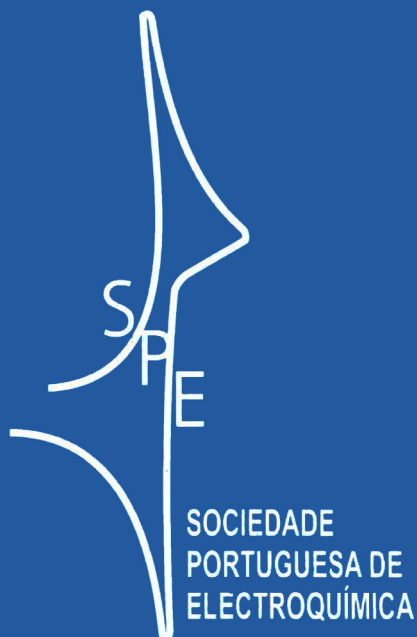


SPECIAL ISSUE

2012

ABSTRACTS BOOK

PORTUGALLIAE
ELECTROCHIMICA
ACTA



XIV Iberic Meeting of Electrochemistry
XVII Meeting of the Portuguese
Electrochemical Society

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XIV Iberic Meeting of Electrochemistry
&
XVII Meeting of the Portuguese Electrochemical Society

11-14 of April 2012

Funchal, Madeira Island – PORTUGAL

Abstracts Book

XIV Iberic Meeting of Electrochemistry & XVII Meeting of the Portuguese Electrochemical Society

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Editor

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(March 22, 2012)

Welcome Message

Dear Colleagues,

It is a great privilege and pleasure to welcome you to the **XIV Iberic Meeting of Electrochemistry (XIV IME) & XVII Meeting of the Portuguese Electrochemical Society (XVII MPES)**, in Funchal, Madeira Island, organized by the Sociedade Portuguesa de Electroquímica (SPE), Electrochemistry branch of the Real Sociedad Española de Química (RSEQ) and Centro de Química da Madeira (University of Madeira).

The islands of Madeira and Porto Santo were officially discovered by the Portuguese navigators Tristão Vaz Teixeira, Bartolomeu Perestrelo and João Gonçalves Zarco in 1419 and are considered the first territorial discovery of the period of the “Portuguese Age of Discovery”. With a subtropical-Mediterranean climate, a laurisilva forest considered by UNESCO a World Natural Heritage, 2170 km of levadas (aqueducts) to carry water from the northwest to the agricultural regions in the south, well served by infrastructures (airport, roads, industrial free zone, hospitals, university), and well connected by direct flights from the main European cities and other countries, the Madeira Islands attract not only tourists from all over the world and during the entire year but also people that want to work and live in a safe and beautiful region.

The main city, Funchal, with five centuries of history, located in a beautiful natural amphitheater, maintains the charming of the old times but remains open to the modernity. Together with one of the few and emblematic buildings that survives from the early period of Madeira colonization (the Gothic Sé Catedral de Nossa Senhora da Assunção from the late fifteenth-century), we are involved by the view of the white villas, tropical gardens, modern buildings and an astonishing sea view with modern cruise ships and ancient boats.

We wish to thank our colleagues and students who helped us with the organization of this meeting, and all institutions and organizations involved for their scientific, technical and financial support.

In the name of the Organizing and Scientific Committee, I welcome all of you in Madeira Island for the XIV IME & XVII MPES and wish you an enjoyable and very fruitful stay.

João Rodrigues,
Chairman of the XIV IME & XVII MPES.

Funchal, Portugal.

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Program

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17:00-18:30 **Registration** (Rectory Building - University of Madeira)

18:30-19:30 **Welcome Cocktail** (Rectory Building - University of Madeira)

THURSDAY, 12 OF APRIL

08:30-09:00 **Registration** (CS Madeira Atlantic Resort & Sea Spa)

09:00-09:30 **Opening Session**

09:30-10:30 **PL1: Victor M.M. Lobo**

“Batteries and super-capacitors for electric vehicles”

10:30-11:00 **Coffee Break**

11:00-12:00

Room A

OC1: Rui Neto

“Vanadium Redox Flow Cell Prototype Result”

OC2: Karel Vyřas

“Recent Investigations on Antimony-based Carbon Paste Electrodes in Stripping Electroanalysis”

OC3: Sorina Motoc

“Carbon-based Electrodes for Electrochemical Detection of Diclofenac”

Room B

OC4: Anamaria Baci

“Silver Modified Carbon Nanotube-based Electrodes for Non-enzymatic Detection of Glucose”

OC5: Joanna Juhaniewicz

“Studies on Electron Transfer Through Electroactive Peptides Self-assembled on Gold Electrode”

OC6: Maciej Karaskiewicz

“Mediator-free, Compartmentless Biofuel Cell Based on Laccase Bioconjugates and Glucose Dehydrogenase”

12:00-12:30 **KN1: Carlos Ruiz**

“Asymmetric Activated Carbon-MnO₂ Supercapacitors in Protic Ionic Liquids”

12:30-13:00 **KN2: Cristina Cordas**

“Electrochemical Behavior of Superoxide Reductases Enzymes”

13:00-14:30 **Lunch**

14:30-15:30 **PL2: Luis Gonçalves**

“From Photovoltaics to Food Quality Passing by the Voltammetry of DNA”

(Young Research Prize SPE 2011)

15:30-16:30

Room A

OC7: Yueh-Yuan Fang

“Control Atomic Ratio of Pt-Ir by Potentiostatic Electrodeposition”

OC8: Magali Camargo

“Electrodeposition of Zn-TiO₂ and Zn-SiO₂: Characterization of Dispersion Baths and Their Deposits”

OC9: Mikhail Zheludkevich

“Synergistic Corrosion Inhibition in Triple Galvanic Combinations”

Room B

OC10: Anca Mazare

“Influence of Anodizing Conditions and Morphology on the Electrochemical Behavior of Ti6Al7Nb TiO₂ nanotubes”

OC11: Javier Izquierdo

“In Situ Monitoring of the Electrochemical Reactivity of Ti-Mo and Ti-Ta Alloys for Biomedical Applications in Simulated Physiological Solution Using SECM”

OC12: Javier Molina

“Electrochemical Characterization of Conducting Fabrics”

16:30-18:00 **Poster Session & Coffee Break**

17:30-19:30 **General Assembly of SPE (Room A)**

FRIDAY, 13 OF APRIL

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“Novel Ti_{0.7}M_{0.3}O₂ Supports with Cocatalytic Functionality for Pt: Advanced Nanoelectrocatalysts for Fuel Cells”

10:00-11:00

OC13: Virginie Roche

“Apparent Potential-dependent CPE Behavior Caused by Geometry-induced Current and Potential Distributions”

OC14: Andrzej Sobkowiak

“Direct Electrochemical Transformations of Cholesterol”

OC15: Romana Sokolová

“On the Oxidation Mechanism of Flavonoids and their Stability under Ambient Conditions”

11:00-11:30 **Coffee Break**

11:30-12:00 **KN3: Ari Ivaska**

“Spectroelectrochemistry at Sensors and Sensor Materials”

12:00-12:30 **KN4: Angela Molina**

“Study of Multielectron Redox Processes by Cyclic Voltammetry and Square Wave Voltammetry at Disc and Spherical microelectrodes”

12:30-13:00 **KN5: Carmen Rangel**

“Effect of the Substrate on the Electrochemical Performance of LaNiO₃ Electrodes”

13:00-14:30	Lunch
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18h30-19:30	Poster Session & Coffee break
20:00	Conference dinner (Free for all registered participants and registered accompanying persons)

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10:20-11:00	Coffee Break
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Plenary Lectures

Victor M.M. Lobo



Victor M.M. Lobo is Professor Emeritus of Electrochemistry at the University of Coimbra, Portugal. Graduation (1963): University of Coimbra; assistant lecturer (1963-1966): University of Mozambique, then Portuguese East Africa; Ph. D. (1971): University of Cambridge, England; lecturer (1971-1980) and Professor (Prof. Catedrático) after 1980.

Titular member of IUPAC for 12 years.

Gold Medal for his diffusion cell, Switzerland 1987; Medal and Honorary Diploma from the Russian Academy of Sciences (2011).

Scientific books and more than 400 scientific papers and communications.

Batteries and super-capacitors for electric vehicles

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Electrical automobiles of practical use were developed after the commercial development of the dynamo, and consequently the widespread use of the rechargeable lead acid batteries (Pb/PbO₂), in the 1880's decade.

Several models will be referred, normally with Pb/PbO₂ batteries, and the advantages they then had over cars with internal combustion engines ("gasoline" cars) as well as cars with steam engines, will be discussed. Up to World War I, electric cars were, in England and in the East Coast of the USA, more popular than "gasoline" cars: for example, in the year 1900, only 1000 of these cars were sold, versus 5000 electric cars! Then, the electric automobile was dominant! Therefore, and against popular understanding, the widespread use of the electric vehicle is not a XXI century "invention".

What led to the decline of the use of the electric car in the 1910's (the last factory close in 1921, in the USA) will be discussed.

The reasons of the tremendous efforts in developing energy storage means of practical use for electrical road locomotion (batteries, super-condensers, etc.) after World War II will be presented, namely a NATO directive (ca. 1960) to implement more than 50% electric cars in Western Europe by 1980, in order to survive an eventual blockade of the flux of petroleum to NATO European countries.

