle model of quinone-modified electrodes previously proposed [1]. The electrocatalytic effect of spontaneously grafted AQ on oxygen reduction was similar to that of the electrochemically grafted electrodes [1,2].

Alternatively, the surface modification was carried out by electrografting using in situ generated AQ diazonium salts. These salts were synthesized in acetonitrile and in acidic aqueous solution using 1- and 2-aminoanthraquinone as starting compounds and the covalent grafting of in situ generated diazonium cations has been demonstrated. The O₂ reduction results are compared with those of surface-bound AQ grafted by the reduction of previously synthesized and purified AQ diazonium tetrafluoroborates. The results obtained are important for the development of fuel cells for peroxide production [4]. The application of peroxide is continuously increasing and there are several advantages of the electrochemical peroxide synthesis over the existing chemical route.

References
Immobilization of Pyranose Dehydrogenase on Graphite Electrodes Modified with Length Fractionated Single Wall Carbon Nanotube and Low Potential Osmium Polymer for Biofuel Cell Applications

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The recent great interest in biofuel cells has caused a renewed interest in sugar oxidizing enzymes other than glucose oxidase (GOx). Even though “wiring” of GOx with Os-redox polymers has reached very efficient levels, GOx still suffers from some drawbacks. GOx oxidizes glucose at the C-1 position, from which follows that only one of the possible anomeric forms is the substrate for this enzyme, i.e., the \( \beta \)-form, which in aqueous solutions constitutes around 64\% of the total glucose content. Additionally it is still a hydrogen peroxide producing oxidase meaning that molecular oxygen will always be competing with any mediator for being the electron acceptor to the reduced form of the enzyme and there is always a risk that some hydrogen peroxide will be formed. A compartment free biofuel cell that relies on using an oxygen reducing enzyme, e.g., laccase or bilirubin oxidase, will of course rely on molecular oxygen being present. These multicopper blue oxidases are sensitive to even trace levels of hydrogen peroxide and therefore its presence should be avoided as much as possible.

During a previous work we investigated different enzymes as an alternative to GOx. Pyranose dehydrogenase (PDH) from \textit{Agaricus meleagris} showed outstanding capabilities to oxidize several aldopyranoses and to communicate with graphite electrodes modified with osmium polymer. This enzyme exhibits an extremely broad substrate tolerance and variable regioselectivity for the oxidation of both mono- and oligosaccharides. The selectivity of PDH for secondary alcoholic group(s) at the C-2, C-3, or C-2 + C-3 allows the enzyme to oxidase the substrate one, two or three times transferring to the electrode up to six electrons. Moreover PDH has no activity at all with molecular oxygen and a long stability. The conjugation of the enzyme with a low potential osmium polymer allows oxidation of glucose and other sugars already at +130 mV vs. NHE. Single wall carbon nanotubes treated with strong acid solution and length separated, improved the electron transfer efficiency up to a factor of five times when immobilized with the redox enzyme and the osmium polymer.
Prediction of Capacitive Deionization performance by BET surface area measurements

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Capacitive Deionization (CDI) is an emerging desalination technology especially suitable to deal with decentral salination problems, such as brackish water sources and irrigation problems due to water logging. CDI is based on the adsorption of ions into an electrical double layer, which is formed when an electrode surface is electrically charged in an electrolyte solution. The sum of the double layer capacity per unit electrode surface area dictates the maximum deionization performance of the electrode. However, this capacity is not unique, since it is dependant on many system characteristics such as salt concentration and surface potential. Furthermore, techniques to obtain this capacity demand extensive characterization setups.

The goal of this research was to establish if easily obtainable electrode material properties, such as the BET surface area, can be used to predict CDI performance at various system characteristics.

The link between BET surface area measurements and CDI performance is based on the electrochemically active area of a material that is defined as the double layer capacity times the amount of double layer per unit material. The dependency of the double layer capacity to system characteristics was tested by performing experiments with electrolyte concentrations of 0.1 mM through 1 M NaCl, cell voltages of 0 through 1.2 V and temperatures of 5 through 45 °C. The experimental results comply with the Stern double-layer model, and yielded double layer capacities similar to literature data.

The validated double-layer model enables us to relate any characterization result in terms of capacitance to an electrochemically active area independent of the system characteristics. Furthermore, we can compare the electrochemically active area to the BET area, to see what fraction of the total BET area is used for CDI, and make detailed conclusions about the relation between BET area and CDI performance of an electrode material.
Effect of Carbon Support on the Kinetic Behaviour of a Metal Hydride Electrode


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Metal hydride alloys are widely used as negative electrodes in rechargeable batteries. The performance of these electrodes is affected by numerous factors such as the kinetics of the processes taking place at the metal–electrolyte interface and the hydrogen diffusion within the bulk of the metal alloy particles [1]. In this paper, we studied the possibility to improve the electrochemical behaviour of AB$_5$ alloy commercial electrodes using different carbons as support, such as carbon blacks and a selection of commercial and in-lab synthesised carbon nanotubes.

The carbons selected for this work present different morphologies (i.e., spherical and tubular). Furthermore, they also present a variation of the porous structure and subsequent surface area, which also are going to influence in their further electrochemical behaviour.

Carbon samples were texturally characterised by adsorption-desorption of N$_2$ and CO$_2$ at 77 K and 273 K, respectively. The carbon structure was also analysed by XRD, Raman, SEM and TEM, and the chemistry of the samples was also characterised by elemental analysis and PZC [2]. The charge and discharge techniques, cyclic voltammetry, rate capability on charge and discharge, and linear polarisation were used for the electrochemical characterisation of the electrodes studied. The electrochemical behaviour of all the samples was related to their morphological, textural and chemical properties.

The results obtained show that there is a clear influence of the nature of the carbon support on the alloy kinetics, as the use of carbon nanotubes improves the kinetic behaviour of the alloy, whereas in the case of active carbons the kinetics decreases with the increase of the surface area of the carbon support.


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Conducting Polymer Composites as New Electrodes for Clean Energy Technologies

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Conducting polymer/inorganic compound composites are in the focus of researches. These new materials give perspectives for various applications by combining together the different properties of the individual components. Recently synthesized representatives open opportunity for the combination of electrical and optical, magnetic or photocatalytic properties, leading to electrodes of special capabilities.

We present the characteristics and possible applicability of different nanocomposites such as
- poly(3-substituted thiophene)/maghemite (POT/ $\gamma$-Fe$_2$O$_3$) and magnetite (PAcT/ Fe$_3$O$_4$)
- polypyrrole/iron oxalate (PPy/Fe-ox)
- polypyrrole/vitamin B12 (PPy/B12).

The composites are characterized on the basis of different electrochemical measurements, including EQCM and a.c. impedance, as well as by ICP-AAS, UV-Vis spectroscopy, XRD, XPS, SEM, EDX.

Iron containing polymer composites are promising as new electrodes possessing magnetic and/or photocatalytic behaviour. The enhanced redox activity of cobalamin, immobilized in PPy/B12 composite electrode, may be exploited in mediated reduction processes in bio-electrochemical systems.

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Decomposition of Various Endocrine-Disrupting Chemicals at Boron Doped Diamond Electrode

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Recently, endocrine disrupting chemicals have been spread over the environment and have deteriorated the generative function of some species of living things on the earth. Among compounds associated with endocrine disruption, Bisphenol A (BPA) and 17α-Ethynyl estradiol (EE2) occupy a prominent place. In recent years, BPA has been detected at considerably higher level ranging from 0.14 to 12.0 μg dm⁻³ in United States river water and up to 10 mg dm⁻³ in leachates from hazardous waste landfill sites in Japan. With regard to possible effects to humans, researchers have found that even in very low concentration levels of BPA and EE2 can cause harmful effects such as abnormal physiological changes, reproductive impairments, and testicular and breast cancer. Considering the serious adverse impacts of these chemicals on human health and environment, it is quite urgent to find an efficient approach for removing such a chemical so as to minimize their contamination. In the past decade, electro oxidation technique is proved to be a well established and an efficient technique to destruct the biologically persistent organic pollutants for water and wastewater treatment. It is mainly due to an appropriate choice of anode material that can allow complete removal of TOC with high current efficiency. Attempts have been made to study the electrochemical removal of BPA using Ti and Pt mesh, Pt/Ti, SnO₂/Ti and carbon fiber electrodes. But Ti, Pt and Pt/Ti electrodes were not effective to achieve total mineralization of BPA due to electrode deactivation and poor generation of more hydroxyl radicals. In the case of carbon fiber electrode, BPA has been totally removed as polymeric products that form on the electrode surface based on anodic polymerization technique. However, the polymerized film should be considered here to avoid secondary pollution. In recent years, boron doped diamond (BDD) electrode has been proved as successful anode material to decompose a variety of organic pollutants such as phenol, 4-chlorophenol and chloromethylphenoxy herbicides. As far as the EE2 concern, no report is available on degradation study by electrochemical methods. Thus, this study aims to investigate the electro oxidation and mineralization behavior of BPA and EE2 in aqueous solutions using BDD anode under galvanostatic control. The result for BPA was shown in the following.

Electrolysis were carried out with solution containing constant initial concentration (20 mg dm⁻³) of BPA under similar experimental conditions (35.7 mA cm⁻², 0.1M Na₂SO₄) with an equal surface area of Pt and GC each as anode, to compare the corresponding oxidizing ability with BDD anode. As can be seen in the figure below, the results are quite explicable in terms of the OH radical generation behavior of anodes. It could be seen that the anodic oxidation with BDD yields a continuous TOC removal up to the total mineralization of BPA within electrolysis time of 14 h whereas in the case of Pt as anode, hardly 20 % TOC removal was obtained under the similar experimental conditions. The better efficiency of BDD with a comparison of Pt can be accounted for the larger generation of oxidant OH radicals on its surface as it exhibits a “non-active” behavior. This is already well documented in our previous study.
Photoelectrochemical Generation of Chlorine and Oxidation of Organics in Superficial Water

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Active chlorine is used in water and wastewater treatment as both a disinfectant and an oxidant agent. Active chlorine is a term referring to all of the species of chlorine in solution and includes molecular chlorine (Cl₂), hypochlorous acid (HOCl), and hypochlorite ion (OCl⁻). Despite the problems caused due to the production of by-products, this process of using chlorine as a water disinfection process remains the primary treatment method of destroying pathogens and thereby used to provide public health protection. Since chloride ions are naturally present in superficial waters at levels from 10 to 250 mg L⁻¹, the electrochemical oxidation of chlorides has been a very successful method of generating chlorine in superficial waters. However, photoelectrocatalysis has also been shown to be efficacious in this regard generating free chlorine in an open-air reactor using a TiO₂ thin-film electrode biased at +1.0 V (SCE) illuminated by UV light. The aim of the present work was to investigate the simplest reactor by which to generate active chlorine by photoelectrocatalytic oxidation under current controlled density (J) using nanoporous Ti/TiO₂ electrodes and UV irradiation. Active chlorine quantitation was monitored by the official method based on chemical reaction with N,N-Diethyl-p-phenylenediamine (DPD). All of the electrolysis experiments were performed using a Galvanostat Micro Química MQGV–01 instrument and employing a photoelectrochemical reactor having 250 mL in volume. Into the reactor chamber we inserted a 125W lamp in a quartz sleeve as well as two electrodes: As a photoanode, we used a Ti/TiO₂ prepared by the sol-gel method (6 cm²). A Pt gauze was used as the cathode. Chlorine production was optimised by testing: controlled current density from 5 to 50 mA cm⁻², chloride concentration from 0.005 to 0.250 mol L⁻¹, pH variation from pH 2 to 12, and interfering salts. Results show that this photoelectrochemical method can produce active chlorine at levels compatible to water disinfection processes using a chloride concentration higher than 0.010 mol L⁻¹ and a current density of 5 mA cm⁻². Maximum chlorine generation is obtained at pH 4 and at a J=30 mA cm⁻². The method was successfully applied to treat superficial water collected from a river in north-eastern Brazil. After 150 min of photoelectrocatalytic oxidation we obtained a decrease of 90% in total organic carbon removal, 100% in turbidity and 74% in discoloration. The financial support of FAPESP, CNPq, CAPES from Brazil and NSF (USA) is acknowledged.
Poster Presentations
Modification of polypyrrole composites with metal nanoparticles: A new material for environmental applications

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The ion-exchange properties of polypyrrole-polystyrene sulfonate composite materials (PPy-PSS) have been already exploited in several applications [1-3]. In this work a forced capture method (FCM) is presented to modify these composites with metal nanoparticles. More specifically, a selected reductive potential was applied to the composites to achieve a potential-controlled capture of copper ions from a copper(II) solution. The copper ions were then reduced to copper metal that could be switched throughout its oxidation states (Fig.1). Cyclic voltammetry (CV), electrochemical quartz crystal microbalance measurements (EQCM), electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM) techniques were used both to characterize the composites and to model the FCM approach.

The FCM has been developed as a new synthetic tool that could be applied to any other metal with significant catalytic properties for environmental applications.

Fig.1

References
Cyclodextrins are naturally occurring cyclic oligosaccharides, which have a rigid torus shape, with an inner hydrophobic cavity and an outer hydrophilic one [1]. They possess a remarkable ability to form inclusion complexes with host molecules and have found applications in the pharmaceutical, cosmetic, food and separation technology [2,3]. Sulfated β-cyclodextrin, in particular, shows a high solubility in water and an anionic behaviour in aqueous solution so it can be electrochemically incorporated in a polymer matrix during an oxidative process.

In this work sulfated β-cyclodextrin has been permanently incorporated within a polypyrrole matrix during electropolymerization and the system has been characterized in detail. The sensor obtained has been used to detect methyl, ethyl and benzyl viologen. Viologens are versatile redox systems and their structures are similar to a variety of pollutants so they represent good molecular models to point out a new strategy in pollution remediation. The interaction between the viologens and the modified polypyrrole was studied using simple cyclic voltammetry and the detection limit was found to be approximately 4 mM. Detection properties have been compared with a corresponding polymer doped with a large non-macrocyclic anion, which is permanently included within the polypyrrole matrix but cannot form inclusion complexes. Results show higher sensitivity for the sensor composed of polypyrrole doped with sulfated β-cyclodextrin. Further investigations are ongoing in order to verify the entrapment of the viologens inside the sulfated β-cyclodextrin cavity. In this case the materials would be able not only to detect viologens but also to remove them from solutions.

Fig.1: β-cyclodextrin.  
Fig.2: CV of the sulfated β-cyclodextrin doped polypyrrole and a bare gold electrode in a 5 mM solution of benzyl viologen.

References
Preparation and Characterization of Nanostructured Films Formed by Poly(allylamine), Albumin and Nickel Phthalocyanine. Sensing Properties Towards Biological Amines

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The fabrication of ultrathin films has contributed to the technologic development in the sensor area. In this work, electrostatic Layer by Layer (LbL) technique was applied to produce nanostructured films containing layers of a polycation (poly-allylamine:PAH), and polyanions (albumin from serum bovine: BSA or tetrasulfonated nickelphthalocyanines: NiPc). Different films were constructed changing the polyanion compound: PAH/BSA, PAH/NiPc, PAH/BSA/PAH/NiPc and PAH/BSA-NiPc. Films were characterized by spectroscopic techniques (UV-Vis, FTIR and Raman). Electrochemical behavior of the films deposited onto ITO was investigated by cyclic voltammetry. The influence of the architecture of the film, and the number of layers in the response was investigated. The effect of other parameters such as the pH, the presence of O₂, the nature and the concentration of the electrolytic solution, the scan rate and number of cycles were also studied.

After the spectroscopic and electrochemical characterization, the ultrathin films were applied as voltammetric sensors for neurotransmitters (dopamine and serotonin) and biogenic amines (dimethylamine, tyramine, and hypoxanthine).

In good accordance with previous results, voltammograms obtained using PAH/BSA LbL electrodes immersed in dopamine showed well-defined reversible redox pair [1,2]. When using PAH/NiPc or PAH/BSA-NiPc films, a noticeable electrocatalytic effect was observed. In addition, films containing NiPc showed an increased sensitivity towards dopamine. The LbL electrodes were also able to detect serotonin and biogenic amines (dimethylamine, hypoxanthine, and tiramine). In all cases well defined voltammograms were obtained.


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Determining of Chromium (VI) by Adsorptive Stripping Voltammetry with Morin

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Redox speciation of chromium has attracted a great deal of interest in view of the toxic properties of Cr(VI) compared with the much less toxic Cr(III). Cr(VI) dominates in effluents from metallurgical and metal finishing industries and Cr(III) exists mainly in tannery, textile and decorative plating industry wastes. The total chromium concentration in unpolluted natural waters is 1-10 µg L⁻¹.¹

A procedure for the determination of chromium in contaminated waters by AdsSV using morin or morin-5-sulfonic acid as adsorbing and complexing agents have been optimized. Cr(VI)-morin complexes are adsorbed into electrode and then reduced to Cr(III)-morin complexes. In the presence of tetrabutylammonium tetrafluoroborate peak current of free ligand decreases and the peak current of complex were lightly enhanced. The variation of peak current with pH, adsorption time, adsorption potential, ligand and quaternary ammonium salt concentration, and some instrumental parameters such as stirring rate in the accumulation stage and step amplitude, pulse amplitude and step duration in the obtaining of the square wave voltamperograms were optimized. The best experimental parameters were pH = 4.0 – 8.0 (Britton Robinson buffers), C_{morin} = 3.5 µmol L⁻¹, C_{TBATFB} = 10.0 µ mol L⁻¹, t_{ads} = 60 s and E_{ads} = -0.50 V vs Ag/AgCl. Under these conditions the peak current was proportional to the chromium concentration over the 0.0-25.0 µg L⁻¹ range, with a detection limit of 0.7 µg L⁻¹. Reproducibility for 6.0 µg L⁻¹ chromium solution was 3.1 % (n = 6). The method was validated with synthetic sea water spiked with 22 metal ions and fortified water GBW08607 (Reference material. Certified value: Cr 0.500µg/g) and applied to analysis of Cr(VI) in the presence of Cr(III) in contaminated waters.

References

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Influence of nitrogen on boron doped diamond electrodes in the nitrate electrochemical response

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Diamond films grown by chemical vapor deposition has been optimized during recent years because of their excellent physico-chemical properties. Due to its wide working potential window and high corrosion resistance, diamond electrodes have been proposed to be beneficial in a range of electroanalytical applications, which are depending of the material aspects\textsuperscript{1}. One of these aspects is the film doping, which can be carried out using boron or nitrogen to turn the diamond films as a semiconductor. Boron doped diamond (BDD) electrodes has been already studied as a new material with extraordinary properties that turn them as a chemical sensors\textsuperscript{2}. Particularly, high overpotential presented by BDD electrodes for hydrogen evolution has demonstrated to be a decisive attribute for studying the detection and reduction of several chemical species. Besides, the nitrogen addition during the BDD growth process (N and B co-doped electrodes) may also enhance this cathodic overpotential\textsuperscript{3}. This work presents the influence of nitrogen on BDD electrodes in response of nitrate ions reduction. Actually, the large use of nitrogen-based compounds in agriculture has increased their ion concentration in the biosphere promoting a significant pollution problem. The working potential window of the N and B co-doped diamond electrode in 1.0 M H\textsubscript{2}SO\textsubscript{4} (Fig. 1A) about of 3.0 V, justifies their performance improvement for nitrate reduction and detection. Furthermore, the variation of N\textsubscript{2} concentration during the BDD growth process was crucial in their electrochemical behavior. Increasing the N\textsubscript{2} concentration favored the occurrence of the nitrate reduction without the interference of hydrogen evolution reaction (Fig. 1B).

Fig 1: (A) cyclic voltammograms and (B) linear sweep voltammograms of nitrate reduction for the BDD electrodes grown in different N\textsubscript{2} concentration. Solutions used (a) 1.0 M H\textsubscript{2}SO\textsubscript{4} and (b) 0.1 M KNO\textsubscript{3} and scan rate at 0.1 Vs\textsuperscript{-1}

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Electrochemical oxidation of maleic acid an import by-product in the phenolic compounds degradation route

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Maleic acid is an important by-product during the oxidation of many phenolic compounds. The aim of this work is twofold: (i) carry out a systematic investigation of the electrochemical oxidation of maleic acid (ii) to show the correlation between electrochemical parameters and electrode composition. Based on our previous investigation [1-2] the following electrode compositions has been applied: Ti/RuO$_2$/Ti$_{0.7}$O$_{0.2}$, Ti/Ru$_{0.3}$/Sn$_{0.7}$O$_{0.2}$ and Ti/Ru$_{0.2}$/Ta$_{0.8}$O$_{0.2}$. They show good electrode stability and photocatalytic and electrochemical activity.

Galvanostatic electrolyses were carried out to determine the products formed in the process. The average composition was 1 mmol L$^{-3}$ of maleic acid, NaSO$_4$ and H$_2$SO$_4$ in suitable amounts to give a pH of 3, $\mu$ = 1.0. The current density of 100 mA cm$^{-2}$ was applied for 5 hours. For all electrode compositions investigated maleic acid do not show oxidation peak (Fig. 1A). The oxidation of the organic compound occurs simultaneous with the OER.

An average of 50% of degradation rate was obtained for all electrode composition investigated (Fig. 1B). An interesting feature observed from HPLC and TOC measurements is the total mineralization of the maleic acid with no intermediate formed. This is very elucidative for a better knowledge of the oxidation mechanism of phenolic compounds which always shows many side products formation. Changes in the current density and maleic concentration is currently under investigation and will be presented.

**Figure 1:** (A) Cyclic voltammogram of maleic acid (H$_2$SO$_4$/NaSO$_4$, pH = 3); (B) Degradation rate in function of electrolysis time ($i = 100$ mA cm$^{-2}$, $A = 2$ cm$^2$)

Multisensor for Electrochemical Determinations

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A new electrochemical multisensor was developed designed and constructed, which is suitable for analysis of small solution volumes (5-200 µL). This multisensor is composed of an array of small sensors - 8 solid working electrodes: 4 different non-toxic solid amalgam electrodes [1, 2], a copper, a gold, a platinum and a glassy carbon electrode. Moreover, solid amalgam composite electrodes can be built-in [3]. The prototype of the tested multisensors contained the following minielectrodes: m-AgSAE (disk diameter Ø 0.8 mm), MF-AgSAE (Ø 0.8 mm), p-AgSAE (Ø 0.8 mm), copper (CuE; Ø 0.6 mm), m-CuSAE (Ø 0.8 mm), gold (AuE; Ø 0.4 mm), platinum (PtE; Ø 0.6 mm) and glassy carbon (GCE; Ø 2.0 mm), and one platinum auxiliary electrode (Ø 0.8 mm). The array has the shape of a Teflon disc of 8-mm diameter. The working electrodes were situated on the circumference of the disc, and a platinum electrode, used as an auxiliary electrode common for all working electrodes, was placed in the centre of the disc. Calomel reference electrode based on silver solid amalgam [4] was prepared in a disc-shaped plug to cover the sensor compartment. The newly developed multisensor is especially suitable for fast finding of the most suitable working electrode for a particular determination and for simultaneous obtaining of information from 8 different electrodes which can greatly increase the information content obtained from a single voltammetric run.

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References
New Silver Solid Amalgam Paste Electrode for Environmental Application

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Modern polarographic and voltammetric methods can be successfully used for large scale monitoring of electrochemically active environmental pollutants [1]. Great attention is devoted to the various possibilities of elimination of problems connected with electrode passivation [2]. One possible solution is the application of the paste electrodes with easily renewable surface.

The silver solid amalgam can be used to prepare the so called silver solid amalgam paste electrode. Pastes can be made from fine powder of the silver solid amalgam mixed with a suitable pasting liquid. These pastes can be stuffed into a Teflon body of the electrode and there is a possibility to easily renew the electrode surface by pulling out and wiping off the paste. In combination with an electrochemical pretreatment of the electrode, it gives a good stability and reproducibility of voltammetric signals. Various types of silver amalgams with various pasting liquids were successfully tested and applied for the determination trace amounts of 4-nitrophenol as a model electrochemically reducible environmental pollutant.

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References


The Use of Solid Amalgam Electrodes as Electroanalytical Sensors for the Determination of Nitroquinolines

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Nitro derivatives of quinoline have been proven to be genotoxic [1], thus their presence in environmental samples is a legitimate cause for concern. Electrochemical detection using advanced electrode materials in batch and flow analysis offers sensitive and relatively selective tool for their determination [2].

In this contribution, it will be demonstrated on the example of 5- and 6-nitroquinoline (5-NQ, 6-NQ). For their determination direct current voltammetry (DCV) and differential pulse voltammetry (DPV) at nontoxic mercury meniscus modified silver solid amalgam electrode (m-AgSAE) were used. Linear calibration curves in the concentration range of 4·10^{-6} – 1·10^{-4} mol L^{-1} were obtained. Further, the polished silver solid amalgam electrode (p-AgSAE) was employed for amperometric detection of 5-NQ in flow injection analysis (FIA). Under optimized conditions (mobile phase 0.05 mol L^{-1} borate buffer, pH 9.0; flow rate 4 mL min^{-1}, detection potential –1.6 V; injection volume 100 µL) the limit of quantitation of ~ 4·10^{-6} mol L^{-1} was achieved. The repeatability of the detector response is satisfactory (RSD ~ 1.3 % for c(5-NQ) = 1·10^{-4} mol L^{-1}). Practical applicability of the method was verified for the determination of micromolar concentrations of 5-NQ in drinking and river water model samples.

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References
Voltammetric Determination of Submicromolar Concentrations of Genotoxic 5-Nitrobenzimidazole at Hanging Mercury Drop Electrode and Carbon Paste Electrode

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5-nitrobenzimidazole (5-NBIA) belongs to the group of genotoxic nitrated heterocyclic aromatic compounds. It can damage natural biological functions of living organisms. The occurrence of 5-NBIA in environment is expected in connection with chemical processes during fossil fuels combustion [1]. 5-NBIA was polarographically determined as a part of photographic processing solutions in the seventies of the last century [2], and it is known as proven carcinogen and mutagen [3].

This work is focused on the optimization of 5-NBIA determination in aqueous medium at hanging mercury drop electrode (HMDE) and carbon paste electrode (CPE) using different voltammetric techniques. The following techniques with mentioned limits of determination (L_D) were used for the determination of 5-NBIA: direct current voltammetry at HMDE (L_D = 2,2×10^{-7} mol·L^{-1}), differential pulse voltammetry at HMDE (L_D = 4,6×10^{-8} mol·L^{-1}), direct current voltammetry at CPE (L_D = 2,4×10^{-5} mol·L^{-1}) and differential pulse voltammetry at CPE (L_D = 3,5×10^{-6} mol·L^{-1}).

An attempt to increase sensitivity using adsorptive stripping voltammetry at HMDE was not successful. Therefore, we have used solid phase extraction for 5-NBIA preconcentration from model and real water samples with limit of determination around 10^{-8} mol·L^{-1}.

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References
Voltammetric Determination of Benserazide Using Carbon Paste Electrodes

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Many widely used drugs now present an environmental problem because they are not removed by biological waste water treatment plants and thus can enter environmental aquatic system where they can have detrimental effects. Therefore, our laboratory pays attention to development of electroanalytical methods capable to detect low concentrations of drugs in aquatic environment. One example of our effort is the determination of the levodopa inhibitor pharmaceutical Benserazide using differential pulse voltammetry (DPV), DC voltammetry and flow injection analysis (FIA) at carbon paste electrodes (CPE). Benserazide as the inhibitor of aromatic L-amino acid decarboxylase is used for the treatment of Parkinson’s disease [1]. Carbon paste electrodes offer high sensitivity, wide choice of compositions tailored to analytes of interest and quite reasonable reproducibility [2, 3].

As optimum media for calibration dependences, BR buffer pH 4 and 0.1M H3PO4 have been selected, with best carbon paste composition consisting of spectrographic graphite with mineral oil as the pasting liquid. The calibration dependences were measured in the concentration range of 4·10^-8 - 1·10^-4M Benserazide. The lowest limit of detection of 6.10^-8 M Benserazide (S/N = 3) was found for DPV in BR buffer pH 4. The attempts to further decrease the limit of detection by adsorptive stripping voltammetry were not successful. The results of voltammetric behavior of Benserazide were used also for FIA determination of this analyte.

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References
Anodic Determination of Oxalic Acid in the Presence of 4-Chlorophenol using Expanded Graphite-Epoxy Composite and Boron-Doped Diamond Electrodes

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In the present study, the comparative electrochemical behaviours of oxalic acid (OA) and 4-chlorophenol (4-CP) in aqueous media using an expanded graphite-epoxy composite (EGE) and an boron-doped diamond electrode (BDDE) has been investigated. The electrochemical performances of both electrodes for the detection of OA in the presence of 4-CP were studied using cyclic voltammetry (CV), chronoamperometry (CA), differential pulse voltammetry (DPV) and square-wave voltammetry (SWV). The EGE electrode was unmodified and used without any additional modification such as addition of an charge transfer mediator or specific reagents. The composite electrodes were prepared using epoxy resin (LY5052, Araldite) and the expanded graphite powder (SGL Carbon) was added under constant stirring. The ratio of the components was chosen to reach 20 % (wt.) expanded graphite. The paste obtained was pressed to a thickness of 1 mm at a temperature of 80 °C for 30 minutes in air. After drying for 14 h at room temperature, the electrode with a surface area of 9 mm² was put on a glass support and electrical contacts were made using silver contacts. The diamond electrode supplied by Windsor Scientific Ltd. for the electroanalytical purposes was a mirror polished polycrystalline industrial doped diamond (microcrystalline; doping degree about 0.1 % boron) disc imbedded in a PEEK(poly-ether-ether-ketone) rod and has been used also unmodified. OA was chosen as target pollutant in the presence of 4-CP, because it represents one of the typical end products or intermediates in aqueous phenol and chlorinated phenol oxidation processes, i.e., ozonation or electrochemical oxidation [1,2]. For both electrodes types were determined the analytical performances concerning the anodic determination of OA in the presence of 4-CP.

Selected references

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Effect of pH, Electrolyte Anion, and Temperature in the Permeation of SAMs by Electroactive Probes

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In our previous work, we studied the electron-transfer (ET) of \([\text{Ru(NH}_3\text{)}_6\text{]}^{3+}\) and \([\text{Fe(CN)}_6\text{]}^{3-}\) redox probes through a SAM of 11-amino-1-undecanethiol (AUT) on polycrystalline Au [1]. A mechanism of selective ion permeation into the monolayer allowed by the slightly disordered structure of the film [2], and driven by the nature of the electrostatic interactions established between the charged amino end-groups and the probes, explained the observed behaviour. These initial properties were reversed with increasing the electrode-solution contact time. Electrolyte anion binding to the charged amino end-groups was suggested to explain this behaviour. However, the kinetics of such a process should be much faster than the observed ($\approx 10^{-4} \text{ s}^{-1}$).

M. J. Capitán et al reported recently that the crystalline order of a monolayer of 1-nonanethiol on Au(111) was disrupted after 30 minutes contact with an ethanol solution [3] showing a similar kinetics ($\approx 2 \times 10^{-5} \text{ s}^{-1}$). The order was recovered when the ethanol was substituted by a helium flow upon 8 h. It suggested that although the thiol heads can keep periodically arranged on the substrate, the alkyl chains should lose its long-range order along the surface normal. It is well known that the lower energy of the chain-chain interactions, with respect to the S-Au bonding, allows a variety of conformational and tilt-order phase transitions that are temperature sensitive [4].

In this work the effect of the pH, the electrolyte anion, and the working temperature on the ET behaviour of the redox probes has been rigorously investigated by Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) in order to get deeper insight about the processes originating the shift observed at long film-liquid contact times.


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Development of environmentally non-aggressive Pb-Sn deposition baths: new alternatives to fluoborate baths.

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The development and characterization of new Pb-Sn deposition baths are of great importance, since most of the industrial baths for Pb-Sn deposition contain fluoborate, which is very corrosive and requires rigorous environmental control of its disposal (ISO 14000). Thus, the aim of this work was to develop less aggressive alkaline Pb-Sn deposition baths containing the organic complexing agents sorbitol, ethylenediaminetetraacetic disodium salt (EDTA) or sodium potassium tartrate (NaKC$_4$H$_4$O$_6$) and to characterize the deposition processes by voltammetric techniques and the morphology, composition and phase composition Pb-Sn deposits by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction spectroscopy (XDS), respectively. The deposition baths were: (1) Pb$^{2+}$ 0.05M + Sn$^{2+}$ 0.05M + sorbitol 0.4M + NaOH 0.8M, (2) Pb$^{2+}$ 0.05M + Sn$^{2+}$ 0.05M + NaKC$_4$H$_4$O$_6$ 0.1M + NaOH 0.4M and (3) Pb$^{2+}$ 0.05M + Sn$^{2+}$ 0.05M + EDTA 0.1M + NaOH 0.4M. A Pt disc (0.196 cm$^2$), a Pt plate and a Hg/HgO/ NaOH (1.0 M) electrode were employed as working, auxiliary and reference electrode, respectively. These baths, newly developed in this study, were found to be stable, i.e. PbO and SnO$_2$ precipitation was impeded. The Pb-Sn voltammetric curves showed two cathodic peaks. Comparing these curves with those of Pb or Sn deposition, it was inferred that in the region of first peak only Pb deposition occurred in sorbitol or tartrate baths and codeposition of Pb and Sn in the EDTA bath, while in the region of the second peak there was always codeposition of Pb and Sn. The analyses of Pb-Sn deposits produced at the second peak, with the same deposition charges, showed codeposition of Pb and Sn, corroborating the voltammetric results and showing that the Sn content in the deposits depends on $q_d$. These results imply that the Pb-Sn codeposition type was normal, since Pb was dominant in these codeposits. SEM results showed that deposits obtained at the first peak potential, where only Pb is deposited, are composed of dendrites in the presence of sorbitol. However, those obtained in the presence of tartrate or EDTA were smooth. The micrographs of Pb-Sn deposits showed more refined crystallites, in the presence of tartrate, sorbitol or EDTA than those obtained from fluoborate baths. It can be concluded that these newly developed baths are promising, not only for the good characteristics of the deposits, but also because there is no effluent discharge problem, since the system does not contain any toxic additive.

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Thiol-functionalised silica films have been deposited on glassy carbon electrode surfaces by spin-coating of sol-gel mixtures in the presence of a surfactante template. Film formation occurred by evaporation induced self-assembly (EISA) [1] involving the hydrolysis and (co)condensation of organosilane precursors on the electrode surface. Extraction of the surfactant from ordered mesoporous films led to a large increase of mass transport rates into the materials and imparted high accessibility to the organic moieties [2].

The performance of thiol-functionalised silica film modified glassy carbon electrode in determination of Hg(II) ions in natural water is described. A typical measurement involves two successive steps: a glassy carbon electrode coated with a thin mesoporous silica film containing 10 % of mercaptopropyl groups (MPTMS/TEOS ratio in the starting sol-gel) was first immersed into the accumulation medium for 15 min, then removed, and finally transferred into a detection solution containing KCl 1.0 mol L⁻¹ where detection was performed by anodic stripping voltammetry. In this medium, the previously accumulated Hg²⁺ species complexed by the thiol groups in the film are desorbed and directly reduced at -0.6 V during 60 s prior to be quantified by a differential pulse anodic scan from -0.6 to 0.3 V vs. (Ag/AgCl). A stripping peak appeared at about -0.01 V, which is directly proportional to the quantity of analyte previously accumulated into the film. The best results were obtained under the following conditions: 100 mV pulse amplitude and 10 mV s⁻¹ scan rate in KCl 1.0 mol L⁻¹ solution pH 2.0. Using such parameters a linear dynamic range from 1.00 to 10.0 x 10⁻⁸ mol L⁻¹ Hg(II) was observed with limit of detection 4.3 nmol L⁻¹ (three times the signal blank/slope) [3]. Hg(II) spiked in a natural water sample was determined with 99.9 % mean recovery at 10⁻⁸ mol L⁻¹ level. The results indicate that this electrode is sensitive for the determination of Hg(II). Zn(II), Cu(II), Pb(II), Cd(II), and Mn(II) did not interfered in the measurements.

References
Comparison between two electroanalytical techniques for atmospheric formaldehyde determination

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In Brazil, the growing fleet of ethanol fueled vehicles causes increased emission and photochemical formation of carboxylic compounds in the troposphere, mainly formaldehyde, acetaldehyde, acetic and formic acids and acetone. The analytical determination of formaldehyde (CH₂O) in air still presents challenges due to the low-level concentrations (sub-ppb) and spatial variability. The present work proposes the use of polypropylene (PP) hollow porous capillary fibers (Oxyphan®, MEMBRANA) to explore CH₂O collection[1] and the comparison between two electroanalytical methods of determination: flow-injection analysis with amperometric detection (FIA-amp) and capillary electrophoresis with contactless conductivity detection (CE-C⁴D)[2].