The present situation of rechargeable batteries (Li-ion, Ni/NiH, etc.) and double layer super-condensers will be presented. Open space successful use of electric vehicles in specific conditions, such as the milk floats in England, garbage collection in urban areas, private cars in the Channel Islands, golf vehicles, etc., will be presented, in parallel with vehicles for closed atmospheres (mines, airports and indoor commercial spaces, etc.).

Luís Moreira Gonçalves



Luís Moreira Gonçalves (b. 1985) is a chemist and a post-doc researcher in Faculdade de Ciências, Universidade do Porto (FCUP), the same university where he has obtained his PhD degree (2011) supervised by prof. Aquiles Araújo Barros and prof. José António Rodrigues. His research interests are wide and include food analysis, analytical chemistry and electrochemistry. He has lived and worked in Tarragona (Spain), Prague (Czech Republic), Oxford (UK) and Araraquara (Brazil). He has published ca. 25 articles and 2 patents and has won several prizes including the Eng. António de Almeida award in 2008.

From photovoltaics to food quality passing by the voltammetry of DNA

Lúis Moreira Gonçalves

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The communication briefly covers 3 areas of research of the author's recent work where electrochemistry has played a major role: a) dye-sensitized solar cells (DSSC), a photovoltaic technology which very promising alternative for low cost production of energy, it is a successful attempt to create an anthropological analogous concept to photosynthesis whereas the photoreceptor and the charge carrier are different elements, state of the art DSSCs achieve more than 11% energy conversion allied to good performance under any atmospheric condition and low irradiance [1-2]; b) the use of graphitic surfaces (like edge-plane pyrolytic graphite electrodes, EPPG) for a bottom-up approach over the voltammetry of adenine and DNA [3-5], with a particularly interesting research detour where it was found that the voltammetric responses in surfaces of carbon could be tailored by electrode modification using adsorbed acetone to switch between adsorptive and diffusive modes [6]; c) food quality, namely the analysis by square-wave voltammetry (SWV) by means of a hanging mercury drop electrode (HMDE) of two relevant chalcones: xanthohumol, a phenolic compound present in hops [7] and cardamonin, a compound of large nutraceutical properties present in cardamon spice [8].

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Bing Joe Hwang



Bing-Joe Hwang studied chemical engineering and received Ph. D in 1987 at the National Cheng Kung University, Taiwan. Following a brief period as a project engineer at China Technical Consultants Inc., he joined the faculty of the department of chemical engineering at the National Taiwan University of Science and Technology as an associate professor in 1988: he was elevated to full professor in 1994. He has been a visiting professor at the University of Düsseldorf (Germany) and at the Massachusetts Institute of Technology (USA) in 1996 and 2002, respectively. His research work has spanned a wide range of subjects from electrochemistry to spectroscopy, interfacial phenomena, materials science and theoretical chemistry. He has established several experimental strategies for the development of new nanoscale materials with a particular emphasis on controlling their morphology, size, structure, and the compositional aspects that define their physical properties. His theoretical work has lead to a better understanding of reaction mechanisms on nanoparticles and to an improved ability to predict the properties of potential new materials for both Li-ion batteries and fuel cells. He has published more than 230 scientific papers in renowned international journals. The international research community acknowledges that the innovative research findings from him are important to the field of spectroscopic analysis. He is currently the president of the Taiwan Hydrogen Energy and Fuel Cell Association. He is a three time recipient of the outstanding research award (1997-1998, 1999-2000, and 2002-2004) from the National Science Council of Taiwan, R.O.C. Due to his excellent achievements in teaching and research and his substantial contribution to local industries, he has won: the 54th National Academic Award (2010) in Engineering and Applied Science given by the Ministry of Education of Taiwan, the 8th Y. Z. Hsu Scientific Chair Professor Award (2010) by Far Eastern Y. Z. Hsu Science and Technology Memorial Foundation, and the TECO award (2011) in Chemical Engineering and Materials Science awarded by TECO Technology Foundation.

Novel $\text{Ti}_{0.7}\text{M}_{0.3}\text{O}_2$ Supports with Cocatalytic Functionality for Pt: Advanced Nanoelectrocatalysts for Fuel Cells

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Due to the high energy yield and low environmental impact Proton Exchange Membrane Fuel Cells (PEMFCs) and Direct Methanol Fuel Cells (DMFCs) represent promising energy conversion technologies. At present, carbon black supported platinum (Pt) catalyst is used for both fuel and air electrodes in PEMFCs and DMFCs at anodes and cathodes.

However, several critical issues still need to be addressed before such cells can be commercialized for automotive applications. For example, the oxygen reduction reaction (ORR) is kinetically limited at the cathode and instability of Pt on the cathode is marked by the loss of Pt electrochemical surface area (ECSA) over time, due to Pt dissolution/ aggregation/Oswald ripening being the major contributors to the degradation of fuel cell performance. This work presents a new approach by exploring robust non-carbon $\text{Ti}_{0.7}\text{M}_{0.3}\text{O}_2$ as a novel functionalized co-catalytic support for Pt. This new approach is based on the novel nanostructure of the $\text{Ti}_{0.7}\text{M}_{0.3}\text{O}_2$ supports which supports an “electronic transfer mechanism” from $\text{Ti}_{0.7}\text{M}_{0.3}\text{O}_2$ to Pt that can modify surface electronic structure of Pt, owing to a shift in the d-band centre of the surface Pt atoms. Furthermore, another benefit of $\text{Ti}_{0.7}\text{M}_{0.3}\text{O}_2$ is the extremely high stability of Pt/ $\text{Ti}_{0.7}\text{M}_{0.3}\text{O}_2$ during potential cycling, which is attributable to the strong metal support interactions (SMSI) between Pt and $\text{Ti}_{0.7}\text{M}_{0.3}\text{O}_2$. Interestingly, $\text{Ti}_{0.7}\text{M}_{0.3}\text{O}_2$ can be fabricated as a much thinner catalyst layer, resulting in significantly improved the mass transport kinetics and performance of the resulting membrane-electrode-assembly (MEA). The new approach presented in this work opens a reliable path to the discovery of advanced concepts that may lead to the design of new catalyst materials that can replace the traditional catalytic structures and motivate further research in this field. [1,2]

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Juan M. Feliu



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Research interest deals with the establishment of relationships between surface structure and composition of metallic electrodes and its electrochemical reactivity, within the framework of Surface Electrochemistry and Electrocatalysis. Both aspects are believed to be strongly interconnected because interfacial properties govern reactivity. To achieve this purpose, single crystal electrodes are prepared and routinely used. The interfacial properties are characterized by using different structure sensitive probes. This method has been extended to rationalize the polycrystalline metal/solution interface, including nanoparticles. Surface composition is modified by adsorption of foreign adatoms in a controlled way. The electrocatalytic reactions under scope are strongly connected with the previous, more fundamental approach, and are mainly focused to the kinetics of oxidation/reduction of adsorbed poisons, oxidation of potential fuels and small nitrogen-containing molecules, as well as the reduction of oxygen and other green chemistry related species.

In relation to these subjects, more than 300 contributions have been published.

Former Chairman (1999-2002) of ISE's Division 1 (Interfacial Electrochemistry).

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Electrocatalysis on controlled surfaces

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A significant number of electrochemical reactions are surface structure sensitive. This means that the reactivity depends on the electrode surface order at atomic level. Even, in some cases, the reaction will not take place on the most efficient catalyst if the surface order is not the appropriate. Consequently, since electrocatalysts may be very expensive and rare materials, as platinum, the knowledge of this surface requirement is crucial for different applications [1].

The most convenient way to check the efficiency of a particular catalyst is by comparison with model surfaces, single crystal surfaces, in contact with a solution of similar characteristics as that used in the real application. In addition, for nanoparticles, the evaluation of the surface structure effect requires the preparation of shape controlled nanoparticles. However, because from fundamental studies it is known that surfaces should be clean to properly evaluate their reactivity, this surface cleanliness should be also maintained when dealing with these shape-controlled materials. Thus, if the surface contains uncontrolled adsorbates, its properties may change accordingly and these changes may be different in the different potential regions. Moreover, one of the most important parameters in Electrocatalysis, the current density, requires the knowledge of the real area of the catalyst that in turn requires clean surfaces to be evaluated [2,3].

Moreover, it is clear that nanoparticles may also contain special sites, different to those observed on model surfaces. To evaluate this effect, it is important to identify the contribution to each type of site to the overall response. In this respect, the estimation of stepped and kinked surface's reactivity becomes important. In some cases, hints of new reaction sites can be anticipated on relatively large nanoparticles with reasonable size and shape uniformity, for which classical size effects are not expected [4]. These studies aim to contribute to a better understanding of electrocatalytic materials for practical uses.

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Key Notes

KN 1

Asymmetric Activated Carbon-MnO₂ Supercapacitors in Protic Ionic Liquids

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Lately, electrochemical capacitors or supercapacitors (SCs) have attracted much attention for their power enhancement compared to batteries and fuel cells, and higher energy densities than common capacitors [1]. SCs use two kinds of energy/storage mechanisms: the double layer that exhibits a non faradic reaction with accumulation of charges at the electrode/electrolyte interfaces, and pseudocapacitance that stores charges via faradic redox reactions [2,3]. Among several transition metal oxides tested as electrode materials for pseudocapacitors [1,2,4], MnO₂ due to its low cost, satisfactory electrochemical performance, natural abundance and environmental compatibility is considered one of the most promising materials in many technological applications ranging from mobile devices to electric vehicles [2,5].

Because the presence of protons is preferred to achieve faradic reactions leading to pseudocapacitance, many studies of metal oxide-based SCs have been limited to aqueous solution [3]. Considering that the energy density (E) of a SC is proportional to the specific capacitance (Cs) and the voltage (V) [$E=C_sV^2/2$] [6], one strategy to enhance the cell voltage in terms of the energy density is to replace the aqueous electrolyte with protic ionic liquids (PIL), which show high ionic conductivity, large electrochemical window of stability, excellent thermal stability, nonvolatility and nonflammability [4,6]. In our work, two PIL obtained by a mixture of a base like 2-methyl or 2-methoxy-pyridine (2-MePy or 2-MeOPy) and an acid (TFA) were shown to sustain pseudocapacitance in MnO₂. Even if these PIL afford to obtain good Cs values, the maximum and minimum cutoff voltage for MnO₂ is limited by the oxidation process of Mn(IV) to Mn(VII) and by the reduction of Mn(III) to Mn(II) [7], that removes active material at each cycle from the electrode. The narrow potential window of these PIL (between 0.8 and 0.6V) limits the SC to reach high energy densities (E) values.

Another strategy [7,8,9], to overcome this problem is to increase the cell voltage by using an asymmetric configuration that combines two kinds of electrode materials: one electrode (Carbon based) stores charge by a reversible non faradic reaction and the other one utilizes a reversible faradic reaction in a transition metal oxide (MnO₂). In this contribution, we will report on the electrochemical behavior of a hybrid AC/MnO₂ supercapacitor in protic ionic liquid electrolytes. Further information about synthesis, characterization by SEM, XRD, CV and performance upon charge/discharge cycling will be reported. Further developments on task-specific ionic liquids for electrolytes in hybrid based supercapacitors are expected to increase their charge storage properties.

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Electrochemical Behavior of Superoxide Reductases Enzymes

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Superoxide Reductases (SORs) are enzymes involved in the protection mechanisms against oxidative stress caused by reactive oxygen species, being responsible for the one-electron reduction of O_2^- to H_2O_2 [1]. The electrochemical features of metalloproteins belonging to the different three classes of SOR enzymes were studied namely, Desulfoferrodoxin (Dfx) from *Desulfovibrio vulgaris* Hildenborough, (class I SOR), Neelaredoxin (Nlr) from *Desulfovibrio gigas* and *Treponema pallidum*, (classes II and III SOR, respectively). In addition, a small protein, Desulfiredoxin (Dx) from *Desulfovibrio gigas*, with high homology with the N-terminal domain of class I superoxide reductases, was also investigated. Also, a substitution of the iron on the center I of class I SOR by zinc was performed and the electrochemical features of the resultant protein were observed.

A comparison of the redox behaviour of all the SOR proteins is presented (Figure 1) and results points to SOR center II being thermodynamically more stable than similar centers in different proteins, probably related with a function of intra molecular electronic transfer [2].

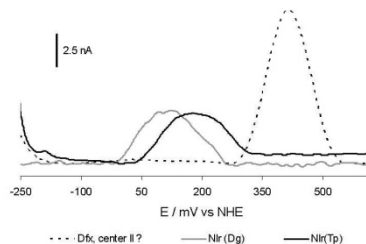


Figure 1. SWV of the three SOR enzymes, on anodic direction.

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KN 3

Spectroelectrochemistry at Sensors and Sensor Materials

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Conducting polymers are nowadays frequently used in chemical sensors [1,2]. Therefore their spectroelectrochemical characterization is of importance [3]. Polypyrrole and poly(3,4-ethylenedioxythiophene), PEDOT, are conducting polymers frequently used in chemical sensors. PEDOT has been electrochemically synthesized and characterized in ionic liquids [4] and polypyrrole has been studied by UV-VIS-NIR and Raman spectroscopy [5]. The pH sensitive properties of polyaniline has been studied by UV-VIS and Raman techniques [6-9]. Polyaniline has also been polymerized in ionic liquids on single walled carbon nanotubes [10]. In-situ UV-VIS-ESR technique has been used in studying charge transport and optical properties of poly[N-methyl(aniline)][11].

FTIR-ATR technique has been used in studying water uptake by PVC, polyacrylate and silicon rubber based ion-selective membranes [12,13]. Diffusion coefficients of water molecules were found to be different in the different membranes. The used technique also showed that water in the membrane has two different diffusion coefficients.

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Study of multielectron redox processes by Cyclic Voltammetry and Square Wave Voltammetry at disc and spherical microelectrodes

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The potential applications of molecules with several redox centers are widely recognized for example in energy conversion, molecular electronic devices, design of new materials and chemiluminiscent analytical methods. These molecules include biological species – such as metalloproteins, enzymes, oligonucleotides–, organometallic compounds, aromatic hydrocarbons and so forth. The differences between the formal potentials of the electron transfers (ΔE^0) and the comproportionation constants are indicative of the degree of interactions between the different redox centers. It has been also demonstrated that systematic variations in solvents and supporting electrolytes enable the change of the formal potential values leading to tailored sequentiation of ΔE^0 and /or the comproportionation constants [2]. Thus, extraction of ΔE^0 values can assist importantly the mechanistic and synthetic study of multielectron reactions [1, 2], giving information about the degree of interaction of the redox centers between them and with the surrounding species.

In this communication, we address the electrochemical characterisation of these systems via Cyclic Voltammetry (CV) and Square Wave Voltammetry (SWV) at microelectrodes of different geometries. Simple analytical equations for multistep reversible electrode processes under transient and steady state conditions are given. These equations are applicable to any electrode geometry both in the case of non uniformly accessible (microdisc) and uniformly accessible (microhemispherical) electrodes [3, 4].

We will also show that, although CV can provide adequate data for ΔE^0 , the SWV technique enables more accurate determination of the formal potentials due to the large reduction of ohmic drop and capacitive effects when SWV is employed together with small electrodes. Moreover, well resolved, peak shaped response is obtained even when microelectrodes are used, making the quantitative determination of experimental parameters more precise and easier.

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KN 5

Effect of the substrate on the electrochemical performance of LaNiO₃ electrodes

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It is well known that the nature and surface characteristics of the substrate play a very important role on the properties of oxide coatings. In this communication we report on a comparative study of LaNiO₃ oxide coatings on two substrates, Ni foam and carbon paper focusing on the properties for the development of a bifunctional oxygen electrode.

The choice of these substrates are due to their specific properties, namely in the case of Ni foam the possibility of high metal oxide loadings and dimensional stability. Concerning the carbon paper it is referred in the literature as ideal for the preparation of porous gas-diffusion electrodes providing extended reaction zones in the solid/liquid/gas interfacial region [1].

Open circuit measurements, cyclic voltammetry and electrochemical impedance spectroscopy were used to characterize the two kinds of prepared electrodes in alkaline media at room temperature, regarding oxygen reduction and water oxidation reactions. To complement the characterization optical and scanning electron microscopy were used.

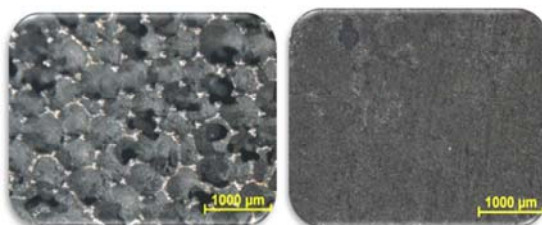


Figure 1. Morphological aspects of LaNiO₃ oxide coatings on Ni foam and carbon paper substrates.

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On the use of scanning microelectrochemical techniques to monitor the anti-corrosion performance of inhibitor films formed on copper

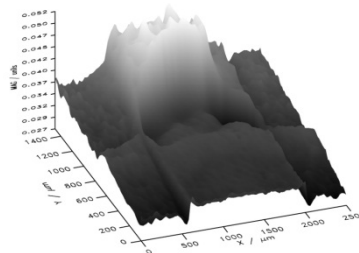
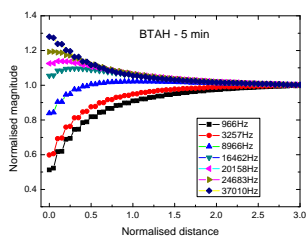
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In recent years, a variety of scanning microelectrochemical techniques has been introduced in the corrosion laboratory facilitating the spatially-resolved investigation of the corrosion reactions and the surface films involved in them, in the micrometric and submicrometric scales. Among them, the scanning vibrating electrode technique (SVET) and the scanning electrochemical microscope (SECM) are regarded the most suitable to gather new information on the anti-corrosion performance of inhibitor films formed on metals. This contribution reports on SECM and SVET studies of the surface films formed by benzotriazole (BTA) and 2-mercaptobenzimidazole (MBI) on copper, investigating the anticorrosion protection characteristics and stability of the layers formed in aqueous solutions. The samples were left unpolarized in the test medium, which was maintained at room temperature and open to air. SECM was operated in either the feedback mode, by adding ferrocene-methanol as redox mediator, or in the alternating current mode (AC-SECM), thus allowing for the surface conductivity properties of the copper-inhibitor films to be determined, and the surface chemical reactivity of samples displaying various regions with different inhibitor coverages to be imaged. On the other hand, SVET was used in order to measure the local distribution of the current density on the copper surfaces with and without inhibitor layers. In this technique, the ionic current flow due to metal corrosion results in a very minute electric field within an electrolyte medium, which can be imaged as the distribution of potentials and currents on the electrolytic phase in contact with the surface of the sample.