The CE-C⁴D determination of CH₂O was performed with the addition of excess of HSO₃⁻ to promote the formation of the charged specie hydroxymethanesulfonate (HMS). The determination of the anion HMS was conducted in MES/Histidine electrolyte (20 mmol L⁻¹) with 0.2 mmol L⁻¹ of CTAB as electroosmotic flow inverter[1]. The FIA-amp determination of CH₂O samples was made on a flat gold working electrode (a slice of gold sputtered polycarbonate from a CD-R[3]), electroplated with Pt[4]. Flow amperometric measurements were carried in phosphate buffer (0.1 mol L⁻¹, pH = 11), at a flow rate of 0.3 mL min⁻¹, injected sample volume of 50 µL, fixing the potential -0.15 V vs Ag/AgCl. The effect of potential interferences was evaluated, considering liquid phase counterparts of species commonly found in air (aldehydes, alcohols, NO₂⁻, H₂O₂ and HSO₃⁻). In relation to the oxidation current of 20 µmol L⁻¹ of CH₂O, a 10% interference level was observed 0.7 µmol L⁻¹ of H₂O₂, 3 µmol L⁻¹ of HSO₃⁻ and 180 µmol L⁻¹ of acetaldehyde. Acetaldehyde interference only causes concern at high acetaldehyde/formaldehyde ratio, a condition not observed yet in the urban atmosphere. A flow reactor filled with catalase enzyme immobilized on Amberlite ion exchanger resin[5], served to decomposes H₂O₂, eliminating any interference in the amperometric signal. The absorption of SO₂ leads the formation of HSO₃⁻ in the acceptor phase, which presents an amperometric signal, and also reacts with CH₂O in solution to form HMS. In alkaline media, this adduct is disrupted liberating the two electroactive species. The interference was solved by adding an excess of H₂O₂ to the alkalized sample, to oxidize S(IV) to S(VI), followed by peroxide elimination with the reactor, as described. To avoid HMS formation during sampling, 1 mmol L⁻¹ H₂O₂ was added to the sampling solution. Comparison of the results with samples spiked or not with extra HSO₃⁻ confirmed the effectiveness of the procedure. The sampling device was validated with a standard CH₂O generator and the amperometric and electrophoretic methods of determination were compared for generated and real air. No significant difference was observed at the 95% confidence level, with both methods presenting a relative standard deviation of 5% for 10 µmol L⁻¹ CH₂O.

Determination of Heavy Metals in Waters of Guarani Aquifer by Voltammetric Methods Using Solid Amalgam Electrode

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Heavy metals are known popularly as environmental pollutants, mainly for presenting characteristics as: high toxicity and bioaccumulation effect in the human beings. Due to that, there is a control in the fiscalization of the concentration of those species in the aquatic matrix for the competent organs. However, the search for new analytical methods of control, which possess a faster and effective answer, is longed for. A viable proposal is the use of voltammetric methods for the determination of those metals in water, versus to the spectroscopic methods with high cost, conventionally used like AAS, ICP-MS and ICP-AES. In voltammetry, mercury liquid material is widely used as indicator electrode, because of its high overpotential of reduction of hydrogen, extending its potential window to very negatives regions, making possible the study of many metallic ions, impossible in other electrodes, as the one of gold and of glassy carbon. However the use of this type of electrode for environmental analysis in the field is restricted, due to its high toxicity. A promising alternative is the use of solid amalgams electrodes which also possess a high overpotential of discharge to hydrogen, and consequently an equivalence in the potential window. However, in compensation, they don’t present the toxicity of the mercury liquid, could be used in field measures. In this present work, the electroanalytical technique used was anodic stripping voltammetry (ASV), in the modality of differential pulse, for the simultaneous determination of the metals Zn, Cd and Pb in natural waters of Guarani Aquifer, with the use of the applicability of the solid amalgam electrode of silver (AgSAE) as indicative electrode. In that modality, some instrumental parameters were optimized as, potential of deposition, time of deposition and effect of pulse width. It was still determined the relative figures of merit to the electrode for each one of the metals in study, as: linear range, sensibility, limit of detection and quantification. The accuracy of the developed methodology was tested by the recovery methodology, being used the standard addition method, with a recovery range for zinc, cadmium and lead of 112,8; 109,0 and 122,1%, respectively.

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Copper nitroprusside was synthesized on the 3-aminopropyl silica gel surface (ASiCuNP) and characterized by IR and atomic absorption. The SiCuNP was incorporated into a carbon paste electrode and the electrochemical studies were performed with cyclic voltammetry. The cyclic voltammogram of SiCuNP into graphite paste electrode exhibit two redox couples (Fig.1) with following mid-point potentials ($E_m$): ($E_m)_1 = 0.34$ V and ($E_m)_2 = 0.76$ V vs SCE (KCl = 1.0M; $v=20$ mV.s$^{-1}$) assigned to the Cu$^{(I)}/$Cu$^{(II)}$ and Cu$^{(I)}$(CN)$_2$NO / Cu$^{(II)}$(CN)$_2$NO respectively. At sweep rates between 20 and 100 mV.s$^{-1}$ the peaks intensity increase linearly with sweep rate. The electrochemical behavior of the SiCuNP was examined in solution of various supporting electrolytes. The nature of the cation affect the $E_m$ as current intensity, shifting the ($E_m)_2$ for more positive potentials, in following order: $\text{NH}_4^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$. The nature of the anion ($\text{Cl}^-$, $\text{NO}_3^-$, $\text{SO}_4^{2-}$, $\text{ClO}_4^-$) practically did not affect the redox couple. The voltammograms obtained with different KCl concentrations (0.01 – 2.0M) exhibit a shift in the ($E_m)_1$ to more positive potentials, this change is linear with the supporting electrolyte concentrations change. The slope of the straight line is 66 mV for decade of the potassium concentration, which indicate a sub–nernstian process. It was verified that the mid-point potential ($E_m)_2$ remained practically constant at pH between 8 and 3. However, a new process with ($E_m)_3$ (0.44 V) appears at pH < 3 and was ascribed to formation of intermediary species. The SiCuNP incorporated into a graphite paste electrode is very stable for several days.

Fig. 1: Cyclic Voltammogram of ASiCuNP.
Gold Nanowires Electrodeposition Using Block Copolymers Films as Templates

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Block copolymers films could be self assembled as periodic porous patterns on different substrates¹: Depending on the experimental conditions, Poly(styrene-vinilpyridine) films could be oriented parallel or perpendicular to the substrate², and in this last conformation, this films could be used as pattern for nanowires electrodeposition². In this work, Poly (styrene-b-vinil pyrydine) porous films were deposited onto conductive glass (ITO) by spin coating of a solution of copolymers (0.1%) and 2-(4'-Hydroxybenzeneazo) benzoic acid (17.8%) in dioxane. The film formed was exposed to dioxane vapours by 24 H, this procedure assure the perpendicular orientation of the porous. The characterization of the films was done by atomic force microscopy (AFM) showing a regular pattern composed by porous of 20 nm diameter, Fig. 1 shows AFM images of films with both orientations.

A)                                             B)

Figure 1: P(S-bVP) films on ITO A) Parallel orientation B) perpendicular orientation.

These films were used to the electrodeposition of gold from HAuCl₄ 1x10⁻⁴ M in 1M HCl. After the electrodeposition the film was removed using dioxane and the gold nanowires obtained, were characterized by AFM, SEM, and electrochemical techniques. These nanowires will be used as substrates to the adsorption of biomolecules (enzymes, antibodies) to design biosensors.

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References
Electrochemical properties of a new nanostructured azido copper (II) octa (3-aminopropyl) octasilsesquioxane using graphite paste electrode

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Nanostructured azido copper (II) octa (3-aminopropyl) octasilsesquioxane (ASCA) was prepared using an octa (3-aminopropyl) octasilsesquioxane as precursory. The main interest in this composite is related to its utilization as a possible sensor towards biological molecules. A preliminary characterization of the precursor and resulting materials was defined using usual spectroscopic and chemical techniques. The electrochemical behaviour of this composite was verified by means of a graphite paste electrode using cyclic voltammetry in a potential range from -0.3 to 1.3 V (vs Ag/AgCl). The cyclic voltammogram of the modified electrode containing ASCA, exhibits one redox couples and an irreversible process. The first redox couple presents a formal potential (E^°') of 0.35 V and an irreversible process at 1.1 V ascribed to the Cu(II)/Cu(I) and N_3/N_2 processes respectively [1]. The electrochemical behavior of the ASCA was examined in solution of various supporting electrolytes. For two processes the nature of the electrolyte does not affect the E^°' and the current intensity. The voltammograms obtained with different NaCl concentrations (0.1 –2.0 mol L^{-1}) exhibit a shift in the E^°' to more positive potentials. It was verified that the E^°' remained practically constant at pH between 8.2 and 4.0. However, a increase of current intensity occur at pH < 4. At sweep rates between 20 and 200 mV.s^{-1} the peaks currents intensity increase linearly with sweep rate. The composite was electrochemically, very stable. In a preliminary study, the peak at 1.1 V presents a sensibility response for nitrite. The modified graphite paste electrode gives a linear range from 1.0 \times 10^{-4} - 5.0 \times 10^{-3} mol L^{-1} for the determination of nitrite with detection limit 0.21 mmol L^{-1} and relative standard deviation \pm 2% (n=4) and amperometric sensitivity 0.08 \mu A/\mu mol L^{-1}.

References

Adsorption and two-dimensional condensation of nucleic acid components

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We have found that purine and pyrimidine derivatives currently occurring in nucleic acids possess an extraordinary high ability of self-association at the electrode surface and can form there by a two-dimensional (2-D) condensation a monomolecular layer (self-assembled monolayer – SAM), a compact film [1,2]. By this high condensation ability nucleic acid bases differ from most of the other purine and pyrimidine derivatives which currently do not occur in nucleic acids. This property was probably significant for the origin of life at the earth [3,4]. For the time being it is not known what is the reason why just the usually occurring components of nucleic acids like adenine, guanine, thymine, cytosine and uracil show the tendency to self-association. Therefore the effect of supporting electrolyte, pH value and substituents on the 2D condensation of nucleic acid bases and/or nucleosides were studied. 5-methylcytosine belongs to one of the most important nucleic acid bases. He is involved in gene silencing and has a great biological impact. 5-methylcytosine adsorbed at the mercury electrode forms at acid pH values physisorbed self-assembled layer at potentials close to the potential of electrocapillarity maximum.

The other part of the lecture is devoted to the study of the adsorption of human blood plasma proteins at the surface of titanium dental implants. The effect of surface treatment of implants on the protein adsorption will be discussed.

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Literature:
A Novel Electrochemical Strategy for the Production of Bimetallic Nanoparticles

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Bimetallic Nanoparticles (BNPs) have attracted much attention because of the size dependent tuning of their electrical, optical and catalytic properties. In fact, bimetallic Ag-AuNPs have been used to transform poisonous carbon monoxide into less-harmful carbon dioxide at room temperature\(^1\). Furthermore, Pd-AuNPs are the most effective catalysts yet identified for remediation of groundwater pollutants such as trichloroethene\(^2\). As BNPs are becoming very important materials (both, in sensors and in water, atmospheric and soil catalytic remediation), the need for developing more environmentally friendly and sustainable methods for their synthesis is evident.

While methods for BNPs synthesis based on wet chemistry occur far from equilibrium, some electrochemical strategies are carried out under thermodynamic control (e.g. Underpotential Deposition (UPD), and ECALE). The least implications of the intrinsic characteristics that each methodology have, are some scaling up difficulties for the wet chemical methods, whereas the electrochemical ones would be limited to conducting substrates.

We describe a currentless method based on solution chemistry in order to prepare Ag-AuNPs. This method use the combination of two well established electrochemical facts: the UPD phenomena and the ability of a redox couple to control the interfacial potential. We have selected the Ag-Au surfaces because they can be taken as a model of bimetallic systems. In general, solution metal cations can be deposited by controlling the interfacial potential. Beside this strategy is commonly used in electroless processes, in our case the potential was carefully fixed in the UPD range in order to work under equilibrium conditions. At these circumstances, bimetallic surfaces can be easily prepared by a simple solution chemistry process\(^3\). Our results are also discussed in relation with the requirements of a green chemistry approach (e.g. water soluble reactive and products; environmental friendly reducing agents\(^4\)).

An Application of Silver Nanoparticles in Environmental Chemistry: Sensing of Nitrates

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Nitrates and other nitrogen-containing compounds are harmful to the environment and pose a particular risk when they become concentrated in drinking water. Consequently, there is an ever-increasing interest in developing reliable, fast and simple sensors to detect low concentrations of nitrate and in developing new environmental technologies to effectively remove nitrates and convert them into harmless products. In particular, modified electrochemical sensors are playing an increasingly important role in environmental monitoring and are the focus of intense research in the effort to develop new and improved techniques.

Electrodes modified with nanosized noble metal particles have attracted considerable interest due to their unique physicochemical properties. Electrochemistry offers a method for size-controlled synthesis of nanoparticles by simply adjusting electrolysis parameters. In addition, it allows for the particles to be directly adsorbed onto a surface, ready for immediate use as a sensor.

In this paper, we show how to simply prepare silver nanoparticles via various electrochemical methods. First, colloidal silver was formed potentiostatically under the protection of the stabilising agent, poly(N-vinylpyrrolidone)\(^1\). Like most methods for synthesising nanoparticles electrochemically, these are prepared by chemical reduction of the metal salt, in this case silver nitrate (AgNO\(_3\)). The stabilising agent immediately coats the particles and therefore prevents agglomeration. These particles were analysed using UV-Visible spectroscopy, which is a very accurate and simple tool to measure the size of the nanoparticles. Silver nanoparticles show a strong absorption band at approximately 420 nm.

Next, we show how silver is directly deposited on a glassy carbon electrode via a potentiostatic single-pulse technique\(^2\). Again it involves the reduction of the metal salt, this time at the electrode surface, for only a few seconds. The longer the deposition time the larger the particles. We investigated this electrodes sensitivity to nitrate using cyclic voltammetry. The electrochemical reduction of nitrate shows two signals, with peak potentials at approximately \(-1.3\) V and \(-1.6\) V. A detection limit of \(5\times10^{-5}\) M KNO\(_3\) was reached.

Evaluation of Lead Concentration in Mussel *Mytella charruana* in the Mundaú Estuarine Lagoon, Maceió, Brazil.

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The Estuary Lagoon Mundaú-Manguaba (ELMM), in the State of Alagoas is a very productive one and is located in Maceió, Brazil. In this estuary, two lagoons (Mundaú and Manguaba) and some streams are connected with the Atlantic Ocean. Due to the input of nutrients, a very rich and highly productive ecosystem was generated, being the nutritional source for the local people [1]. Among those organisms, the bivalve mollusk *Mytella charruana* has a huge nutritional significance, being very easy to catch. For this reason the elevated productivity of this mollusk is essential. The estuary has suffered the impact of some human activities and the most important are related to sugar cane, culture, sugar/alcohol production allied to MVC and PVC industries and in \textit{natura} sewage release local cities, including the capital of the state, Maceió. The present work aims to evaluating lead concentration in the tissues of *Mytella charruana*, since those organisms can be used as biomonitors of heavy metals pollution [2]. The mollusk was first washed with Water Milli-Q, until complete elimination of incrusted sediments. After removal of the soft tissue from the shells, with plastic spoons, excess humidity was eliminated using paper filter. Digestion was performed using 2.0 (± 0.0001) g (wet wt) of mollusk tissue in 10 mL of concentrated HNO\(_3\) [3]. After filtration through 0.45 µm membrane, the solution was made up to 100 mL using citrate buffer (pH 3). Lead concentration in the digest was determined by anodic stripping voltammetry, using square wave voltammetry. The mercury film was generated on a carbon vitreous surface (BAS) from Hg(NO\(_3\))\(_2\).H\(_2\)O solution, with 5 minutes of deposition. The pre-concentration of the analyte was also of 5 min. In the optimized conditions (citrate buffer, pH 3), calibration curves were built with linearity between 3.5 and 160 ppb. The mollusk digest was analysed, yielding 1.7 µg/g of Pb. Recovery tests in the sample were performed in the determination of Pb with addition of 360 µL and after 550 µL of one solution of 1 mg/L of Pb. The results obtained were 94 e 76% for the first and second additions, respectively. The used methods were adequate concerning extraction and Pb determination, in the analysis of mollusk *Mytella charruana*. The content of Pb in he mollusk does not compromise is use as a nutritional source [4].


CTHIDRO/CNPq.
Development of a Modified Biosensor by a Crude Extract of Guariroba (*Syagrus oleracea*) for the Analysis of Phenolic Compounds in Environmental Samples

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The use of plant tissues as a cost efficient enzymatic source for electrochemical biosensors have recently increased. In this research, a carbon paste biosensor modified with a crude enzymatic extract of Guariroba (*Syagrus oleracea*) has been developed. The later biosensor has shown potential use for phenolic determination in environmental samples. Furthermore, the use of this Brazilian Palm tree as a poliphenoloxidase source is consistent with the sustainable use of local biodiversity. The enzyme catalyzes the oxidation of phenols to their quinone sub products. The resulting current in the electrochemical reduction of each product is attributed to phenolic concentration in solution. The crude extract was prepared by grinding slices of guariroba which was mixed with a 0.1 molL$^{-1}$ phosphate buffer (pH 7.0) and blended in order to obtain a concentration of 10% w/v. The detected enzymatic activity (2800 U/mL) was measured by spectrometric method. The immobilization of the enzyme was made by combining 110 mg of graffite with 1 mL of the extract. The resulting mixture was dried at room temperature and mixed for a minimum of 20 minutes in a mortar with 50 mg of mineral oil to produce the final paste. The cyclic voltammetric study scanned potentials from +0.8 to -0.5 V and indicated a good stability of the Carbon Paste modified with Guariroba extract (CPG). The CPG has reusability up to 80 cycles and a shelf life of more than 2 months when stored at 4 °C. Differential pulse voltammetric (DPV) measurements were performed at 25°C in unstirred and non-aerated 0.1 molL$^{-1}$ phosphate buffer solutions (pH 7.0). The DPV voltammograms were obtained by scanning the potential from 400 mV to 0 mV at a scan rate of 30 mVs$^{-1}$ and potential pulse amplitude of 50 mV. The response for phenol compounds has shown to decrease in the following sequence: catechol ≥ hydroquinone > resorcin > aminophenol > nitrophenol > chlorophenol, being consistent with the literature data. A good linear calibration curve for catechol concentrations from 4.5 x 10$^{-5}$ to 5.5 x 10$^{-4}$ molL$^{-1}$ ($r = 0.9996$) and good repeatability (RSD = 2.99%, for n=9) was obtained. The detection limit was of 5 x 10$^{-6}$ molL$^{-1}$ (Fig. 1).

**Fig. 1** – Calibration curve and the DPV voltammograms for different catechol concentrations.
**Lactoperoxidase Activity at Gold Surfaces: Amperometric Response to Hydrogen Peroxide**

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Detection of hydrogen peroxide is of a great interest in many fields including industrial, pharmaceutical, clinical, food, and environmental analysis. \( \text{H}_2\text{O}_2 \) can be found in drinkable, rain, sea waters, and snow at the levels of mg/L [1]. As low as submicromolar hydrogen peroxide concentrations are, however, harmful for mammalian cells. Lactoperoxidase (LPO, EC 1.11.1.7) has been found to be useful for determination of low concentration of hydrogen peroxide as well as organic peroxides, aromatic amines, and phenolic compounds [2]. Currently, our interest is to understand how lactoperoxidase activity depends on the properties of electrode surfaces, especially, when lactoperoxidase is coadsorbed with other proteins or polymers. Lactoperoxidase modified gold surfaces were constructed by the adsorption of lactoperoxidase alone or in combination with bovine serum albumin or different mucins. Before protein adsorption the surfaces were cleaned electrochemically in 0.5 M \( \text{H}_2\text{SO}_4 \) and the electrode area was determined via analysis of the stripping peak of gold oxide reduction. The formation of LPO containing protein films was monitored by in situ null ellipsometry technique, which allowed studies of protein adsorption kinetics, adsorbed amount, thickness, and the stability the protein layer.

Several systems were studied: LPO adsorbed directly on bare gold surface and LPO adsorbed on the layer of other proteins such as bovine serum albumin, bovine submaxillary mucin and human mucin. The adsorption was carried out for 1 h at room temperature from 10 mM phosphate buffer pH 7.0 with 100 mM NaCl and 1 mM CaCl\(_2\) containing 10 µg/mL of LPO. Ellipsometry showed that LPO monolayer on bare gold surface contains 3 mg/m\(^2\) of adsorbed protein with 35Å thickness. The amount of LPO adsorbed on the other protein layers was much lower. However, surface bound LPO adsorbed with other proteins appeared to be far more active than directly adsorbed on bare gold surface. The activity was determined by amperometry measurement of the response of LPO-gold electrodes to \( \text{H}_2\text{O}_2 \). The applied potential was -50 mV vs. Ag/AgCl and the buffer contained 0.1 mM catechol. The LPO-gold electrodes had the following characteristics: sensitivity to \( \text{H}_2\text{O}_2 \) of \( 4\times10^3 \) Am\(^2\)M\(^{-1}\), detection limit of 300 nM, and linear range between 0.3 – 25 µM. Electrochemical studies of other enzymes incorporated in polymers or proteins multilayers are in the scope of our further investigations.

Monitoring the electrochemical oxidation of a mixture of phenol compounds on boron-doped diamond electrode using fluorescence and multiway methods

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Boron-doped diamond (BDD) electrodes are being applied with success for treatment of wastewaters containing non-biodegradable organic compounds, such as the phenolic compounds (PC). Improvements are being reported in this area and for efficient evaluation, the concentration of the analytes involved in the degradation process needs to be quantitatively determined. The individual monitoring of PC in the mixture during electrochemical oxidation is a very important task in this context, because the efficiency of the process strongly depends on the organic pollutant, and the degradation of the most toxic is considered a priority.

The usual methods of analysis of a PC mixture involve time-consuming analytical procedures such as chromatography, which are not appropriated to analyze the chemical process in real time. On the other hand, phenolic compounds can be determined by molecular fluorescence. However, in complex mixtures, spectral overlapping is often a serious drawback. To avoid very time-consuming separation techniques, multiway methods [1] that can solve and identify species present in complex mixtures can be a viable alternative approach.

This work shows the use of multiway methods such as multilinear partial least squares (N-PLS) and parallel factor analysis (PARAFAC) [1] to monitor individual electrooxidation in a mixture of PC in aqueous media using data matrices consisting of excitation–emission fluorescence spectra (EEM).

The bulk electrolysis was carried out in a non-divided nylon cylindrical cell. The BDD anode was grown according to the previous work [2] using a square wafer of p type silicon of 1.15 cm$^2$ of area as substrate and a stainless steel (AISI 304) with 1.5 cm$^2$ of area was used the cathode. The evaluated PC were: hydroquinone (HYDR), phenol (PHEN) and catechol (CATE). The minimum, medium and maximum concentrations used in the mixture design for the model building were: 0.5, 2.4 and 5.0 µmol L$^{-1}$ for HYDR; 0.5, 2.8 and 5.0 µmol L$^{-1}$ for PHEN and 1.0, 4.4 and 8.0 µmol L$^{-1}$ for CATE. The initial concentration levels for degradation were: 5.0 µmol L$^{-1}$ for both HYDR and PHEN, and 10.0 µmol L$^{-1}$ for CATE. The volume of the solution was 500 mL and the current density applied was 30 mA cm$^{-2}$. The maximum time of degradation monitoring was 25 h. Aliquots of 10 mL of the electrolyte were collected during the degradation in defined time intervals. The degradation was monitored in each aliquot using EEM. The scan settings of the fluorescence spectroscopic measurements were: excitation wavelengths of 245–300 nm (recorded every 2 nm), emission wavelengths of 270–380, and scan rate of 120 nm s$^{-1}$. 
Use of fluorescence intensity for aromaticity monitoring of phenolic compounds during the electrochemical oxidation on boron-doped diamond electrode

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Industrial processes generate residuals containing refractory organic compounds of high toxicity, such as phenolic compounds (PC), which are needed to be recovered or eliminated before discarding or reusing [1]. Recently, boron-doped diamond (BDD) electrodes are being successfully applied for the treatment of wastewater. The monitoring of degradation of organic compounds is usually performed using global parameters such as total organic carbon content (TOC). In this work, it will be presented the use of fluorescence intensity as a procedure capable of monitoring total degradation, as well the degradation of aromatic ring of the PC mixtures.

Bulk electrolysis was carried out in a non-divided nylon cylindrical cell. The employed anode was BDD grown according to previously described procedure [2] with area of 1.15 cm$^2$. A stainless steel with 1.5 cm$^2$ was used as cathode.

PC used to prepare the mixture was as follows: phenol (PHEN), catechol (CATE), hydroquinone (HYDR), $p$-cresol (pCRE), $m$-cresol (mCRE) and guaiachol (GUAI). The initial concentration levels of these compounds were: level A (higher concentration) – 80 µmol L$^{-1}$ for all compounds and level B (lower concentration) – 1.75 µmol L$^{-1}$ for HYDR, GUAI and PHEN; 0.63 µmol L$^{-1}$ for pCRE and mCRE and 3.5 µmol L$^{-1}$ for CATE. The volume of the solution was 500 mL.

The maximum time of degradation monitoring was 45 h for the level A and 25 h for the level B. An aliquot of 10 mL of the electrolyte was collected during the degradation in defined intervals of time. The degradation was monitored by TOC and fluorescence spectroscopy (Fluor) in each aliquot. The intensities collected only in the wavelengths ($\lambda$) of 275 nm for the excitation and 320 nm for the emission were used. In the investigated wavelengths the intensities were extremely selective for aromaticity.

It was observed that the remotion of aromaticity is significantly higher than the remotion of TOC. These results indicate that the breach of aromatic ring occur rapidly during the degradation, while the TOC is removed more slowly. It can be explained by the necessity of several steps after the ring breach until the full mineralization of the generated intermediaries. Besides, for level B concentrations, the electrochemical oxidation is extremely efficient. This advantage of BDD for degrade organics compounds in low concentration makes this type of electrode an excellent alternative for perform water disinfection destined for human consumption.

References
Electrochemical monitoring of some phenol derivatives at modified electrodes

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There are many organic pollutants with a phenolic structure dispersed throughout the environment. Thus, there is a continuously increasing demand for selective and sensitive detection of phenols since these toxic compounds are present in the wastewaters of large number of industries including coal conversion, wood preservation dyes, petroleum refining, resins and plastics\textsuperscript{1,2}. These polluting chemicals are easily absorbed by animals and humans through the skin and mucous membranes\textsuperscript{3}. Many phenols are known for their persistency in the environment and propensity for bioconcentration and biomagnification\textsuperscript{4}.

A sensitive electrochemical sensor for phenols compounds, based on composite inorganic redox material-organic conducting polymers, were developed. Phenol derivatives have been determined with square wave voltammetry (SWV) using both mono and bilayer modified electrodes. These electrodes based on PB, azulene and 3-[(E)-2-azulene-1-ylvinyl] thiophene have been prepared by electrochemical methods in various configurations onto Pt substrate. The modified electrodes show a linear response range of 10 – 100 and 20 – 140 nM, with a sensitivity of 57.17 and 13.88 nA/nM for phenol and nitrophenol, respectively.


Incorporation of Fe(III) into a poly (5-Amino 1,10 phenanthroline) matrix.

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The 5-Amino, 1,10 phenanthroline (5-Aphen) has the capacity to be a quelating agent with different metallic ions such as: Mn(II), Fe(II), Co(II), Ni(II), y Os(II)[1]. The 5-Aphen can be polymerized by using chemical or electrochemical procedure. Ellis et al.[2] studied the electopolymerization of the 5-Aphen and incorporated metallic ions such as Ru(III), Fe(II) y Co(II) in a non aqueous medium. Galicia et al.[3], have shown that the 5-Aphen is susceptible to electropolymerization in aqueous medium at a carbon-paste electrode at pH = 0.3. Furthermore, carbon-paste electrode modified with poly(5-Aphen) shows a good pH sensor. W. Ting et al.[4] obtained modified electrodes with Poly[5-Aphen] and Poly[Fe(5-Aphen)2+] in a non aqueous medium and they were used as glucose sensors, and the Poly[Fe(5-Aphen)]3+ presented de best behavior. Lozano et al.[5] has reported the kinetic and thermodynamic behaviour of Fe(II)/5-Aphen complexes in solution, by spectrophotometric and electrochemical methods. Nevertheless in the literature exists few information about the electrochemical behavior of the 5-Aphen and complex [Fe(5-Aphen)3+ in aqueous medium. Therefore, the objective of this work, is to obtain modified electrodes, by the incorporation of ion Fe(III) to a poly(5-Aphen) matrix, in aqueous medium.

Results
It was carried the electrooxidation of 5-Aphen in the presence of Fe(III) on carbon-paste electrode and obtained a modified electrode with poly [Fe(5-Aphen)]3+, at different pH values. Figure 1, shows typical voltammograms obtained for the 5-Aphen electropolimerization in sulfuric media applying successive potential cycles (70) at a 100mv/sec sweeping rate.

![Fig. 1. Typical voltammograms for the last formation cycle of the modified CPE with the 5-Aphen in the presence of Fe(III). (a) pH=0.3  b) pH= 1.14 and (c) pH = 3.07.](image)

The Voltammograms were obtained at different pH values. It can be observed that the Fe(III) incorporation to the polymer matrix is pH dependent. At low pH values the Fe (III) incorporation is not evident, only the poly(5-Aphen) electrochemical behavior is detected. As the pH increases the Fe(III) is electrochemically detected in the voltammogram, the curve shows two redox peaks that can be associated to the film and the Fe(III) signals. The former study makes it possible to determine the most adequate experimental conditions for the controlled Fe(III) insertion into the poly (5-Aphen) matrix.
The Availability of Boron-Doped Diamond Electrode for Anodic Determination of Nonylphenols Etoxylates

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In this work, boron-doped diamond electrode (BDD) was used as the working electrode for the electrochemical determination of nonylphenol etoxylates (NPEs). NPEs are widely used in industry as dispersing agents in paper and pulp industry, as flotation and emulsifying agents in latex paints and in pesticide formulation [1]. Their presence in aquatic environment is owing industrial waste and wastewater, landfill leachates and sewage effluents from treatment plants. In the last years, interest for these non-ionic surfactants has increased because of their oestrogenic activity [2]. The performances and availability of BDD electrode to determine electrochemically NPE were studied by cyclic voltammetry (CV), linear-scan voltammetry (LSV), and differential pulsed voltammetry (DPV). Prior to use, the working electrode was polished on a felt-polishing pad by using 0.3 µm alumina powder (Metrohm, Switzerland) in distilled water for 5 minutes, cleaning with ethanol, and rinsing with distilled water. All measurements were carried out using a potentiostat/galvanostat PGSTAT 30 (Eco Chemie, The Netherlands) controlled with GPEES 4.9 software and a three-electrode cell, with a saturated calomel electrode as reference electrode, and a platinum counterelectrode and BDD working electrode. Britton-Robinson buffer and 0.1 M Na\textsubscript{2}SO\textsubscript{4} solution were used as supporting electrolyte used for the detection experiments. Standard stock solutions of 0.1 g·L\textsuperscript{-1} from two types of technical grade nonylphenols with ethylene oxide average units of 6 and 9 were prepared in distilled water. The optimum potential ranges for useful anodic amperometric signals were determined. Several aspects regarding fouling effects, cleaning of electrode surface and the limiting concentration were investigated. The quantitative determination of NPEs was achieved at relative low and limited concentrations using BDD electrode and the limits of detection varied between 0.1 and 0.5 mg·L\textsuperscript{-1}, function of supporting electrolyte, electrochemical technique used, and the etoxylation degree.

Selected references

Acknowledgements
Funding for this project was provided by the Romanian National Research of Excellence Program- CEEX, Grant 62/03.10.2005 - Advanced Treatment
Evaluation of a carbon paste electrode modified with organofunctionalised amorphous silica in the simultaneous determination of lead, copper and mercury ions in natural water

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The use of functionalised silica has been widely described in several areas of chemistry [1-3]. In analytical chemistry it can be an interesting support for different groups which can be used for preparation of stationary phases in chromatographic methods, extraction of several species from solutions and improvement of selectivity and sensitivity in the preparation of electrodes for electroanalysis. Walcarius presented extensive reviews about the preparation and application of silica modified electrodes showing their importance as electroanalytical sensors [4,5]. The determination of Pb(II), Cu(II) and Hg(II) in natural water samples using a carbon paste electrode modified with organofunctionalised amorphous silica with 2-benzothiazolethiol was investigated by differential pulse anodic stripping voltammetric procedure. The fact that three stripping peaks appeared on the voltammograms at the potentials of -0.58 V (Pb\textsuperscript{2+}), -0.27 V (Cu\textsuperscript{2+}) and +0.02 V (Hg\textsuperscript{2+}) vs. SCE demonstrates the possibility of simultaneous determination of Pb\textsuperscript{2+}, Cu\textsuperscript{2+} and Hg\textsuperscript{2+}. The best results were obtained under the following optimised conditions: 50 mV pulse amplitude, 2 min accumulation time at -0.90 V, 5 mV s\textsuperscript{-1} scan rate in KCl 0.1 mol L\textsuperscript{-1} solution, pH 2.0. Using such parameters, calibration graphs were linear in the concentration ranges of 4.0 to 12.0 µmol L\textsuperscript{-1} for Pb\textsuperscript{2+} and Cu\textsuperscript{2+}, 4.0 to 15.0 µmol L\textsuperscript{-1} for Hg\textsuperscript{2+}. Detection limits of 1.9 x10\textsuperscript{-7} mol L\textsuperscript{-1} (Pb\textsuperscript{2+}), 9.9 x10\textsuperscript{-7} mol L\textsuperscript{-1} (Cu\textsuperscript{2+}) and 9.5 x10\textsuperscript{-7} mol L\textsuperscript{-1}(Hg\textsuperscript{2+}) were obtained at the signal noise ratio (SNR) of 3. The proposed electrode was applied for DPASV determination of Pb(II), Cu(II) and Hg(II) spiked in a water sample from Universidade Federal de São Carlos in São Carlos/SP-Brazil. The Pb(II), Cu(II) and Hg(II) concentrations spiked were 5 µmol L\textsuperscript{-1} and that determination in the present work was 4.71 µmol L\textsuperscript{-1} for Pb(II), 5.05 µmol L\textsuperscript{-1} for Cu(II) and 4.9 µmol L\textsuperscript{-1} for Hg(II). There were no significant differences between the calculated and added concentrations, indicating that carbon paste electrode modified with organofunctionalised amorphous silica can be used for simultaneous determination of lead, copper and mercury in water samples, under the optimized conditions and using the standard addition procedures.

References
The correlation between boron content and surface modifications on the nitrate reduction for Boron-Doped Diamond Electrodes

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Nitrate ions represent a great problem of contamination of natural water sources, mainly attributed to the use of high amount of fertilizers. High nitrate concentrations in potable water may cause several health problems and its quantity control becomes a challenge, nowadays\(^1\). Boron-Doped Diamond (BDD) films have appeared as a new promising electrode for applications in nitrate reduction studies, particularly, due to their wide potential window to detect many electroactive species at high anodic and cathodic potentials. Besides, there are few reports involving the correlation between the electrochemical behavior and the physical, chemical and electronic properties of these electrodes. Such properties can be influenced by the quantity and kind of doping, film morphology features, defects, crystallographic orientations and surface terminations (hydrogen or oxygen). This work propose to investigate the electrochemical reduction of nitrate onto BDD electrodes prepared at different boron doping level and its correlation with H-terminated surface produced by cathodic polarization (water reduction). According to literature\(^2\), H-terminated surface can enhance the conductivity and electrochemical activity of BDD electrodes. BDD films were grown by the hot filament chemical vapor deposition (HFCVD), varying the boron/carbon (B/C) ratio in the precursor mixture at 5000 ppm and 10000 ppm. Afterwards, BDD electrodes were subjected to cathodic pre-treatment by applying -3.0 V for 30 min. Comparing the results before and after cathodic pre-treatment it was observed a loss of the reversibility for the Fe(CN)\(_{6}^{4-/3-}\) redox reaction for 5000 ppm-BDD electrode, while for 10000 ppm-BDD electrode this change of reversible behavior was not observed. The better response for the nitrate reduction was also obtained for the 10000 ppm BDD electrode, after cathodic pre-treatment, which may be associated with its higher stability. Furthermore, the boron content increase, during the growth process, produces BDD films with high electrical conductivity and more active surface for nitrate reduction.


Fig 1: Linear sweep voltammograms of nitrate reduction and cyclic voltammograms for the Fe(CN)\(_{6}^{4-/3-}\) (insets) using BDD electrodes with different boron contents.
Conducting Polymers modified with Cyclodextrins and their ability to detect the Pollutant Paraquat

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Methyl viologen or Paraquat, as it is more commonly known, is a toxic herbicide composed of bipyridilium ion with a methyl group attached to each ring (Fig. 1). Paraquat is used mainly in weed control and can resist microbial and photolytic degradation [1]. However due to its high toxicity, concentration limits have been set by the Environmental Protection Agency (EPA) and the European Community [2]. Electrochemically, it exhibits two redox states (Fig. 2). Even though there are other methods for its detection and characterisation (spectrophotometric and chromatographic), electrochemistry is the most efficient as it eliminates extensive pretreatment. In this paper, results are presented on the sensing performance of polypyrrole films, doped with either dodecylsulfate or sulfated $\beta$-cyclodextrin, for paraquat. Cyclic voltammetry, differential pulse voltammetry and square wave voltammetry were the techniques used. The detection limit was 10 $\mu$M. Although the interaction is predominantly electrostatic, using sulfated $\beta$-cyclodextrin as a dopant introduces the possibility for formation of an inclusion complex. Using cyclic voltammetry, a decrease in peak current with respect to increasing sulfated $\beta$-cyclodextrin concentration, showed that at a three-fold excess of sulfated $\beta$-cyclodextrin all paraquat in solution had been complexed. In order to confirm inclusion within the polymer matrix of polymerised pyrrole and sulfated $\beta$-cyclodextrin, differential scanning calorimetry (DSC) was carried out. This method of trapping the pesticide within the cavity of the cyclodextrin is effective in the process of environmental remediation but also as a means of extracting the pollutant.