KN 7

Hydroxylation of benzoic acid by electrochemical generated hydroxyl radicals

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The generation of hydroxyl radicals is an important process in many applications such as organic synthesis [1], oxidative stress studies [2] and detoxification of effluents [3].

Due to the high instability of these radicals they are usually produced in situ by means of different methods, such as disproportionation of peroxyxynitrous acid or dissociation of hydrogen peroxide by UV action. The generation of hydroxyl radicals based on metal catalyzed decomposition of hydrogen peroxide, Fenton or Fenton-like reactions, is the most spread method.

The electrochemical generation of hydroxyl radical, as an intermediate in the oxygen formation from the oxidation of water is a well-known process. The ability of boron doped diamond electrodes (BDD) to produce hydroxyl radicals is extensively described on the oxidation of organics for wastewater [4]. Although the mineralization of several electroactive species is reported, the role of hydroxyl radicals in the initial phase of these reactions is not well established.

In this work we present a study on the performance of Pt and BDD anodes on the hydroxylation of benzoic acid (a non-electroactive species) comparatively to electroactive species, such as quinol and p-hydroxybenzoic acid.

The reactions were monitored by fluorescence, cyclic voltammetry and HPLC (UV detection).

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Cerium- and Praseodymium-Doped SrTiO₃ for Solid Oxide Fuel Cells Anodes: Redox Behavior and Electrochemical Performance

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Donor-doped strontium titanate-based perovskites are stable in a wide range of oxygen partial pressures, exhibit moderate thermal expansion and significant level of electronic conductivity under reducing conditions, and can be considered, therefore, as an alternative to conventional Ni-based cermets for solid oxide fuel cells (SOFCs). The present work was focused on the evaluation of Ce- and Pr-doped SrTiO₃ as components of SOFC anodes with emphasis of the electrochemical activity of porous anode layers and properties relevant for fuel cell applications.

Dense ceramic samples of Sr_{0.90-x}A_{0.10}TiO₃ (A = Ce, Pr; x = 0, 0.05, 0.10) with cubic perovskite-like structure were prepared via conventional solid-state synthesis route and sintered in air (1700°C), under reducing conditions (10%H₂-90%N₂, 1500°C), or reduced at 1500°C after sintering in air. Characterization of the ceramic materials included XRD, SEM/EDS, XPS, DSC, controlled-atmosphere dilatometry and thermogravimetry, measurements of the total conductivity (4-probe DC method and impedance spectroscopy) and Seebeck coefficient as function of temperature and p(O₂).

XPS studies indicated that cerium and praseodymium substitute into strontium sublattice in mixed 3+/4+ oxidation state. All prepared ceramics exhibit moderate, nearly p(O₂)-independent, thermal expansion (TEC = 11.5-12.0×10⁻⁶ K⁻¹) and rather negligible dimensional changes on reduction, ensuring thermomechanical compatibility of anode layers with common solid electrolytes and their dimensional integrity in redox cycles. Ce- and Pr-doped SrTiO₃ ceramics are n-type electronic conductors. Sintering or high-temperature treatment in reducing atmospheres results in significant level of electrical conductivity, which increases with introduction of cation vacancies into Sr sublattice and depends strongly on thermal pre-history of ceramics. At temperatures characteristic for SOFC operation, the transition between oxidized and reduced forms is kinetically stagnated, as indicated by the measurements of electrical properties and thermogravimetric studies, and associated, apparently, with a slow reconstruction of perovskite-related lattice.

Submicron Sr(Ce,Pr)TiO₃ powders for anode fabrication were synthesized by glycine-nitrate combustion technique. The electrochemical activity of porous Sr(Ce,Pr)TiO₃ and Sr(Ce,Pr)TiO₃+Ce_{0.9}Gd_{0.1}O_{2-δ} layers in contact with (La_{0.9}Sr_{0.1})_{0.98}Ga_{0.8}Mg_{0.2}O_{3-δ} solid electrolyte was evaluated using electrochemical impedance spectroscopy and steady-state polarization technique in atmosphere of diluted wet hydrogen at 600-900°C.

Oral Communications

OC 1

Vanadium Redox Flow Cell Prototype Results

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The utilization of renewable energy is subject to intermittency and so its use requires a correct integration into the electricity grid. At a country level the network fluctuations can be absorbed by reversible pumping at dams, but for small networks, especially for homes in isolated areas, antennas and other telecom applications the common solution are conventional lead acid batteries. The main limitations of these batteries are that electrical storage is connected to the power and the durability is limited to one thousand cycles of charge/discharge. To store large amounts electricity the energy storage should be independent of power capacity so the paper addresses the use of flow batteries.

Flow batteries are electrochemical devices where the electrolytes are stored outside the fuel cell constituted by the electrodes and an ion selective membrane across which ions are transferred generating a correspondent current of electrons through an electrical circuit. The electrolytes in the case of a Vanadium Redox Flow Batteries are redox couples in sulphuric acid as the negative and positive half-cell electrolytes respectively, that are expected to have about 10 times the cycles of conventional lead acid batteries. The vanadium battery consequently uses reservoirs to store two electrolytes (energy module) which are pumped through a battery stack (power module) where the electrochemical energy stored in the electrolytes is converted to electrical energy. By separating the power source (battery stack) from the energy source (electrolyte tanks) gives high flexibility for appropriate solutions adapted to end uses needs.

The present paper presents a series of activities based on literature [1-5] to build a prototype of a flow cell and perform its characterization. This work also presents a new process for the electrolyte preparation. This simplifies and reduces the production time of electrolyte compared to traditional processes reported in the literature. This work presents the results of the use of the electrolyte prepared including performance curves, charge / discharge of the cell and analyzes the relevant issues that affect its performance.

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Recent investigations on antimony-based carbon paste electrodes in stripping electroanalysis

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In the past decades, mercury-based electrodes have proved themselves as inevitable detection tools in electroanalysis thanks to their simple renewability, high selectivity, reproducibility and mainly, reliability in electrochemical stripping analysis. Despite the dominant position of these electrodes in stripping techniques and in electroanalysis as such, toxicity of mercury and especially its compounds has led to search some alternative and more environmentally friendly materials. Antimony belong to one of them; after some initial studies [1], the first successful attempt to prepare an antimony-based electrode was reported in 2007 when a glassy carbon fibre substrate was used [2] followed by antimony film carbon paste electrodes (SbF-CPEs) [3-5].

Antimony, as an electrode material, has proved an attractive electrochemical behaviour imposing the need for its further systematic investigation [6]. In this contribution, our very recent observations are presented and some new procedures of both stripping voltammetric and stripping chronopotentiometric determinations employing SbF-CPEs [7-12] are presented and numerous examples are given.

Acknowledgments: Support of Ministry of Education, Youth and Sports of the Czech Republic (projects MSM0021627502 and LC06035 is gratefully acknowledged.

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OC 3

Carbon-based electrodes for electrochemical detection of diclofenac

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The electrochemical oxidation and determination of sodium diclofenac (DCF) at multi-wall carbon nanotube-epoxy composite (CNTE) electrode was assessed in comparison with conventional glassy carbon (GC) envisaging a new alternative of quantitative determination of DCF in aqueous solutions. In comparison with GC electrode and our previous results[1,2], CNTE electrode exhibited enhanced electrocatalytic effect towards DCF oxidation, allowing its determination in aqueous solution with enhanced electroanalytical parameters. Figure 1 shows CVs recorded at both CNTE and GC electrodes in 0.1 M Na₂SO₄ and in the presence of various DCF concentrations. No oxidation peak was evidenced on GC electrode, while for CNTE electrode two peaks corresponding to DCF oxidation were noticed. The linear dependences of the oxidation peak current versus DCF concentrations were reached for the concentration range between 0.2 μM-20 μM. Also, the electroanalytical parameters for DCF determination at CNTE electrode were determined using pulsed voltammetric/amperometric techniques.

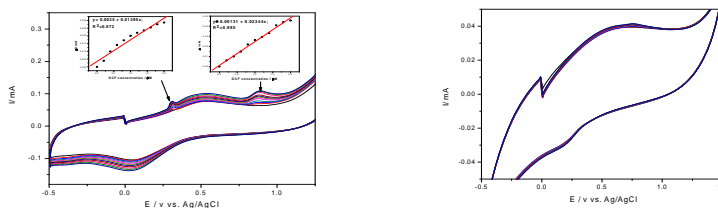


Figure 1. CVs recorded at a) CNT and b) GC electrodes in 0.1M Na₂SO₄ supporting electrolyte (curve 1) and in the presence of various IBP concentrations: 0.2 μM-20 μM (curves 2-11); potential scan rate of 50 mVs⁻¹. Inset a: Calibration plots of peak current vs. IBP concentration.