References
Determination of 4-Nitrophenol in natural waters using a multi-wall carbon nanotubes sensor

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The 4-nitrophenol (4-NP) presents high environmental impact due to both, its toxicity and persistence. Moreover, 4-NP is involved in most of the degradation pathway of organophosphorous pesticides like fenitrothion, methyl-parathion, etc, which are decomposed by light or micro-organism in the environment producing 4-NP either as an intermediate or as one of the final product of the reaction [1]. Electrochemical determination of 4-NP has been carried out on several carbon electrodes as boron-doped diamond, glassy carbon and also on noble metals electrodes [2]. However, the electro-oxidation of 4-NP oxidation on such materials occurs at quite positive potential values, thus allowing the interference of many substances usually present in the matrices. An alternative to electrochemical determination of 4-NP is the multi-wall carbon nanotubes (MWCNT) electrode, whose electrocatalytic property [3], can shift the 4-NP oxidation potential toward less positive values.

The work electrodes used were glassy carbon (GC), boron-doped diamond (BDD) and glassy carbon recovered with carbon nanotubes (GC/MWCNT). To prepare the GC/MWCNT electrode, 1.0 mg of MWCNT, previously treated in sulphonic solution for 12 hours, was dispersed with the aid of ultrasonic stirring for 30 min in 1.0 mL dimethylformamide (DMF). After that, the obtained suspension was dropped over highly purified glassy carbon surface. All electrodes were initially evaluated using cyclic voltammetry in PBS (pH 6.0) containing 5.0 mmol L\(^{-1}\) of 4-NP, between -0.7 to 0.8 V with a scan rate of 50 mV s\(^{-1}\). All surfaces presented a well-defined oxidation peak, which was associated to 4-NP, but different potential regions. The GC/MWCNT electrode showed a shift of 600 mV (to less positive potential) for the 4-NP oxidation peak, when compared with BDD electrode.

The 4-NP was further quantified using square wave voltammetry (SWV, with optimized parameters as frequency of 100 Hz, amplitude of 50 mV and step potential of 2 mV). An analytical curve was obtained for GC/MWCNT electrode which showed a linear region represented by the equation: \(I_{pa} (\mu A) = 2.15 (\mu A/\mu mol L^{-1}) + 0.73 [4-NP] (\mu mol L^{-1})\), with a correlation coefficient of 0.9987 (for n = 7) in a range of 1.0 to 16.6 \(\mu mol L^{-1}\) 4-NP concentration. The 4-NP detection and quantification limits were 0.54 and 1.81 \(\mu mol L^{-1}\) respectively, determined using a 3σ/slope ratio, where σ is the standard deviation of the mean value for 10 voltammograms of the blank, determined according to the IUPAC recommendations.

A natural water sample from a dam in the Federal University campus, in São Carlos County was spiked with 3.2 \(\mu mol L^{-1}\) of 4-NP, had the pH controlled by addition of PBS (pH 6.0) and analyzed by the standard addition method using the GC/MWCNT electrode, without any further purification step. The recovery procedure yielded a value of 96.5% for such sample, thus confirming the suitability of this methodology to determine 4-NP.

**Octhyl dimethyl PABA Detection in Natural and Artificial Aquatic Systems based on a PANI/FeTSPc Sensor**

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This work describes the studies carried out in order to construct a cheap, sensible and selective electrochemical sensor for detection of the sunscreen octhyl dimethyl PABA (ODP) in aquatic systems. Since, still does not have an official method for its quantification and no regulation for its maximum levels in aquatic environments is established, although it is known that currently is being launched to the environment, in great amounts.

The sensor was constructed used a stainless steel 302 electrode modified with polyaniline (PANI) electrochemically synthesizing in presence of the iron (III) tetrasulfonated phthalocyanine (FeTSPc). The PANI/FeTSPc electropolimerization procedure was performed potentiodynamically (cyclic voltammetry) in the potential range of −0.2 and 1.6 V vs Ag/AgCl at a scan rate of 50 mV s⁻¹, during 20 cycles, in a 0.5 mol L⁻¹ H₂SO₄ solution containing 0.12 mol L⁻¹ of aniline and 5.0 mmol L⁻¹ of FeTSPc. In order to prove the FeTSPc immobilization in the electrode surface, experiments used AFM (atomic force microscopy) technique, were carried out. The proposed sensor presented the best performance in 70:30 (v/v) 0.1 mol L⁻¹ H₂SO₄/Tetrahydrofuran (THF) mixture, dissolving the ODP in THF and applying a potential of 0.0 V vs Ag/AgCl. Under these conditions the sensor showed a linear concentration range from 0.15 up 1.00 mmol L⁻¹, a sensitivity of 24961 µA L mol⁻¹ and detection and quantification limits of 8.0 and 25.0 µmol L⁻¹, respectively. The measurement repeatability, in terms of the relative standard deviation (RSD) of seven sensitivities obtained from seven analytical curves, was 1.7% and the reproducibility in the sensor constructions (RSD) was 3.2% (n = 4). The selectivity study was carried out evaluating the sensor response in nine sunscreens, derivates of PABA (p-aminobenzoic acid), benzophenones, camphor and methoxynamates, which are the more common groups employed in the commercial formulations preparation, and the results obtained confirmed the high selectivity of the sensor for ODP.

In the analysis of cosmetic formulations, the sensor presents better performance than classics instrumental methods like HPLC and UV/vis spectrophotometry. The initial results suggest that this sensor should be applied satisfactorily in the selective detection of this sunscreen in different aquatic environments, becoming a really alternative methodology for the ODP detection.

CNPq, FAPESP
Accumulation and Determination of Pb and Cd Using an Alginic Acid-Modified Carbon Paste Electrode

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Alginic acid is a linear, binary copolymer of 1,4-linked α-l-guluronic acid and β-d-mannuronic acid, usually isolated from brown algae but also present in some species of bacteria. This compound contains carboxyl and carbonyl groups capable of forming complexes with metal ions. Many studies have been made on the application of alginic acid in the aqueous-phase separation of heavy metals, and the possibility of using it as an adsorbent material has been suggested [1, 2]. Due to its non-toxic nature and excellent metal-binding properties, it can be applied in wastewater treatment. On the other hand, use of this biopolymer would be a much less expensive means of collecting metal ions than the use of synthetic resins.

The main purpose of this study was to developed an inexpensive, simple, and especially highly selective modified alginic acid carbon paste electrode for the anodic or adsorptive stripping voltammetric determination of Pb(II) and Cd(II). Alginic acid obtained from Chilean brown algae will be used as adsorbent in the solid phase extraction of these metals and arsenic. First, the modified carbon paste electrodes were prepared by mixing different ratios of graphite powder, alginic acid and paraffin with the purpose of obtaining good stability and reproducibility in the measurements. Alginic acid is a hygroscopic compound and during the measurements the area of the electrode increases slightly. Spectroscopic measurements of some electrodes were made. Operational conditions such as pH of the electrolyte solution, accumulation time and potential, scanning parameters, voltammetric waveform, and interference were studied and optimized to allow the quantitative determination of Pb(II) and Cd(II). The study as a function of accumulation potential between -1.0 and 1.0 V vs. Ag/AgCl/KCl 3M showed that the highest current due to the presence of Pb and Cd is obtained at 1.0 V. A linear calibration graph was obtained in the 0 to 450 ng mL⁻¹ concentration range for Pb(II) (n=7, r=0.9991, E_{acc}= -900 mV, t_{acc} = 60s) and 0 to 400 ng mL⁻¹ for Cd(II) (n=7, R=0.9909) with 60 s of preconcentration time. The detection limit was 23 ng mL⁻¹ (Pb) and 27 ng mL⁻¹ (Cd). The method was applied to the analysis of contaminated waters.

References

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A New Electro catalytic Sensor for Hydrogen Peroxide Prepared by Ferricyanide Immobilized on Organically Modified MCM-41

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MCM-41 molecular sieves are a new class of mesoporous aluminosilicates, having regular, well-defined, and uniform channels with diameters between 1.5 to 10 nm. Their synthesis was first reported by researchers of the Mobil Oil Corporation [1]. These solids with very high surface areas (up to about 1000 m\textsuperscript{2} g\textsuperscript{-1}) and silanol groups in their internal surface have been widely employed to anchor specific groups onto surface silanols, by covalently grafting of various organic species into the channel walls using typically organochlorosilanes or organoalkoxysilanes as precursors for the surface modifications [2].

The organically modified mesoporous aluminosilicates have recently attracted considerable attention and gave rise to a wide range of applications, mainly in analytical separation, electrochemistry and sensors [3-6]. Using organically modified porous adsorbents as electrode modifiers provide possibility of various electroactive guests.

In this work we prepared aminopropyl-grafted MCM-41, which was characterized with XRD and FTIR methods. Experimental results show that carbon paste electrode modified with this material has observational anion exchange capacity after protonation of amino group in acidic medium; therefore we used this electrode for open circuit accumulation of ferricyanide and then for electrocatalytic reduction of hydrogen peroxide. This chemically modified electrode can be applied for electroanalysis of hydrogen peroxide in environmental samples.

References:

CMEs used for Pb and Cu detection in soil samples by Osteryoung Square Wave Stripping Voltammetry

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Heavy metal detection in solid and aqueous industrial wastes is traditionally a domain of standard methods as atomic absorption spectrometry (AAS) and inductively coupled plasma (ICP) that are very accurate and allow multidection; however, both of them require expensive instrumentation. Other alternative is the UV-Vis spectrometry that is characterized by the consumption of very exclusive reagents to form stable metal complexes suitable to be detected. In addition, the stability of metal complexes does not allow to get back the original sample neither to recycle those exclusive reagents (ligands). Attending this necessities (non expensive detection and recyclable reagents), electroanalytical methods are presented as an appropriate alternative. Electroanalytical methods have the advantage of using very small amounts of sample that even can be returned to its original state and reuse the detection devise (sensor electrode); however a right comprehension of phenomena involved in the detection process are the key to have a successful determination.

In this work amperometric electrodes are proposed as Pb and Cu sensors for soil and water analysis in a practical, accurate and non expensive way. The use of non modified carbon paste electrodes (CPE) and chemical modified electrodes (CME) in conjunction with the Anodic Stripping Voltammetry with Osteryoung Square Wave (OSWSV) showed to be a very suitable option to analyze the lead and Cu content in samples of dangerous residues collected from a historically polluted site in Tijuana B.C., Mexico. The addition standard method was used. Results are presented in table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Electrode</th>
<th>Sensibility for Pb $(\mu\text{A/mgL}^{-1})$</th>
<th>Sensibility for Cu $(\mu\text{A/mgL}^{-1})$</th>
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</thead>
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<tr>
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<td></td>
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<td>1.35</td>
<td>3.52</td>
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<td></td>
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<td>7.49</td>
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Table 1. Sensibility of different electrodes for 3 different soil samples washed with NH$_4$CH$_3$COO.
Disperse dyes are environmental interesting because of their widespread use and their mutagenic and toxicity potentiality. They present low removal rate during aerobic waste treatment as well as under advanced chemical oxidation process. Active chlorine (Cl₂, HClO, NaOCl) is extensively used in disinfection and treatment of water and wastewater. Although the formation of disinfection byproducts in drinking water caused by the reaction between natural organic matter and chlorine or other disinfectants is well known in the literature, disinfection processes in water and wastewater treatment systems still rely mainly on chlorine and chlorine-based compounds. This work reports the feasibility of the degradation of disperse dyes, Disperse Orange 1, Disperse Red 1 and Disperse Red 13, as model of azo disperse dyes, Figure 1, using conventional chlorination and photoelectrocatalytic oxidation. The photoelectrocatalysis was performed using Ti/TiO₂ prepared by sol-gel method as working electrode, a reference electrode Ag/AgCl and Pt gauze as counter electrode. Test solutions containing chlorine or sulphate as electrolyte were tested using NaCl or Na₂SO₄ 0.1 mol L⁻¹, pH 4, in 0.8 g L⁻¹ of surfactant Emulsogen used to dissolve disperse dye in water. The photoelectrolyzed solutions were monitored by HPLC, spectrophotometry and TOC measurements. In the same experimental conditions, 60 minutes of treatment on Ti/TiO₂ electrode at +1 V and UV irradiation, photoelectrocatalytic oxidation carried out on NaCl was more efficient to degrade the dyes, Disperse Orange 1, Disperse Red 1 and Disperse Red 13, compared to photoelectrocatalysis in Na₂SO₄. The mineralization results showed 60% of total organic carbon removal after photoelectrocatalysis in chloride medium. The conventional chlorination method promoted discoloration but did not degrade the dyes with TOC removal less than 8%. The formation of Cl⁺, Cl₂ and/or active chlorine becomes the method more efficient to degrade dye pollutant than conventional chlorination method. The photodegradation is very effective and could be appropriate to treat wastewater effluents reaching the public sewage treatment plants. Acknowledgement: CNPq, CAPES

Disperse Red 1: R₁- H; R₂- C₂H₅; R₃- C₆H₄OH
Disperse Red 13: R₁- Cl; R₂- C₂H₅; R₃- C₆H₄OH
Disperse Orange 1: R₁- H; R₂- H; R₃- C₆H₄

Figure 1 - Molecular structure of disperse azo dyes.

Electropreparation of Ascorbic Acid Imprinted Polypyrrole and Overoxidized-Polypyrrole: A Comparatively Study

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AA is an important preservative and antioxidant agent used in the food industry. [1]. Electrodes, modified with electrogenerated polymers, possess many interesting characteristics that can be exploited for numerous sensor applications. Particularly, electroanalysis of biologically important substances are presently under intense studies with the use of chemically modified electrodes [2]. The electro-oxidation of ascorbic acid has been investigated on various modified electrodes, such as polypyrrole [3,4], poly (3,4-ethylenedioxythiophene) [5] etc. Imprinting by electropolymerization in particular is a very attractive approach for development of electrochemical sensors. This method is very easy and provides deposition of a sensitive layer with high precision on electrode surface [6].

In this work, preparation of a molecularly imprinted polypyrrole (MIPPy) and overoxidized-polypyrrole (MIPOPpy) film and its recognition property for ascorbic acid were investigated. The polypyrrole (PPy) films were synthesized by electrochemical method in the presence of a supporting electrolyte (LiClO₄) with and without a template molecule (AA) through on a pencil graphite electrode (PGE). The performance of the imprinted and non-imprinted (NIP) films was evaluated by differential pulse voltammetry (DPV). Several important parameters controlling the performance of the polymer electrodes was investigated and optimized. Linear calibration curves were obtained in the concentration range for AA with MIPPy and MIPOPpy 2.5x10⁻⁴-7.0x10⁻³ M (at pH 8.5) and 2.5x10⁻⁴-7.0x10⁻³ M (at pH 4.0), respectively. The detection limits (3σ) of AA are 7.4x10⁻⁵ M and 1.9x10⁻⁵ M for MIPPy and MIPOPpy, respectively. The effect of various interfering species on the determination of ascorbic acid was studied in standart solutions and in pharmaceutical preparations. The results show that molecularly imprinted PPy can be used as electrode for the determination of ascorbic acid in various samples. Although linear calibration ranges for MIPPy and MIPOPpy were approximately same, the detection limit of MIPOPpy was lower than that of MIPPy.

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References:
Simple and Low Cost Voltammetric Determination of Catechol at a Pencil Graphite Electrode

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Aromatic or phenolic compounds are released into the environment by a large number of industries [1]. Analysis of phenolic compounds is important since many of these compounds have establish a prominence for their toxicity and continuation in the environment [2]. Dihydroxybenzenes such as catechol, hydroquinone etc. are polluting substances that are hazardous to human health occur frequently in the environment [3]. In addition to, some phenolic compounds such as catechol even in low concentration may cause in general genetics, mutagenics and cancerous alteration [4,5]. Therefore, it is very important to develop simple and rapid analytical methods for the determination of these substances [6].

In this work, a simple electrochemical method for the determination of catechol has been developed using a pencil graphite electrode (PGE). Several important parameters controlling the performance of the PGE was investigated and optimized. The determination of catechol was evaluated by differential pulse voltammetric (DPV) method in 0.04 M Britton-Robinson buffer (pH 2.0). The oxidation peak current of catechol is linear over a range from 5.0x10^{-6} M to 1.0x10^{-3} M (r^2:0.998) with the detection limit of 1.3x10^{-6} M.

Financial support of Anadolu University Research Found (Project No: 051060) is greatfully acknowledged.

References:
Glassy carbon electrode modified with ruthenium oxide hexacyanoferrate as an electrochemical sensor for hydrogen peroxide determination in rainwater

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Hydrogen peroxide, \( \text{H}_2\text{O}_2 \), performs an important role in atmospheric and biochemical processes. Atmospheric hydrogen peroxide is formed from the interactions of hydroperoxyl and hydrated hydroperoxy radicals, which are produced by the photochemical reactions of atmospheric trace gases, such as ozone and volatile organic compounds [1]. Prussian Blue (PB) has been considered to be an interesting material for \( \text{H}_2\text{O}_2 \) electrocatalysis for years. The fast electron transfer rate of PB makes PB-modified electrodes a very rapid and versatile sensor with respect to \( \text{H}_2\text{O}_2 \) detection [2]. Notwithstanding, the operational instability of PB has represented the main limitation to the use of PB modified electrodes [3]. Problems of penetration of large cations in the PB lattice represent another important drawback. Hence, the deposition of ruthenium oxide hexacyanoferrate (RuOHCF) onto a glassy carbon surface has been investigated since the incorporation of ruthenium in the structure of hexacyanoferrate films increases its stability [4]. Furthermore, determinations in samples containing different cations such as \( \text{Na}^+ \) can also be done. To evaluate the performance of the proposed modified electrode towards hydrogen peroxide determination, a comparison of amperometric signals between RuOHCF and PB films in acid medium containing KCl was performed. Better sensitivity was found with the PB film, whereas the poor linear range associated with the film loss during the experiments confirmed the above mentioned problems. The analytical applicability of the RuOHCF modified electrode for the determination of hydrogen peroxide at 0.0 V was examined. A linear response was found in the 100 to 600 \( \mu\text{mol} \text{L}^{-1} \) \( \text{H}_2\text{O}_2 \) concentration range (\( R^2 = 0.9991 \)), with a detection limit of 3.7 \( \mu\text{mol} \text{L}^{-1} \). The repeatability for injections of a 100 \( \mu\text{mol} \text{L}^{-1} \) \( \text{H}_2\text{O}_2 \) solution in a FIA experiment was found to be 4.0 % (\( n = 10 \)). The usefulness of the method was demonstrated by an addition-recovery experiment with rainwater samples (102 %). Hydrogen peroxide concentration values in two rainwater samples were (17.4 ± 0.7) and (60 ± 1) \( \mu\text{mol} \text{L}^{-1} \) \( \text{H}_2\text{O}_2 \). Further studies will be directed to explore new approaches to reduce the limit of detection and to investigate the influence of interferences on the response of the proposed sensor. Correlations between the \( \text{H}_2\text{O}_2 \) levels in rainwater samples and pollutant species components (hydrogen ion, nitrate and non-seasalt sulfate) are also of interest. Financial support: FAPESP and CNPq.

Electroflotation as an alternative treatment for water containing suspended solids and emulsions

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The formation of hydrogen and oxygen bubbles generated from water electrolysis can help to float suspended solids, oils and insoluble compounds. The first proposal of electroflotation was done by Elmore in 1904 for the separation of minerals containing gold. The involved factors in electroflotation are: pH, current density, and position of the electrodes, among others. Recently some authors have mentioned the bubble size also need to be considered in electroflotation process.

In this paper we present voltamperometric studies to determine the formation of hydrogen and oxygen using several electrodes as Pt, Au, Ti/RuOx, Ti/IrOxTaOx and Ti/IrOxSnOx. When potential ranges were determined the electroflotation cell will be designed to treat cafeteria waste water (with high level of suspended solids and oil emulsions). For the evaluation of the electroflotation process applied to the waste water of cafeteria, pH, conductivity, DBO, DQO and suspends solids will be measured before and after the treatment.

NaCl in the water has been the main used factor in the literature to obtain microbubbles. For that reason in this work we want to study the influence of the concentration of Cl- in the efficiency of the electroflotation using different electrodes.

In figure 1 the 5 different electrode materials are represented in a voltammetric study for water containing 0.1M NaCl. It can be observed that Ti/RuOx shows a better behavior since oxygen evolution overpotential is 590 mV. For hydrogen evolution the better material is Pt. Further studies are in course in order to complete the cell design and evaluation of treatment for waste water from the ITT cafeteria.
Study of the Electrochemical Behavior of Self-Assembled Films Used in Environmental Applications

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Recently, the self-assembly method has been used to prepare environmental sensors based on conducting polymers to determine pesticides and humic substances [1, 2]. This method allows alternated layers which are sensitive with specific recognition sites [3]. However, the studies of the electrochemical behavior and stability of these films are important to enhance their properties. In this work, a transmission-line model was used to characterize the electrochemical degradation of polyaniline/polystyrene sulfonated self-assembled film. Figure 1 shows the obtained transmission-line model for the analyzed films. The obtained values are presented in Table 1.

Table 1. Nominal values of the elements of the circuits presented in Figure 1

<table>
<thead>
<tr>
<th>Polarize time at 0.55V (minutes)</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>R polymer (Ω)</td>
<td>12.74</td>
<td>15.91</td>
<td>18.09</td>
<td>20.58</td>
</tr>
<tr>
<td>Rct (Ω)</td>
<td>130.69</td>
<td>301.08</td>
<td>1479.63</td>
<td>10974.15</td>
</tr>
</tbody>
</table>

Analyzing the Table 1 it was observed that the degradation of the polymer occurred mainly at the polymer / solution interface. The resistance of the polymer and capacitance (values not showed) remains practically unchanged.

References
Stable and electroactive polypyrrole (PPy) films were produced by electropolymerization of polypyrrole in alkaline solutions containing nitrate or chloride. It is well known that PPy films electrosynthesized in acid or neutral media suffer a decrease of electrochemical activity in alkaline solutions [1]. On the contrary, the films formed in alkaline medium can be cycled in acid or in alkaline media without losing electrochemical activity [2]. Thus, these PPy films should be suitable materials for the construction of electrodes to be used in alkaline solution, a medium which is preferred for several electrochemical reactions related with environmental protection such as nitrate or oxygen reduction. A deeper understanding of properties of these films should be helpful in improving the performance of the polymers.

We present the results of ongoing research to understand the different behaviour of PPy films synthesized in both acid and alkaline media. The polymers were electrodeposited onto vitreous carbon electrodes at 0.9 V vs SCE from 0.1 M HCl and 0.1 M NaCl solutions of pH 12 and 13 containing 0.25 M Py. The electrochemical characterization was performed using cyclic voltammetry and electrochemical impedance spectroscopy. Infrared and Raman spectroscopy were conducted to observe the changes during acid and base treatments as well as during thermal ageing. Treatments include exposition to different media during prolonged period (60 days).

The IR and Raman study of PPy samples synthesized in acid and alkaline media indicates only little differences between their molecular structures.

The stability in alkaline solution of the film formed in the same medium is maintained even if the polymer is exposed to alternating treatment with base and acid. On the other hand, the study of redox cycling of the polymers in the presence of different mobile anions and impedance data indicate that ions diffuse faster in the film electrosynthesized in acid medium.

The obtained results are discussed in terms of differences between polymeric chains organization. A less open structure may be formed as the solution pH increases, which is less accessible for reactants. Then, the formation of covalent bonds between PPy and OH⁻ is hindered. The film synthesized in a basic solution is not damaged even if it is exposed to a strongly alkaline medium for a short time. Moreover the closed polymer structure remains unaltered in a low pH solution.

References
Chlorinated aliphatic hydrocarbons, such as 1,2-dichloroethane (EDC), are frequently found in many surface and ground waters, as a result of their widespread use in industry and in various household products and their poor biodegradability. Presently, 1,2-dichloroethane belongs to those chemicals with the highest production rates. Average annual growth rates higher than 10% were achieved during the past 20 years. Although these growth rates declined during the past several years, in the long run 1,2-dichloroethane is expected to maintain its leading position among the chlorinated organic chemicals [1]. EDC is one of the more toxic common chlorinated substances [1]. It can cause depression of the central nervous system, mental confusion, dizziness, nausea, and vomiting. EDC is present on the US Environmental Protection Agency priority list of pollutants with a limit of 0.005 mg l-1 in drinking water while a limit of 0.003 mg l-1 has been fixed by European Community.

Both destructive and non-destructive methods have been used to remove dichloroethane and other chlorinated aliphatic hydrocarbons. Destructive methods include aerobic/anaerobic degradation [2], chemical reaction via zero-valent iron [3], chemical and photochemical oxidation [4-5], electrochemical reduction [6-9] and oxidation [10,11]. In the present work, the electrochemical treatment of water solutions containing dichloroethane was performed by both electrochemical reductive and oxidation processes.

Stripping Voltammetric Determination of Inorganic Mercury Using a Polyaniline, Polyaniline-poly(vinylsulfonate) and Polyaniline-poly(methylene blue) Coated Glassy Carbon Electrode

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Inorganic mercury ions (Hg²⁺) in laboratory prepared solutions were determined with a glassy carbon electrode coated with either polyaniline [¹], polyaniline-poly(vinylsulfonate) [²,³] and polyaniline-poly(methylene blue) [⁴] polymer layers. The electrically-conducting polymers were prepared by electrochemical polymerisation of monomer solutions of aniline, aniline-poly(vinylsulfonate), and consecutive solutions of aniline followed by methylene blue on a glassy carbon electrode. Anodic stripping voltammetry (ASV) was used to evaluate a solution composed of [1 x 10⁻⁶ M HgCl₂, 0.1 M H₂SO₄, 0.5 M HCl], in the presence of the three different polymer combinations. The Hg²⁺ ions were determined as follows, i) pre-concentration and reduction on the modified electrode surface, and ii) subsequent stripping from the electrode surface during the positive potential sweep. The experimental conditions optimised for Hg²⁺ determination included the supporting electrolyte concentration and the accumulation time [⁵,⁶]. The detection limits for the [1 x 10⁻⁶ M HgCl₂, 0.1 M H₂SO₄, 0.5 M HCl] solution in the presence of the polyaniline, polyaniline-poly(vinylsulfonate) and polyaniline-poly(methylene blue) modified glassy carbon electrodes were 166 ppb, 27 ppb and 30 ppb, respectively. The results of the study will be presented to report the use of a conducting polymer modified electrode as an alternative transducer for the voltammetric stripping and analysis of Hg²⁺ ions.

Keywords: Inorganic mercury; Anodic stripping voltammetry; Polyaniline; Polyaniline-poly(vinylsulfonate); Polyaniline-poly(methylene blue)

On the use of ultrasound-assisted electrochemical methods for the determination and removal of model pollutants

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The determination and elimination of toxic substances and their residues in the environment are important due their high persistency in natural waters, food and soils. Electrochemical methods have been used for detection and removal of pesticides and their degradation products and for the determination of inorganic substances. These organic molecules usually adsorb on the surface of solid electrodes hindering their use in analytical determinations. Moreover, the sensibility of the direct determination of these analytes in complex matrices is reduced due to the adsorption of interfering species that lead to electrode fouling. In the case of removal of contaminants, the electrode surface is often passivated by the adsorption of oxidation products minimizing the efficiency of the process. Power ultrasound has been employed to overcome such electrode fouling problems due to its ability for cleaning the electrode surface, enhancement in the mass transport and for the production of hydroxyl radicals.

In this work, the square wave sonovoltammetric determination of 4-nitrophenol, methylparathion, carbaryl and nitrite was studied on a boron-doped diamond (BDD) electrode. In all cases, significant improvements in the analytical sensibilities were observed due to electrode surface cleaning and the enhancement in the transport of species provided by ultrasound. Limits of detection (LOD) diminished in all cases. For the oxidation and reduction process of 4-nitrophenol, the LOD diminished from 11.7 to 3.87 and from 6.38 to 2.57 µg L⁻¹, respectively. For the reduction of methylparathion, from 10.8 to 4.86 µg L⁻¹; for the oxidation of carbaryl, from 2.96 to 2.08 µg L⁻¹ and for the nitrite sonoelectrooxidation, the limit was 0.782 µg L⁻¹, a value eight times smaller than that obtained in the absence of ultrasound (6.44 µg L⁻¹).

On the other hand, potentiostatic electrolyses of pentachlorophenol were performed on a BDD electrode. Electrolyses at 0.9 V showed that the blockage of the electrode surface was faster in the sonoelectrolysis than in the absence of ultrasound due to the formation of a dimeric compound on the electrode surface. Electrolyses at 2.0 V showed that after 120 minutes, with periodic reactivation of the diamond surface in both cases (using –3.0 V for 30 s), 25.0 and 44.5 % of the initial compound concentration were consumed in the absence and presence of ultrasound, respectively, forming p-chloroanil. Meanwhile, after 90 min of electrolytic process at 3.0 V, without the intermediary reactivation of the electrode surface, 35.8 % (149.0 mC cm⁻²) of the pesticide concentration was consumed by sonoelectrolysis, while 16.9 % (90.08 mC cm⁻²) was degraded by electrolyses without ultrasound.

The results have shown that the ultrasound associated to SWV and electrolyses using BDD electrodes can be a powerful alternative for the determination of organic and inorganic substances and for the removal of toxic compounds from wastewater. This is due to the increase of mass transport, cleaning/activation the electrode surface and to the added generation of hydroxyl radicals by both ultrasound and BDD surfaces.

Acknowledgements: to CNPq and FAPESP, Brazil, for financial support to this work.
Adsorption of microorganisms on mercury surface

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The implantation of a biomaterial into the human body is influenced by susceptibility of an infection. Bacteria or yeast can be also bound on the proteins adsorbed on the metal surface. Microbial colonization and biofilm formation on any substratum proceeds by a series of complex physical and biological processes.

We have studied the processes of adsorption of microorganisms on metal surface. We used bacteria (Escherichia coli) and yeast (Saccharomyces cerevisiae) cell cultures to find the mechanisms of microorganism binding to surface.

The electrochemistry was used for estimation of the degree of adsorption. We performed capacitance, voltammetric and impedance measurements. We measured dependence of electrochemical quantities on concentration of microorganism, on the time of adsorption, on different initial potential, on frequency etc.

We observed different values of physical quantities for different microorganisms. We were able to found difference between adsorption of bacteria and yeast. We also were able to observe the forming of biofilm on electrodes.

The rate of forming of biofilm depends on initial concentration of cells in medium. The dependence is linear in smaller initial concentration of yeasts and it is saturated for higher initial concentrations.

Electrochemical methods for assessment of cell concentration seem good tool for practice. Differences of capacitance in yeast cultures with different cell concentration provide us possibility to estimate yeast concentration without special pretreatment of sample in the culture medium.

The method can be interesting also for medicine application, it is possible to estimated biofilm formation for different metal materials used for implantology. It can help to understand the biofilm formation.

The work was supported by the Grant Agency of Czech Republic (310/07/P480) and by the Project of Ministry of Education of Czech Republic – Stomatology Research Centre No 1M0528.
Characterization of soil samples from a heavy metals contaminated site and the possibility of using *in-situ* electrokinetic remediation

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The electrokinetic treatment applied to heavy metal contaminated soil is known as a good laboratory alternative but very rarely used in real places. In Tijuana, B.C. (industrial frontier city where the daily generation of corrosive, reactive, toxic, inflammable, biological and infectious residues is considerable) few enterprises have been aware of keeping a strong control in residues disposition. For that reason there are contaminated sites requiring an urgent attention. For example the site known as Metales y Derivados S. A. de C.V. where tons of lead residues are mixed with native soil.

After sampling the site in 8 different points, a physicochemical characterization have been performed, including Cation Exchange Capacity (CEC), pH, humidity, conductivity, and texture. Another analysis was the determination of lead and copper content using an electroanalytical methods commonly used in our laboratory. All the collected data represent the initial conditions of contaminated soil that allowed making a diagnostic. After analyzing results of 8 different sampled, two were selected to perform an electrokinetic treatment.

The electrokinetic experiments were performed for soil samples containing 216.13 and 10.702 ppm Pb, and with a CEC of 0.544 and 0.599 mmol/kg .The electrochemical cell was the new model OSMIC-I developed by Murillo and coworkers. During the experiment pH profiles were measured, at the end of experiments lead content was determined for both samples. Results are shown in table 1.

<table>
<thead>
<tr>
<th>X</th>
<th>ppm OSWSV</th>
<th>mg/kg</th>
<th>mol/ kg</th>
<th>sample description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>10.702</td>
<td>1070.225</td>
<td>5.165</td>
<td>Initial simple</td>
</tr>
<tr>
<td></td>
<td>0.276</td>
<td>27.642</td>
<td>0.133</td>
<td>catodic comparment</td>
</tr>
<tr>
<td></td>
<td>13.636</td>
<td>1363.570</td>
<td>6.581</td>
<td>[0-2]</td>
</tr>
<tr>
<td></td>
<td>15.895</td>
<td>1589.496</td>
<td>7.671</td>
<td>[2-4]</td>
</tr>
<tr>
<td></td>
<td>42.106</td>
<td>4210.645</td>
<td>20.322</td>
<td>[4-6]</td>
</tr>
<tr>
<td></td>
<td>14.224</td>
<td>1422.387</td>
<td>6.865</td>
<td>[6-8]</td>
</tr>
<tr>
<td></td>
<td>71.467</td>
<td>7146.741</td>
<td>34.492</td>
<td>[8-10]</td>
</tr>
<tr>
<td></td>
<td>3.162</td>
<td>316.240</td>
<td>1.526</td>
<td>anodic comparment</td>
</tr>
</tbody>
</table>

Table 1. Results of digestions done after Electrokinetic treatment for both samples.
Mediated enzyme reactions form the basis of many applications, ranging from biosensors, through biocatalytic fuel cells, to applications in industrial electrolysis. This presentation will briefly review some of our efforts to date on redox mediation of enzyme reactions for such applications.

Our initial research in this area focused on mediated reactions of laccases, a class of copper-based oxidase enzymes that catalyze the four-electron reduction of oxygen to water. Immobilization of the enzyme in a redox mediating hydrogel yields reagentless biosensors, as monitoring of mediated reduction currents for oxygen, present in solution, permits detection of any modulator of enzyme activity.

Furthermore, co-immobilization of a redox mediator and an affinity recognition element, such as DNA or antibody, provides a generic platform for the amplified detection of complementary affinity partners (DNA or antigen) that are labelled with redox enzymes.

Our studies on laccase biosensors demonstrated, also, that laccases co-immobilized in redox hydrogels can reduce oxygen at relatively high potentials and current densities, suggesting possible applications as cathodes in implantable biofuel cells when combined to oxidation of a fuel, such as glucose, at the anode.

Covalent coupling of enzymes and mediators on the electrode surface can appreciably improve the fuel cell stability. Also, improvements in the design of the redox polymers (in terms of structure and redox potential) help to increase the biofuel cell power output. Our approach at improving the stability and the power output of the biofuel cell will be presented.

Figure showing slow-scan cyclic voltammograms (left) for electrodes modified with a laccase integrated with redox mediators of different redox potentials (red and black) in the presence of oxygen, in physiological buffers. Scheme illustrated the flow of electrons (represented by arrows) on the right.
The determination of hydrogen peroxide ($H_2O_2$) is of great importance because $H_2O_2$ plays an important role in food, pharmaceutical, and environmental analysis. The development of a sensor amperometric for electrocatalytic determination of hydrogen peroxide on platinum electrode coated with Nafion® membrane containing $[(bpy)_2(H_2O)Ru^{III}-O-Ru^{III}(H_2O)(bpy)_2]^+$ complex. The polypyridyl ruthenium-oxo complex was prepared according to a previously described procedure [1]. All the voltammetric measurements were carried out in a 30 ml thermostated glass cell at 25 ºC, in a three-electrode configuration: modified electrode as the working electrode, saturated calomel reference (SCE) and platinum auxiliary electrodes. During the measurements the solution in the cell, de-aerated 0.5 mol L$^{-1}$ KCl solution. Cyclic voltammetry was applied to study the electrochemical behavior of the modified electrode and the electrocatalytic activity of the complex in the hydrogen peroxide oxidation. The voltammetric response of the modified electrode for $H_2O_2$ is based in two cycles, initiating with an electrochemical step (Eq. 1) and followed by chemical step (Eq. 2):

$$[Ru^{III}-O-Ru^{IV}]^{4+}_{(electrode)} \rightarrow [Ru^{III}-O-Ru^{V}]^{4+}_{(electrode)} + e^- \tag{1}$$
$$2[Ru^{III}-O-Ru^{IV}]^{4+}_{(electrode)} + H_2O_2 \rightarrow [Ru^{III}-O-Ru^{III}]^{4+}_{(electrode)} + 2H^+ + O_2 \tag{2}$$

The oxidation of hydrogen peroxide occurred at less negative potential on modified electrode (+0.63 V vs. SCE) compared to bare platinum electrode (+0.85 V vs. SCE). Performing the voltammograms under different scan rates for the modified electrode showed that the catalytic peak current of the hydrogen peroxide oxidation was linearly proportional to the square root of the scan rate within the range (2–50 mVs$^{-1}$), suggesting that the hydrogen peroxide oxidation follows a diffusion-controlled mechanism. The modified electrode was shown to be good amperometric sensor for the detection of hydrogen peroxide. The linear range is from $8.0 \times 10^{-7}$ to $4.0 \times 10^{-5}$ mol L$^{-1}$ with a correlation coefficient of 0.998. The limit of detection was $5.6 \times 10^{-7}$ mol L$^{-1}$, which was obtained through experimental determination based on a signal-to-noise ratio of three.