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Silver modified carbon nanotube-based electrodes for non-enzymatic detection of glucose

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This study is focused on the comparison of two types of multi-wall carbon nanotubes-based composite electrodes, one with silver nanoparticles decorated surface (AgCNT) and the other with silver-exchanged natural zeolite in composition (CNTAgZ), for non-enzymatic oxidation and determination of glucose. A similar behavior was recorded at both tested composite electrodes in the presence of glucose in alkaline medium, with a better electroanalytical performance for AgCNT electrode, *i.e.*, electrode sensitivity recorded by linear sweep voltammetry technique (see Figure 1) was 6.4 times higher and the limit of detection for glucose is 10 times lower at AgCNT electrode in comparison with CNTAgZ.

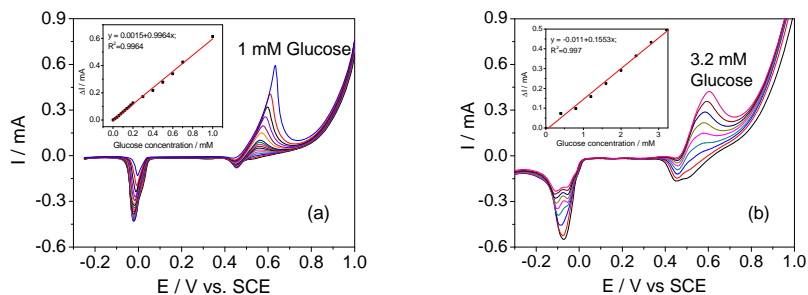


Figure 1. Linear-sweep voltammograms recorded in 0.1 M NaOH supporting electrolyte and in the presence of different glucose concentrations at (a) AgCNT and (b) CNTAgZ electrode.

Acknowledgments: This work was partially supported by the strategic grants POSDRU/89/1.5/S/57649, Project ID 57649 (PERFORM-ERA), POSDRU/89/1.5/S/63700 and POSDRU/88/1.5/S/50783, Project ID 50783, co-financed by the European Social Fund – Investing in People, within the Sectoral Operational Programme Human Resources Development 2007-2013 and partially by the PN-II-ID-PCE 165/2011 and PNII-RU-PD129/2010 Grants.

OC 5

Studies on electron transfer through electroactive peptides self-assembled on gold electrode

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Downscaling of electrical devices is nowadays one of the most important and rapidly developing branches of nanotechnology. The design, synthesis and characteristics of new nanostructural biomaterials are extremely important in the development of new technologies such as molecular wires, diodes, transistors or molecular switches [1]. One of the most promising tools to unravel the aforementioned electrical circuit elements seem to be peptides. Moreover, studies on electrical properties of peptides may also contribute to the development in the field of medicine. Most biochemical processes occurring in living organisms are based on electron transfer [2]. Understanding the mechanisms which determine its efficiency in biological systems is crucial for control of individual biochemical reactions. This is particularly important in the development of effective anticancer treatments or analytical biosensors.

We have designed and synthesized a short thiolated peptides derivatives containing tyrosine or tryptophan and cysteine residues. The compounds were further used for preparation of self-assembled monolayers on gold. The electrochemical and quartz microbalance measurements have provided information about the quality and properties of resulting films. In the next step we have used STM-based molecular junction approach, in order to determine the conductance of the peptides molecules. Based on the conductance measurements we have verified the influence of the oxidation state of the amino acid residue on the electron transfer efficiency.

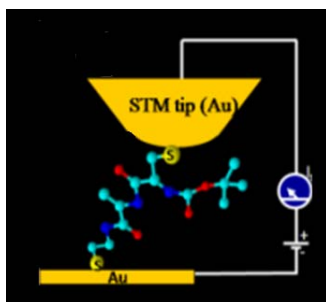


Figure 1. Gold-peptide-gold molecular junction formed using scanning tunneling microscope

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Mediator-free, compartmentless biofuel cell based on laccase bioconjugates and glucose dehydrogenase

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Biofuel cell is an electrochemical device that converts chemical energy into electrical using enzymes as catalysts and simple, natural substances e.g. glucose as fuel. [1,2] We modified the glassy carbon electrodes (GCE) with laccase from *Cerrena unicolor* bonded to single-walled carbon nanotubes (SWCNTs) or anchored on aromatic moieties covalently bound to arylated SWCNTs. [3] Such cathodes were successfully employed in the biofuel cell. The anode was GCE electrode decorated with pristine SWCNT and liquid crystalline cubic phase doped with glucose dehydrogenase (GDH) or GDH covalently attached to SWCNT. The highest power density of described devices was $131 \pm 4 \mu\text{W}/\text{cm}^2$.

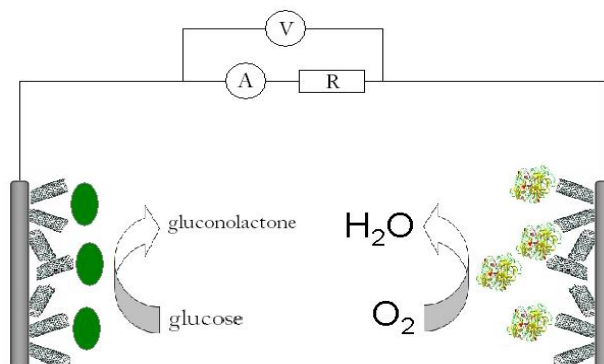


Figure 1. Scheme of biofuel cell constructed with previous described biocathodes and GDH-based (green objects) bioanodes.

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OC 7

Control Atomic Ratio of Pt-Ir by potentiostatic electrodeposition

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Pt-Ir alloy have excellent physical and chemical properties and highly catalytic activation so it is of intense interests to the applications of bioelectrodes [1], fuel cells and sensors [2]. Electrodeposition is one of the methods to deposit Pt or Ir thin film. Petrossians et al. provided a method to deposit different atomic ratio of Pt-Ir by cyclic voltammetry[1]. Otherwise, lack of study discusses about how to manipulate the atomic ratio of Pt-Ir by electrodeposition. In this paper, we demonstrate how to manipulate different atomic ratio of Pt-Ir by potentiostatic electrodeposition.

H₂PtCl₆•6H₂O (1g/L) in 0.01M HCl and IrCl₃ (10g/L) in 0.01M HCl were used as the electrolytes. Table 1 lists the parameters for electrodeposition. The atomic ratio of the Pt-Ir films was examined by X-ray photoelectron spectroscopy (XPS). Based on the XPS data, S1 (Pt₀Ir₁₀₀), S2 (Pt₁₀₀Ir₀), S3 (Pt₈₀Ir₂₀), S4 (Pt₆₇Ir₃₃), and S5 (Pt₈₃Ir₁₇) were successfully fabricated by electrodeposition (Figure 1). Further, the hydrogen absorption/ desorption characteristics (Figure 2) indicate that the Pt-Ir deposited by electrodeposition has more electroactive surface area than the Pt film deposited by e-beam evaporation. This property implies that the Pt-Ir fabricated by electrodeposition may have better performance as the catalytic layer in the future application.

Table 1. The electrolyte volume, applied potential (v.s. Ag/AgCl) and deposition time using for electroplating Pt-Ir. (Stirring rate: 100 rpm; Temperature:30°C)

	H ₂ PtCl ₆ •6H ₂ O (ml)	IrCl ₃ (ml)	Applied voltage (V)	Time (s)
S1	0	15	-0.7	7000
S2	15	0	-0.8	7000
S3	7.5	7.5	-0.65	7000
S4	7.5	7.5	-0.7	7000
S5	7.5	7.5	-0.8	7000

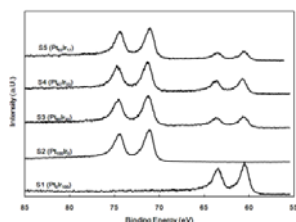


Figure 2. XPS data of S1~S5

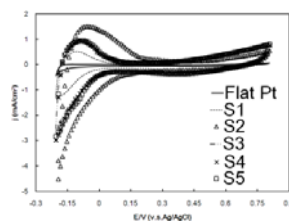


Figure 3. CV of flat Pt and S1~S5 in 0.5M H₂SO₄

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Electrodeposition of Zn-TiO₂ and Zn-SiO₂: characterization of dispersion baths and their deposits

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Electrodeposition of zinc dispersion coatings is a promising route for the production deposits that can provide improved corrosion resistance, hardness and wear resistance. An ideal dispersion coating involves the embedding of well dispersed particles in a metal matrix during the plating process. However, it is also possible to obtain deposits whose particles are only adsorbed or entrapped; these situations would not lead any significant enhancement of the composites properties [1].

In this work, the incorporation of SiO₂ and TiO₂ nano-particles into the zinc matrix will be studied in relation to the dispersion stability of the plating baths. Furthermore, the influence of cationic and anionic surfactants was investigated.

To study dispersion stability in chloride/sulphate based electrolytes, two important parameters were determined: size distribution and zeta potential of nano-particles at different pH values.

The electrodeposition experiments were carried out galvanostatically at different direct current densities currents at a rotating disk electrode.

Other studies about zinc dispersion coatings [2,3] have determined the incorporation of particles by using EDX technique. In this work, in order to get better information about the particle content in the deposits, the chemical composition of the layers was determined as depth profile analysis by glow discharge optical emission spectroscopy (GD-OES). The role of various process parameters (current density, surface charge of the particles, etc.) in the electrocodeposition process will be discussed.

Acknowledgments: *Deutscher Akademischer Austauschdienst (DAAD).*

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OC 9

Synergistic corrosion inhibition in triple galvanic combinations

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Multi-material approaches are promoted because of strategy of weight reduction of future vehicles aiming in the lower fuel consumption and consequently in the reduction of carbon dioxide emission. The light car design is based on application of new grades of high strength steels instead of mild steel and on use of other alternative materials with comparable mechanical properties and lower weight. Thus Mg alloys, Al alloys and carbon fiber reinforced plastics (CFRP) are considered by car producers for different structural parts of car body. These materials play an increasing role in construction of new aircrafts as well. However the galvanic corrosion can become a limiting factor for different multi-material applications in corrosive environments. The current anti-corrosion approaches are mainly suitable for single-material structures. The issue of effective corrosion protection becomes even more challenging when different multi-material combinations are used in the same structures. The need for active corrosion protection of different metallic structures calls for the development of new more efficient corrosion inhibitors. The most recent trend is to introduce the corrosion inhibitors into the protective polymer coatings aiming in active self-healing functionality [1].

In the present paper group of organic and inorganic corrosion inhibitors was investigated for different galvanic combinations of industrial relevance such as Al-Cu-CFRP and Zn-Fe-CFRP. Novel micro-electrode multi-metal array cells combined with Scanning Vibrating Electrode Technique (SVET) [2] were employed to study the kinetics and inhibiting efficiency. It was demonstrated that combination of inhibitors can provide an important synergistic effect when used in the case of galvanic couples. This effect is observed even in the cases when the same combination does not show any synergy on the uncoupled single metals. Moreover significant suppression of the cathodic electrochemical reaction on CFRP was observed in the cases of inorganic corrosion inhibitors.

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Influence of anodizing conditions and morphology on the electrochemical behavior of Ti6Al7Nb TiO₂ nanotubes

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Nowadays, TiO₂ nanotubes are relatively easily obtained by electrochemical anodizing [1]. However, the emphasis is on tailoring their morphology in order to better correlate with their intended applications. Furthermore, the morphology is also influenced by the metallic substrate, in our case Ti6Al7Nb – a two-phase alloy, which is well known for having a very good behavior in bioliquids.

The present study is focussed on tailoring the morphology of TiO₂ nanotubes obtained on Ti6Al7Nb alloy [2] and evaluating their electrochemical behaviour in Hank bioliquid [3]. By modifying the anodizing parameters (electrolyte, time, applied potential) different diameter and nanotube length TiO₂ nanotubes were obtained. Moreover, the presence of the α and β phase leads to different diameters on the sample – which in turn affects the electrochemical stability. Electrochemical behaviour analysis consisted of Tafel plots, cyclic voltammetry and electrochemical impedance spectroscopy.

Electrochemical behaviour data was correlated with morphology data obtained from Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), e.g. SEM images are shown in Figure 1, with the corresponding anodizing conditions.

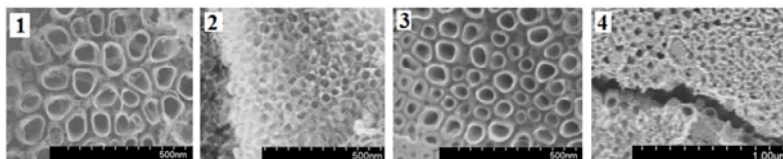


Figure 1. Nanotubes obtained in 1) 1M H₃PO₄ + 0.5wt.%HF, 20V, 2h; 2) 1:7 CH₃COOH:H₂O + 0.5wt.% HF, 10V, 2h; 3) 60:40vol.% Glycerol:H₂O + 0.5wt.% NH₄F, 20V, 2h; 4) Ethylene Glycol + 0.5wt.% NH₄F + 2M H₂O, 50V, 1h.

The aim of the morphological modification of the surfaces was done for further use in biocompatibility testing. Electrochemical tests showed that these modifications did not make the modified Ti6Al7Nb alloy susceptible to the corrosion phenomena on the studied potential range.

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OC 11

***In situ* monitoring of the electrochemical reactivity of Ti-Mo and Ti-Ta alloys for biomedical applications in simulated physiological solution using SECM**

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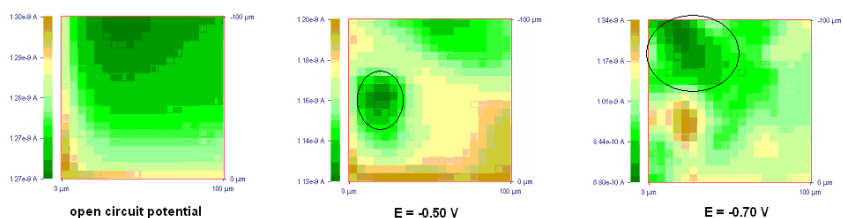
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Scanning electrochemical microscopy (SECM) was employed for in situ observation of electrochemical reactivity of various Ti-Ta and Ti-Mo alloys for biomedical application. In this work the differences in surface reactivity for different Ti-Ta and Ti-Mo alloys were analyzed when they were polarized in 0.1 M NaCl solution and Ringer’s physiological solution using SECM, and results compared to those for the unbiased samples. The analysis of the shape of the approach curves obtained for the Ti-Ta and Ti-Mo alloys shows different behaviors to be distinguished depending on the nature of the alloying element. There are also differences among the various Ti-Ta alloys tested, that originate changes in the shape of the approach curves with the value of the polarization applied to the substrate, defining a transition potential between -0.3 and -0.4 V vs. Ag/AgCl(3M) in most of the systems under study. Furthermore, from the line scans and array scans, a change in reactivity of the surface has been found corresponding to the activation of localized sites on the surface of the materials which occurs selectively with the applied potential.



Electrochemical characterization of conducting fabrics

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The development of fabrics with new properties and applications has received great attention during the last years; one of these properties is the electrical conductivity. Different methods have been employed to produce conducting fabrics, such as the synthesis of conducting polymers on the fabrics. Different works have been published concerning the production of polypyrrole (PPy) or polyaniline (Pani) coated fabrics to produce conductive fabrics. The applications of conducting polymer coated fabrics are numerous, such as: ammonia sensor, electromagnetic shielding, static charge dissipation, electromechanical devices, or precious metals recovery. Our research group has worked for years in this topic, as well as the employment of electrochemical techniques in the characterization of these materials, [1-7].

Electrochemical Impedance Spectroscopy (EIS) was employed to measure the conducting properties of original polyester (insulating) and the conducting fabrics.

Scanning Electrochemical Microscopy (SECM) has been applied for the first time in the study of the electroactivity of these materials, [4-7]. The conducting fabrics behaved like a conducting material, showing positive feedback. A study of the electroactivity with the pH was also performed, [5-7]. Higher pHs produce the deprotonation of conducting polymers and there is a decrease of its electroactivity.

Cyclic voltammetry (CV) was also employed to characterize the electroactivity of the conducting fabrics. It was shown the importance of the scan rate in the characterization of these materials, [4-6]. Higher scan rates such as 50 mV s^{-1} do not allow the observation of the characteristic oxidation and reduction processes of conducting polymers; on the other hand, lower scan rates (5 mV s^{-1} and 1 mV s^{-1}) allow their observation. The nature of these materials (conducting polymer on insulating polyester) makes the charge transfer process slower than when metal electrodes are employed. This is why the redox processes are only observed with lower scan rates.

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OC 13

Apparent potential-dependent CPE behavior caused by geometry-induced current and potential distributions

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CPE behavior is usually found in the literature to depend on experimental variables such as the electrode potential. In this work we show that this dependence may be not real but caused by the influence of geometry-induced current and potential distributions in the high frequency domain [1,2]. The crossover to this geometry-dominated regime establishes an upper cutoff frequency in the experimental frequency range employed to characterize CPE behavior from EIS measurements. In many circumstances this crossover may prevent the experimental results to reveal the real underlying CPE behavior and thus lead to erroneous conclusions as seen in Figure 1 for the estimation of the CPE exponent α : low overpotentials lead to the estimation of a biased 0.78 value instead of the actual 0.92. However, when corrections due to this effect are properly taken into account, our results show that CPE exponent α and characteristic capacitance C_0 can be independent magnitudes of the interface, i.e. not dependent on the applied potential. This conclusion is along the line of some proposed interpretations of CPE parameters.