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Environmental analytical electrochemistry: monitoring the planet

Electrochemical Sensor for Sulfite Determination Based on Copper-Salen Film Modified Electrode

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Sodium sulfite is widely used as a reducing agent in applications such as bleaching of paper pulp and dyeing of textiles. The determination of the sulfite concentration in water, atmosphere and other materials is of great importance for environment protection and quality control. The present work describes the electrocatalytic oxidation of sulfite on platinum electrode modified with copper-salen (salen = N,N’-ethylenebis (salicylideneiminato)) polymer films. The complex was prepared and electropolymerized at a platinum electrode (surface = 0.1952 cm²) in acetonitrile/0.1 mol l⁻¹ tetrabuthylammonium perchlorate by cyclic voltammetry between 0 to 1.4 V vs. SCE. The resulting polymer exhibited stable and reversible redox processes when submitted to voltammetric repeated scans, whatever the nature of the metal or the structure of the ligand. Cyclic voltammetric measurements were performed using this modified electrode, a saturated calomel reference electrode (SCE) and a Pt auxiliary electrode. All measurements were made in a deaerated 0.5 mol l⁻¹ KCl solution. The surface concentration of electroactive species (I_Cu(salen) mol cm⁻²) was estimated from the background-corrected electric charge. After cycling the electrode in 0.10 mol L⁻¹ KCl solution, the estimated surface concentration was found to equal 1.61 x 10⁻¹⁰ mol cm⁻². This is typical behavior for an electrode surface immobilized with a redox couple which can be usually assumed like a reversible single-electron reduction/oxidation of the copper(II)/copper(III) couple. The ratio of cathodic to anodic peak currents at various scan rates was almost unity. Cyclic voltammetry was applied to study the electrochemical behavior of the modified electrode and the electrocatalytic activity of the complex polymer in the sulfite oxidation. The voltammetric response of the modified electrode for sulfite is based in two cycles, initiating with an electrochemical step (Eq. 1) and followed by chemical step (Eq. 2):

\[ \text{Cu(II)·salen}_{\text{electrode}} \rightarrow \text{Cu(III)·salen}_{\text{electrode}} + e^- \]  \hspace{1cm} (1)

\[ 2\text{Cu(III)·salen}_{\text{electrode}} + \text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow 2\text{Cu(II)·salen}_{\text{surface}} + \text{HSO}_4^- + \text{H}^+ \]  \hspace{1cm} (2)

Catalytic oxidation of sulfite anion is performed at platinum electrode at +0.9 V versus SCE, but a significant decrease in the overpotential (+0.57 V) has been obtained using the modified electrode, minimising the effect of oxidizable interferences. Anodic peak current \( (I_{pa}) \) versus sulfite concentration for cyclic voltammetry at the modified electrode, which is linear in the 4.0 x 10⁻⁵ to 4.4 x 10⁻⁴ mol l⁻¹ concentration range. The detection limit (taken as the concentration that gives a signal equal to blank plus three times its standard deviation, calculated from calibration curve) was 2.2 x 10⁻⁵ mol l⁻¹.

Acknowledgements: FAPESP (05/01296-4)
Oxidation of 2,4,6-trichlorophenol at a GC electrode modified with metal phthalocyanines

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There is considerable interest in the determination and degradation of phenolic compounds, since they are persistent pollutants. Their mineralization at different electrode surface and electrolytes has been tried. The rate-determining step is the loss of the first electron, with formation of the phenoxy radical, which usually polymerizes at the electrode surface, fouling it and thereby impeding further reaction. We have found that different bare electrodes (Au, GC, ITO) modified with Ni(II) porphyrins and phthalocyanines yield better results for the electrooxidation of chlorophenols (CPs) and a lower degree of fouling. Agboolola et al. reported that both monomeric and aggregated Cotetrasulphophthalocyanine (CoTSPC) catalyzes CP oxidation by hydrogen peroxide. It is also known that a GC electrode modified with CoTSPc catalyzes the electroreduction of oxygen to hydrogen peroxide. Thus, in this work we study the electrooxidation of 2,4,6-trichlorophenol using a GC electrode modified with polyNiTSPCoTSPc, in the presence and absence of oxygen in the electrolyte. The results indicate a better performance of polyNiTSPCoTSPc/GC electrodes with adsorbed CoTSPc.

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Electrochemistry Applied to Detect Potentially Toxic Elements (PTE’S) in Contaminated Soils by Mining Residues

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Mining industry in Mexico has been one of the main productive activities of the country (after the conquest); today, the environmental impact generated by the high volumes of sulfurous residues left in the jales dams, is the problem to solve. Climatic characteristics of the sites where the residues are deposited have provoked their dispersion or mobility through an extended area urban or rural, giving place to soils contaminated by Potential Toxic Elements (PTE’s) between which are As, Pb, Zn and Cd. On the other hand, voltammetric techniques using carbon paste electrodes (CPE) have been a powerful tool to characterize the oxidation and reduction processes of the pure sulfurous minerals [1-5] (galena, pyrite and arsenopyrite, etc.). However, the characteristics of those minerals are far away from that of the soils. The objective in this work is to detect PTE’s in contaminated soils from mining district of Zimapán, Mexico using 0.1 M NaNO₃ (pH 6.5) and a soil leached solution as electrolytes.

In this work, experimental tests were carried out concentrating the oxidation products on the CPE surface. The samples used were soils contaminated with low and high concentration of the contaminants. Voltammetric responses of the contaminated soils allowed identifying oxidation and reduction processes clearly defined for As, Pb, Zn y Cd species present in the soil. This conclusion was made when a comparative study was carried out through the responses of pure sulfurous minerals [6-7]. The soils showed oxidation and reduction processes in the same potential ranges of the pure minerals. According to the results it is possible to conclude that, the voltammetric methodology with CPE’s to detect PTE’s in contaminated soils resulted convenient and it can be used in obtaining additional information of the mobility of its species.

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Evaluation of food quality is connected with numerous questions. One of them is undesirable occurrence of pathogenic microorganisms, which are dangerous to human health. Their detection, usually based on classical cultivation methods, is tedious and, on the other hand, financially and materially demanding. For those reasons, a search for new methods that are rapid and applicable for wider spectrum of microbes is very important and actual. One of the perspective solutions can be based on applications of electroanalytical techniques combined with procedures used in microbiology and immunology.

As an example of electroimmunoassay of bacterial cells, an amperometric method for *Salmonella* detection is presented. The method is based on the reaction of salmonella with an enzyme-linked specific antibody (alkaline phosphatase) forming salmonella-antibody-alkaline phosphatase (SAAP) conjugates. After their hydrolysis, the products formed (phenols) are detected amperometrically using a carbon paste electrode; current signals are monitored at 0.65 V vs. Ag/AgCl/satd. KCl in a medium of pH 10.0 which was found as the best. Amount of phenol generated by SAAP is proportional to the number of *Salmonella* Enteritidis in a sample.

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Simultaneous Photoelectrochemistry Reduction of Cr(VI) and Dye Oxidation in a Leather Effluent

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The extensive use of chromium in the metallurgic, leather tanning, electroplating, lumber, electricity generating, and other industries have promoted enormous ecological impact on numerous sites that are being contaminated by chromium. Possible hazards arising from the use of chromium (VI) is in evidence, especially in leather industry, where chromium is currently used. Cr(VI) exhibits remarkable toxic activity and it is included in the list of priority pollutants of the US EPA. In addition, the European Union has also been concerned with this chemical species setting a maximum concentration limit for chromium in drinking water at 50 ppb. The treatment of Cr(VI) is generally accomplished by transforming Cr(VI) to Cr(III), which is considered non-toxic and an essential trace metal in human nutrition. This work concerns about the application of a photoelectrocatalytic technique for the removal of both an acid red dye and Cr(VI), using nanoporous Ti/TiO₂ thin-film anodes. Red 151 dye is a commercial dye widely used in leather dyeing industry. All photoelectrochemical experiments were conducted using Ti/TiO₂ thin-film photoelectrodes prepared by sol-gel methods. The photoelectrolyzed solutions were monitored by HPLC, spectrophotometry and TOC measurements. Cr(VI) abatement was followed by the official colorimetric method based on reaction with diphenylcarbazide. The method was applied by testing the photoelectrocatalysis of a solution containing 0.03% (w/v) acid dye, 0.009% (w/v) commercial surfactant assigned as Tamol® and 9.32 ppm Cr(VI) in Na₂SO₄ 0.1 mol L⁻¹ using a one compartment electrochemical reactor. The photoelectrolysis experiments performed using a potentiostat EG&G Instruments model 383, using a working electrode of Ti/TiO₂ (25 cm²) prepared by the sol-gel method, a reference electrode of Ag/AgCl (KCl 3 mol L⁻¹) and a Pt net as an auxiliary electrode. After 120 min of treatment using the best experimental condition of applied potential of +1.0V, it was possible to suppress 100% of the color, 100% of the surfactant, 75% of the total organic carbon and 96% of Cr(VI). A comparison of photolysis, photocatalysis and photoelectrocatalysis for Cr(VI) reduction for these three methods increased from 0%, 44% and 96%, respectively. Simultaneous increases in the discoloration rate constant were also obtained from -0.092 min⁻¹ to -0.018 min⁻¹, respectively. Effects of other electrolytes, dye concentration, surfactant concentration, pH and applied potential have been investigated and the best conditions to promote both oxidation of acid dye and reduction of Cr(VI) are discussed. Acknowledgment is given to FAPESP, Process 04/07353-7, CNPq, CAPES from Brazil and NSF (USA) for funding these studies.
Voltammetric and ellipsometric study of platinum electrodes in acid solutions containing sulphur dioxide

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Hydrogen evolution and the oxidation of methanol are intensively studied reactions due to their significance in alternative energy production [1-2]. The efficient catalytic oxidation of methanol is crucial in fuel cell development. The catalytic process on platinum electrodes is ruled by the adsorption of several adsorbed intermediates, CO, HCO or COH, whose excessive accumulation leads to the electrode poisoning. On the other hand, the adsorption of SO₂ and other S compounds coming from SO₂ reduction modifies the kinetics in some cases improving but in others decreasing the efficiency of the catalyst. Recently several other adsorbed species have been detected, such as formiate, incipient oxides, non-coordinated water as well as metal surface restructuring, which can alter the electrooxidation process. Moreover, even in the absence of dissolved SO₂, the pretreatment by strong cathodisation produces an increase of catalytic activity in methanol electrooxidation [2].

Unlike oxide films, the sulphur compounds may form clusters or adsorbed species containing S-S bonds of different magnitude. In aqueous electrolytes SO₄²⁻ and HSO₄⁻ ions are strongly adsorbed on platinum. However, these ions are considered as not reducible on inert cathodes, except in very high acidity media and in the absence of water. Possible reduction routes in 1 M H₂SO₄ solution are through SO₃ or S₂O₃ intermediates. Under intensive hydrogen bubble detachment, localised changes in concentration and temperature may produce variations in the equilibrium of the SO₂ - H₂SO₄ - H₂O system, with accumulation of low oxidised sulphur species.

The effects of the cathodisation is investigated in the presence of dissolved sulphur dioxide using electro-chemical and surface analysis techniques such as voltammetry, energy dispersive X-ray analysis (EDAX), scanning electron microscopy (SEM), and in-situ ellipsometry. In 1 M H₂SO₄ solution the initial adsorption of SO₂ at open circuit for a time between 15 and 150 min produce a continuous change in the ellipsometric parameters Δ and Ψ. These results show the progressive growth of a layer with practically constant optical density and increasing thickness between 1 and 140 nm that indicates the formation of adsorbed SO₂ multilayers. For a time longer than 150 min the optical parameters shows the nucleation and growth of an elemental sulphur film.

Wiring of *Escherichia coli* With Different Electron Transport Mediators

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Gram-negative *Escherichia coli* strain JM109 looks promising for energy generation in biofuel cells. The cells we are using over express the di-heme membrane protein from *Bacillus subtilis* succinate:quinone reductase. This protein has two $b$-type hemes: heme $b_L$ with a midpoint potential of -132 mV vs NHE and heme $b_H$ with a midpoint potential of +16 mV vs NHE. The protein is present in the inner cell membrane and can potentially be used to enhance the wiring between the cell and different electron transfer mediators. The role of mediators in microbial biosensors and biofuel cells is to take electrons from the oxidizing enzymes and/or respiratory chain and transport them to the surface of the electrode and thus to replace the natural electron acceptor – oxygen, in the case of aerobic bacteria for example. In this way artificial electron shuttles can enhance electron transfer between microbial cells and electrodes.

It is well known that different water-soluble mediators such as 2,6-dichlorophenol indophenol (DCPIP) or ferricyanide (FeCN) and hydrophobic ferrocene derivatives can be effectively used for coupling microbial metabolism and electrodes [1]. One recent trend in wiring of living cells and electrodes is to use polymeric mediators, which exhibit efficient electron shuttling properties for multiple layers of microbial cells [2,3].

In the current study the application of different artificial electron transport mediators for efficient electrical wiring of gram-negative bacteria *E. coli* JM109 were investigated. Different characteristics of the system containing a graphite electrode modified with cells, a Ag|AgCl (0.1 M KCl) electrode and a platinum wire used as reference and auxiliary electrodes, respectively, were evaluated in flow analysis mode when glucose was used as a substrate. The influence of pH of buffer solution and presence of oxygen on the current response was evaluated.

*E. coli* JM109 cells immobilized on the surface of graphite electrode did not show any direct electron transport. We have not been able to show any current response from the cells in the presence of DCPIP-solution or ferrocene immobilized on the surface of the electrode. However we obtained very good results with a flexible osmium redox polymeric mediator and the water-soluble mediator – ferricyanide.

Electrochemical and Photo-Assisted Electrochemical Degradation of Real Textile Effluent

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The textile industry is one of the most polluting sectors in terms of volume and complexity of effluent discharge. Textile wastewater is characterized by high chemical oxygen demand (COD) and total organic carbon (TOC), as well as, strong color. Conventional treatment of textile wastewater generally consists of coupling chemical coagulation with biological treatment. However, these methods cannot be employed where the wastewater is resistant to biological treatment. An alternative path could be the application of electrochemical technology, which benefits from advantages such as versatility, environmental compatibility and potential cost effectiveness. The present study evaluates the efficiency of electrochemical (EC) and photo-assisted electrochemical (PAEC) degradation of real textile effluent under galvanostatic conditions. The effluent was provided by the Brazilian textile company Tecelagem São Carlos SA. It was collected in two stages: (a) without any pretreatment and (b) after biological treatment. A single-compartment photo-electrochemical filter-press cell was used with a commercially available Ti/Ru0.3Ti0.7O2 - DSA® electrode (area = 14 cm²) with a Ti-mesh cathode (area = 14 cm²). The UV radiation was provided by a 250 W Hg lamp. A constant temperature of 28°C was used. All electrolyses were performed adding NaCl and Na2SO4 as the supporting electrolyte in different proportions, keeping constant ionic strength at 0.15 mol L⁻¹. For the study of the effect of current density the following values were: 10, 20, 40, 60, 80 and 120 mA cm⁻². When the untreated (no electrolyte addition) effluent is treated there is little or no color or TOC removal, even at the higher current densities. As the conductivity of the effluent is low (~2 mS cm⁻¹), electrochemical treatment of the as-received effluent is extremely inefficient. When salts are added to the effluent, the efficiency of the process improves. As a result when the current density is increased there is a concurrent increase in the extent of colour removal and TOC. The effect of substituting stepwise the Na2SO4 with NaCl was studied and it was observed that the color, COD and TOC removal increases almost linearly with the chloride ion concentration. This is due to the in-situ formation of the Cl₂ and free chlorine species in solution (e.g. OCl⁻). With the addition of the salts the conductivity of the effluent increases (17 mS cm⁻¹) and as a result the operating cell potential is reduced and the energy consumption is lower. Overall the photo-assisted method is observed to be more efficient than the purely electrochemical system. When the biologically treated effluent is electrochemically treated, analogous results to those obtained for the untreated effluent are obtained – inefficient color removal in the absence of salts and increased efficiency with NaCl – however, the energy efficiency is much greater. These results indicate that the EC and PAEC methods are best employed as a final treatment process (polishing) after biological treatment. As Cl₂ is formed in-situ the results will also be presented with a determination of the extent of formation of harmful chlorinated degradation by-products.

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Electrochemical degradation of the Blue Reactive 19 dye in a filter-press reactor using a carbon-fiber/PbO$_2$ anode in the presence or absence of chloride

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In the last decades, environmental problems have become increasingly critical and frequent, due to population growth and the increase of industrial activities. In the attempt of avoiding the exhausting of natural resources so essentials for humanity, like water, new techniques have been developed for the treatment of pollutant containing wastes before their discarding into the environment. Among the alternatives to conventional methods, the use of electrochemical technologies is also being tested as quite promising processes for this end. Thus, electrode materials with good chemical activity, high superficial area and stability at high potential values have called the attention for the electrochemical treatment of wastewaters, mainly those from textile industries. PbO$_2$ fulfills these criteria and has been considered a good electrode material for the treatment of dye containing wastewaters. So, considering the high superficial area of carbon fiber (CF) and taking into account that studies on lead dioxide deposition on CF are, at this moment, unknown, the purposes of this work were to produce and characterize PbO$_2$ films on a CF substrate and also to evaluate their performance in the oxidation of simulated wastewaters containing the Blue Reactive 19 (BR 19) dye using a filter-press reactor. The PbO$_2$ films were electrodeposited (20 mA/cm$^2$ for 34 min) on the CF substrate (PWB-3/Stackpole - USA) using a four-electrode one-compartment cell, containing the following aqueous solution, kept at 65 °C and magnetically stirred: 100 mM Pb(NO$_3$)$_2$ + 0.5 g/L sodium lauryl sulfate in 0.1 M HNO$_3$. In order to investigate the effect of the operating parameters on the BR 19 dye (100 mg/L in 0.1 M Na$_2$SO$_4$) oxidation, electrolyses were carried out at different flow rates (2.5 - 7.0 L/min) and current densities (10 - 70 mA/cm$^2$), in the presence or absence of different chloride concentrations (10 - 70 mM). According to SEM micrographs, the PbO$_2$ films deposited on the CF were homogeneous and well distributed on the fibers. When these films were used for the oxidation of the BR 19 dye, the best values obtained for the operating parameters were: 7.0 L/min, 30 mA/cm$^2$, and 70 mM NaCl. In the absence of chloride ions, the total charge per unit volume ($Q_f$) needed to achieve 100 % decolorization of the simulated BR-19 wastewater was 2.0 A h/L. The BR-19 wastewater color intensity decreased exponentially with $Q_f$, indicating a mass-transfer controlled process. On the other hand, in the presence of chloride ions the $Q_f$ value decreased twentyfold (0.1 A h/L) and the BR-19 simulated wastewater color intensity decayed linearly with $Q_f$, indicating a charge-transfer controlled process. This result was due to the hypochlorite ions electro-generated on the electrode surface, which selectivity oxidized the BR 19 anthraquinone chromophore group.

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Electrochemical degradation of the Reactive Red 141 dye
on Ti-Pt/\(\beta\)-PbO\(_2\) and DSA anodes

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The contamination of water has been one of the greatest current challenges, as
it is becoming a scarce natural resource. The textile industry, in particular, stands in a
delicate position due to the large volume of water used and wastewater produced. The
latter is characterized by an intense color originated by un-reacted dyestuff, as well as
by a high organic load and temperature oscillations. In this context, new technological
processes, such as electrochemical oxidation, for the treatment of wastewater are being
improved, due to the development of new electrode materials, and the combination of
different degradation techniques. Thus, this work aimed to compare the electrochemical
degradation of a simulated wastewater containing the Reactive Red 141 (RR 141) dye,
by the use of Ti-Pt/\(\beta\)-PbO\(_2\) or DSA (from Denora) anodes, with and without the
addition of NaCl to the wastewater. The electrochemical degradation experiments were
done in a one-compartment filter-press reactor. \(\beta\)-PbO\(_2\) films were electrodeposited (20
mA cm\(^{-2}\) during 34 min) on a Ti-Pt substrate from the following electrodeposition bath:
100 mM Pb(NO\(_3\))\(_2\) + 0.5 g L\(^{-1}\) sodium lauryl sulfate in 0.1 M HNO\(_3\), at 65 °C. The
concentration of RR 141 in the simulated wastewater (300 mL, at 25 °C) was 100 ppm
in 0.1 M Na\(_2\)SO\(_4\). A set of initial experiments was done in which the flow rate, current
density and concentration of NaCl were varied separately. Chemical oxygen demand
(COD) measurements were also carried out. The best results obtained for the initial
conditions were 7.0 L min\(^{-1}\), 75 mA cm\(^{-2}\), and 30 mmol L\(^{-1}\) NaCl. This set of
parameters was applied in the electrooxidation using DSA anodes. Initially, the
electrooxidation in the absence of NaCl led to total color removal in 35 minutes (\(Q_t =
1.7\) A h L\(^{-1}\)) using Ti-Pt/\(\beta\)-PbO\(_2\), while for DSA the color removal was only 33 %. After
the addition of NaCl, the time required for decolorization decreased significantly due to
indirect oxidation by electro-generated hypochlorite ions. Nevertheless, while for Ti-
Pt/\(\beta\)-PbO\(_2\) a total color removal was reached in 12 min (\(Q_t = 0.5\) A h L\(^{-1}\)), only 45 % of
decolorization was reached for the DSA anode. Furthermore, COD measurements
indicated 77 % or 5 % RR 141 mineralization using the Ti-Pt/\(\beta\)-PbO\(_2\) or DSA anode,
respectively, after 60 min (\(Q_t = 2.9\) A h L\(^{-1}\)) and in the absence of NaCl. The rate of
mineralization in the presence of NaCl increased, reaching 74 % or 68 % for the Ti-
Pt/\(\beta\)-PbO\(_2\) or DSA anode, respectively, after 20 min (\(Q_t = 1.0\) A h L\(^{-1}\)). The results
obtained for the Ti-Pt/\(\beta\)-PbO\(_2\) anode showed a high efficiency for color and COD
removal. On the other hand, the DSA anode exhibited a worse efficiency, which
improved by the addition of NaCl to the simulated wastewater due to its intrinsic
property of indirect oxidation by electro-generated hypochlorite ions.

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Recent advances in polymer electrolyte fuel cells technology demand operation at high working temperatures to improve efficiency, tolerance of contaminants and for an easy water management. High temperature operation influences significantly carbon black corrosion, platinum dissolution and sintering [1]. The scope of this work is to evaluate the high temperature performance and stability of the catalysts in the presence of perfluorosulphonic membranes and to correlate these properties with the physicochemical characteristics both in terms of electro-catalytic activity for oxygen reduction and resistance to degradation under fuel cell conditions. We have overcome the constraints related to the dehydration behaviour of the membrane at high temperature by pressurizing the PEM single cell and operating the humidifiers at the same temperature and pressure of the cell [1]. Although, the operating conditions do not exactly reproduce those aimed by the automakers, i.e. ambient pressure and 25% relative humidity (RH), the present approach may provide a basis to identify the high temperature degradation mechanism for conventional PEMFCs and alleviate through proper preparation procedures the performance loss. An investigation of carbon-supported Pt/C and PtCo/C catalysts was carried out with the aim to evaluate their stability under high temperature polymer electrolyte membrane fuel cell (PEMFC) operation. Carbon-supported nanosized Pt and PtCo particles with a mean particle size between 1.5 nm and 3 nm were prepared by using a colloidal route. A suitable degree of alloying was obtained for the PtCo catalyst by using a carbothermal reduction. The catalyst stability was investigated to understand the influence of carbon black corrosion, platinum dissolution and sintering in gas-fed sulphuric acid electrolyte half-cell at 75 °C and in PEMFC at 130 °C. Electrochemical active surface area and catalyst performance were determined in PEMFC at 80 °C and 130 °C. A maximum power density of about 700 mWcm⁻² at 130 °C and 3 bar abs. O₂ pressure with 0.3 mg Pt cm⁻² loading was achieved. The PtCo alloy showed a better stability than Pt in sulphuric acid after cycling; yet, the PtCo/C catalyst showed a degradation after the carbon corrosion test. The PtCo/C catalyst showed smaller sintering effects than Pt/C after accelerated degradation tests in PEMFC at 130 °C. The results have been interpreted in terms of structural and surface properties of the catalysts.

References
Metal hydride electrodes studied by QCM technique

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The use of Ni–MH batteries for traction applications in electric and hybrid vehicles is increasingly attractive and reliable. Besides the energy and power handling, and the cost issues, high tolerance to abuse is an important aspect of the Ni–MH technology. We have studied the LmNi₄.₁Co₀.₄Mn₀.₄Al₀.₃ [1,2] in thin thick layer deposition on QCM crystal. We have studied the absorption/desorption of hydrogen. The electrochemical quartz crystal microbalance (QCM) was applied to the study of LmNi₄.₁Co₀.₄Mn₀.₄Al₀.₃ thin layer electrodes as measure technique. We have used the Pt and Au crystal matrix for deposition. We have compared their mass changes dependents on absorption-desorption and oxidation-reduction reactions in metal hydride thin layer electrodes of hydrogen. The deposit was prepared by mixing of alloy with carbon black in mixed by the ball mill. We activated the material after deposition on crystal in galvanostatic and potentiometric way. The effect of the hydrogen evolution in the different substrates was analyzed with the change of the mass.

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Effect of the catalyst composition in the Pt$_x$(Ru–Ir)$_{1-x}$/C system on the electro-oxidation of methanol in acid media

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The need for more efficient energy conversion systems is a strong reality for two important reasons, namely, the future shortage of fossil fuel sources and the urgency in reducing the contamination levels in urban centers. Fuel cells are very promising alternative energy sources due to the high efficiency of the electrochemical combustion in comparison with the chemical one thus minimizing the formation of by-products that pollute our planet. Among the different systems under investigation, the use of methanol has been the subject of numerous studies since considerable advances has been achieved using that fuel [1].

Pt shows the highest activity for the electro-oxidation of methanol but the performance of pure Pt electrodes is not very satisfactory due to the formation of strongly adsorbed intermediates (particularly CO). Efforts to reduce the amount of adsorbed CO are centered on the use of co-catalysts and, to date, the addition of ruthenium into the platinum catalyst has yielded the best reported results [2–3]. Thus, the aim of this work is to report the effect of composition in the catalyst system Pt$_x$(Ru–Ir)$_{1-x}$/C on the methanol electro-oxidation in acid media for $x$ values of 0.25, 0.50 and 0.75.

The catalysts were prepared by the sol–gel method and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), atomic absorption spectroscopy (AAS) and energy dispersive X-ray (EDX) analyses. The nanometric character (2.8 – 3.2 nm) of the sol–gel deposits was demonstrated by XRD and TEM while EDX and AAS analyses showed that the metallic ratio in the compounds was very near to the expected one. Cyclic voltammograms for methanol oxidation revealed that the reaction onset occur at less positive potentials in all the ternary catalysts tested here when compared to a Pt$_{0.75}$Ru$_{0.25}$/C (E-Tek) commercial composite. In addition, steady-state polarization experiments showed that the Pt$_{0.25}$(Ru–Ir)$_{0.75}$/C catalyst is the more active one for methanol oxidation as revealed by the shift of the reaction onset towards lower potentials (~284 mV in relation to the Pt/C from E-Tek). Furthermore, constant potential electrolyses suggest that the addition of Ru and Ir to Pt decreases the poisoning effect of the strongly adsorbed species generated during methanol oxidation. Consequently, the Pt$_{0.25}$(Ru–Ir)$_{0.75}$/C composite catalyst is a very promising one for practical applications.

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Bromate formation on BDD anodes

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Bromate is known to be disinfection by-product in drinking water disinfection by ozonation. Therefore, bromide concentration is limited by regulations.

In this paper, results are presented obtained from electrochemical treatment of aqueous systems containing bromide ions in ppm (mg L\(^{-1}\)) range of concentration and using boron doped diamond (BDD) anodes. A cell with rotating anode located 4.5 mm above a mixed oxide cathode (expanded mesh) was used [1]. Temperature was varied between 5°C and 30 °C in thermostated experiments, rotation rate was between 100 rpm and 500 rpm. A constant current density mode was applied up to highest current densities of 200 A m\(^{-2}\). All species were analyzed by HPLC.

Bromate formation was strongly dependent on current density applied (Fig. 1). The high reaction rate can be explained by EC mechanisms with participation of \( ^{*} \mathrm{OH} \) radicals and ozone that is an intermediate. The formation of bromate proceeds much faster compared with experiments using mixed oxide anode (not shown here). Higher bromide concentrations results in higher bromate concentration at same side conditions.

![Fig. 1](image)

There were only neglecting bromate concentration changes varying mass transfer conditions (rotation rate). At higher temperature, lower bromate concentration was measured, whereas the bromide depletion remained constant. Stripping effects may explain this behavior.

When chloride was added to the bromide solution chlorate, perchlorate and bromate ions could be detected. New peaks in chromatograms show obviously the presence of perbromate. The results demonstrate the high potential of bromate formation on BDD anodes. More research work is necessary to get better information about the reaction paths.

**References**


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The study of anion exchange materials for electrodeionization

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Electrodeionization (EDI) is a technology combining ion exchange and electrodialysis for continuous operation in loading/regeneration of ion exchangers. Firstly, it was applied for the production of ultra-pure water. This work presents results of a research project for studying processes in precision plating industry. The work was focused on diluted solution treatment (rinse waters) containing chromate, chloride and sulphate ions in ppm range. Several materials of ion exchange resins and ion exchange membranes were tested. The determination of resin conductivities, exchange capacities and kinetic parameters was a significant part of the studies. As one result of the work, a 2-compartment technology was worked out for concrete conditions of application. In addition, other variants were suggested [1]. The paper presented here mainly describes results of resin studies. Three anion exchange materials were chosen for comparison (Lewatit MPC 64, Lewatit Monoplus MP64 and Wolfatit SZ 30). Measurements of conductivities in dependence on metal ion concentration and pH were carried out at room temperature. Other parameters determined were adsorption capacity and equilibrium coefficient. Kinetic parameters were measured or calculated for the exchange process. Typical ranges of anion concentrations used were 0.02...15 mmol L−1 in solutions and 0.1... 2.8 mol L−1 inside the resins.

Tab. 1 presents calculated values of ion exchanger conductivity. It is apparent that the lowest conductivities were observed for materials in the chromate form, the biggest for the OH− form. This is a clear indication that chromate transport during electrodeionization can be expected to large extent by ionic flow in the electrolyte phase between the bed particles.

Table 1 Specific conductivity in mS cm−1 of several ion exchange materials.

<table>
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<tr>
<th>Material</th>
<th>Cl− form</th>
<th>SO42− form</th>
<th>OH− form</th>
<th>(CrO4)2− form</th>
</tr>
</thead>
<tbody>
<tr>
<td>System I</td>
<td>1.66</td>
<td>1.34</td>
<td>19.14</td>
<td>0.067</td>
</tr>
<tr>
<td>System II</td>
<td>2.4</td>
<td>2.28</td>
<td>5.05</td>
<td>0.049</td>
</tr>
<tr>
<td>System III</td>
<td>16.2</td>
<td>8.0</td>
<td>75.0</td>
<td>0.049</td>
</tr>
</tbody>
</table>

It was found that absorption capacity was much higher for one selective anion exchange material compared with the others. The calculated equilibrium constants for main and side ions were nearly of same order of magnitude. This may lower process efficiency for chromate removal in some cases.

Both from the results obtained and theoretical consideration, conditions for further experiments in laboratory EDI cells were defined. In addition, the results allowed concluding a general and practicable solution for the process technology.

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Development of a Bipolar Electrochemical Reactor with Rotating Cylinder Electrodes of Woven-Wire Meshes for Effluent Treatment

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The electrochemical treatment of effluents claims the use of three-dimensional electrodes in order to increase the space time yield of the electrochemical reactor. Likewise, the bipolar connection is appreciated due to the more simple constructive features of these devices. This contribution reports experimental results obtained using woven-wire meshes packed in a cylindrical configuration in order to conform an electrochemical reactor with rotating electrodes, which is shown in Figure 1. The reactor was made part of an electrolyte circulation system. Thus, the solution flows from a thermostated tank to the lower part of the current feeder of the terminal cathode, passes following a zigzagged path through the bipolar electrodes and is collected in another tank. It was not recycled so that the inlet copper concentration remained constant.

The test reaction was copper deposition from 1 M Na₂SO₄, pH 2, with an inlet copper concentration of approximately 350 mg dm⁻³. During the experiment, samples of solution were taken at intervals from the reactor outlet in order to determine the copper concentration by atomic absorption spectroscopy. All experiments were performed at 30°C under galvanostatic control, 1 A. Figure 2 shows the conversion, \( x \), and current efficiency, \( \beta \), as a function of the number of bipolar electrodes.

For a small number of bipolar electrodes the conversion increases linearly and the current efficiency is high, however when \( n \) is higher than 2 both figures of merit decrease suddenly. This behaviour can be attributed to the accumulation of gases inside the stack because the evacuation of the gases evolved at the electrodes becomes more difficult when the number of bipolar electrodes is increased. In a long term experiment with two bipolar electrodes and 2.1 mm separator thickness it was obtained a conversion of 47\%±5\% with 54\%±5\% of current efficiency. The specific energy consumption was 3.27 kWh kg⁻¹ with a normalized space velocity of 23.05 h⁻¹.
Comparative Study of Concentration-Time Relationships in Recirculating Electrochemical Reactor Systems

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One possible mode of operation for effluent treatment is to associate the electrochemical reactor to a reservoir by conforming a recirculating electrochemical reactor system. In the design of this system it is important to be able to predict the temporal variation of concentration in the reservoir. The purpose of this paper is to outline the mathematical models which permit such calculation. Taking into account the plug flow model to represent the electrochemical reactor and the reservoir as a well mixed tank, assuming that at \( t = 0 \) the concentration along the reactor is \( C_0 \) the following rigorous equation is obtained for the concentration in the reservoir:

\[
C_i(t) = C_0 \exp\left( -\frac{t}{\tau_R} \right) \times \left[ 1 + \frac{1 + \beta \frac{\tau_M}{\tau_R} \exp(\beta)}{1 + \beta \frac{\tau_M}{\tau_R}} \right] \times \exp\left( -\frac{\tau_M}{\tau_M} t \right) \sum_{n=0}^{\infty} \frac{(z - n \tau_R)^n}{n! \exp(\beta) \tau_M^{n+1}} \exp\left( -\frac{z - n \tau_R}{\tau_M} \right) dz
\]

When the reactor residence time, \( \tau_R \), is lower than the reservoir residence time, \( \tau_M \), the temporal behaviour is given by the simplified equation:

\[
C_i(t) = C_0 \exp\left( -\frac{t}{\tau_M} \left[ 1 - \frac{1}{\tau_M} \exp(\beta) \right] \right)
\]

Likewise, considering the stirred tank model for the electrochemical reactor the concentration in the reservoir is

\[
C_i(t) = \frac{C_0}{r_2 - r_1} \left[ r_1 \exp(r_1 t) - r_1 \exp(r_2 t) \right], \quad r_{1,2} = \frac{1 + \frac{1 + \beta \tau_M}{\tau_R} \pm \sqrt{1 + \frac{1 + \beta \tau_M}{\tau_R}}^2 - 4}{2 \tau_M \tau_R}
\]

For \( \tau_R << \tau_M \) the simplified equation \( C_i(t) = C_0 \exp\left( -\frac{t}{\tau_M} \left( \frac{\beta}{1 + \beta} \right) \right) \) is valid,

where \( \beta = \frac{ka_e \tau_R}{\varepsilon} \), being \( k \) the kinetic constant, \( a_e \) the specific surface area and \( \varepsilon \) the porosity.

In this contribution the temporal behaviour according to the above equations is compared. When \( \tau_R < 50 \tau_M \) the simplified equations, Eqs. 2 and 4, agree well with those of the rigorous models, Eqs. 1 and 3 respectively. As expected a reactor according to the plug flow model associated to a reservoir shows the best performance.
**Corrosion Resistance and Electrochemical Stability of Ti-Mo Alloys For Biomedical Applications**

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**Introduction:** Nowadays, the population of most countries is increasing; so the demand for artificial implants has been growing [1-2]. There are only a few reports focusing electrochemical methods to analyze Ti-Mo alloys applied as biomaterials, the goal of this work was to carry out stabilities studies of these alloys in electrolyte simulating physiological media as function of immersion time.

**Materials and Methods:** The Ti-Mo alloys (6 to 20 Mo wt.%), were cast in an arc-melting furnace by and characterized by the authors [3]. Working solution was natural aerated aqueous Ringer solution (NaCl 8.61 g/L, CaCl₂ 0.49 g/L, KCl 0.30 g/L), at 37°C, and the alloys were studied on as-cast conditions. After alloys polish (1500 grade silicon carbide paper), the open-circuit potentials values, $E_{oc}$, and Electrochemical Impedance Spectroscopic, EIS, were record after 1, 24, 48, 72, 168, 240 and 360 h. EIS measurements were carried out at open circuit potential in the frequency range from 100 kHz to 10 mHz with a perturbing signal of 10 mV.