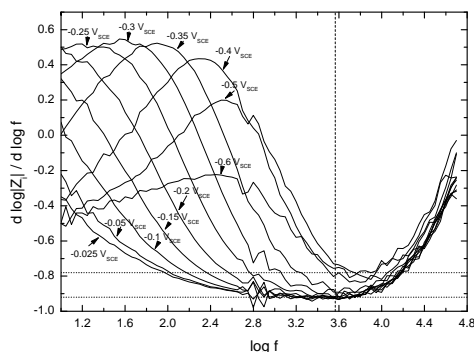


Figure 1. Behavior of α as function of the logarithm of frequency for different cathodic overpotentials. The results have been calculated from EIS data obtained with a rough Fe rotating disk electrode (3000 rpm) in 1M NaOH + 0.1M K₃[Fe(CN)₆] at 25°. Vertical dashed line indicates the upper cutoff frequency. Horizontal dotted lines indicates the values $\alpha=0.78$ (biased) and $\alpha=0.92$ (correct).

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Direct Electrochemical Transformations of Cholesterol

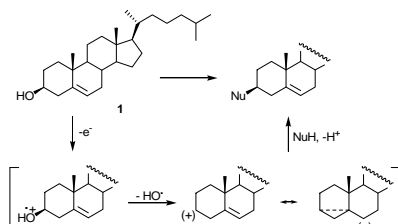
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Cholesterol is the most common steroid in our body. It can be subjected to different oxidative processes including oxidation of the hydroxyl group, the double bond, allylic oxidation and oxidation of the hydrocarbon part. Electrochemical oxidation of cholesterol (**1**) was studied during last two decades but most reports concern indirect oxidation with various mediators. Our study on direct electrochemical oxidation of cholesterol has shown that the process strongly depends on condition applied. Thus, the reaction performed on platinum electrode in glacial acetic acid led to allylic acetoxylation of cholesterol (at C7) [1]. The reaction carried out in dichloromethane in divided cell afforded dicholesteryl ether in relatively high material yield. Depending on electrolysis conditions (composition of supporting electrolyte and type of electrolytic cell applied) various by-products with 3 β -chloro, 3 β -acetoxy, and 3 β -acetyl amino groups were obtained [2]. The electrochemical oxidation of cholesterol proceeds probably at the oxygen atom. The cation-radical underwent heterolysis of the C3-O bond leading to the homoallylic carbocation, which can react with any nucleophile present in the reaction media.



An attempt to use carbohydrates as nucleophiles has shown the possibility of application of the new electrochemical method for glycoconjugates synthesis [3].

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OC 15

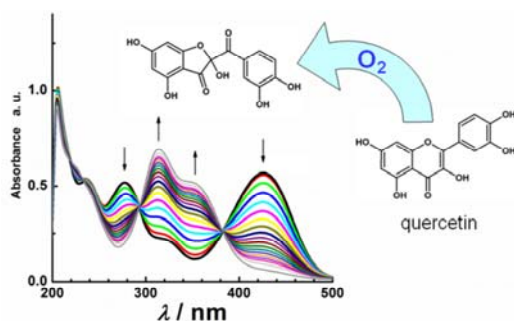
On the Oxidation Mechanism of Flavonoids and their Stability under Ambient Conditions

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Hematoxylin and quercetin belong to a large group of naturally occurring flavonoid compounds. These intensively colored polyphenolic compounds were used in the past as colorants in old tapestries [1,2]. This study concerns the analysis of degradation pathways and decomposition products of the original dyes by electrochemical means. Degradation products formed during the ageing process can be used



as fingerprints for the determination of the original color. The oxidation mechanism of hematoxylin is proposed. The electrochemical step is followed by subsequent chemical reactions, leading to hemathein [3]. The strong influence of air oxygen on the distribution of oxidation products of bioflavonoid quercetin was monitored by LC-MS and LC-DAD analysis. The oxidation mechanism of quercetin leads to the formation of 2-(3',4'-

dihydroxybenzoyl)-2,4,6-trihydroxybenzofuran-3(2H)-one [4], which further decomposes in several oxidation products in the presence of air oxygen [5]. The fast formation of oxidation products under ambient conditions is a crucial aspect not only in the analytical determination but also in the efficiency of these antioxidants on the prevention of diseases.

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Synthesis and electrochemical characterization of novel octupolar metallodendrimers

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Metal-containing dendrimers can provide an attractive strategy for the enhancement of electronic, photo-optical and biological properties of simple organic dendrimers [1].

Taking advantage of the electronic properties of *s*-triazines cores and the presence of two different metal moieties, our goal is to build-up new redox-active heterometallic dendrimers with improved non-linear optical properties (NLO).

In this work we will show our latest results in the synthesis and characterization of, 2,4,6-tris(((4-ethynylphenyl)ethynyl)phenyl)-1,3,5-triazine and 2,4,6-tris(4-ethynylphenyl)-1,3,5-triazine based, vinylidene-, alkynyl- and ferrocenyl-ruthenium metallodendrimers. The redox behaviour of these metallodendrimers were investigated by means of cyclic voltammetry and correlated with the NLO results.

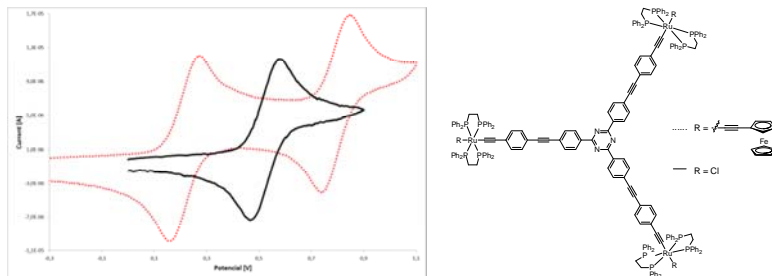


Figure 1. Cyclic voltammetry of the capped and uncapped zero generation metallodendrimer.

Acknowledgments: The Portuguese Fundação para a Ciência e a Tecnologia (FCT) is acknowledged for funding through the research project PTDC/QUI/64202/2006, the NMR and MS Portuguese Networks (REDE/1517/RMN/2005, REDE/1508/REM/2005), the pluriannual base funding of CQM (PEst-OE/QUI/UI0674/2011) and the Ph.D scholarship granted to M. Jardim (SFRH/BD/65036/2009). The support from CS Madeira is also gratefully acknowledged.

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Poster Communications

PA 1

Diffusion coefficients of hydrocortisone in different media

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Hydrocortisone (HC, cortisol), used in oral administration, intravenous injection or topical application is a drug with a great significance in many fields, among them medical and pharmaceutical applications. For example, its primary functions include increasing blood sugar through gluconeogenesis, suppress the immune system, and aid in fat, protein and carbohydrate metabolism. While some studies have been carried out on thermodynamic behaviour of this drug in cyclodextrins aqueous solutions of cyclodextrins (CD) [1, 2] (e.g., on evaluation CD solubilization of HC, having in mind its lower solubility [1]), as far as the authors know, no data on the mutual diffusion coefficients of this drug in aqueous solutions, containing or not cyclodextrins.

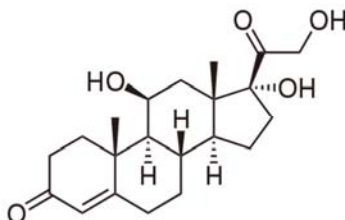


Figure 1. Structural form of hydrocortisone in aqueous solutions.

The present work intends to fill this gap with the experimental data of diffusion coefficients measured by the Taylor dispersion method for binary (HC/H₂O) and ternary systems (HC/CD/H₂O), at concentrations from (0.00 to 0.0008) mol.dm⁻³ of each component, at 298.15 K. From these data, we have estimated some thermodynamic and transport parameters, such as the hydrodynamic radius and ionic conductance the limiting diffusion coefficient for HC, as well as the number of moles of each component transported per mole of the other component driven by its own concentration gradient, contributing this way to a better understanding of the structure of these systems and of their diffusion behaviour in aqueous solution.

Acknowledgments: C.I.A.V.S. thanks the "Fundação para a Ciência e Tecnologia" for the SFRH/BD/45669/2008 PhD grant.

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Diffusion coefficients of paracetamol in aqueous solutions

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Paracetamol (PA, *N*-(4-hydroxyphenyl)acetamide) is a drug with a great significance in many fields, such as biomedical, medical and pharmaceutical applications. For example, it is an important analgesic drug and antipyretic agent, and in combination with opioid analgesics, it can also be used in the management of more severe pain such as post surgical pain and provide palliative care in advanced cancer patients.

Some studies have been carried out on the thermodynamics behaviour of drugs aqueous solutions, such as solubilities of paracetamol in organic solvents, at different temperatures [1], as well as the study of the dissolution behaviour of this drug in the presence of a range of selected potential excipients [2]. However, data on the transport behaviour of these systems are more limited, particularly in what concerns diffusion coefficients in aqueous solutions.

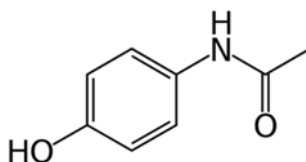


Figure 1. Structural form of paracetamol in aqueous solutions.

The present work intends to fill this gap with the experimental determination of binary diffusion coefficients, D , measured by the Taylor dispersion method, for aqueous solutions of paracetamol at concentrations from (0.00 to 0.05) mol dm⁻³ at 25 °C.

From these data, we have estimated some thermodynamic and transport parameters, that is, activity coefficients, the hydrodynamic radius, values of degrees of dissociation, and the limiting diffusion coefficient and ionic conductance, contributing this way to a better understanding of the structure of these systems and of their thermodynamic behaviour in aqueous solution at different concentrations (e.g., interactions ion-solvent).