**Results and discussion:** $E_{oc}$ values shifted towards more positive potentials, reaching a quasi-stationary value at 72 h, not changing significantly after that (Fig. 1a). Ti-15Mo had the highest $E_{oc}$ values, while Ti-20Mo had the lowest. EIS studies showed high impedance values for all samples, increasing with immersion time, indicating an improvement in corrosion resistance of the spontaneous oxide film. Fitting suggested the presence of a single passive film on the surface of the alloys, with its resistance improving with immersion time (Fig. 1b). The higher polarization Resistance, $R_P$, values were found to Ti-15Mo alloy and Ti-20Mo the lowest ones showing that the Ti alloy with 15 Mo wt.% present a better corrosion resistance among the alloys studied.

**Conclusions:** The results suggest that Ti-15Mo alloy is promissory to be applied for orthopaedic devices, once electrochemical stability is directly associated with biocompatibility and one necessary condition for applying a material as biomaterial.

**References**

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Photoelectrochemical and Impedance Studies of Passive Films on Different Ti-Mo Alloys

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Ti-based materials are widely employed for several biomedical applications, including artificial prostheses [1]. In fact these materials present high mechanical strength, low elasticity modulus, elevated corrosion resistance and excellent biocompatibility. The latter originates from the very low metal release and toxicity of corrosion products of Ti, Zr, Nb, Ta and Mo, at variance with stainless steels and Co-Cr alloys [2,3].

Ti-Mo cast alloys with different compositions were melted in an arc furnace with a non-consumable W electrode and a water-cooled copper hearth under ultra-pure argon atmosphere [1,2]. Alloys were passivated in acidic or neutral aqueous solutions by linear potential sweep, up to different potentials. Upon anodizing, barrier-type oxide films were formed on the alloys surface, showing interference colours depending on their thickness. The kinetics of film growth was influenced by Mo content in the alloy; formation efficiency was lower in acidic solution than in neutral ones, likely due to Mo partial dissolution.

Passive films were investigated by photoelectrochemical and impedance experiments. It was found that behaviour of the films changed with their thickness and with Mo content in the metallic alloy. For low Mo contents in the alloy films show always semiconducting behaviour, irrespective of thickness, in agreement with the behaviour of Ti oxide films. For higher Mo contents behaviour changes from semiconducting to insulating with increasing thickness. Moreover, EIS experiments show that, at corresponding thickness, films become more resistive with increasing Mo content in the alloys. XPS analysis confirms the presence of Mo into passive films.

Results can be interpreted assuming the formation of mixed Ti-Mo oxide films, where MoO$_3$ groups partially compensate oxygen deficiencies of TiO$_2$.

References

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The electrochemical-oxidation process promises versatility, environmental compatibility, and potential cost-effectiveness for the degradation of different organic pollutants. Accordingly, this method has been considered to be of practical interest, particularly for wastewaters containing biorefractory organic pollutants or microtoxic substances, which are not amenable for conventional biological abatement.

The evaluation of the treatment costs is, at moment, one of the aspect which needs more attention for the fully introduction of electrochemical reactors as an attractive alternative for advanced oxidation process. The overall costs are represented by the sum of the capital costs, the operating costs and the maintenance. For a full-scale system these costs strongly depend on the nature and the concentration of the pollutants, the flow rate of the effluent and the configuration of the reactor (at fixed electrodes performance). Galvanostatic conditions are preferred for simplicity of the power supply as well as for process post calculation. Conversely, optimization on the applied current density seems to be the most relevant tool for enhanced the economy of the process.

For constant controlled current, and in the case of direct electrooxidation, first order reaction are consider and, for a batch purification operation, the efficiency will tend to substantially decrease as the impurity is removed.

Efficiency could be improved if the currents are not kept constant but instead programmed to decrease as impurity removal progresses, keeping the imposed current just near or a little above the mass transfer limiting current value, minimizing the amount of current used to electrolyze water to oxygen. A validated model of abatement, considering the performance of the reactor at fixed current density, should be enough to program a modulation on the applied current density, but it implies a loss in the characteristic easiness of the electrochemical cell operation. In alternative, a modular system can be adopted, where the applied current density (constant) for step, can be changed considering the inlet organic pollutant concentration. For each of these steps, is possible to derive an optimal constant current density by using an optimization procedure based on the classical definition of total cost of electrolyzers, the Ibl’s formula [1]. This calculation was completed with one experimental value (giving a semi-empirical equations), obtained from a series of runs for a specific target compound (dyes, drugs, phenolic compounds) determining the kinetics of abatement versus the applied current, maintaining invariable all the others operative parameters.

In the operation of the electrochemical reactor, and in accordance with other studies [2], increasing the applied current density above the limiting value (diminishing on the current efficiency) an increase on the specific energy consumption is expected. However, the reduction on the electrolysis time to reach a selected conversion compensate, in term of energetic consumption (cell potential * current * time) and cost, this loss in current efficiency. Consequently, for the cases studied, the estimated optimal current densities were largely superior to the limiting current values.

The expression obtained could be useful for quantitative estimations of optimum current density to carry out the process for real systems carrying direct electrooxidation process.

Model Validation of Ni-MH Batteries Under Constant Discharge Current

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A simple model of a Ni-MH battery with constant oxygen pressure is derived and validated by using constant current discharge.

The model considers the kinetics of the reactions taking place at the electrodes and the mass transport of H atoms in the MH particles and Ni active material. It can be stated from the following reactions:

1) \[ \text{NiOOH} + \text{H}_2\text{O} + e^- \rightleftharpoons \text{Ni(OH)}_2 + \text{OH}^- \]

2) \[ \text{MH}_{x} + x\text{OH}^- \rightleftharpoons x\text{H}_2\text{O} + \text{M} + e^- \]

The charge and discharge processes can be described by the cascade of two subsystems. The first is a dynamical stage given by the diffusion transport of hydrogen in the MH particles and Ni active material. By using space discretization, this stage is mathematically described as a set of differential equations. From this step the hydrogen concentration profile in both electrodes is obtained. The second stage considers the equations required to describe the kinetics of the electrochemical processes:

\[
I_{\text{cell}}(t) = a_Ni \left( \frac{z_Ni}{z_Ni(t)} e^{\frac{F}{RT} \eta_Ni(t)} - (1 - \frac{z_Ni}{z_Ni(t)}) e^{\frac{-F}{RT} \eta_Ni(t)} \right)
\]

\[
I_{\text{cell}}(t) = \frac{a_{\text{MH}}}{x_{\text{MH}}(t) + K_{eq}[1 - x_{\text{MH}}(t)]} \left( \frac{z_{\text{MH}}}{z_{\text{MH}}(t)} e^{\frac{F}{RT} \eta_{\text{MH}}(t)} - (1 - \frac{z_{\text{MH}}}{z_{\text{MH}}(t)}) e^{\frac{-F}{RT} \eta_{\text{MH}}(t)} \right)
\]

\[
E_{\text{cell}}(t) = \eta_{\text{MH}}(t) + E_{\text{MH},\text{ref}} - \eta_{\text{Ni}}(t) - E_{\text{Ni},\text{ref}} - I_{\text{cell}}R_i
\]

where \(x_{\text{Ni}}\) and \(x_{\text{MH}}\) are hydrogen concentrations, \(I_{\text{cell}}\) and \(E_{\text{cell}}\) are cell current and potential, \(\eta_{\text{Ni}}\) and \(\eta_{\text{MH}}\) are over-potentials. The remaining parameters are constants.

**Identification and validation:** A constant current discharge, potential/time curve was used together with a set inversion procedure. In the figures the potentials and currents obtained are shown.

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The high power density, very good cyclability and high specific energy of the nickel hydroxide electrode, make it very competitive for an extended range of applications such as electrode material for Nickel /Hydrogen and Nickel /metal hydride batteries. The electrochemical energy storage in the nickel hydroxide electrodes is related to the reversible characteristics of the redox couple nickel hydroxide/oxihydroxide. The active material in the electrode undergoes an intercalation process where hydrogen atoms are inserted during the discharge process and de-inserted during charge. The complex nature of the whole process has been the subject of many research works, however there are still many questions not well understood, such as the changes in conductivity, mass transport properties and porosity, during charge/discharge operation.

In this study two types of nickel hydroxide working electrodes, were prepared by electrodeposition on sintered and foam nickel substrates. Nickel hydroxide was electrodeposited using 1,8 M Ni(NO$_3$)$_2+ x$ M X(NO$_3$)$_y$ aqueous solution, X being Na and Co. Experiments were carried out in 7 M KOH, using electrochemical charge-discharge cycling and electrochemical impedance spectroscopy (EIS). The results obtained by EIS for different states of discharge (SOD) of the electrode are analysed in terms of a physicochemical model based on the classical theory of flooded porous electrodes in concentrated binary electrolytes\[1,2\], taking into account the electrochemical reaction at the active material/electrolyte interface, the diffusion of hydrogen atoms in the active layer and the transport processes in the electrolyte. The parameter identification procedure, allows the estimation of structural parameters such as, active area per unit volume, porosity and thickness of the active layer as a function of SOD. These changes are discussed considering the volume expansion taking place during discharge.

References

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Symposium: “Electrode Materials and Processes for a Cleaner Planet”
Advances in the electrocatalysts systems for the hydrocarbons oxidation

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The hydrocarbons (HCs) are typical air pollutants causing photochemical smog or greenhouse effect. With the aim of producing new electrocatalysts for the butane oxidation reaction, and possibly other electrochemical oxidation processes, we have investigated the preparation and characterization of novel systems electrocatalysts for the oxidation of butane to produce less contaminant.

Due to the feasibility to control the size and distribution of particles, the underpotential deposition was used. This method is very effective for the preparation of Mo-Ni Zr-Ni, Mo-Sn and Mo-Ni-Sn systems supported on the glass carbon (GC) at room temperature.

The study of the codeposition process and the catalytic evaluation of different systems was performed in a thermostated three-electrode cell (T=22ºC), using a microcomputer-controlled potentiostat/galvanostat Autolab with PGSTAT30 equipment and GPES software. Codeposits were prepared on glass carbon – based substrates (surface area 1 cm²). The reference electrode was an Ag/AgCl /1 mol dm⁻³ KCl electrode mounted in a Luggin capillary. The counterelectrode was a graphite rod. All solutions were prepared using reagent-grade chemicals [(NH₄)₂ Mo O₄, 99.5 %, BDH), (NiSO₄.6H₂O, 99%, Sigma), ( SnCl₂.2H₂O, 99%, BDH), (ZrOCl₂.8H₂O, 99%, Merck) (H₃PO₄ , p.a. Merck ) and ultrapure water (18.0 MΩ cm⁻¹) Milli-Q system. The n-butane (Matheson C.P., 99.99%) oxidative reaction was carried out with saturation in aqueous 0.5 M phosphoric acid solution, at 22°C. The n-butane is inert on GC under the experimental conditions of this work.

Electrolytic phase formation of different systems on glassy carbon electrode was investigated using cyclic voltammetry and potential step techniques. Analysis of the current-time transients obtained for each alloys, indicated that distinct mechanisms of nucleation are involved during the early stages of codeposits (1). Detailed analysis of these mechanisms will be presented. Evaluation of electrocatalytic activity for butane oxidation in 0.5 M H₃PO₄ solution showed interesting performance for Mo (29,9 %)-Ni (2,7%)-Sn(67,4%) / GC and Ni (28,97%)-Zr (71,03%)/GC. The calculated exchange current density (i₀) were 1.2 x 10⁻¹² and 5.13 x 10⁻⁹ A.cm⁻², respectively. This fact is highly significant and promising for other HCs.

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Reference
An Experimental Study of the Morphological Characteristics of Copper Electrodeposits in Three-Dimensional Electrodes

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The adoption of the bed thickness in three-dimensional electrodes is an aspect of great importance. Actually, the bed thickness is adopted considering that all points work under limiting current condition in order to achieve a maximum in the space time yield of the electrochemical reactor. However, the three-dimensional electrode presents a potential distribution even though the current density is uniform - limiting value - along the bed thickness. The potential distribution makes the deposited metal show different morphologies, which affects the local value of the specific surface area and consequently the macrokinetic current density. The aim of this contribution was to determine the change of the morphological characteristics of electrodeposits as a function of the position in the electrode.

The experiments were performed in a cylindrical three-dimensional electrode, made of woven-wire stainless steel, with a flow-by configuration. Two arrangements with respect to the electrode position were used. The first one was a cylindrical concentric configuration with inner position of the counter electrode and the second design used the counter electrode in outer position. In both situations a plastic separator was placed between them. The reactor was mounted in a flow circuit system consisting of a reservoir, a pump, a flow meter and connections to maintain the temperature at the preset value, 30°C. The electrolyte solution was 1 M Na$_2$SO$_4$ and H$_2$SO$_4$ to obtain pH 2, with a copper concentration of approximately 300 mg dm$^{-3}$. The copper deposition and copper dissolution were the cathodic and anodic reactions respectively. The experiments were performed potentiostatically, the potential was controlled at the side of the working electrode nearest the counterelectrode and the working electrode potential of the region farthest from the counterelectrode was also measured. After the experiments, an epoxy resin was added to the three-dimensional cathode. Cross sections of the cathode were polished and examined with a metallurgical microscope in order to determine the morphology of the electrodeposits and the thickness distribution of the deposit along the electrode thickness, and photographs were taken for the characterization. It was observed that the deposits obtained in the zones near the counterelectrode show dendritic characteristics, those electrodeposited in the central part of the three-dimensional electrode are nodular and a more compact nature is detected in the deposited copper in the region far from the counterelectrode, where lower values of overpotential are achieved. Likewise, the thickness of the deposits are similar in all the perimeter of a wire and only a small thickness was observed in the intersection of two wires, as one of them has a shielding effect on the other.
The occurrence of estrogen hormones in natural systems like surface water, soil and sediment has become a subject of significant concern. There are many sources of estrogenic pollution which include effluent from municipal and industrial wastewater treatment plants, livestock wastes, biosolids, septic tanks and landfills. The complete removal of estrogens does not occur in municipal wastewater treatment plants, and which then end up in the natural system [1]. The great oxidation ability of the electro-Fenton process is due to the large production of hydroxyl radicals (•OH) in the medium from electrochemically assisted Fenton’s reaction which takes place between electrogenerated H₂O₂ and Fe²⁺ formed by cathodic reduction of O₂ and Fe³⁺, respectively [2]. These radicals are able to oxidize many organics until their mineralization. The degradation of hormones, β-estradiol and tibolone, has been investigated by electro-Fenton process using a titanium anode and dimensionally stable electrode containing tin and iridium oxide (Ti/Sn₀.₉₉Ir₀.₀₁O₂) as cathode. The influences of operating parameters including electrolyte Na₂SO₄ concentration, cathodic potential, pH, Fe²⁺ concentration and initial methyl red concentration were investigated. The results obtained have shown that the potential applied was the main influential parameters on the degradation rate. At the conditions of cathodic potential of −1.0 V versus Ag/AgCl, pH 3, Fe²⁺ concentration of 0.1 M, β-estradiol and tibolone initial concentration of 5 mg/L could be removed 60 % and 65 % in 60 min for β-estradiol and tibolone, respectively. Due to the formation of hard-to-treat intermediates during treatment, the removal of both hormones were found degraded at two different stages, and the second stage was much slower than the first one. Under the obtained conditions, kinetic analysis for both hormones degradation showed a pseudo-first order reaction. The by-products of the hormones degradation were analyzed by liquid chromatography/UV-vis spectrometry (LC/UV) and gas chromatography/mass spectrometry–mass spectrometry (GC/MS–MS). The results show the efficiency of the electro-Fenton process to remove the hormone from aqueous medium.

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Charge-Discharge Simulation of Lithium Ion Batteries in a Cogeneration Load-Leveling Context

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The advent of Time-of-Use electricity prices for residential dwellings may provide an opportunity for lithium ion batteries at about a 1 kW power level, to become a common component of household electrical power equipment in a cogeneration context. A battery is a power storage device which can deliver DC electricity in response to an imposed current draw. Under load, current is generated by the migration of lithium ions from a higher chemical potential state in the anode, across a separator zone, to the cathode. The battery microstructure consists of discrete dispersed solid phases in both the anode and cathode regions where lithium is stored, and a continuous electrolyte phase through the entire cell through which lithium ions diffuse.

To simulate the transient discharge behaviour of a battery, an interphase lithium ion flux can be calculated based on the initial charge state, which in turn drives the lithium ion diffusion, regulated by electric potential fields distributed spatially in the solid and electrolyte phases. A full field solution requires output from four highly coupled partial differential equations, driven by the interphase lithium ion flux. The lithium ion concentration and the electrical potential in the electrolyte phase are solved over the entire battery, the solid phase potentials must be solved in different anode and cathode sub-domains, and the solid phase lithium ion concentration is solved on individual pseudo-domains, representing the interior of spherical particles distributed spatially in the anode and cathode regions of the battery.

In cogeneration, a device such as a Stirling engine is envisioned as running on natural gas to generate electricity, and at the same time thermal losses would be sufficient for home heating. The electricity produced in this way could be used to offset peak price period power demand, along with power stored over the course of a day in a lithium ion battery. Off-peak times would be used for charging the lithium ion battery.

The project will investigate household power requirements, cogeneration outputs, and how these fit with lithium ion battery technology. The simulation can output charging or discharging behaviour based on fundamental battery electrochemistry. The analysis of a cogeneration system containing a battery can serve to demonstrate economic advantages of this type of power storage, as well as to identify size, material and performance criteria suitable for designing a lithium ion battery unit meeting the real demands of a cogeneration power storage and output application.
The aim of our work was to study the decolorization and mineralization of the dyes Reactive Black 5 and Basic Yellow 28 in aqueous solutions using Ni-PVC and Co-PVC as electrodes and TiO$_2$ as catalyst. The combination of the electrochemical-photocatalytic treatment, the influence of potential, pH and time on the electrochemical and photocatalytic degradation rate was studied using HPLC, UV-VIS, IR spectroscopy, COD and TOC measurements. The electrochemical study showed that during the bulk electrolysis (at potentials greater than -2 V vs SCE) the RB5 and BY28 dye solutions were decolorized as a result of the reductive cleavage of the N=N and C=N bonds respectively. Also the decolorization and mineralization of these two dyes occurred by photocatalytic treatment using TiO$_2$ as catalyst and during the combination treatment: Electrochemical-photocatalytic. The by-products formed during the bulk electrolysis [1, 2] were photocatalytically degraded in TiO$_2$ suspension (Fig. 1). The optimum pH for the photocatalytic treatment was 5.0 and $\lambda_{UV} = 366$ nm. The mineralization was partial (COD = 21 mg L$^{-1}$ and TOC = 6 mg L$^{-1}$) when 15 ppm of BY28 dye solution was electrochemically treated on the Co-PVC electrode at –2.0 V vs Ag/AgCl (3M KCl) during 120 min in phosphate buffer pH 5.0. The photocatalytic treatment of the 15 ppm BY28 dye solution during 240 min at pH 5.0 yielded a COD and TOC percent removal of 78 and 75, respectively. After 480 min photocatalysis the removal efficiency of COD and TOC was respectively 64 % and 96 %. Studies by HPLC, UV-Vis and IR spectroscopy revealed that the extent of photocatalytic degradation products depended on the time, pH, dye concentration and mass of the catalyst.

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References
Silver-zinc electrodeposition from a non-cyanide solution

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Abstract: The few works dealing with silver-zinc electrodeposition are in cyanide solutions [1-3], which lead to environment problems. Hence, the aim of this study was to investigate the silver-zinc electrodeposition from a thiourea solution by voltammetry and to characterize the deposit by scanning electronic microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD). The voltammetric study indicated that silver and zinc deposition on platinum, from 2.5 x 10⁻² M AgNO₃ + 5.0 x 10⁻³ M Thiourea and 1.0 x 10⁻¹ M Zn(NO₃)₂ + 5.0 x 10⁻³ M Thiourea solutions, occurred at potentials (E referred to Hg/HgCl₂, 1.0 M KCl) more negative than -0.425 V and -1.350 V, respectively. In relation to solutions containing 1.0 x 10⁻¹ M Zn(NO₃)₂ + 5.0 x 10⁻³ M Thiourea and various AgNO₃ (1.0 x 10⁻³ M, 5.0 x 10⁻³ M, 1.0 x 10⁻² M and 2.5 x 10⁻² M), the voltammetric studies indicated that silver and zinc deposition potential (E_d) shifted to more positive values, i.e., from -0.560 V to -0.425 V and from -1.350 V to -0.950 V, respectively. The shift of silver E_d was a result of polarization by concentration, while the shift of zinc E_d was due to zinc deposition on silver. In addition, voltammetric curves with various cathodic-reversed potential between -0.410 V to 0.470 V showed loops, indicating that silver deposition occurred by nucleation. SEM analyses of silver-zinc deposits obtained by step potential from 0.000 V to various values of final potentials (-0.900 V, -1.200 V and -1.500 V), with various charge density values (q_d = 2.0 C cm⁻², 5.0 C cm⁻² and 10.0 C cm⁻²) indicated that increasing q_d or depositing at E more negatives led to dendritic deposits or clusters of nodular crystallites. EDX analysis of the silver-zinc deposit obtained at -0.900 V with various q_d indicated co-deposition of these metals (silver percent greater than 80% wt). Moreover, the silver-zinc deposits obtained at -1.200 V and -1.500 V with various q_d showed silver percentage between 30% to 55% wt. SEM and EDX analyses of silver-zinc deposits obtained at -1.200 V, from solutions containing 1.0 x 10⁻¹ M Zn(NO₃)₂ + 5.0 x 10⁻³ M Thiourea and various AgNO₃ (1.0 x 10⁻³ M, 5.0 x 10⁻³ M, 1.0 x 10⁻² M and 2.5 x 10⁻² M), showed that the morphology and composition of deposit depends on the solution composition. The silver-zinc deposit obtained at -1.200 V from solution containing 5.0 x 10⁻³ M AgNO₃ showed the highest zinc content (Zn 72.8 wt + Ag 16.4% wt + S 10.8% wt). EDX analyses indicated sulfur incorporation in all deposits. XRD analysis of silver-zinc deposit indicated that it was amorphous, independently of its composition and morphology.

Acknowledgements: The financial support from Brazilian agencies FAPESP is gratefully acknowledged.

Reference:
Investigation of Pt-M/C tolerance in presence of Ethanol acid solution for the Oxygen Reduction Reaction

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2-CNR-ITAE, Via Salita S. Lucia sopra Contesse 5 – 98126 Messina, Italy

The influence of ethanol crossover on the oxygen reduction reaction has been investigated on carbon supported Pt/C and PtFe/C catalysts, in the presence of different ethanol concentrations at various temperatures. The catalysts have been prepared using colloidal and incipient wetness methods. These materials were studied in terms of structure, morphology and composition using XRD, XRF and TEM techniques. The electrocatalytic behavior for ORR of the carbon supported PtFe was investigated using the rotating disk technique and compared to that of a pure Pt catalyst with similar particle size. A significant improvement in performance has been observed with the Pt-Fe/C compared to Pt/C catalyst. PtFe/C shows similar performance in absence and in presence of a low alcohol concentration, 0.005M. (Fig 1). This means a better ethanol tolerance with respect to the Pt/C catalyst. The latter shows a significant decrease of performance in the presence of ethanol. The results have been interpreted in terms of electronic properties of the bimetallic catalysts.
Electrochemical Deposition Technology of Organic Coating to Protect the Environment

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The deposition technique of the organic films on the metallic substrates represents a decisive factor for their protective performances and consequently for the diminution of the environmental pollution with corrosion products. This paper presents results concerning the electrochemical monitoring of performance of the electrodeposited epoxy films in comparison with the films deposited by immersion and brushing.

The paint films were formed during the anodic and cathodic electrodeposition of the modified epoxy resin on carbon steel substrate.

<table>
<thead>
<tr>
<th>Epoxy resin</th>
<th>Deposition technique</th>
<th>Film curing</th>
<th>Dry film thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>cationic modified with secondary amine</td>
<td>cataphoresis</td>
<td>30 min. at 180°C</td>
<td>18-20 μm</td>
</tr>
<tr>
<td>anionic modified with carboxylate group</td>
<td>anaphoresis</td>
<td>30 min. at 180°C</td>
<td>18-20 μm</td>
</tr>
</tbody>
</table>

The electrochemical experiments (electrochemical impedance spectroscopy and stepwise polarization) were conducted in stagnant naturally aerated 3% NaCl solution under ambient conditions, for a period of up to 5000 immersion hours.

Modeling (two time electric equivalent circuit) and time monitoring of metal/organic film interface has permitted to determine: the presence of double layer under coating, the active area of the metal surface, the corrosion rate, water uptake and area of the conductive pathways in coating and consequently the protective properties of the coatings.

Water saturation value (≈2.5%) in films emphasizes a low water permeability of the electrodeposited coatings and area of conductive pathways (≈0.007% from film area) show a reduced ionic transport through coating.

Electrochemical reactions at metal/electrodeposited film interface were much slowed down (≈ 40 times) in comparison to those at the metal/immersion or brushing deposited films interfaces; paint film efficiency does not decrease in time (90%).

It resulted a good performance of the electrodeposited coatings in comparison with the coatings deposited by immersion and brushing. So, the life duration of the organic film in service increase very much reducing the corrosion and implicitly the negative impact on the environment. Also, the maintenance works are necessary after longer periods and consequently a decrease of the materials and energy consumption.
Towards the Mechanism of Electrochemical Hydrogen Storage in Nanostructured Carbon Materials

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Carbon nanotubes (CNTs) combine unique chemical and physical properties which have attracted the interest of numerous researchers for applications such as supercapacitors, chemical sensors and energy storage devices. One of the most exciting application fields for CNTs is hydrogen storage. The storage of hydrogen in a light element like carbon could lead to the formation of power supplies for mobile applications with higher energy densities. Dillon et al. reported for the first time excellent hydrogen storage properties of single walled carbon nanotubes (SWNTs). Thereafter, many research groups started to carry out hydrogen storage experiments. Most of the studies on hydrogen storage in CNTs were conducted by temperature-programmable desorption measurements and electrochemical methods. From the literature results it is quite difficult to reach a common conclusion for maximum adsorption capacity. The variation of hydrogen storage capacity may arise due to the differences of CNTs used (SWNT or multi walled carbon nanotubes), purity, chirality of tubes, tube diameter, bundle appearance and possible presence of metals used as catalysts in the synthesis procedure. Besides the debate of hydrogen storage capacity, there are other important tasks to be achieved such as the understanding of the mechanism for hydrogen storage. Thus, the aim of this work is to study the electrochemical absorption and desorption of hydrogen in SWNTs and to elucidate the reaction mechanism. The hydrogen sorption ability has been evaluated electrochemically in a three-electrode cell in an aqueous 6M KOH medium, where activated and purified SWNT is used as the working electrode, nickel mesh as the counter electrode and Hg/HgO/6M KOH as the reference electrode (+0.098 V vs. NHE). In order to evaluate the efficiency of SWNT toward hydrogen storage, several electrodes containing different ratios SWNT : carbon Vulcan® are employed. From the electrochemical results obtained through cyclic voltammetry, galvanostatic charge-discharge and impedance spectroscopy one can infer that the hydrogen storage capability increases with the quantity of SWNT within the electrode. Impedance measurements corroborate the porous nature of the electrode allowing also an estimation of their interfacial area. Consequently, the higher hydrogen current density measured for those electrodes containing SWNT can be ascribed not only to the interfacial areas calculated but also to a strong catalytic effect on the hydrogen evolution reaction.

Acknowledgments. This work was supported by Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Facultad de Ciencias Exactas, UNLP, and the Agencia Nacional de Promoción Científica y Tecnológica.
Electrokinetic extraction of surfactants and heavy metals from a municipal wastewater sludge

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via L. Borsari 46 – 44100 Ferrara (Italy)
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The disposal of sewage sludge from domestic wastewater treatment plants is a growing problem worldwide. The European Community has developed the draft of “Working document on sludge” to promote the (re)use of sewage sludge. In Italy, sewage sludge could be disposed on agricultural lands but, in last years, this use has been limited by Italian legislation to avoid the contamination by and the accumulation of both heavy metals and organic compounds in the soils. Analogous regulations have decreased the maximum attainable limit for these pollutants. In order to increase the recycling of sludge on agricultural lands, thus avoiding their accumulation, we need a powerful treatment as electroremediation. The present work reports on a laboratory investigation on the use of an electrokinetic method for the removal of anionic surfactants like linear alkylbenzenesulphonate (LAS) and heavy metals from wastewater sludge.

![Removal efficiencies](image-url)

<table>
<thead>
<tr>
<th>[M] (mg/Kg)</th>
<th>Test A</th>
<th>Test B</th>
<th>Test B'</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>19</td>
<td>-21%</td>
<td>-64.9%</td>
</tr>
<tr>
<td>Cd</td>
<td>4.03</td>
<td>-3%</td>
<td>-10.2%</td>
</tr>
<tr>
<td>Co</td>
<td>12</td>
<td>-8%</td>
<td>-71.9%</td>
</tr>
<tr>
<td>total Cr</td>
<td>88</td>
<td>-19%</td>
<td>-36.3%</td>
</tr>
<tr>
<td>Cu</td>
<td>563</td>
<td>-18%</td>
<td>-40.4%</td>
</tr>
<tr>
<td>Ni</td>
<td>61</td>
<td>-25%</td>
<td>-56.7%</td>
</tr>
<tr>
<td>total Cr</td>
<td>88</td>
<td>-19%</td>
<td>-36.3%</td>
</tr>
<tr>
<td>Cu</td>
<td>563</td>
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<td>Cu</td>
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<td>Ni</td>
<td>61</td>
<td>-25%</td>
<td>-56.7%</td>
</tr>
<tr>
<td>total Cr</td>
<td>88</td>
<td>-19%</td>
<td>-36.3%</td>
</tr>
</tbody>
</table>

Removal efficiencies (%)

As: 19 -21% -64.9% -47.6%
Cd: 4.03 -3% -10.2% 16.7%
Co: 12 -8% -71.9% -78.4%
total Cr: 88 -19% -36.3% -30.2%
Cu: 563 -18% -40.4% -21.1%
Ni: 61 -25% -56.7% -54.1%
total Cr: 88 -19% -36.3% -30.2%

All heavy metal contents could be reduced, and removal efficiencies increased by prolonging the application time and raising the current density. Concerning LAS, removal efficiencies between 18% and 43% were obtained; no important improvements could be obtained by prolonging the application time to more than 16 hour.
Chloramphenicol oxidation via electro-fenton reagent on a flow reactor using modified gas diffusion electrodes

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\textsuperscript{2}Universidade São Francisco, CEP: 12916-900, Bragança Paulista, SP, Brazil
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Chloramphenicol (CAP) was the first antibiotic to be synthetically manufactured on a large scale basis; it is effective on a wide variety of microorganisms and it is still in use in many countries. This paper reports the experiments of CAP oxidation on a filter-press type reactor connected to a recirculating flow system. The antibiotic was dissolved in 1.3 L of a 0.1 mol L\textsuperscript{-1} H\textsubscript{2}SO\textsubscript{4} plus 0.1 mol L\textsuperscript{-1} K\textsubscript{2}SO\textsubscript{4} solution. Gas diffusion electrodes, either a non-modified (GDE) or modified with 10% of 2-ethylanthraquinone (MGDE) were used as cathodes [1]. A commercial DSA\textsuperscript{*} type plate was used as anode and a Pt/AuAg/AgCl system as pseudo-reference electrode. The hydrogen peroxide concentration was determined with a UV-Vis spectrophotometer [1]. The H\textsubscript{2}O\textsubscript{2} electrogeneration process (oxygen pressure of 0.16 bar was kept through the reverse side of the electrode) was studied as a function of the applied potential and the results showed that the modification of the gas diffusion electrode led to a significant increasing in H\textsubscript{2}O\textsubscript{2} yield reaching 1126 mg L\textsuperscript{-1}. The overpotential for oxygen reduction was shifted by 500 mV less negative compared to the values obtained with a non-modified electrode. As a result, a decreasing in the energy consumption was observed. Experiments for CAP (50 mg L\textsuperscript{-1}) oxidation were performed using the controlled potential technique by applying an optimized potential value for H\textsubscript{2}O\textsubscript{2} production, i.e., -2.5 V for GDE and -2.0 V vs Pt//Ag/AgCl for MGDE. The following experiments were carried out: electrochemical oxidation on the DSA anodes (without H\textsubscript{2}O\textsubscript{2} generation), with electro-generation of H\textsubscript{2}O\textsubscript{2} and with electrogeneration of Fenton’s reagent (with 10 mM of FeSO\textsubscript{4} in solution). After each electrolysis, solutions were analyzed by HPLC and the total organic carbon concentration (TOC) was also determined. An UV/Visible detector (280 and 254 nm), a C\textsubscript{18} column (250x4.6 mm) and a mobile phase with methanol, water and acetic acid (45:55:0.1) was used for HPLC analyses with flow rate of 1.0 mL min\textsuperscript{-1}. The results are shown in Table 1. Both, HPLC and TOC analysis showed CAP concentration decay. However the presence of CAP intermediates is still subject of a going on investigation. Results have shown an improved performance of the MGDE by 2-ethylanthraquinone.

Table 1: HPLC and TOC analyses of chloramphenicol (CAP) degradation

<table>
<thead>
<tr>
<th></th>
<th>GDE (E = -2.5 V vs Ag/AgCl)</th>
<th>MGDE (E = -2.0 V vs Ag/AgCl)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HPLC / TOC</td>
<td>HPLC / TOC</td>
</tr>
<tr>
<td></td>
<td>After 30 min.</td>
<td>After 2 hours</td>
</tr>
<tr>
<td>Electrolysis</td>
<td>9% / 0%</td>
<td>35% / 0%</td>
</tr>
<tr>
<td>H\textsubscript{2}O\textsubscript{2} oxidation</td>
<td>12% / 0%</td>
<td>44% / 4%</td>
</tr>
<tr>
<td>H\textsubscript{2}O\textsubscript{2}/Fenton</td>
<td>65% / 4%</td>
<td>100% / 11%</td>
</tr>
</tbody>
</table>

Acknowledgements: FAPESP (Brazil)
A variety of ceramic anodes was prepared based on (La,Sr)CoO$_3$ perovskites and La$_2$NiO$_4$-based materials. The kinetics of electrochemical oxygen evolution resembles the behaviour of Ni-based anodes with hydroxide surface scales, thus suggesting similar mechanisms. In addition, one found that the overpotential of (La,Sr)CoO$_3$-based anodes decreases with time under prolonged galvanostatic tests. Cyclic voltammetry is also consistent with the formation of Co(OH)$_2$ or CoOOH, as for metallic electrodes with surface modifications by electrochemically deposited hydroxide or oxy-hydroxide scales. Model Pt electrodes with mixed Co(OH)$_2$+La(OH)$_3$ scales were used to confirm the close relation between ceramic anodes and the corresponding metallic electrodes with hydroxide modifications. In contrast to cobaltites, the behavior of La$_2$NiO$_4$-based anodes seems to significantly differ from that of Ni oxy/hydroxide due to large amount of lanthanum hydroxide. It was also shown that ceramic anodes with La-deficiency perform better than for ceramics with unit stoichiometric ratio (La+Sr):Co=1:1. The best performance was found for cases when off-stoichiometry or prolonged electrochemical treatment yield formation of Co-rich precipitates.
Nanostructured magnetic thin films are materials found in many applications such as in memory devices, high density magnetic storage media and in magnetic sensors. Particularly these materials have a fundamental role in the development of better methods in biosciences such as in recognition, handling and controlling bio-molecules and cells. CoNi and CoNiP magnetic thin films have received much attention because of their magnetic properties. Electrodeposition is a suitable method to obtain films with desired properties because on controlling deposition parameters and bath composition one can easily achieve a material with a certain microstructure and morphology and hence, magnetic properties. Analysis of the first stages of the electrodeposition process is particularly critical as they determine the properties and dimensions of the resulting film. This paper discusses the kinetics of the first stages of the electrocrystallization of Co and Ni thin films. Experimental current-time transients were analyzed using the existing models reported in literature and the best model that adjusted to our data is an instantaneous/progressive, three-dimensional nucleation and mixed charge transfer/diffusion controlled growth model. The results show that the electrocrystallization kinetics of Co in a bath containing citrate, in equimolar ratio or with an excess of the additive, follows an instantaneous, three-dimensional nucleation model, which is not influenced by the applied potential or by the pH (from pH 4.0 to 8.0). Using a bath containing glycine, [Co^{2+}]/[Gly] = 1, the electrodeposition of Co^{2+} follows the progressive, three-dimensional nucleation model for all pH’s at low potentials. However, if the applied cathodic potential is higher than -1.2 V, the mechanism changes to instantaneous nucleation. When there was an excess of glycine the nucleation mechanisms varied according to the applied potential and pH. As for Ni electrocrystallization, only partial conclusions could be made. I/E Potentiodynamic experiments showed that the electrodeposition is influenced by the pH, for both additives. Moreover, at pH = 7.0, the deposition contributes to the formation of two distinct metallic phases. The best models to describe the mechanism of Ni deposition [1] were used and although the fittings were quite good in some conditions, the resulted parameters had no physical meaning. These models treat the current-time transients in three different sections and also take into account the hydrogen evolution, the cessation of growth and renucleation of growth centers (“death and rebirth” processes [1]) It is observed that for both Co and Ni the use of glycine containing baths results in attaining better current efficiencies, considering all the pHs tested and a wide range of applied potentials.

FAPESP, CNPq
As already mentioned in Part 1 of this study magnetic nanoparticles are key elements for new developments in the field of magnetic sensors. For example, the possible use of these materials for the detection of pathogenic organisms has been studied. Besides, the use of magnetic nanoparticles as contrast agents can improve detection of certain diseases in their early stages. CoNi and CoNiP are hard magnetic materials that present high coercivity and therefore, the studies leading to the synthesis of nanoparticles of such materials with desired magnetic properties, by electrodeposition, are very interesting from the applied viewpoint. As it is known, analysis of the first stages of a electrodeposition process is particularly critical as they determine the properties and dimensions of the resulting film. In this second part of this study we discuss results on the study of the electrocrystallization of CoNi thin films onto glassy electrode from a glycine containing bath. Cyclic voltammetry and potentiostatic steps were used to investigate the nucleation and growth processes. The I/E potentiodynamic profiles for pure Ni(II) and Co(II) and for the solution containing both metals revealed a nucleation crossover indicating the existence of nucleation in the early stages of these electrodepositions processes. During the potentiodynamic deposition of the alloy only one reduction peak was observed, whilst one or more oxidation peaks were observed depending on the adopted cathodic limit potential. Two nucleation peaks can be observed on the current transients when the applied potential was lower than -1.05 V. Each peak is associated with the formation of two distinct metallic phases and were analyzed independently. In the case of the phase associated with the first peak, the electrodeposition kinetics of a CoNi film follows a progressive, three-dimensional nucleation model. As for the second metallic phase, in most cases, this model was also valid. However, if the applied cathodic potential is higher than -1.30 V, there is a coupling of progressive and instantaneous nucleation and only one peak is observed. The $j_{\text{max}}^2b_{\text{max}}$ product and the diffusion coefficient are constant for a given nucleation mechanism, as predicted. This is another diagnostic criterion for the choice of the appropriate mathematical model, along with the non-linear fits of the “nucleation-growth” transients [1]. The kinetic parameters $N$ e $AN_0$, namely the number of nuclei density (in case of instantaneous nucleation) and the rate of nucleation (progressive nucleation), increase exponentially with the increase of the applied cathodic potential, for all the systems tested.


FAPESP, CNPq
Electropolymerization Of Mono, Bi, Ter and Tetra-thiophene

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In this research a comparative study of the start unit chain lengths effect on the electropolymerization of polythiophene (PTh) was carried out. Therefore, the monomer relative mass was maintained constant, ensuring the same quantity of thiophene units on the solution.

Hypothetically the oxidation potential (OP) would be lower, as the length of the start unit chain increase, because the aromatic character increases. Also, in the nucleation and growth mechanism (NGM) established from chronoamperometric results, less and more homogeneous contributions would be expected, as the start unit chain is longer.

Results of CV (Interface Pt | 0,25 g·L⁻¹ start unit + 0,1M TBAPF₆, CH₂Cl₂) evidence a decrease on the OP from 1920 to 1185mV, as the start unit chain is longer.

The deconvolved transients (figure 1) allows to state that the growth of PTh is governed by the same NGM reported for PTh obtained by electro-oxidation of the monomer, which is constituted by three contributions indicated on figure 1. However, the contribution of each to the net charge varies with the start unit chain length. Additionally a decrease on the number of contribution to the PTh NGM and a predominance of the instantaneous contribution is shown, as the length of the start unit chain increase. Further studies would consider atomic force microscopy on PTh film in order to confirm this behavior and the NGM proposed.

Acknowledgements. The authors thank Fondecyt Chile trough grant 1060598.
Environmental friendly coatings for aerospace industry applications

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The main reason for preventing the use of chromium in surface coatings is their high ambient impact in their applications. This work aims at creation and investigation of new anticorrosion environmental friendly coating system without chromium addition. The hybrid organic-inorganic sol-gel coating was prepared by TEOS (tetraethoxysilane), titanium alcoxides and additives which provide corrosion protection for magnesium alloy. The coating exhibits excellent adhesion to the substrate and prevents corrosion attack in 5 mM sodium chloride solution for 9 days of standard immersion test. The morphology and the structure of the sol-gel coatings were characterized with SEM/EDS, TEM and AFM techniques. Corrosion behaviour of substrates treated with sol-gel derived coatings was tested by Electrochemical Impedance Spectroscopy. Different composition of sol-gel systems show enhanced protection of magnesium alloy.
**Introduction.** Arsenic (As) contamination in ground water of Mexico is well known. In this research, the As was removed from wells groundwater by the electrocoagulation (EC) technique. The arsenic removal efficiency during EC process decreased notably when well groundwater was treated, this due to the interference of several ions that are present in this water. Thus, in this work we compare the arsenic removal efficiency from this well groundwater with and without addition of a compound (A) that dissolved in water withdraw those ions that interfere with the arsenic removal during the EC process.

**Experimental.** The analysis of the natural water by inductively coupled plasma (ICP) technique, showed an arsenic concentration of 146 µg L⁻¹, which is higher than the permissible As level established by the World Health Organization (WHO: 10 µg L⁻¹). In addition, this underground water exhibited high contents of others ions such as Ca (46.23 mg L⁻¹), silica (67.63 mg L⁻¹), etc. In order to decrease the interference of these ions, an adsorbent compound A in a concentration of 1 g L⁻¹ was added to the well groundwater. The current density applied during the EC process was 4.5 mA cm⁻². Energy dispersive X-ray spectroscopy (EDX) technique was used to characterize the solid precipitates formed during the EC process.

**Results and discussion.** Fig. 1 shows the change in the arsenic concentration as function of time for experiments carried out with and without A compound, WA and W respectively. In this figure, we can see that the arsenic concentration in W, decreased down to the limit level in 6 min. Whereas, this time decreased almost 50% (3.5 min) when the A compound was added (WA). The EDX analysis in Fig. 2(b) indicates that the agglomerates obtained exhibit high content of Si and Ca. On the other hand, Fig. 2(a) shows a significant reduction of Si and Ca peaks. Comparing the EDX spectrum obtained from W with respect to that obtained from WA it is clearly seen that the Si dissolved species are those that compete mainly with arsenic for the adsorption sites on FeOOH flocs surface, forming Fe-Si complexes. When the A compound is added into natural water (WA), the Si dissolved species continue competing with arsenic for adsorption sites on FeOOH surface, however the As adsorption is significantly increased because of the A compound has greater affinity by the Si species.
One of the most important aspect to be improved for the real application of PEFC in portable and stationary devices, especially when processed hydrogen is fed as a fuel, is to overcome the CO poisoning problems. Many approaches were used for this aim, in particular the development of non noble metal electrocatalysts, the increase of working temperature until $T = 150^\circ$C, the introduction of a small amounts of air mixed to the fuel at the anode side, the employment of transition metals oxides ($WO_x, MoO_x$) or heteropolyacids (like PWA, PMoA, SiWA etc.) [1], the replacing at the anode Pt catalysts by Pt-M alloys. Among these approaches the Pt-M alloys seem to be the most promising when processed hydrogen is used, in particular the Pt-Ru alloys remain the most popular CO tolerant electrocatalyst.

A further approach to enhance the electrodes CO tolerance is the introduction of a Ru catalyst layer between the diffusive and catalytic (Pt) layers at the anode side, that acts as a filter [2-3]. On the basis of this assumption, in this work anodes with different amount of Ru catalyst in the diffusive layer (GDL) were prepared.

The catalytic layer was obtained by using a 30 %wt Pt/Vulcan as an electro-catalyst (0.5 mg/cm$^2$) mixed to a Nafion solution. The diffusive layer was obtained by mixing different amounts of 20% wt/wt Ru/C with Shanwiningan Acetylene Black (SAB). A Nafion 115 was used as an electrolyte for the membrane electrode assemblies (MEAs) realisation before the electrochemical tests. All MEAs were characterised at $80^\circ$C by feeding the cell with air as oxidizer and pure H$_2$ and H$_2$-CO(100ppm) as fuel.

The Ru/C and SAB carbon ratio was found to influence the performance and potential loss when H$_2$-CO mixture was used. The electrodes with the best performance in pure H$_2$ showed the highest potential loss when operating with H$_2$-CO. On the contrary, the MEA with the poorest performance in pure H$_2$ was not affected by the used fuel.

Moreover, when a 20% Ru/C or unsupported Ru were used for preparation of diffusion layers different performance were recorded, even if the same amount of Ru was introduced. This behaviour could be attributable to the different chemical-physical properties of used catalysts, like crystallite size and the dispersion of catalysts on carbon support.

Textile dye Reactive Orange 16 degradation using DSA®
electrode

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Reactive orange 16 (RO16) is an azo dye, that presents a N=N group linked to aromatic ring [1,2]. Reactive dyes have an electrophilic group (reactive), capable of forming covalent bonds with cellulose fibers, hydroxyl and amino groups of polyamides. Reactive dyes are widely utilized because application is simple and they are stable during washing [3,4]. However, a disadvantage of this type of dye is its low fixation rate, and to improve this fixation, an electrolyte species is sometimes added (generally NaCl)[4]. The synthetic and complex aromatic molecular structure of dyes increases the stability and so biological, physical and chemical treatments can be ineffective. RO16 degradation was performed in a single-compartment filter-press cell, using a commercial Ti/Ru0.3Ti0.7O2 DSA® plate (geometric area = 2 cm²) and a stainless steel cathode of the same area. All potentials are referred to the reversible hydrogen electrode (RHE). The distance between anode and cathode was controlled with viton® and Teflon® spacers. The electrolyte flow through the cell was 1.24 L h⁻¹ and the dye solution was pumped from the electrolyte reservoir, through the cell using a peristaltic pump. In this work, the degradation of RO16 was studied in terms of potential (1.8 and 2.2 V) and NaCl concentration (0.004 to 0.017 mol L⁻¹) added to medium, being that the electrolysis was carried out in 0.5 mol L⁻¹ H₂SO₄. Fig.1 presents the UV-vis spectrum of RO16 before and after electrochemical degradation, using 0.017 mol L⁻¹ NaCl at 1.8 V. The colour removal was initiated in the first 15 min, being that in this time approximately 76.6 and 88.7% of colour was removed at 1.8 and 2.2 V, respectively. After 60 min at these potentials, removals of 97 and 98% were obtained (fig.1), however the energy consumption at 2.2 V was four times greater than at 1.8 V (fig.2).

Fig. 1 – UV-vis spectra (--) before and (--) after 60 min of electrolysis, using 0.017 mol L⁻¹ NaCl, at 1.8 V.

Fig. 2 – Electrical energy per unit mass consumed in electrolysis at 1.8 and 2.2 V, with different concentrations of NaCl.

References
Increasingly stringent legislation for effluents calls for reliable and cost-efficient processes for the purification of waste water. Electrochemical reactors with bipolar three-dimensional electrodes are promising devices to treat large solution volumes with small concentration of dangerous species. In this contribution a simplified mathematical model to represent bipolar three-dimensional electrodes, of thickness $L$, is proposed assuming that the electrochemical reaction has a mass-transfer control at low overpotentials. Thus, the overpotential distribution inside the bipolar electrode is given by

$$\eta(x) = \eta(0) \frac{\sinh \left( \Omega \left( \frac{L}{2} - x \right) \right)}{\sinh \left( \frac{\Omega L}{2} \right)}$$

where

$$\Omega = \sqrt{\rho_e A_s \frac{j_l v_e}{RT}}$$

being $\rho_e$ the effective electrolyte resistivity, $A_s$ the specific surface area, $j_l$ the limiting current density, $v_e$ the charge number of the electrode reaction and $RT/F$ the usual meaning in electrochemistry. Likewise, the by-passed fraction of the total current through the bipolar electrode is

$$\frac{I^*}{I} = 1 - \frac{\sinh \left( \frac{\Omega L}{2} \right)}{\frac{\Omega L}{2} \left[ \cosh \left( \frac{\Omega L}{2} \right) - 1 \right] + \sinh \left( \frac{\Omega L}{2} \right)}$$

Where $I^*$ corresponds to the leakage current and $I$ is the total current.

Taking into account the above equations, the effect of kinetic, electrochemical and geometric variables on the leakage current is discussed. Likewise, the combined effect of all the variables is lumped into one dimensionless number, $\Omega L$, whose influence on the performance of the electrode is analyzed.
Electrical Wiring of Living Bacterial Cells Using Flexible Osmium-Redox Polymers

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Artificial redox mediators offer the possibility for an enhanced electron transfer rate between microbial cells and electrodes. The important role of these mediators in whole cell biosensors and microbial fuel cells is to replace the natural electron acceptor e.g., oxygen in the case of aerobic bacteria, and Fe(III) oxides/complexes in the case of anaerobic organisms. Usually small monomeric redox mediators have been used, however, polymeric mediators recently proved also to exhibit efficient electron shuttling properties and enabling connection with multiple layers of microbial cells. Moreover they promote a stable binding onto the electrode surface in contrast to the monomeric ones.

Recently we could show that two different flexible osmium redox polymers; poly(1-vinylimidazole)\textsubscript{12}\{Os-(4,4'-dimethyl-2,2'-di'pyridyl)_2Cl\textsubscript{2}\}^2+/+ (osmium redox polymer I) and poly(vinylpyridine)-[Os-(N,N'-methylated-2,2'-biimidazole)]^2+/3+ (osmium redox polymer II) could wire efficiently gram negative bacteria (\textit{Gluconobacter oxydans} \cite{1} and \textit{Pseudomonas putida} and \textit{P. fluorescence} \cite{2,3}). These studies have now been extended also to cover gram positive bacteria and to include \textit{Bacillus subtilis}.

The characteristics of the electrodes modified with \textit{B. subtilis} cells were evaluated for their response to succinate, fumarate and glucose as substrates in both batch and flow modes using both gold and graphite electrodes. The influence of the presence of oxygen in the buffer on the current response was evaluated. The efficiency of the electron transfer with the osmium redox polymer was compared with that of a soluble mediator (ferricyanide).

Prediction of the Secondary Current Distribution and Leakage Current in Bipolar Electrochemical Reactors

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The use of bipolar electrochemical reactors becomes promising for industrial processes due to their simplified construction. However, the main disadvantage of these devices is the leakage current, $I^*$, which flows through the manifolds of the electrolyte inlet and outlet by-passing the electrodes.

In this contribution, the secondary current distribution in a bipolar reactor is calculated by solving of the Laplace equation with the finite difference method considering a Tafel kinetics at the electrodes, and it is compared with experimental results. The experimental current distribution was obtained with the segmented electrode method using the hydrogen and oxygen evolution from 1 M NaOH or 3 M NaOH as cathodic and anodic reactions. The bipolar stack, shown schematically in the figure on the left, consisted of two undivided reactors electrically connected in series constituting a bipolar stack with one bipolar electrode. Each electrode was made with 15 nickel segments isolated by means of an epoxy resin layer. For symmetry reasons only one half of the stack was considered and the inlet manifold was simulated by a Teflon tube interconnecting the electrolyte of both reactors. A typical current distribution at the terminal electrodes is shown in the figure on the right. The symbols 1 and × represent the experimental values with and without the electrolyte by-pass whereas the vertical segments show the standard error. $\sigma$ is the standard deviation of the experimental results. The full line corresponds to the theoretical prediction and $d_r$ is the mean relative deviation, which quantifies the predictive capability of the theoretical treatment. A good agreement is observed between experimental and theoretical results.

\[
\begin{align*}
\sigma_{\text{without by-pass}} &= 0.02129 \\
\sigma_{\text{with by-pass}} &= 0.03253 \\
R_{\text{by-pass}} &= 75.41 \, \Omega
\end{align*}
\]
Effect of solid proton conductor Hydronium-$\beta''$-$\text{Al}_2\text{O}_3$ in the electrode on the performance of PEFC

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Polymer electrolyte fuel cells (PEFC) are attracting considerable interest as alternative power sources for automobiles, stationary and portable applications. The effective three-phase interfaces in the electrodes are important for the performance of PEFC. The presence of the Nafion ionomer covering the accumulated Pt-C catalyst particles in the electrode provides H$^+$ path from catalyst site to the membrane. However, the pores in the electrode will be blocked while Nafion expansion happens in the process of PEFC operation. If a solid proton conductor is used to play part of the Nafion’s role in the electrode, the porosity will increase but the H$^+$ path will not reduce. The fine solid proton conductor particles may also be possible as the H$^+$ path from Pt site in the Pt-C accumulation, while Nafion plays the roles as the H$^+$ path from the surface Pt site of accumulated Pt-C to the membrane.

Hydronium-$\beta''$-$\text{Al}_2\text{O}_3$ ($\text{H}_3\text{O}^+$-$\beta''$-$\text{Al}_2\text{O}_3$) had ever been reported to be a relatively fast solid proton conductor. The polycrystalline Na$^+$ form (Na$^+$-$\beta''$-$\text{Al}_2\text{O}_3$) with the chemical formula of Na$_{1.67}$Mg$_{0.67}$Al$_{10.33}$O$_{17}$ was synthesized by high temperature vapor reaction. Na$^+$ form $\beta''$-$\text{Al}_2\text{O}_3$ was ion-exchanged to the $\text{H}_3\text{O}^+$-$\beta''$-$\text{Al}_2\text{O}_3$ in the condensed H$_2$SO$_4$, the ion exchange ratio was higher than 90%. XRD were taken for Na$^+$ form and H$_3$O$^+$ form $\beta''$-$\text{Al}_2\text{O}_3$, which prove that they have the similar $\beta''$ structure, and the lattice constant indicates the change of ions (Na$^+$ to H$_3$O$^+$) in the conduction plane. The main form of (H$_2$O)$_n$H$^+$ in Hydronium-$\beta''$-$\text{Al}_2\text{O}_3$ is H$_3$O$^+$, which was confirmed by FTIR. The $\beta''$ structure of H$_3$O$^+$-$\beta''$-$\text{Al}_2\text{O}_3$ is stable at 360°C at least, and the H$_3$O$^+$ in the $\beta''$ structure can be kept at least at 200°C.

The MEA with the H$_3$O$^+$-$\beta''$-$\text{Al}_2\text{O}_3$ in the electrode has been fabricated. The PEFC performance tests on the application of H$_3$O$^+$-$\beta''$-$\text{Al}_2\text{O}_3$ in the PEFC electrode are on going. The effect of adding the solid proton conductor in the electrode structure of PEFC will be reported in the meeting.
Preparation and optimization of Photoelectrochemical parameters for synthesis of silicon nanoparticles from n-type wafers

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Si nanoparticles (Si-NP) of diameter size of a few nanometers show strong photoluminescence due to quantum confinement with maximum wavelength emission strongly depending on size. The strong luminescence and photostability in aqueous suspensions of suitable surface modified nanoparticles makes them excellent candidates for use as specific luminescent markers in biological environments for in vitro and in vivo applications.

Si-NP have been prepared by different physical and chemical approaches, the route of the electrochemical etching is one of the most used for its ease to implement. It`s known that the current voltage curves in diluted HF solution for p and n-type silicon are different. However, under illumination p-type or n-type Si shown same current voltage behaviour except for a cathodic voltage shift of about 500 mV, which is due the differences in Fermi energies of the different material. This gives a new degree of freedom in electrochemical experiments: one can vary the (photo-) current and the voltage independently. As a consequence we have a broad region where we can produce porous silicon.

In this contribution we report results from the synthesis of Silicon nanoparticles using a combined route photoelectrochemical using n type silicon wafers. Crystalline, Si(100) oriented, 1-10 Ω cm. resistivity, n-type Phosphorus doped wafer were photoelectrochemically etched in a teflon cell with an electrolytic solution mixture de HF, HNO$_3$, CH$_3$OH and H$_2$O in different proportions. The silicon wafer anode is vertically immersed in the etchant and is advanced at slow speed of approximately 1 mm per hour; a wire Pt was used as cathode. For the synthesis of the Si nanoparticles a current density in the range form 0.5-20 mA/cm$^2$ was applied while illuminated with a light source of 50 watt 12 V. for 24 hours. Finally, the thus treated silicon wafer is removed, washed with methanol, and transferred to an ultrasonic toluene or methanol bath bubbled with argon for 30 minutes. Sonication crumbles the very top layer into a suspension of silicon nanoparticles. Optimum conditions for obtaining Si particles in the range 1- 10 nm were studied changing the parameters such as the current density, electrolyte composition, anodisation and ultrasonic time.

Depending on the particular experimental conditions, the Si nanoparticles show, either, a bright blue or red luminescence when irradiated with an UV lamp. The emission and excitation spectrum were measured with a Perkin Elmer LS50B spectrofluorometer. The size of the silicon nanoparticles was determined by direct imaging using transmission electron microscopy (TEM) and the nature of the surface groups determined by FTIR and Raman spectroscopy.

References:
Atrazine degradation by electrochemical and photo-assisted electrochemical methods: Toxicity assessment

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Amongst the many pesticides that have been studied with a view to developing alternative treatment systems, atrazine (ATZ) has received considerable attention. ATZ is a triazine herbicide used on a wide spectrum of crops (e.g. corn and sugarcane). Of the methods suggested by the WHO for reduction of contamination by pesticides are high-temperature incineration and disposal in landfill sites. However, both of these can result in pollutant transfer. In this light the development of clean treatment technologies, as well as mobile units that enable treatment on site, is desirable. In this context, electrochemical technology is a promising alternative and is extremely adaptable, being able to help both large scale industries and the small-scale farmer in the disposal of pesticide containing waste. The aim of this study is to evaluate the toxicity of simulated effluents containing ATZ before and after three different forms of treatment: Electrochemical (EC), photochemical (PC) and photo-assisted electrochemical (PAEC) degradation. The studies were performed in an electrochemical flow-cell using a Ti/Ru0.3Ti0.7O2 anode (14 cm²) as the working electrode. Experiments were performed by applying a current (40 mA cm⁻²) simultaneously with application of UV radiation for 3h. NaCl (0.10 M) Na₂SO₄ (0.033 M) were used as electrolytes and ATZ was present at 20 mg/L in all cases. The acute toxicity (48h) of the solutions before and after treatment was evaluated using nauplius of Artemia sp. as the test organism. As previously observed [1], the rate of ATZ removal is greatly enhanced when the PAEC method is employed when compared to the isolated EC and PC methods. This is true in solutions containing both NaCl and Na₂SO₄ as supporting electrolytes. After 3h of electrolysis the reduction in chemical oxygen demand (COD) depended on the treatment process employed and the electrolyte employed. For EC degradation, the presence of NaCl enhances both ATZ and COD removal due to the formation of powerful chlorine-based oxidizing agents (i.e. Cl₂, HOCl and OCl⁻). For the PAEC method, both electrolytes exhibited increased efficiency when compared to the EC and PC methods individually. The starting solutions of ATZ presented an acute toxicity of ~60 % (in 0.10 M NaCl) and 0% (0.033 M Na₂SO₄). After the EC treatment, both electrolytes an increased level of toxicity was observed. This is probably due to the formation of Cl₂, HOCl and OCl⁻ in the case of NaCl and S₂O₄²⁻ in Na₂SO₄. Interestingly, the use of the PAEC method resulted in a reduction in the acute toxicity, with the solutions being considered non-toxic for both electrolytes. The results will be discussed by considering the photolytic break-up of the electro-generated species and their effect on the toxicity. Overall the present study demonstrates that the level of toxicity of pesticide-containing waste can be significantly reduced by applying the PAEC method, even in the presence of NaCl and its toxic electro-generated products.

Deposition of Diamond-like Carbon films using a liquid phase electrodeposition

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Protective coatings are used for a great variety of applications, as for example different chromium films used for protection against corrosion, wear and to enhance the surface finishing. However, The European Union regulations [1] established that from the first of July 2006 on it will be prohibited the use of Pb, Hg, Cd, and Cr+6 in electric/electronic equipments. So, a process substitution or the development of new coatings is a world reality. Recently, much attention has been focused on diamond-like carbon films that present outstanding properties, such as chemical inertness, high hardness and are composed just by carbon and hydrogen atoms. In this way, the present work proposed the deposition of this kind of films by an electrochemical way. The films were obtained by applying a high voltage (1200V), at room temperature during 4 hours, in an organic solution. The organic solutions used to deposit the films were acetonitrile and N,N-dimethyl formamide (DMF). The morphology of the films was verified by atomic force microscope (AFM) and scanning electron microscope (SEM). Raman spectroscopy, one of the most used techniques to characterize diamond-like carbon films, was performed with a NTEGRA SpectraNanofinder (NT-MDT) operating in a blue laser (488nm) laser at room temperature. The Raman spectra indicated the presence of diamond-like carbon films.

Electrochemical oxidation of methamidophos in aqueous solution: Role of the electrode material

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The anodic mineralization/incineration of toxic organic substrates in aquatic media is an important goal in industrial electrochemistry, whose achievements in synthesis and energetics already greatly contribute to the reduction of the environmental impact in chemical production of goods and in energy conversion. Electrochemical incineration of organic pollutants can be attempted by direct or indirect oxidation. 1 Recently, degradation of organophosphorous pesticides has been under study since they are extensively used and have shown to be environmentally persistent. 2 Therefore, electrochemical oxidation of methamidophos (O,S-dimethylphosphor amidothioate: C2H8NO2PS), an organophosphorous pesticide, has been studied at Pb/PbO2, Ti/SnO2 and diamond (BDD) anodes. In this work, the electrooxidation of methamidophos was carried out on these anodic materials at 30°C in sodium sulphate aqueous media under different pH conditions and at different current densities of electrolysis. According to reverse phase HPLC studies using UV-Vis detection, it was found that at pH 2.0 and using a Pb/PbO2 electrode, the concentration of methamidophos decreases from 50 ppm to non-detectable concentrations (less than 5 ppm) during the first 40 minutes of reaction, whereas Ti/SnO2 and diamond are less efficient towards methamidophos oxidation. Methamidophos undergoes cleavage through the following reaction: C2H8NO2PS + 8·OH → 2CH2O + NH4+ + SO42− + PO43− + 8H+ + 4e−. In basic media (pH 8.5), it was observed that pH decreases as a consequence of hydrogen ions formation. FTIR studies based on attenuated total reflectance (ATR) lead us to confirm that aqueous formaldehyde (IR bands: 1028, 1218, 1368, 1740, 2910, and 2971 cm−1), was the main product of reaction when using a Pb/PbO2 anode at pH 2.0 and at 20 mA/cm2. Under the same conditions, SnO2 shows poor formaldehyde production compared to Pb/PbO2, while BDD does not show this species formation. However, FTIR/ATR studies on diamond electrolyses performed at pH 12.0 and at 20 mA/cm2 show the appearance of carbon dioxide (IR bands: 2361 and 2338 cm−1) and phosphate (IR strong bands: 3005 and 1006 cm−1) spectra, which suggest a direct mineralization step of methamidophos: C2H8NO2PS + 10·OH → 2CO2 + NH4+ + SO42− + PO43− + 14H+ + 16e−.

Electrocatalysis of nitrite reduction using a polyaniline/nordihydroguaiaretic acid composite film

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Polyaniline subjected to cyclic voltammetry in the presence of nordihydroguaiaretic acid (a naturally occurring bis-catecholic compound) undergoes covalent modification to form a novel composite material exhibiting complex electrochemical behavior in a wide pH range.

The plausible mechanism of the modification reaction will be presented and discussed. The composite films prepared on a polycrystalline gold supporting electrode will be used as electrocatalysts for the reduction of nitrite in acidic electrolyte. Some kinetic data obtained from the RDE measurements will be presented as well. When operating at constant potential of 0.0 V vs. Ag/AgCl a linear relationship between nitrite concentration and reducing current is observed over wide concentration range with sub-micromolar detection limit.
Titanate-based compounds can be considered promising materials for application in solar cells or in photocatalysis. This contribution reports on the study of titanate film deposited onto transparent electrode, glass coated with fluorine-doped tin oxide (FTO) for use in solar energy conversion. Titanate was prepared from a mixture of TiO$_2$ particles and K$_2$CO$_3$ through a solid state reaction at 640 °C for 8 hours. Aqueous HCl solution was added and the suspension was maintained under magnetic stirring for 5 hours for ion exchange. Then, polyethylene glycol was added to the protoned titanate (H$_2$Ti$_2$O$_5$) and a film of this suspension was deposited onto the conductive side of the glass-FTO followed by heating at 450 °C for 30 minutes. Scanning Electron Microscopy (SEM), Figure 1, revealed a porous surface consisted of agglomerate rods (160 nm diameter and 400 nm length) and spherical particles (c.a. 500 nm diameter). X-Ray Diffraction analysis confirmed the intrinsic layered structured of titanate in 2θ = 10°.

The electrochemical properties of the titanate electrode were investigated by Cyclic Voltammetry using Ag/AgCl as reference and a platinum wire as counter-electrode. In aqueous Na$_2$SO$_4$ solution, a wide potential window was observed, limited at -0.1V and +1.3V due to H$_2$ and O$_2$ evolution reactions (Figure 2). Defined peaks were observed for the electron transfer reaction of ferri/ferrocyanide redox couple, as can be seen in the insert in Figure 2. However, the difference between the anodic and cathodic peaks was higher than 59 mV (the expected value for this reaction), and enlarged with increasing scan rates. Under irradiation, the electrochemical response of the titanate electrode varied with the light intensity. In supporting electrolyte, the open circuit potential, which corresponded to 0.30 V in the dark, changed to -0.12 V under 100 mW cm$^{-2}$ of polychromatic irradiation. This effect can be attributed to the electron injection into the conduction band of the titanate after the $e^-/h^+$ charge separation and is an indicative of the semiconductor behavior of the titanate electrode. Acknowledgments: Capes,CNPq, Fapesp, Faepex-Funcamp.

Figure 1. SEM image of the surface of titanate film deposited onto glass-FTO.

Figure 2. Cyclic voltammetry of electrode in aq. Na$_2$SO$_4$ (a) and K$_4$Fe(CN)$_6$ (b), 20 mVs$^{-1}$. 

Optimization of operational conditions for nitrobenzene (NBE) degradation by Electro-Fenton methods.

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Aromatic nitro compounds are commonly used in the manufacture of pesticides, dyes and explosives, and are often detected in industrial effluents, in ambient freshwater. In addition, nitroaromatic hydrocarbons are naturally generated as a result of photochemical reactions produced in the atmosphere. These substances show high toxicity, provoking serious health problems.

Electrochemical methods can lead to an efficient destruction of such compounds. Among them, indirect electrooxidation methods based on the cathodic generation of hydrogen peroxide such as electro-Fenton and photoelectro-Fenton are being developed for the destruction of toxic pollutants in acidic wastewaters. These environmentally clean electrochemical methods are usually performed in an electrolytic cell where H$_2$O$_2$ is continuously produced in the contaminated solution from the two-electron reduction of O$_2$ at mercury pool, reticulated vitreous carbon, carbon-felt, activated carbon fiber or carbon-polytetrafluoroethylene (PTFE) O$_2$- diffusion cathodes.

The electro-Fenton method involves the addition of small quantities of Fe$^{2+}$ as catalyst to the acid solution to enhance the oxidizing ability of H$_2$O$_2$ because of the production of the strong oxidant $\cdot$OH through the Fenton’s reaction.

In this contribution we report results from the degradation of nitrobenzene (NBE) using electro-fenton methods in aqueous solutions. Two different aproaches were tested: (a) In situ electrochemical production of H$_2$O$_2$ by reduction of O$_2$ using two different carbon-based electrodes. (b) Electro-Fenton degradation of NBE in excess of hydrogen peroxide and catalytic concentrations of Fe(III) or Cu(II) salts using Pt cathodes.

The cathodic H$_2$O$_2$ production in acid media was studied in two different carbon materials and the kinetic profiles of H$_2$O$_2$ obtained in several conditions are presented. The rates of O$_2$ reduction depend on the applied potential and the supporting electrolyte concentration.

The results of both thermal and electrochemically-enhanced oxidation of NBE are also compared. The kinetic profiles of the thermal processes induced by Fe(III) or Cu(II) salts show an autocatalytic behavior. A Slow initial phase is followed by a Fast phase were both NBE and H$_2$O$_2$ consumption rates are increased. For the electrochemically enhanced oxidation, the rates of the Slow phase are substantially increased for both Fe(III) and Cu(II) catalyzed systems, though the effects of the electrochemical treatment on the fast phases are less evident.

References
**Proton Conductive Silicate/Phosphate Composite Membranes**

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**Introduction.** — Polymer electrolyte fuel cells (PEFCs) are extensively studied as a new energy conversion device. To improve energy conversion efficiency and to avoid CO poisoning of catalysts, PEFCs which can operate in the intermediate temperature range (100-200°C) are strongly desired. Phosphates have been reported to show high proton conductivity at intermediate temperature. We have synthesized porous phosphate films with uniform nanopores [1,2]. Mesoporous materials prepared by a surfactant-assisted method have a large pore volume for water adsorption. In addition, periodic order of their pore structure may improve the proton conductivity. A structure of the silicate/phosphate composite membranes and their proton conductivity are shown here.

**Experimental.** — Surfactant molecules were deposited on a silicon substrate by a spin-coating method. The precursor solution was prepared using Brij 30 \((C_{12}EO_4)\), \(H_3PO_4\), EtOH, and deionized water with the mole ratios of 1.5 \(H_3PO_4\): 0.75 Brij 30: 50EtOH: 100H_2O. The surfactant-solvent mixture was dropped onto the silicon substrate while it was spinning at 500 rpm, and then the substrate spun up to 4000 rpm for 60 s. The \(H_3PO_4\)/Brij 30 composite film was arranged to lie vertically in a closed vessel (50 cm³). Small amount of TEOS and HCl was placed in the bottom of the vessel apart from the substrate. The vessel was placed in an oven at 120 °C for 1.5 h. Calcination was performed at 300°C in air for 5 h with a heating rate of 1°C /min to remove surfantant.

**Results and discussion.** — The results of FE-SEM and XRD measurements indicate the films have ordered pore channels with a hexagonal arrangement parallel to the film surface. In Figure 1, proton conductivity of the silicate/phosphate composite film as a function of temperature at different water vapor pressures was shown. Relative humidity at water vapor pressure of 2, 10 and 20 kPa at 50°C corresponds to 16, 82 and 100%. The proton conductivity for the mesoporous silicate/phosphate composite films was 0.07-0.38 S cm⁻¹. The proton conductivity was not much affected by water vapor pressure. The activation energy for the proton conduction was low (13 kJ mol⁻¹). These results suggest that the proton conduction is governed by the Grotthus mechanism.

From the EDX analysis, the molar ratio of P/Si in the film was determined to 0.13. It seems like the high P-OH group content and the ordered periodic mesostructure contributed to the high proton conductivity. Stable inorganic membranes with high conductivities at high temperature can be widely applied for possible electrolyte alternatives for PEMFCs. But, for applying this material in a fuel cell, self-standing membranes are preferable. We have developing inorganic-organic hybrid materials with the silicate/phosphate composites. The proton conductivity of the hybrid materials will be reported in the future.

Non-polluting indirect electrochemical synthesis of 6-methyl-1,5-diazabicyclo[3.1.0]hexane

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It is known that the diaziridine derivatives, including their bicyclic analogues – 1,5-diazabicyclo[3.1.0]hexanes 1 are interested as potential neuropeptide compounds. The classical method for the synthesis of compounds 1 is based on an interaction of carbonyl compounds, diaminopropane and unstable and toxic NaOCl. Recently an electrosynthesis of the parent 1,5-diazabicyclo[3.1.0]hexanes was realized by galvanostatic electrolysis of 0.1M solution of equimolar quantities of the diaminopropane and formaldehyde and additives of NaHCO₃ in the anodic space of a diaphragm cell. The electrolyte was a 4M solution of NaCl in a 20-% aqueous MeOH. However this method did not allow to isolate the final product due to its very low concentration in spite of the yield was rather high.

In the given work we suggest the preparative version of the non-polluting electrochemical synthesis of compounds 1 on an example of the 6-methyl-1,5-diazabicyclo[3.1.0]hexane 1a. 6-Methyl-1,5-diazacyclohexane 2a was used as a starting material. The direct electrochemical oxidation of compound 2a in MeCN with Bu₄N·PF₆ as a supporting electrolyte on a glassy carbon anode at the potential of 1.2 V vs Ag reference electrode did not afford 1a. Only olygomer products were obtained under these conditions. The indirect electrochemical oxidation of compound 2a in MeCN with Bu₄N·PF₆ as a supporting electrolyte on a glassy carbon anode at the potential of 1.2 V vs Ag reference electrode did not afford 1a. Only olygomer products were obtained under these conditions. The indirect electrochemical oxidation of compound 2a appeared to be more effective. The electrolysis was conducted in undivided cell in aq. acetonitrile 3 M NaCl solution on Pt-10%Ir alloy anode at current density 30 mA/cm². The conditions found were not optimal – the yield of the target 6-methyl-1,5-diazabicyclo[3.1.0]hexane 1a was only 25%. Nevertheless we consider this approach to the electrosynthesis of 1,5-diazabicyclo[3.1.0]hexanes 1 to be prospective as the concentration of compound 1a in our case is several times more than that described in work³.

References

Однако этим методом final product не был выделен поэтому он представлял только теоретический интерес и by this method final product has not been allocate therefore it(he) represented only theoretical interest
Anodic Oxidation of Propham in Water using BDD Electrode

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It is well known that lots of wastewaters are formed during the production of pesticides and their application process [1]. Although activated carbon adsorption, chemical oxidation, biological treatment, etc are used for the treatment of these wastewaters, these processes are not sufficient. In order to remove these pollutants from aqueous solutions, the development of new technologies such as Advanced Oxidation Processes (AOPs) has been attracted great attention during the last two decades because of their ability which allows to reach the total mineralization [3-6]. Anodic oxidation is an electrochemical advanced oxidation process with many advantages. In this manner, boron doped diamond electrode (BDD) is the most widely used anode material in wastewater treatment processes [5-6]. This electrode allows to produce large quantities of hydroxyl radicals from water electrolysis. These radicals are very powerful oxidizing agents and they react unselectively with organics until their total mineralization is achieved.

This study aims the removal of propham from aqueous solution by anodic oxidation with a BDD anode and identification of degradation by-products. The effects of operational system variables such as applied current, temperature, pH, and supporting electrolyte on the degradation and mineralization rate of propham were examined. The obtained results showed that applied current exerts a prominent effect on the TOC removal rate of the system. The maximum TOC removal values was obtained at 35 °C in the presence of 0.05 M Na₂SO₄. The pH of the medium slightly effects the mineralization rate and higher mineralization rates were observed at acidic pH values. The degradation by-products were identified by HPLC, GC-MS, LC-MS and IC and a mineralization pathway was proposed.

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References
Removal of Basic Blue 3 from Water by Electrochemically Generated Fenton’s Reagent

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The huge production rate of synthetic dyes and their intense usage in the textile and other industries produce large amount of colored wastewaters. Colored agents interfere with the transmission of light through water and hinder photosynthesis [1], resulting in ecological imbalance. On the one hand, many dyes or their metabolites have toxic as well as carcinogenic, mutagenic and teratogenic effects on aquatic life and humans [2]. Therefore, it is evident that removal of such colored agents from aqueous effluents is of significant environmental, technical, and commercial importance. The electro-Fenton technology can be seen a suitable tool for the treatment of such kinds of wastewaters. This process is based on the continuous supply of electrochemically generated H₂O₂ to a contaminated acid solution containing Fe²⁺ or Fe³⁺ as catalyst [3-5]. Hydroxyl radical, ·OH, is produced in the medium by the Fenton’s reaction between ferrous ion and hydrogen peroxide. This catalytic reaction is propagated from Fe²⁺ regeneration, which mainly takes place by the reduction of Fe³⁺ at the cathode [3]. The formed hydroxyl radicals leads to the mineralization of the organics present in the solution.

In this study, we used the electro-Fenton technology for the removal of Basic Blue 3 (BB3) from its aqueous solution. The absolute rate constant of the BB3 hydroxylation reaction has been determined as (2.61 ± 0.06) x 10⁷ M⁻¹ s⁻¹ by using competition kinetics method. The effects of the applied current and catalyst concentration on the degradation kinetics of BB3 were examined and optimal values were found as 300 mA and 0.4 mM, respectively. The mineralization of BB3 and its derivatives was followed by total organic carbon (TOC) measurements. More than 98% of BB3 and the intermediates generated during the electrolysis can be mineralized in 8 h electrolysis. Degradation reaction intermediates such as aromatic compounds, carboxylic acids and inorganic ions were identified by HPLC, LC-MS, and IC and a mineralization pathway is proposed.

Financial support of Anadolu University Research Fund (Project No: 061022) is greatly acknowledged.

References
Electrochemical oxidation of the dye Reactive Orange 16 using a low cost Pt film electrode prepared by Pechini method


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Electrochemical degradation of textile dye Reactive Orange 16 (RO16) was performed in an electrochemical flow-cell [1], using as working electrode platinum sheet, Pt, and platinum thin film deposited on a titanium substrate prepared by the Pechini method [2], Pt/Ti. The Pt films were used to investigate its electrocatalytic activity compared to a Pt bulk electrode. Due to its small thickness, its cost is about US$ 3.00 (three dollars) per square centimeter. The experiments were performed in 0.017 mol L⁻¹ NaCl and 0.017 mol L⁻¹ NaCl + 0.5 mol L⁻¹ H₂SO₄ solutions for Pt/Ti and Pt electrodes, respectively. Two different potentials, 1.8 V or 2.2 V were used during the electrolysis. Pt electrodes presented good colour removal (fig.1) at 492 nm, at 2.2 V, but only in 0.017 mol L⁻¹ NaCl + 0.5 mol L⁻¹ H₂SO₄ solutions. The Pt/Ti presented a better color removal than the Pt, and as a result, its was possible to use an applied potential of 1.8 V for 15 min of electrolysis and even in this mild condition to obtain more than 80% of color removal. Beside, these experiments were performed in a 0.017 mol L⁻¹ NaCl, without the need to add 0.5 mol L⁻¹ H₂SO₄. As show in table 1 the operational cost is a half for the Pt/Ti electrode comparing with those results obtained for Pt electrodes at 2.2 V which are the best removal condition for polycrystalline platinum electrode. Considering the results presented, the Pt/Ti electrodes are very promising as an environmental electrochemical tool due to its high efficiency as well as its, electrode and operation cost.

Table 1: Parameters of electrochemical degradation of dye RO16, in electrolysis at potential of 2.2V, using Pt and Pt/Ti electrode.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Pt</th>
<th>Pt/Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour removal (%)</td>
<td>93</td>
<td>98</td>
</tr>
<tr>
<td>K (min⁻¹)</td>
<td>0.024</td>
<td>0.069</td>
</tr>
<tr>
<td>Energy (kW m⁻³)</td>
<td>1.06</td>
<td>0.49</td>
</tr>
</tbody>
</table>

Fig. 1 – Colour removal at fixed potential of 1.8 and 2.2 V, with addition of NaCl (0.017 mol L⁻¹) for all experiments. (Δ) Pt/Ti 1.8 V and (○) Pt/Ti 2.2 V in aqueous medium, (▲) Pt 1.8 V and (■) Pt 2.2 V in 0.5 mol L⁻¹ H₂SO₄ medium; (○) Pt 1.8 V and (●) Pt 2.2 V in aqueous medium.

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References
Metallic Nanostructures of Pt/Bi/Pt for the Oxidation of CO Molecules

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On Pt electrodes, CO$_{ads}$ has been identified as the main intermediate formed in the adsorption of many small molecules. A possible alternative to decrease CO$_{ads}$ poising is the use of Pt alloyed with elements such Ru. From an experimental point of view, our group has been worked with nanostructureds of metallic multilayer to electrooxidation of small molecules, e.g., ethanol, methanol, formic acid, formaldehyde and CO. In view of this fact, the aim of this work is to electrodeposit Bi/Pt mono and multi layers to investigate the electrocatalytic activity for methanol and CO electrooxidation. The Bi and Pt layers were deposited in different times following the factorial design $2^2$, where two variables (Bi and Pt layers deposition) in two different times (40 and 180 s).

In Figure 1a, the voltammetric profiles for Pt, Pt/Bi and Pt/Bi/Pt are presented. The monolayer thickness of Bi change between 1.3 to 6.5 and 1.0 to 2.7 to Pt when the deposition time in changed from 40 to 180 s. The voltammetric profile is the same to different time deposition.

Figure 1: a) Voltammetric profile of Pt electrode, Pt/Bi and Pt/Bi/Pt multilayer and b) CO stripping. The electrolyte was 0.1 M HClO$_4$, $v = 50$ mV s$^{-1}$. $T = 25$ °C.

The voltammetric overlap of the H adsorption to Pt and Pt/Bi/Pt agree with the no change in the surface area. This indicates that the roughness factor did not change. As the Bi oxide reduction process is not observed in the voltammogram of Pt/Bi/Pt, it is probable that no free Bi sites are present on the bilayer surface. The electrooxidation of CO monolayer is important to study the mechanistic and applied properties. In Figure 1b, all stripping peak of CO electrooxidation is displaced 160mV to more negative potential. In summary, different approach for the development of electrocatalytic materials was employed and the electrooxidation of CO molecule was used as a probe reaction. On the basis of the results presented here, a new material has been obtained that, even though it presents the same voltammetric profile as Pt in acidic medium, presents distinct features for small organic molecule oxidation.

Acknowledgements
The authors gratefully acknowledge CNPq and FAPESP (03/09933-8 and 05/04708-1).
Comparative Study of Methanol and Ethanol Oxidation on Amorphous Ni$_{59}$Nb$_{40}$Pt$_{(1-X)}$Y$_X$ (Y =Sn, Ru; X =0, 0.4% ) IN ACID MEDIA.


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The aim of this work was to investigate the modified carbon paste electrodes (MCPEs), working in perchloric acid solutions, have been made by adding amorphous alloys powders with compositions Ni$_{59}$Nb$_{40}$Pt$_{(1-x)}$Y$_x$ (Y =Sn, Ru; x =0, 0.4% at.), and obtained by mechanical alloying, to the mixture of powdered graphite and paraffin. It was observed that both Ni$_{59}$Nb$_{40}$Pt$_{0.6}$Ru$_{0.4}$ and Ni$_{59}$Nb$_{40}$Pt$_{0.6}$Sn$_{0.4}$ containing MCPEs, shift the onset potential for CO (ca. 0.23 V) to lower potentials compared to Ni$_{59}$Nb$_{40}$Pt$_{1}$ electrodes. While ruthenium promoted the catalytic activity for ethanol and methanol electrooxidation, tin showed the same enhancing behaviour for a shorter period of time, probably due to the facile dissolution of tin from the surface.

Concerning the reactivity of ethanol and methanol, the current density are drastically decreased with the presence of tin, susceptible to the potential range, followed by the Ni$_{59}$Nb$_{40}$Pt$_{1}$ and Ni$_{59}$Nb$_{40}$Pt$_{0.6}$Ru$_{0.4}$ alloys. However, these new electrodes show a very interesting behaviour, taking into account their high tolerance to CO molecules, and the decrease of the onset potential for methanol electrooxidation, which are the main causes of poisoning of anode materials in fuel cells (DAFC).

Reference


Acknowledgement

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Preparation of Pt Rare Earth/C electrocatalysts using the alcohol-reduction process for ethanol electro-oxidation

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Fuel cell employing alcohols directly as combustible (Direct Alcohol Fuel Cell - DAFC) are attractive as power sources for mobile, stationary and portable applications. Compared to hydrogen-fed fuel cells which need a reforming system, or have hydrogen storage problems, DAFC uses a liquid fuel simplifying the fuel system. Methanol has been considered the most promising fuel, because it is more efficiently oxidized than others alcohols, however, slow anode kinetics are observed and it is a toxic product. Ethanol offers an attractive alternative in relation to methanol as a fuel in low temperature fuel cells because it can be produced in large quantities from agricultural products and it is the major renewable biofuel from the fermentation of biomass. However, its complete oxidation to CO$_2$ is more difficult than that of methanol due to the difficulty in C–C bond breaking and to the formation of CO-intermediates that poison the platinum anode catalysts. In this context, more active electrocatalysts are essential to enhance the ethanol electro-oxidation. In recent years, it is found that certain metal oxides, such as RuO$_2$, SnO$_2$ and CeO$_2$, can enhance the catalytic activity for ethanol or methanol electro-oxidation through synergetic interaction with Pt. Among those, rare earth oxides exhibit a number of characteristics that make them interesting for catalytic studies. In this work, Pt Rare Earth/C electrocatalysts (Rare Earth = La, Ce, Pr, Nd, Sm, Tb, Dy, Ho Er, Tm and Lu) were prepared in a single step by an alcohol reduction process using ethylene glycol as reduction agent and solvent and Vulcan XC 72 as support. The obtained materials were tested for ethanol oxidation in acid medium using cyclic voltammetry and chronoamperometry. The EDX analysis showed that the Pt:RE atomic ratios obtained for all electrocatalysts were approximately 60:40 and were similar to the ones used in the preparations. The X-ray diffractograms of Pt Rare Earth/C electrocatalysts showed the typical fcc structure of platinum and the presence of rare earth (III) hydroxides. The average particle size were calculated using Scherrer equation using the reflections of Pt(220) peak and the values are in the range of 6-15 nm. The final current values after holding the cell potential at 0.5V versus RHE for 30 min are following: PtLu/C > PtTb/C > PtEr/C ≈ PtNd/C ≈ PtCe/C > PtHo/C > PtLa/C > PtDy/C > PtTm/C > PtPr/C > PtSm/C > Pt/C. The superior activity of Pt Rare Earth/C electrocatalysts in relation Pt/C could be attributed probably to the bi-functional mechanism were Pt acts on ethanol adsorption and dissociation and Rare Earth provides oxygenated species at lower potentials for oxidative removal of adsorbed CO.
PtRuNi/C electrocatalysts prepared by an alcohol reduction process for methanol electro-oxidation

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Fuel cells employing alcohols directly as combustible (Direct Alcohol Fuel Cell - DAFC) are attractive as power sources for mobile, stationary and portable applications. Compared to hydrogen-fed fuel cells, which need a reforming system, or have problems of hydrogen storage, DAFCs use a liquid fuel simplifying the fuel system. Methanol has been considered the most promising fuel, however, slow anode kinetic is observed. PtRuNi electrocatalysts prepared by different methodologies have been shown more active than the corresponding PtRu electrocatalyst. We have prepared active PtRu/C electrocatalyst for methanol electro-oxidation by an alcohol reduction process. In this work, PtRuNi/C electrocatalysts were prepared with different Pt:Ru:Ni atomic ratios and tested for methanol electro-oxidation. PtRuNi/C electrocatalysts (20 wt%) were prepared using H₂PtCl₆·6H₂O, RuCl₃·1.5H₂O and NiCl₂·6H₂O as metal sources, ethylene glycol as solvent and reducing agent and Carbon Vulcan XC72R as support. The electrocatalysts were analyzed by EDX, DRX, TGA and cyclic voltammetry. The activity towards methanol oxidation was evaluated by chronoamperometry in acid medium. We have already observed that if the synthesis of PtRuNi/C electrocatalyst was performed in acid medium only Pt(IV) and Ru(III) ions were reduced by ethylene glycol and no reduction and/or incorporation of Ni(II) ions on the carbon support were observed. Adding KOH in the reaction medium (KOH/metals ratio of 8), the reduction and/or incorporation of Ni(II) ions occurs and Pt(IV) and Ru(III) ions were also reduced. In this manner, PtRuNi/C electrocatalysts with Pt:Ru:Ni atomic ratios of 50:40:10, 50:25:25 and 50:10:40 were prepared. Pt:Ru: atomic ratios obtained by EDX were similar to the nominal ones. The X-ray diffractograms of the electrocatalysts showed peaks at about 2θ = 40°, 47°, 67° and 82° characteristic of the fcc structure of platinum and platinum alloys. No diffraction peaks that could be attributed to pure ruthenium and nickel or their oxides/hydroxides were observed. However, the peaks of fcc structure showed a slight shift to higher angles compared to the ones of PtRu/C electrocatalyst, suggesting the incorporation of Ni into the fcc structure. On the other hand, the total quantities of metals deposited on the carbon support were smaller than the nominal value (20wt%). The following values were obtained: PtRu/C 50:50 (8 wt%) and PtRuNi/C 50:40:10 (10 wt%), 50:25:25 (13%) and 50:10:40 (18wt%). The electro-oxidation of methanol was studied at room temperature by chronoamperometry at 0.5V. The current values were normalized by gram of Pt considering that methanol adsorption and dehydrogenation occurs on Pt sites at room temperature. The performances of PtRuNi/C electrocatalysts were higher than that of PtRu/C electrocatalyst; being the PtRuNi/C electrocatalyst with Pt:Ru: Ni atomic ratio of 50:40:10 the best.
Aiming to elucidate the corrosivity of seven different soils found in South Brazil and the effects of cathodic protection on the composition changes due to ionic migration and electrolysis of contained water the ionic composition and pH profiles were determined as function of applied cathodic currents, time an soil type under laboratory conditions and from the field. The soils were collected along a pipeline running from the ocean coast to the continent. An increase of pH up to 13-14 was observed at the surface of the buried pipe in, as well as under laboratory conditions associated to the depletion of aggressive chlorides and sulfates and enrichment of several metal cations (K⁺, Na⁺, Mg²⁺, Ca²⁺). These composition changes have major influence on the corrosion of pipelines and anodes for the application of cathodic protection. Additionally, EIS measurements of these soils were carried out between two AISI 316 electrodes, searching for an association between soil properties as specific surface area, particle size distribution and composition. Fig. 1 shows Nyquist plots of two different soils in dependence of the relative humidity. Two capacitive loops are found in the impedance spectra: One (low frequency) was attributed to the electrode-soil interface or contact impedance and the other (high frequency), to the bulk soil response, The capacitive behavior of the soil is explained by the adsorption of ionic species on the soil particles surface and is affected by the soil texture and composition.

Fig. 1. Nyquist plots for AISI 316 stainless steel in (a) silt-clay soil and (b) sandy soil.
Synthesis, Characterization and Electrochemical Evaluation towards Alcohol Oxidation Reaction of Ordered Intermetallics Nanostructured PtSn and PtSb

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Ordered intermetallics platinum electrocatalysts have been recently proposed as very efficient electrocatalysts materials for reactions involved in low temperature fuel cells [1]. This class of compounds presents the synergetic effect of suitable adsorption properties and inhibition of poisoning effect provided by Pt and transition metals sites, respectively. In spite of the great deal of reliable and valuable scientific information resulted from such methodological approach, the bulk material configuration is still far from the actual use in a fuel cell. In order to overcome such technological constraint some efforts have been dedicated to obtain ordered intermetallic nanoparticles of Pt based electrocatalysts [2-4]. This paper describes the experimental method of obtaining and characterizing PtSn and PtSb ordered intermetallic nanoparticles via a modified poliol route. The characterization of the synthesized materials showed the successful attainment of the designed electrocatalysts in a nanosized scale. X-ray powder diffraction technique unequivocally confirmed the intermetallic identities and made possible the estimation of the mean particles size of 7 nm and 13 nm respectively for PtSn and PtSb by using Scherrer’s equation as well crystalline structure, hexagonal (P63/mmc) for both materials. SEM images at different magnification shows the nanostructured morphology of the samples. The produced materials have showed to be predominantly homogeneous and well distributed on networks intertwined and the particles seemed to be intensely aggregated. The quantitative EDX spectrum provided the composition of the final product as 48.6 ± 0.3 atom% Pt, 51.4 ± 0.3 atom% Sn and 46.5 ± 2.2 atom% Pt, 53.5 ± 2.2 Sb atom% for the materials PtSn and PtSb respectively, thereby corroborating the effectiveness of the synthesis. The electrocatalytic activity of intermetallics nanostructured was evaluated by cyclic voltammetry through the oxidation of methanol, ethanol and ethylene glycol. The intermetallics showed high current densities for all fuels analyzed.

References
Treatment of wastewater of paper industry by Electrocoagulation process using aluminum electrodes

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Turbidity, COD and BOD₅ decreasing of paper effluent were made by Electrocoagulation. The study aims to determine the best current density of treatment which maximizes the process efficiency. The current was determined from micro-electrolyses studies utilizing aluminum micro-electrodes. Once determined the current, batch mode was studied applying 10 and 20 A m⁻² using monopolar and bipolar electrodes. The best configuration was 20 A m⁻², monopolar electrodes and 4 electrode plates. Electrocoagulation treatment present 2 different behaviors: adsorption-destabilization and sweep coagulation (Amirtharajah et al., 1982)

Figure 1. Turbidity removal percent at 10 and 20 A m⁻². Monopolar electrodes, 4 aluminum plates, electrode separation = 1 cm, [Turbidity]₀ = 120 NTU
Theoretical Study of the Primary Current Distribution in Cylindrical Electrodes

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The primary current and potential distributions were obtained for an electrochemical reactor with an inner cylinder electrode solving the Laplace Equation by the finite difference method. The studied configuration presents an inner electrode, 2.54 cm diameter and 8 cm active length, with an outer counterelectrode made of four plates symmetrically collocated around of the cylinder. The current distribution was obtained for the axial and radial coordinates considering a cylinder with an insulating cover of 0.5 cm, with a minimal cover and without insulating end cap as well as varying the width of the counterelectrode. The results show that the best arrangement is a cylinder without insulating cover, with 2.5 cm counterelectrode width for an interelectrode gap of 1 cm.

Figure 1. Current distribution as a function of the axial position.

Figure 2. Current distribution as a function of the radial position parametric in the counterelectrode width.
Design and development of Cooper gas diffusion electrodes (Cu-GDE) applied to the electrochemical reduction of carbon dioxide

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The electrochemical reduction of carbon dioxide continues receiving considerable attention not only as a technological tool for conversion to useful materials, but because of the need to reduce its concentration in the atmosphere since it is one of the main contributors to the "greenhouse effect". Many workers have extensively studied the electrocatalytic reduction of CO\(_2\) using various metal electrodes in aqueous electrolytes. As a result, it has been determined that the electrocatalytic activity of the electrode depends strongly on the metal used. Also, it is known that copper provides good electrocatalysis for promoting CO\(_2\) reduction in aqueous electrolyte to either gaseous or condensed species dependent upon experimental conditions.

In this contribution we report results from CO\(_2\) reduction using a copper gas diffusion electrodes (Cu-GDE). The Cu-GDE electrodes were prepared mixing carbon black (Vulcan XC-72R) from Cabot with Teflon 30 B from du Pont to provide the hydrophobic layer. Cooper powder of three different sizes (micro and nanometer range), was supported on sulphonated Vulcan XC-72R carbon by mixing the carbon powder with Teflon and water. The resulting paste constitutes the hydrophilic reaction layer. Finally, the electrode is assembled by pressing both layers. The catalytic ability and stability of the electrodes for the CO\(_2\) reduction in aqueous 0.5 M K\(_2\)SO\(_4\) and 0.2 M NaClO\(_4\) aqueous solutions was evaluated in a three-electrode electrochemical cell. The Cu-GDE working electrode compartment was separated from the anodic counter electrode compartment by a Nafion\textsuperscript{R} membrane. A platinum mesh was used as counter electrode. The morphological characteristics of the electrodes before and after the process of reducing the CO\(_2\) are evaluated through optical, scanning electron and transmission microcopies. Different parameters such as optimum Teflon content in both the hydrophobic and hydrophilic layers, hydrophobic carbon to hydrophilic carbon ratio in the reaction layer, molding pressure, copper content and copper particle size were studied. The potential dependence of the faradic efficiency in Cu-GDE’s was evaluated measuring the total organic carbon from the electrolyte and by chromatographic techniques. The results show that Cu-GDE’s have a faradic efficiency for CO\(_2\) reduction of about 100 times higher than that observed for a bulk copper electrode. The efficiency is largely dependent on the copper particle size and its distribution in the hydrophilic layer. The size and shape distribution of electrocatalyst particles, as well as the roughness and non-Euclidean characteristics of the electrodes was determined and correlated to the electrochemical data.
Electrochemical studies of secondary phases in hydride-forming AB$_2$ alloys

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In a previous work on the electrochemical behavior of a AB$_2$-type ZrCrNi alloy, prepared in an arc melting furnace, it was shown that the as-melted material had different electrochemical characteristics as compared to the annealed one. The effect was ascribed to the presence of secondary phases Zr$_x$Ni$_y$ formed during solidification of the melt. Further studies on ball milled mixtures of annealed ZrCrNi alloy with powders of the phases Zr$_7$Ni$_{10}$, Zr$_8$Ni$_{21}$, and Zr$_9$Ni$_{11}$ indicated that the main secondary phase responsible for the improvement of their properties is Zr$_8$Ni$_{21}$. The aim of this work is to study the electrochemical behavior of these secondary phases by impedance spectroscopy in order to determine the physicochemical parameters responsible for the improvement of the alloy performance.

A ZrCrNi alloy was prepared by arc melting adequate proportions of the composition elements. Alloys corresponding to the secondary phases Zr$_7$Ni$_{10}$, Zr$_8$Ni$_{21}$, and Zr$_9$Ni$_{11}$ were prepared by following the same procedure. The base alloy ZrCrNi was heat-treated for 30 days at 1250 K plus 15 days at 1273 K, whereas the alloys corresponding to the secondary phases were heat-treated for 30 days at 1273 K. Finally, powders of each secondary phase were mixed with powder of the base ZrCrNi alloy in a 20 wt.% proportion using a RETSCH S-1/2 ball mill. Samples of these mixtures were used in the preparation of the working electrodes.

Different electrochemical studies, such as cyclic voltammetry, galvanostatic charge-discharge cycling, and rate capability were performed. Electrochemical measurements were carried out using a 7M KOH solution, a Ni mesh as counter-electrode, and Hg/HgO as reference electrode.

The hydriding/dehydriding process is described in terms of the Volmer-Heyrovsky-Absorption (HAR) scheme coupled with hydrogen diffusion in the alloy material. Experimental impedance data were simulated in terms of the proposed model, exhibiting good agreement in the whole frequency range.

The parametric identification allow us to conclude that electrodes prepared with the Zr$_8$Ni$_{21}$ alloy exhibit the highest values for the hydrogen diffusion coefficient, D, exchange current density, and the HAR kinetic constant, in accordance with the electrode improved performance. It was also determined that the kinetic constant related to the HAR process is more than one order smaller for electrodes prepared with Zr$_9$Ni$_{11}$, and the diffusion coefficient, D, three orders smaller for this alloy than for electrodes prepared with Zr$_8$Ni$_{21}$ or Zr$_7$Ni$_{10}$.

Acknowledgments
This work was supported by Consejo Nacional de Investigaciones Científicas y Técnicas of Argentina and the Agencia Nacional de Promoción Científica y Tecnológica.
Oxidation of Dyes on Pt and Ti/Ti_0.7Ru_0.3O_2 Electrodes in Chloride Medium. Effect of Chloride Concentration and Current Density

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Effluents from textile and paper industries contain large quantities of organic compounds and reactive dyes. The release of colored wastewater in the environment is a considerable source of non-aesthetic pollution and eutrophication. Therefore, proper treatment of these wastewaters has drawn increasing attention.

In this work, the electrochemical bleaching of a simulated effluent containing 30 mg L⁻¹ of Blue Reactive 19 dye is proposed. Chloride was added to the electrolyte in order to improve the reaction rates since electroactive intermediates are generated.

A three-level factorial design was used to investigate the influence of current density and chloride concentration on the generation rate of active chlorine and dye bleaching. For each experimental condition, the absorbance (given in terms of absorbance unit – a.u.) was recorded curing a certain time and in all cases, the kinetics has shown a first order behavior. The rate constant for the bleaching process (k_b) was calculated using the slope of these curves.

The results shown in Figure 1 and 2 indicate that the active chlorine concentration has a secondary effect on the bleaching rate. On the other hand, current density and mainly the chloride concentration are very important variables governing the reaction rate. The best conditions for the dye bleaching were found to be at the high level of chloride and current density, but these conditions should be optimized in terms of current efficiency and energy consumption.

Figure 1. k_b against k_{Cl^-}. Pt electrode.  Figure 2. k_b against i and C_{Cl^-}. Pt electrode.

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Phenol Oxidation on Commercial Ti/Ti$_{0.7}$Ru$_{0.3}$O$_2$ Electrodes in Chloride Medium. Effect of Chloride Concentration, Current Density and Flow Rate

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In this work, phenol has been used as a model compound to study the influence current density and flow rate during its electrochemical oxidation in aqueous medium containing different concentrations of sodium chloride. Chloride was added as an attempt to improve the reaction rate through electrogenerated chlorine species in order to make electrochemical degradation of organics using commercial electrodes of Ti/Ti$_{0.7}$Ru$_{0.3}$O$_2$ a suitable process to be effectively used.

Experiments were done for eight hours and the results of active chlorine formed (expressed as Cl$_2$) and chemical oxygen demand (COD) were plotted against the reaction time. The results have indicated a first order reaction for both Cl$_2$ and COD. The results shown in Figure 1 indicate that the amount of active chlorine generated is not the major factor affecting the reaction rate when COD depletion is considered. In fact, the operational parameter flow rate and current density have a strong and complex influence on $k_{\text{COD}}$. As expected, for current density of 150 mA cm$^{-2}$ the higher the flow rate the higher $k_{\text{COD}}$ since the process is mass transfer controlled. However, for low current density, the opposite effect was observed, suggesting that the residence time could be affecting the reaction rate.

Figure 2 shows that chloride concentration has a strong influence on COD depletion, being its effect more important for low flow rates. It can be noted that when the concentration of 5 g L$^{-1}$ NaCl was used, a brownish precipitated appeared in the electrolyte, but it was not observed on the concentration of 1 g L$^{-1}$.

Figure 1. Comparison between rate constants for active chlorine generation and COD depletion.

Figure 2. Rate constant for COD against current density. (●) 4.56 L min$^{-1}$/ 5 g L$^{-1}$ NaCl; (■) 0.83 L min$^{-1}$/ 5 g L$^{-1}$ NaCl; (▲) 4.56 L min$^{-1}$/ 1 g L$^{-1}$ NaCl; (▲) 0.83 L min$^{-1}$/ 1 g L$^{-1}$ NaCl;

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Microstructural and electrochemical characterization of environmentally friendly sol-gel based layers on Al alloys

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The heterogeneous microstructure of aluminum alloys makes them particularly susceptible to localized corrosion [1]. The alloy Al2024 is widely used in the aerospace industry because of the optimal strength-to-weight ratio. However, this alloy is one of the most susceptible to localized corrosion. Corrosion protection for Al alloy components in military and commercial aircraft is provided mainly by a chromate conversion coating. However, due to the high toxicity of Cr\(^{6+}\), environmentally benign alternatives to chromates are strongly needed. Thus, the purpose of this work is to present the results of microstructural characterization of cerium oxide conversion coatings prepared by the sol-gel method using different deposition conditions (T: 200, 300 and 400 °C). The role of microstructure is discussed in terms of corrosion performance of coatings on the aluminum alloy 2024–T3.

Scanning electron microscopy (SEM) analyses revealed that cerium oxide was homogeneously deposited on the electrode surfaces as compact layers of ceramic aspect with thickness in the range between 11 and 19 µm. Furthermore, some thin cracks of approximately 500 nm and 1 µm of width were observed on the deposits prepared at 300 and 400 °C, respectively, which were not observed on the deposits prepared at 200 °C. Energy dispersive X-ray analyses indicating the formation of cerium oxides on the surfaces and X-ray diffractometry measurements confirmed the formation of CeO\(_2\).

Polarization curves carried out in a very wide range of potentials, from –1.5 to 2 V vs. SCE, displayed very resistive behaviors for the protected alloys with very low corrosion current density values (~0.49 pA cm\(^{-2}\)) and also presented a positive shift of ~0.80, ~1.23 and ~1.63 V in the corrosion potential for the coatings prepared at 400, 300 and 200 ºC, respectively. Note that the corrosion current density value observed for the untreated Al–2024 alloy was 1.68 µA cm\(^{-2}\). Thus, the corrosion resistance of the coatings prepared at 200, 300 and 400 ºC was somewhat dependent on the microstructure of the coatings. The layers prepared at 200 °C do not present cracks on their surfaces and presented the best corrosion protection in the polarization curves. However, it is worth to mention that SEM images taken before and after performing the polarization curves did not show observable differences, demonstrating that all the coatings are efficient for corrosion protection even when high potentials (until 2 V vs. SCE) are used. Moreover, EIS measurements performed with all the electrodes protected by CeO\(_2\) coatings presented very high resistances for the charge transfer in the order of gigaohms, clearly indicating that these coatings are very passive and could be efficient for corrosion protection in practical applications.

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Formation, Characterization and Electrocatalytic Activity of Pt-W Particles for the Oxygen Reduction Reaction

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In this work we evaluate the electrocatalytic activity of Pt-W particles for the oxygen reduction reaction. The Pt-W particles were synthesized by thermal decomposition of (NH₄)₂PtCl₄ and W(CO)₆ used as precursors. The thermal decomposition process from room temperature until 760°C was performed using thermogravimetric analysis (TGA). The obtained product was analyzed by X-ray diffraction and infrared spectroscopy (FTIR). Transmission electron microscopy was using for observation of the particles. The electrochemical characteristic of Pt-W particles supported on vitreous carbon electrodes were obtained by cyclic voltammetric in 0.5 M H₂SO₄. The oxygen reduction reaction was studied by using a rotating disk electrode. The result of X-ray diffraction indicates that the decomposition of the precursors leads to formation of metallic Pt and tungsten oxides with predominance of WO₂ (Fig. 1a). A set of current-potential curves obtained in 0.5 M H₂SO₄ O₂-saturated solution at various electrode rotation rates (Fig.1b) shows the contribution of the diffusion of oxygen from the surface process involved in the oxygen reduction reaction. Kinetic analysis of the current-potential curves was made in the mixed kinetic diffusion control region.

Fig. 1a. X-ray diffractogram of the thermal decomposition of (NH₄)₂PtCl₄ and W(CO)₆; 1b. Polarization curves for oxygen reduction on Pt-W particles supported on vitreous carbon electrodes in 0.5 M H₂SO₄ O₂-saturated solution.
Reduction of Nitrate Ions on Supported Pd-Cu Nanocrystals Obtained by Electrodeposition

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The use of synthetic fertilizers is a necessary practice in the production of food and fiber to meet the growing needs of human and livestock consumption. However, increasing use of nitrogen-based fertilizers has raised concerns over the possible nitrate (NO$_3^-$) contamination of drinking water supplies. Nitrate can cause several health problems in humans, and a maximum contaminant level of 50 mg L$^{-1}$ was indicated for the potable water. The denitrification process by electrochemical methods is receiving increased attention because its convenience, environmental respectability, and low cost-in-use. For this purpose, the Pd–Cu system appears as an interesting electrocatalyst material.

The aim to this work was to obtain Pd-Cu bimetallic nanocrystals onto a vitreous carbon (VC) support and to evaluate the electrocatalytic behavior of such electrode for the nitrate reduction. VC was chosen as foreign substrate because of its high overpotential for hydrogen evolution and its properties as inert material.

Initially, the electrodeposition process of Pd nanocrystals on the VC substrate, from a PdCl$_2$ acid solution, was studied by conventional electrochemical techniques and atomic force microscopy (AFM). Within the potential range analyzed, the kinetics of the Pd electrodeposition followed a model including progressive nucleation on active sites and diffusion controlled cluster growth. The AFM images clearly corroborated the progressive nucleation mechanism proposed by the electrochemical analysis. The formation of the bimetallic Pd-Cu nanocrystals was performed in a sequential way with an adequate control of the potential applied. The substrate surface was initially modified by electrodeposition of Pd nanoparticles as was previously indicated, and subsequently, after solution replacement, Cu electrodeposition was produced from a solution containing Cu$^{2+}$ ions. These experiments were performed both in a conventional electrochemical cell and in the AFM electrochemical fluid cell. The AFM showed the formation of bimetallic particles having a Pd core and a Cu shell. Nevertheless, these bimetallic particles were very stable and their dissolution occurred at relatively high positive potentials. Therefore, the formation of a Pd-Cu alloy was not disregarded.

The different modified substrates VC/Pd, VC/Cu and VC/Pd-Cu, characterized in this way were used as electrodes for reduction of nitrate anions, and clearly, the last one showed the lowest overpotential for this reaction.
Reduction of Nitrate Ions on a Au(111)/Pd/Sn Electrode

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Pollution of ground and surface waters by nitrate ions is a common environmental problem throughout intensive agricultural areas. In fact, a high concentration of the nitrate ion has detrimental effects on health and environment, and its removal has gained renewed attention. Possible technologies for the treatment of nitrate ions include ion exchange, biological treatment, reverse osmosis, heterogeneous catalysis and electrochemical reduction. The electrochemical reduction of nitrate ions has been performed using different type of metallic or bimetallic electrodes and, recently, it was indicated that a gold substrate modified with Sn and Pd showed a relatively high activity for this reaction [1].

The aim of this work was to prepare and characterize a Au(111)/Sn and Au(111)/Sn/Pd modified surfaces, using conventional electrochemical techniques and STM (Scanning Tunneling Microscopy) technique and to correlate these results with the corresponding activity for the electrochemical reduction of nitrate.

Sn nanocrystals were formed on the Au(111) surface by the immersion method. Initially, the gold single crystal surface was immersed in 1 mM SnSO$_4$ + 0.5 M H$_2$SO$_4$ deaerated solution under open-circuit conditions for different immersion times, $t$ (5 $t$/s 90), followed by sufficient rinsing with pure water. Then, the electrode was introduced into another electrochemical cell or the STM cell containing 0.5 M H$_2$SO$_4$ supporting electrolyte, at a controlled potential in order to characterize the modified surface. The STM images showed two dimensional islands nucleated on the flat terraces and on step edges. The number and size of these islands increase as the immersion time, $t$, increases and they tend to merge forming interconnected structures of monatomic high. This type of structure showed practically no catalytic activity for the electroreduction of nitrate when it was used as an electrode in a 0.1 M Na$_2$SO$_4$ + NaNO$_3$ 0.1 M solution.

On the other hand, the subsequent immersion of this type of Au(111)/Sn modified surface in 1mM PdCl$_2$ + 0.1 M Na$_2$SO$_4$ solution produced an increase in the surface activity. This behavior, ascribed as a synergetic effect of Pd and Sn is discussed in the work, considering the surface morphology changes observed by in-situ STM after the immersion in the Pd(II) containing solution.

Performance of biogas-fueled SOFC with different fuel compositions
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Biogas, mainly consists of ca. 60 % methane and 40 % carbon dioxide, is obtained from biomass such as excrement of livestock. The effective production of electrical energy from chemical energy of biogas through solid oxide fuel cell (SOFC) system is attractive in development of an environmental-friendly energy conversion system [1]. However, trace of impurity such as $\text{H}_2\text{S}$ in actual biogas poisons the anode material resulting in lower performance of SOFCs [2]. Electrolyte-supported SOFCs using LSM-ScSZ, ScSZ and Ni-ScSZ as cathode, electrolyte and anode materials, respectively, were fabricated. Mixtures of CH\textsubscript{4} and CO\textsubscript{2} were directly fed into anode compartment with 25 ml min\textsuperscript{-1}, and the cell voltages were monitored at the operating temperature of 900 and 1000 °C under a constant load current.

Cell voltage at 900 °C in supplying simulated biogas (CH\textsubscript{4}:CO\textsubscript{2} = 3:2) was measured. In spite of the fact that carbon deposition is thermodynamically predicted [3], direct supply of the CH\textsubscript{4} rich biogas brought about stable and rather high voltage over 200 h (ca. 0.98 V at 200 mA cm\textsuperscript{-2}) comparable with the case of hydrogen. After operation, carbon deposition was not observed on anode material in FESEM-EDS analysis.

During the galvanostatic measurement, 1 ppm $\text{H}_2\text{S}$ was mixed in fuel gas. At 900 °C, $\text{H}_2\text{S}$ contamination caused rapid degradation of SOFC within 30 min resulting from a rapid increase in anodic overvoltage. The results obtained at 1000 °C were shown in Fig. 1. Although initial voltage drop of 50-100 mV occurred, the influence of $\text{H}_2\text{S}$ contamination was remarkably suppressed in comparison with the case of 900 °C. Moreover, biogas with higher CH\textsubscript{4}/CO\textsubscript{2} ratio was found to be more tolerant to $\text{H}_2\text{S}$ contamination.

It was revealed that direct-biogas SOFC operated at a higher temperature and a higher CH\textsubscript{4}/CO\textsubscript{2} was more tolerant to $\text{H}_2\text{S}$ contamination. In these experiments, small button cells with the electrode area and thickness of 0.64 cm\textsuperscript{2} and about 50 μm, respectively, were used. Therefore, more stable operation could be expected for larger cells or anode-supported cells having larger amount of reforming catalysts. Considering this point, direct-biogas SOFC would be feasible if the impurity concentration is sufficiently low.

Enhanced corrosion resistance of aluminum alloys treated by nitrogen plasma immersion ion implantation

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Aluminum alloys widely used on aeronautical industry were treated by nitrogen plasma immersion ion implantation (PIII) for improvement of their corrosion resistance. This technique allows surface modification without film formation. It is an alternative technology to the nitriding process, that besides modifying the surface threedimensionally targets with complex geometry, it does not generate any type of toxic residues. Surface analysis methods have shown improvements of the corrosion resistance of the Al5052 and Al7475 alloys, after PIII treatments. Polarization curves obtained in chloride medium were used to verify that the corrosion current densities decreased ten times in relation to the untreated samples. The Al7475 alloy presented corrosion current density of about ten times smaller values than before the treatment. The corrosion current density of the Al7475 was of the order of $10^{-5}$ A/cm$^2$ before PIII and after the treatment it passed to $10^{-6}$ A/cm$^2$. This new performance of the alloy can be attributed to the formation of aluminum nitride during nitrogen implantation, identified by X ray diffraction and in AES, where it was verified that nitrogen ions had been implanted to the depths of about 70 nm. AES nitrogen profiles indicated relatively small nitrogen concentrations, between 5 – 10 at. %, in the surfaces of treated alloys which resulted in corrosion protection layer. The Al5052 alloy presented the same behavior but its implanted layer was of 140 nm thickness. This layer contains Al$_2$O$_3$ and Al$_x$N$_y$O compounds which conferred to the treated surface a more noble characteristics. On the scanning electron microscopies we observed that the surface was less corroded after the nitrogen implantation. It is hoped that treatments like these offer a good way to increase the life and performance of industrial parts with components and devices made of these alloys.

More corrosion tests will be performed applying electrochemical impedance spectroscopy for a better study of behavior of these alloys before and after N-PIII.
Microbial fuel cell: A prospective technology for power production from wastewater

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In Brazilian big cities are generated millions of liters of domestic sewage daily. According to the IBGE, 53% of municipalities have sewage collection system, from these only 15% receive treatment. Thus, the sector of sanitation represents about 50% ($1.4 billion) of the market environment. However, it is estimated that the sector for the treatment of sewage in Brazil has the potential to move around US $30 billion. To improve the sanitation conditions of the population so environmentally friendly, we are looking for a new alternative wastewater treatment by Microbial fuel cell (MFC). MFCs are bioelectrochemical devices that convert chemical energy in the chemical bonds biodegradable material to electrical energy through biotransformation reactions of microorganisms under anaerobic conditions. In these conditions the microorganisms need to change from the oxygen electron acceptor to an insoluble acceptor, such as the MFC anode. The electrons flow through an external electrical circuit with a load to the cathode. At the cathode, an electron acceptor is chemically reduced. For this propose the oxygen is the best, because produce water. Therefore, to improve the oxygen reduction reaction (ORR) performance is an important challenger.

The microorganisms are bacteria, such as *Escherichia coli*, *Pseudomonas*, *Proteus*, and *Bacillus* that are unable to effectively transfer electrons derived from central metabolism so they need the redox active species (mediator) to the transfer electrons derived from central metabolism to the outside of the cell. On the other hand outside of the some metal-reducing bacteria like *Shewanella putrefaciens*, *Geobacter sulfurreducens*, *Geobacter metallireducens* and *Rhodoferax Ferrireducens* can produce their own mediators.

In this work, in collaboration with the Serviço Autônomo de Água de Volta - SAAE we are prospecting the use of domestic sewage from the treatment plant sewage to be used in MFC. The work will be the isolation, identification and multiplication of bacteria capable of generating electricity using as substrate, organic matter derived from the sewage. The electrochemical performance will be analyzed by voltage/current and power/current profile.

The wastewater treatment by MFC is still new, the low power obtained today is typically 30 mW/m². However it is expected that in the near future this technology is mature enough to make their commercial application. The application of this technology can be expanded to generate electricity to move small equipment or generate electricity in remote places and difficult to access.

A combination of both electricity production and wastewater treatment would reduce the cost of treating primary effluent wastewater.

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Environmental electrochemical engineering: protecting the planet

Oxygen reduction reaction on platinum electrodes prepared by decomposition of polymeric precursors

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The increasing in the energy consumption and in the environmental pollution made the research of new non-pollutant and more efficient technologies into an interesting challenge. Fuel cells are one of the alternatives for energy generation in an efficient and clean way. These devices make possible the transformation of chemical energy in electric energy without damaging the environment. They operate using the gaseous oxygen, that are reduced in the cathode, and gaseous hydrogen or small organic molecules, that are oxidized in the anode. Methanol and ethanol are promising substances to substitute hydrogen but the cross-over of these alcohols through the protons exchanging membrane causes a reduction in the cell performance.

Many efforts have been made in order to find an efficient catalyst for the oxygen reduction reaction (ORR) which presents high electroactivity even in the presence of methanol or ethanol. These catalysts must also present a reduced amount of noble metal for the operation of the fuel cell. The objective of this work is the preparation of electrocatalysts containing Pt powder dispersed onto carbon surface by the decomposition of polymeric precursors.

The prepared materials were characterized by X-ray diffraction, transmission electron microscopy, cyclic voltammetry and polarization curves. The obtained results showed that the catalytic activity depends on the preparation temperature which may be an influence of the particles morphology and catalyst dispersion. The metal load was also investigated and the best results were obtained for catalyst containing 20% of Pt.

![Figure 1: (A) XRD diffractogram of Pt/C electrocatalysts (40% metal loading) prepared by thermal decomposition of polymeric precursors. (B) Mass-transport corrected Tafel plots for the ORR on the Pt/C materials in H_2SO_4 0.5 mol L^{-1} at 25°C. Currents are per unit of Pt surface area, as obtained by cyclic voltammetry.](image-url)
The investigation of the process of electrochemical extraction of copper from the vaste electrolyte using electrochemical reactor with rotary drum electrode were carried out from two main reasons:
1. Founding out of the behaviour of electrochemical reactor with a rotary drum electrode in respect to the current efficiency, during the treatment of higher concentratrated electrolytic solutions and
2. Checking the selectivity of the investigated reactor.

The compositions of vaste electrolytic solution from the electrolytic plant of copper electrolisis in Bor, Serbia, used in the investigations, were in mol m\(^{-3}\): Cu 660.7 \(\rightarrow\) 707.9; H\(_2\)SO\(_4\) – 1459.2; As – 57.4; Fe – 17.9; an Sb – 4.1. The amount of the treating electrolyte in each experiment was one litter. The process of electrochemical extraction was driven under the next experimental conditions: the current density of 35 A m\(^{-2}\), the speed rotation of drum of 80 min\(^{-1}\) and voltage on the system of 5 V. The samples of electrolytic solution have been taken periodicaly in order to determine the concentration change of copper and arsenic into solution during time. The concentrations of copper in investigated solution were determined by colorimetric and electrogravimetric method but arsenic by destilation and titration with potassium carbonate.

The results obtained show that the copper can be selectively removed from the treated electrolytic solution with the current efficiency of 95%. Namely, the concentration of other components into treated electrolytic solution, remained unchanged during treatment in this reactor.
Protection of bronze patina by an environment friendly corrosion inhibitor

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From antiquity bronzes have been widely used to produce sculptures and other objects of art. Bronze forms a thin layer of corrosion products, called patina, when exposed to atmosphere, soil or water. This patina is stable with time and protects the underlying metal, becoming a part of building or object it covers. Because of the increased air pollution (acid rain), patina that covers and protects bronze artifacts becomes more soluble. This is the reason why it has become necessary to protect the patina that covers bronze artifacts. In order to preserve metal works from the aggressive atmosphere, organic inhibitors are often required. Many inhibitors are toxic, so it has become a big concern to find new non-toxic inhibitors. Previous investigations have shown that imidazole derivatives are good copper corrosion inhibitors in different media. In this work the efficiency of a non-toxic organic inhibitor: 1-phenyl-4-methyl-imidazole, was examined on the Cu-6Sn bronze patina by the potentiodynamic methods and EIS, as well as by spectroscopic methods.

In order of studying the patina protection it is necessary to obtain an artificial patina with a defined chemical composition similar to the patina formed spontaneously in urban atmosphere. To gain a composition characteristic for patina obtained in urban atmosphere it was formed potentiostatically in an aerated solution composed of 0.2 g L\(^{-1}\) Na\(_2\)SO\(_4\) + 0.2 g L\(^{-1}\) NaHCO\(_3\) at pH 8.5 and 30°C. The SO\(_4^{2-}\) ions are one of the main pollutants in urban atmosphere due to the industrial activity and the emission by automotive vehicles. The morphology and crystallographic structure of artificially obtained patina were examined with SEM, EDS analyses and Raman spectroscopy. The results have shown that the patina consists of a crystallic structure of malachite and a smooth structure of copper and tin oxides.

The electrochemical measurements were made in the sulphate and carbonate solution, acidified to pH5 by addition of a dilute sulphuric acid, at room temperature. The results have shown that the studied environment friendly inhibitor efficiently protects Cu-6Sn bronze patina in sulphate-carbonate media.

Effect of compaction pressure on the behaviour of metal hydride pellet electrodes: New modelling

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Metal hydride alloys are commercially used in electrodes for rechargeable batteries. AB\textsubscript{5}-type alloys show high capacity and good kinetics in the hydriding/dehydriding reactions. These reactions occur on the metal particle surfaces, but the influence of the structural properties of the electrode such as porosity, active area and electrode length, affect the response of these electrodes.

In previous works [1] the constant current discharge response of these electrodes was simulated in terms of a physicochemical model based on the classical theory of flooded porous electrodes [2]. In this work the effect of structural parameters, determined by the compaction pressure during electrode preparation, on the discharge potential /time curves is analysed.

Working electrodes were prepared with Carbon Vulcan, PTFE and AB\textsubscript{5}-type alloy. Using a Helium Pycnometry method the dependence of the electrode porosity and volume with pressure was derived. The dependence of the active area per unit volume with pressure was calculated in terms of a model taking into account plastic deformation and fragmentation effects [3]. This analysis predicts a maximum in active area and porosity at low pressures, leading to an improvement in discharge performance and rate capability with diminishment of the compaction pressure.

Experimental data show these effects too, but these electrodes have a limiting low pressure when a disaggregation effect appears.

References

Acknowledgments
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Electrocatalysis of the Hydrogen Oxidation Reaction on W₂C-Dispersed Platinum Catalysts in Acid Medium

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Tungsten carbide dispersed on a high surface area carbon (W₂C/C) prepared by a sonochemical method in two compositions (10% and 60% W₂C/C, nominal) was used as supports of Pt-based electrocatalysts (Pt-W₂C/C). The resulting materials were tested as catalysts for the hydrogen and CO oxidation reactions in acid medium. The catalysts were analyzed by EDX (energy dispersed X-ray) and X-ray diffraction (XDR) analyses. The electrochemical techniques considered were cyclic voltammetry, steady state polarization curves and linear sweep curves, obtained utilizing an ultrathin catalyst layer in a rotating disk electrode (RDE). A remarkable activity for the hydrogen oxidation reaction was observed for the W₂C/C supports, as shown in Fig. 1a. In the case of the Pt-W₂C/C catalysts, an increased electrocatalysis for the hydrogen oxidation reaction was observed, when compared to the standard Pt/C material (Fig. 1a). For Pt-W₂C/C (10 % W₂C/C) the reaction mechanism is the direct discharge process, similar to Pt/C (Figure 1b), while for Pt-W₂C/C (60 % W₂C/C) the mechanism is composed by the Heyrovsky-Volmer steps. The most probably mechanism for the 10 % W₂C/C support is composed by the Heyrovsky-Volmer steps at low overpotential and the direct discharge irreversible mechanism at high overpotentials (Fig. 1c).

Fig. 1(a). Steady-state current-potential plots for the hydrogen oxidation at 300 rpm rotation speed, in 0.5 molL⁻¹ H₂SO₄ solution; (b) Mass transfer corrected Tafel plots assuming reversible kinetics for the hydrogen oxidation on Pt-W₂C/C. (c) Mass transfer corrected Tafel plots assuming irreversible kinetics for the hydrogen oxidation on W₂C/C.
A method for detoxifying industrial wastes is presented, aiming at a safer management and reuse. Focusing, in particular, on bottom ashes from a Municipal Solid Waste Incinerator (MSWI), the proposed treatment allows to extract soluble salts (e.g. chlorides), “washing” the ash by means of an electric field, instead of water, and using the same electric potential to move ions and let stabilizers (e.g. phosphate anions) to react with metal ions. The paper presents the results of six experiments, which were carried out varying the voltage between the electrodes (2-2.4 V cm⁻¹), the amount of phosphoric acid (0.9-1.5% – weight of acid/weight of ash) and fixing the time of treatment (24 hours). A significant leaching reduction was observed after each electrochemical test, namely 92% for Pb, 97% for Ba, 90% for Cu and 80% for chlorides; the latter are oxidized at the anode, and definitively leave the ash in the form of gaseous chlorine.
A new resistant alloy based on titanium was obtained. This alloy contains components, which directly facilitate the passivity (Ni and Mo), and a noble element (Pd) which decreases the cathodic processes. The effects of the alloying elements are to confer a very high stability, a good anticorrosion resistance, avoiding the environmental pollution by corrosion.

The new Ti-0.8Ni-0.3Mo-0.1Pd alloy was obtained by high vacuum melting, in electric furnace; it is an un-polluted, clean method.

The electrochemical behaviour of this alloy in comparison with titanium in aggressive acid environments (10% acid oxalic, 1% and 10% hydrochloric acid and 5%, 10%, 20% and 30% sulphuric acid) at different temperatures (25°C, 50°C and 75°C) was studied using electrochemical potentiodynamic and linear polarisation methods.

The effects of the alloying elements on the electrochemical behaviour of Ti-0.8Ni-0.3Mo-0.1Pd alloy are to shift the open circuit potential to more electropositive values and leading to self-passivation by the forming on its surface of a compact, protective titanium dioxide film. This passive layer improved all electrochemical parameters of the corrosion processes in studied acid solutions and decreased very much (hundred times) the alloy corrosion rates in comparison with base metal (Ti).

Modeling of the alloy electrochemical behaviour in sulphuric, hydrochloric and oxalic acid solutions resulted different mechanisms for the formation of protective titanium dioxide (TiO₂): in sulphuric acid solutions, titanium oxidizes as Ti⁴⁺ ions and then formed TiO₂ oxide; in hydrochloric acid, titanium directly oxidizes to Ti³⁺ ions and then to Ti⁴⁺ ions, forming compact, protective TiO₂ oxide; in oxalic acid, titanium succeeds all its valence states, respectively II, III and IV, finally resulting the same resistant TiO₂ oxide. This passive film provides a high resistance against the corrosion in acid environment.

Using this alloy for to produce the chemical reaction vessels, tanks, cisterns, etc., their service life will increase. On this way, the pollution due to the corrosion will be reduced, the production costs will decrease and the natural resources will be preserved.
Electrochemical Corrosion Resistance Modeling of Some Alloys for a Clean Industry

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A healthy planet means to protect the environment, to prevent the pollution by the obtaining of the usual materials by clean technologies, by using of long life materials for to save the natural resources.

The new Romanian Ti-0.5Mo-1Ni alloy was obtained (by vacuum clean technology) in casting (Ti-0.5Mo-1Niₜ) and forging (Ti-0.5Mo-1Niₕ) state with the aim to provide long term anticorrosion resistance in acid, neutral and alkaline aggressive chemical liquids, preventing the pollution in different industries.

This passive alloy revealed a better corrosion resistance than titanium, due to the insoluble compounds of the alloying elements, which are incorporated in its passive film and consolidate this layer.

In concentrated chloride solutions (30%KCl, 23%NaCl, 25%NH₄Cl, 60%CaCl₂.6H₂O, 50%MgCl₂.6H₂O, 40%LiCl.6H₂O, 30%AlCl₃.6H₂O, 20%CuCl₂.2H₂O, 20%NiCl₂.6H₂O) at 23°C, 50°C and 75°C, the Ti-0.5Mo-1Ni alloy has lower corrosion rates than titanium and does not present pitting corrosion, being very resistant.

In sulphuric acid solutions of different concentrations (5% – 30%) and temperatures (23°C – 75°C), the stability of the alloy passive film is improved by the enlarging of the passive potential range, the decreasing of the dissolution current density and of the corrosion rates. The alloy is more resistant than the pure titanium.

In very concentrated (5% and 10%) oxalic acid at high temperatures (until 75°C), all electrochemical parameters of this alloy are better than of the base metal. Also, its corrosion resistance is higher than of titanium, in “very stable” domain.

In alkaline solutions of 5% and 25%NaOH, 10% and 25%KOH and saturated Ca(OH)₂ at 75°C, the alloy corrosion rates have very low values and, therefore, Ti-0.5Mo-1Ni alloy is very resistant in all these environments.

The metallurgical working by forging improved the resistance of the passive film to the corrosion in acid, neutral and alkaline solutions. This fact is confirmed by the corrosion rates, which show that the forging alloy is more resistant than the casting alloy.

It resulted that Ti-0.5Mo-1Ni alloy, apart from its low corrosion rate in many aggressive solutions, has good mechanical properties and is by the mechanical and economical interest to use this alloy in many industries for to reduce the quantity of corrosion products and to protect the environment.
Effect of Solution Concentration and pH on Tartrate Ions
Transport Properties through an Anion-Exchange Membrane

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Electrodialysis has been used as electrochemical membrane technique to concentrate tartaric acid from ion-exchange regeneration waters obtained in grape juice treatment in order to decrease the effluent pollution and recover their insoluble salts. To assure a good performance of this process is useful to know the transport number of the ions through the ion-exchange membranes. It is also important to respect some specific conditions of the electrochemical processes such as the limiting current density. So in this work the limiting current density and the transport number of tartrate ions through a commercial anion-exchange membrane were determined by current-voltage curves. The effect of solution concentration and pH was evaluated. The transfer of tartrate ions from the feed solution to the concentrated one was also evaluated using a cation-exchange/anion-exchange membrane pair electrochemical cell. The obtained results show that the solution concentration and pH affect the limiting current density value. While the limiting current density increases with the increase of the tartrate ion concentration in solution it decreases with the decrease of the solution pH. The obtained results revealed also that the tartrate transport number through the membrane is similar for the evaluated range of concentrations (0.01 – 0.05 M). However it is lower than the transport number of chloride ions. The estimated tartrate ion transport number through the membrane was 0.76 while the chloride ion transport number for the evaluated membrane is 0.95. The electrodialysis experiment shows that the transfer of tartrate ions from the feed solution using a fixed current density depends on the experimental time. With 3 hours of electrodialysis approximately 43% of tartrate ions were transferred from the feed solution to the concentrated one using a current density of 3.6 mA/cm².


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Adsorption of Human Blood Plasma Proteins and Oligonucleotides at the Titanium Surface

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Titanium is frequently used as a biomaterial for hard tissue replacement, such as dental and orthopaedic implants. The surface morphology influences the final interactions of the implant with the surrounding environment. Since most implants are exposed to blood during implantation, the initial protein film is mainly composed of plasma proteins. We have investigated the application of diffraction optical element (DOE) in aim to investigate permittivity change and fluctuation in optical roughness of titanium surface when this biomaterial surface is located in the immersion or buffer liquid. The DOE sensor utilises non-coherent response for permittivity changes and coherent response for optical roughness changes. We have started with the investigation of adsorption of oligonucleotides. The effect of solvent and mechanical (polished, etched and/or gritted surface) or chemical modification of titanium surface on the purine (AAG) and pyrimidine (TTC) oligonucleotide adsorption are determined. The adsorption of human blood plasma proteins on the titanium surface was studied using ODE, ellipsometry and electrochemical methods.

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Conducting polymer composites are in the focus of researches. These new materials give perspectives for various applications by combining together the different properties of the individual components. Recently synthesized representatives open opportunity for the combination of electrical and optical, magnetic or photocatalytic properties, leading to electrodes of special capabilities.

We present the characteristics and possible applicability of different nanocomposites such as
- poly(3-substituted thiophene)/maghemite (POT/ $\gamma$-Fe$_2$O$_3$) and magnetite (PAcT/ Fe$_3$O$_4$)
- polypyrrole/iron oxalate (PPy/Fe-ox)
- polypyrrole/vitamin B12 (PPy/B12).

The composites are characterized on the basis of different electrochemical measurements, including EQCM and a.c. impedance, as well as by ICP-AAS, UV-Vis spectroscopy, XRD, XPS, SEM, EDX.

Iron containing polymer composites are promising as new electrodes possessing magnetic and/or photocatalytic behaviour. The enhanced redox activity of cobalamin, immobilized in PPy/B12 composite electrode, may be exploited in mediated reduction processes in bio-electrochemical systems.

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Environmental electrochemical engineering: protecting the planet

Electrochemical Oxidation Treatment of Refractory Organic Pollutants in Aqueous Media

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There are many industries which discharge wastewaters with certain pollutants which cause a serious impact to the environment. High molecular weight organic, such as lignin and humic acid are the typical refractory pollutants always cause high strength of chemical oxygen demand (COD) and color in wastewater [1,2]. Also, the high molecular weight organic, are poorly biodegradable and consequently, they often remain in the effluents. Therefore it is necessary to find effective methods to degrade such pollutants.

The electrochemical oxidation of lignin and humic acid in aqueous media has been investigated. Electrochemical oxidation process was performed by potentiostatic electrolysis with electrodes type dimensionally stable: Ti/RuPb(40%)Ox as cathode and Ti/PtPd(10%)Ox as anode. The wastewaters investigated in this study were prepared at laboratory using pure chemical, including lignin (Sigma) and humic acid (Merck) in aqueous media. The pollutant concentration in the synthetic wastewater was 0.25 g L⁻¹ and sodium chloride was used as the supporting electrolyte.

The operating factors such as potential difference, sodium chloride concentration, pH and electrolysis time on the degradation of contaminants has been studied. The process effect has been followed through the dependence of chemical oxygen demand (COD), color and Total Dissolved Solids (TDS). The results suggested that the Ti/PtPd(10%)Ox anode has the highest electrocatalytic activity and increasing with chloride concentration and electrolysis time, consequently both COD and color removal efficiencies were improved.

References
Experimental and theoretical investigation of the adsorption behaviour of new triazole derivatives as inhibitors for mild steel corrosion in acid media

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Three triazole derivatives (4-chloro-acetophenone-O-1′-(1′,3′,4′-triazolyl) metheneoxime (CATM), 4-methoxyl-acetophenone-O-1′-(1′,3′,4′-triazolyl) metheneoxime (MATM) and 4-fluoro-acetophenone-O-1′-(1′,3′,4′-triazolyl) metheneoxime (FATM)) have been synthesized as new corrosion inhibitors for the corrosion of mild steel in 1M HCl solutions. The inhibiting efficiency of the different inhibitors is evaluated by means of weight loss and electrochemical techniques such as electrochemical impedance spectroscopy (EIS) and polarization curves. Then the surface morphology was studied by scanning electron microscopy (SEM). The studied compounds following the Langmuir adsorption isotherm, and the thermodynamic parameters were determined and discussed. The effect of molecular structure on the inhibition efficiency has been investigated by ab initio quantum chemical calculations. The electronic properties such as highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) energy levels, energy gap (LUMO–HOMO), dipole moment and molecular orbital densities were calculated.
The tremendous increase in worldwide energy consumption, along with the threat that fossil energy resources might soon run out, have encouraged the search for alternative energy sources. However one of the main drawbacks renewable energy projects has to face these days is the extraordinary cheap price of fossil energy, disregarding the consequential damage costs of its production and consumption. The field of photovoltaics is of major importance among renewable energy sources, as solar energy is largely abundant, surpassing our present global annual energy needs. Harnessing this enormous potential of free energy represents an exciting challenge to scientists and politicians as well as the global economy. One promising technology is the solar cell based on the sensitization of mesoscopic oxide films by dyes.

TiO$_2$ electrode coated with a thin film of SrTiO$_3$ was synthesized for photoelectrochemical application and was analyzed by several methods including $J-V$ curves and photovoltage decay measurements under short-circuit condition. The results indicate that the TiO$_2$-SrTiO$_3$ core-shell electrodes provide a significant increase in photovoltage due to a minimization in the recombination reaction (recombination of the photoinjected electrons with the dye cation) resulting in an improvement of the conversion efficiency of the solar cell.

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Direct versus indirect electrochemical oxidation of pesticide polluted drainage water containing sodium chloride

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Drainage water from a depot of chemical waste, polluted with a mixture of organophosphates and degradation products was treated by a direct as well as an indirect electrochemical method using a Ti/Pt-Ir anode and Stainless Steel 304 cathode. With a concentration of 0.7%, sodium chloride was the main electrolyte. The direct electrochemical treatment showed a first order degradation of COD with an optimal energy consumption of 110 kWh/kg COD. At constant current, addition of sodium chloride resulted in increased degradation up to 2%, whereas no further degradation was obtained at higher concentrations. Analyses of the actual pollutants, Me-Parathion, parathion, malathion and degradation products, confirmed that the concentrations of all initial pollutants were eliminated during the treatment. The only exception was O,O,O-triethyl-phosphoric acid, a degradation product which was formed during the treatment. Indirect electrochemical treatment, where a highly oxidized brine solution was added to the drainage water, revealed immediately reduction in COD, and similar to the direct treatment, degradation of all of the pesticide pollutants was obtained except for the O,O,O-triethyl-phosphoric acid.

The experiments proved that the obtained degradation of pesticide solely was caused by indirect electrochemical oxidation, mainly due to the electrolytic formation of hypochlorite during the treatment, and that direct electron transfer from the pesticide substances at the anode surface didn’t significantly contribute to the degradation. Experiments with addition of aqueous sodium hypochlorite solution to the drainage water revealed that hypochlorite was the main oxidizing agent responsible for the indirect oxidation.

The experimentally obtained results for the pesticide degradation were compared to theoretic calculations of rate constants using the actual experimental conditions and reactor design. These calculations showed that assuming first order degradation rate, direct oxidation of the non-ionic pesticide substances due to mass diffusion, despite of
Electrochemical Studies of Cephalexin Using Dimensionally Stable Anodes

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Process of water treatment practised in the Stations of Treatment of Effluents (ETEs) has not been efficient in the soluble and recalcitrant antibiotic removal, needing new technologies for removal of these pharmacs. Electrochemical processes using dimensionally stable anodes (A.D.E.®), that is, immobilized conducting oxides in metallic titanium, showed to be efficient and promising in this direction. Behavior of electroxidation of the antibiotic cephalexin (CFX) was investigated in the presence of materials of electrodes of different nominal compositions, such as Ti/RuO₂, Ti/Ru₀.7Ti₀.3Ο₂ and Ti/Ru₀.3Ti₀.7Ο₂, in buffer solutions of pH 2.10 (citric acid/Na₂HPO₄) and pH 4.70 (CH₃CO₂H/CH₃CO₂Na). Chemical stability of CFX was investigated through spectrophotometry, whose absorbance was monitored at λ=260nm for a period of up to 24 hours. This study was carried out in buffer solutions of pH 2.10 and 4.70 and showed that CFX remained stable. Electrochemical experiments have been carried out through a potenciostate/galvanostate, using as reference and counter electrodes the Ag/AgCl, sat. and a wire of platinum, respectively. The working electrodes were Ti/RuO₂, Ti/Ru₀.7Ti₀.3Ο₂ and Ti/Ru₀.3Ti₀.7Ο₂. Studies at various scan rates (ν) were carried out between 20 and 120 mV s⁻¹, whose graphical analyses of current vs. ν¹/², showed that the electroxidation of 2.01x10⁻³ mol dm⁻³ CFX occurs via diffusional control for all investigated nominal compositions of electrode. Studies of concentration of CFX as a function of catalytic anodic current showed that at higher concentrations than ~2.00 x10⁻³ mol dm⁻³ of CFX, it occurs the formation of a current plateau, suggesting the formation of an organic film that block the active surface sites for the three investigated electrode materials. The highest catalytic activity for the electrodegradation of CFX was showed by the Ti/RuO₂ electrode. Kinetic studies carried out using the electrode of composition Ti/RuO₂ showed that the electrodegradation of CFX is of pseudo-first order.

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Formation of Ultrathin Films on Au(111) used as Electrocatalysts for Nitrate Reduction

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The reduction of nitrate ions present in the groundwater has attracted special attention due to environmental problems such as over-fertilization and the increasing costs of the purification of drinking water. For this purpose, the electrochemical method has demonstrated to be a useful tool [1]. Furthermore, it is well known that the modification of the electrode surfaces by metal adatoms is an effective way of enhancing their electrocatalytic activity [2].

In the present work a Au(111)/Ag/Cd heterostructure was prepared by sequential electrochemical deposition of Ag and Cd on a Au(111) substrate, and analyzed by in situ STM and conventional electrochemical techniques. The catalytic effect of this structure for the reduction of nitrate ions was also investigated and compared with the response obtained for the structures Au(111)/Ag and Au(111)/Cd.

The results indicated that it was possible to prepare a bimetallic ultrathin film consisting of Au(111)/1 ML Ag/1 ML Cd. This system had the advantage that both metals (Ag and Cd) present separated UPD (Under Potential Deposition) regions, and their depositions occur following a layer by layer mechanism. In situ STM images showed that the subsequent Cd deposition on a modified Au(111)/Ag substrate, started with the growth of step edges and the formation of Cd islands until a monolayer was completed at potential values near the equilibrium potential of Cd/Cd$^{2+}$. The topography of the underlying Ag layer was practically reproduced by the Cd layer. It was also demonstrated that this heterostructure could be transformed into an alloy structure depending on the polarization conditions.

The behavior of this ultrathin bimetallic film in nitrate anions containing solutions indicated a much higher catalytic effect than the structures Au(111)/Ag and Au(111)/Cd, exhibiting a synergistic effect of both metals. In the later case, the electroreduction of nitrate ions occurred at even lower overpotentials. The reaction products were also analyzed.

References
Evaluation of Nafion-SiO₂ Hybrids as Electrolytes in PEMFC operating at High Temperature

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Nafion-SiO₂ hybrid membranes were prepared by the incorporation of SiO₂ into commercial Nafion 115 and evaluated as electrolytes in H₂/O₂ proton exchange membrane fuel cells (PEMFC). Hybrid membranes were produced by in-situ sol-gel method with different SiO₂ contents by using Tetraethyl Ortosilicate (TEOS) as the silicon precursor. The catalytic parameters, such as the nature of alcohol (methanol, ethanol, and 2-propanol); concentration of the acid catalyst (HNO₃, 0.2-2.0 mol L⁻¹); reaction temperature (25-90°C); and the precursor concentration (0.5-2.0 mol L⁻¹) were studied. Gravimetric analysis revealed that degree of incorporation of SiO₂ is in the 4-10 wt% range. The obtained values are strongly dependent, mainly, on both the alcohol nature and TEOS concentration. Energy dispersive X-ray analysis (EDX) showed that the inorganic phase is well distributed across the membrane thickness, indicating that the synthesis methodology provides homogeneous dispersion of the nanoparticles into the polymeric matrix. The stability of the hybrids was evaluated after successive washings in H₂SO₄ 0.5 mol.L⁻¹ and water at 70°C employed to remove surface residues. The water uptake data have showed a ~50% increase for the hybrid membranes in comparison to Nafion 115. Gas diffusion electrodes were prepared with Pt/C catalyst (E-TEK, 20 %wt) with a loading of 0.4 mg cm⁻² for both anode and cathode. Polarization curves of fuel cells operating with water-saturated hydrogen and oxygen gases were obtained galvanostatically with 5 cm² electrode area single cells. Measurements were carried out in the 80 - 130°C temperature range with total absolute pressure of 3 atm (RH=100%) and at 130 °C with reduced relative humidity (RH = 75 and 50%).

Polarization curves show that the addition of an inorganic insulating phase has not changed significantly the ohmic drop polarization of fuel cells and up to 120°C both the pure Nafion and Nafion-SiO₂ hybrids display comparable performances. With further increase in the operating temperature to 130°C the performance of the Nafion-SiO₂ hybrid was maintained and, in contrast, the unmodified Nafion showed a pronounced decrease of the performance. Such different temperature dependence represents a performance of ~40% superior of the Nafion-SiO₂ hybrid at 130°C. This response is probably attributed to the higher water retention capacity of the hybrids, in agreement with the water uptake data.

In summary, hybrids based on Nafion-SiO₂ were effectively prepared by the incorporation of the inorganic phase into commercial Nafion by an optimized sol-gel route. A significant enhancement of the fuel cell performance was evidenced at 130°C, indicating that ionic conductivity was sustained at high temperature, probably, due to the increase of the water retention capacity of the hybrids conferred by the hygroscopic property of the SiO₂.

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Facetted Platinum Catalysts With Preferential Crystal Orientation For Low Temperature Fuel Cells

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The design and preparation of carbon-supported facetted platinum catalysts with preferential crystal orientation for PEM fuel cells are described. The nanomorphology and surface structure of the platinum catalysts were studied by using XRD, STM and SEM techniques. The characterization studies of the carbon-supported platinum catalysts reveal the presence of facetted platinum crystallites having a predominant (111)-type preferential crystal orientation.

In order to study the effect of platinum crystallite surface nanomorphology on the performance of a hydrogen/oxygen PEM fuel cell, two types of platinum/carbon electrocatalysts incorporated into gas diffusion cathodes were tested: (i) high surface area (111)-type facetted platinum crystallites electrodeposited on carbon substrates by applying a pulsating electrolysis technique, and for comparative purposes, (ii) commercial polycrystalline platinum crystallites supported on Vulcan XC-72 carbon, with a metal loading of about 0.2 mg/cm2.

Typical cell potential-current density curves for hydrogen/oxygen PEM single cells at 60 ºC and 1 atm gas inlet pressure show an improvement in the fuel cell performance with (111)-type facetted platinum catalysts as compared to that with commercial platinum catalysts. This improved performance should be assigned to the presence of (111)-type facetted platinum crystallites in the fuel cell cathode, which favours the four-electron route in the overall oxygen electroreduction process by diminishing the blocking effect of the electrode surface by intermediate peroxide species.

Acknowledgements
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In the present work, different coverage degrees of osmium nanodeposits were obtained by spontaneous deposition on Pt(100) and Pt(111). The catalytic activity of Pt(100)/Os and Pt(111)/Os towards the ethanol electrooxidation was investigated through cyclic voltammetry and these results are correlated with FTIRS studies. It is observed that Pt(111) showed better catalytic activity than Pt(100) for ethanol oxidation at lower potentials, after osmium modification. The complementary studies of composition of the reaction intermediates and products for ethanol oxidation, carried out by *in situ* FTIRS, suggested that this reaction can follow three different pathways on Pt(100)/Os and Pt(111)/Os, as a function of the osmium coverage degree. Thus, as can be seen in Figure 1, on low osmium coverages, the reaction takes place by cleavage of ethanol C–C bond (pathway 1); on higher osmium coverages, this reaction follows the way to produce acetaldehyde and acetic acid (pathway 2); and on an almost complete osmium layer (\( \theta_{Os} = 0.92 \)), the ethanol was directly oxidized to acetic acid at lower potentials (pathway 3).

![Figure 1: Scheme of simplified mechanistic pathways proposed for ethanol electrooxidation on: (—→) Pt(100)/Os and (—>) Pt(111)/Os.](image)


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