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PA 3

Study of the electrochemical degradation of synthetic solutions containing H-XEL bifunctional dyes according to real effluents conditions

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The electrochemical treatment of wastewaters from textile industry is a promising technique for substances which are resistant to biodegradation, [1]. In this work, the electrochemical treatment of reactive bifunctional dyes was investigated. The selected dyes correspond to the tricromy HEXL. These dyes present two azo groups as chromophore groups and two monochlorotriazinic groups as reactive groups. This study consisted of an initial investigation where synthetic solutions containing just one of these dyes, Procion Yellow HEXL, were studied (Solution A). According to previous investigations, the best conditions to carry out the electrochemical treatment correspond to the oxidation-reduction at 125 mA cm^{-2} , [2, 3]. Once concluded this first part, the same study was performed in the same working conditions with synthetic solutions containing the three dyes of the tricromy H-EXL: Procion Yellow, Procion Crimson and Procion Navy, (Solution B). In this second case, the concentrations were selected considering the real effluents conditions. In order to evaluate the decoloration/mineralisation obtained, Total Organic Carbon (TOC) and the Chemical Oxygen Demand (COD) were measured. Moreover, these parameters allowed knowing the Average Oxidation State (AOS) after electrolyses as well as the efficiency at which the process takes place by means of calculating the Carbon Oxidation State (COS) and the Average Current Efficiency (ACE). The UV-Visible spectroscopy also permitted to observe the decoloration differences between the initial and final stage. As it can be seen in Figure 1, a complete decoloration was obtained in the two cases.

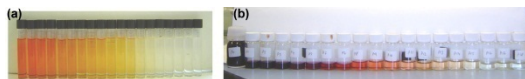


Figure 1. Decoloration obtained after the electrochemical treatment of solutions A and B.

Moreover, the High Performance Liquid Chromatography (HPLC) gave information about the intermediates generated as well as the decoloration kinetics.

Acknowledgments: *The authors would like to acknowledge to Spanish Ministry of Science and Innovation (MICINN) for the financial support (CTM2010-18842-C02-02 and CTM 2011-23583) as well as FEDER funds.*

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Indomethacin and Acemethacin Determination by Differential Pulse Adsorptive Stripping Voltammetry

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Electrochemical techniques have been widely used to determine pharmaceutical drugs in a variety of solutions. Adsorptive stripping voltammetry coupled with carbon modified electrodes are commonly used to identify as well as to quantify pharmaceutical drugs. Indomethacin and acetaminophen were determined on urine samples using differential pulse adsorptive stripping voltammetry coupled with a mercury electrode [1, 2]. According to the authors, both pharmaceutical drugs were determined with good results and without the need for tedious prior separations. Microelectrodes are currently used as biosensors towards a multiplicity of analytes and fields, such as toxicity testing or biomedical applications, presenting several advantages over conventional sized electrodes [3, 4]

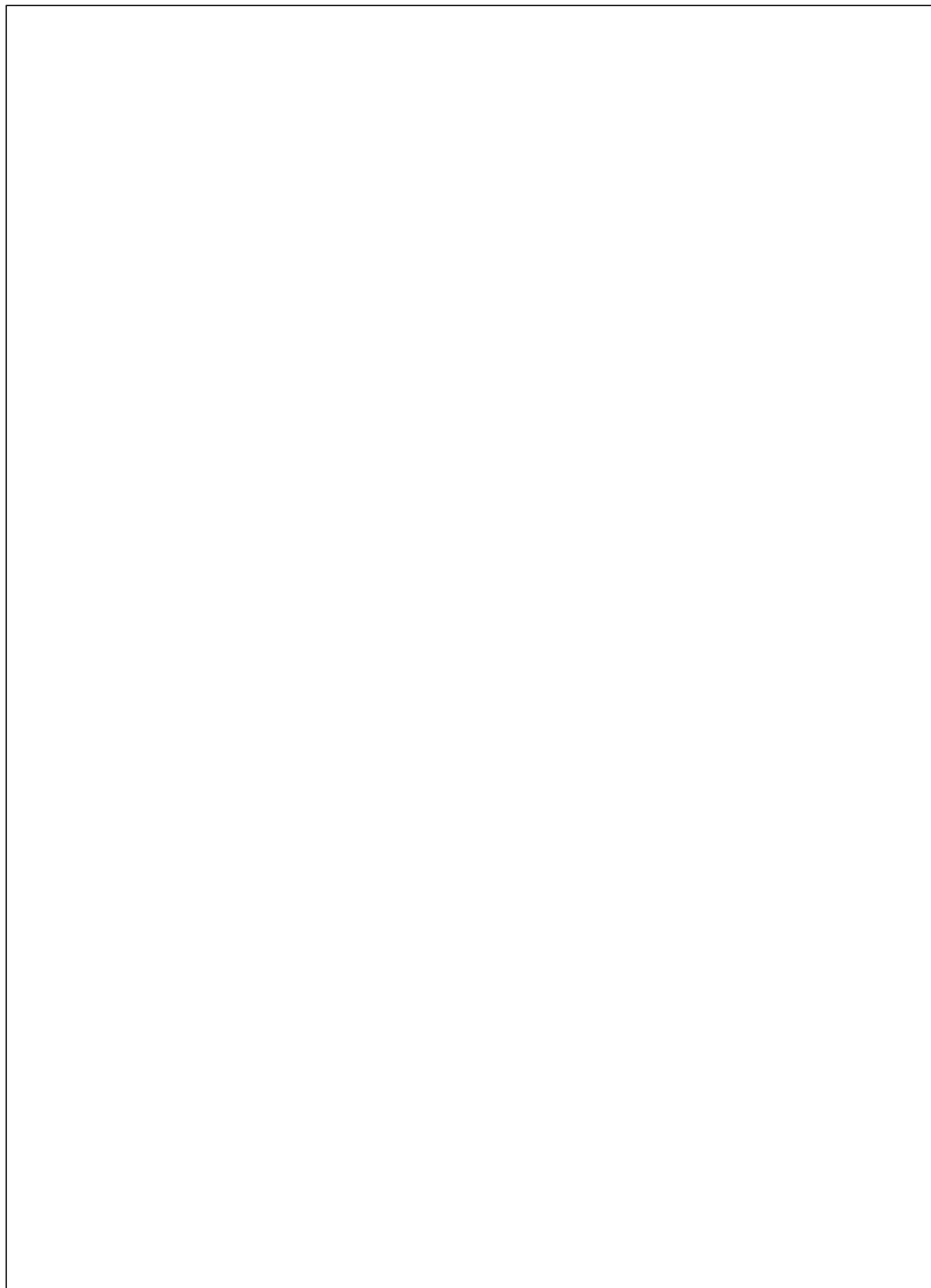
In the present study, we have used carbon microelectrodes (diameter of 5 μm) modified with a mercury thin layer through the application of differential pulse adsorptive stripping voltammetry to determine both pharmaceutical drugs at trace levels. The use of different biosensors as well as different electrochemical techniques (e.g. potentiometry, linear and cyclic voltammetry) is under study.

Acknowledgments: *Requimte is funded by grant PEst-C/EQB/LA0006/2011 from FCT/MCTES.*

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PB 2



Comparative study of the antioxidant activity and polyphenol content of Douro wines by chemical and electrochemical methods

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Cyclic voltammetry (CV) was the first electrochemical method applied to measure wine antioxidant activity (AA) and polyphenols content (PC) [1]. In spite of the utility of the cyclic voltammetry technique, differential pulse voltammetry (DPV) is known to be more sensitive and to have a higher resolution. Recently, DPV was used to determine red wines' AA and PC, and compare its values with those obtained by other methods [2]. This technique was also used to quantify red wines anthocyanin composition in order to distinguish young from old wines [3].

The aim of this work was to evaluate the AA and PC of Douro wines by electrochemical methods (CV and DPV) and compare them with those derived from chemical methods (ABTS and Folin-Ciocalteu essays). It was found that AA and PC values are underestimated by CV. On the other hand, DPV technique demonstrated its excellent reliability in evaluating the radical scavenging activities of antioxidants.

The ranking order on the PC and AA of Douro wines, determined both by chemical and electrochemical methods, was: red > ruby > tawny > muscatel > white wines.

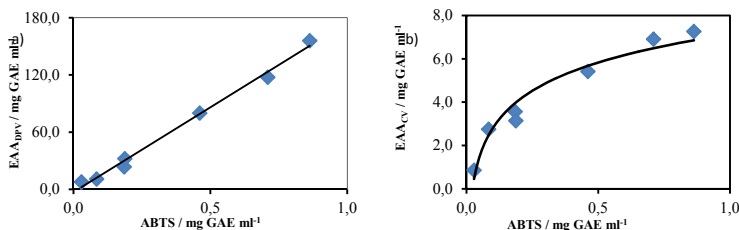


Figure 1. Correlation between antioxidant activity by ABTS essay of Douro wines, DPV (a) and CV (b).

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PB 4

**The employment of electrochemical immunosensors
fabricated on nanohybrid screen-printed carbon electrodes for
the diagnosis of celiac disease**

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Celiac disease (CD) is an autoimmune enteropathy that affects the gastrointestinal tract of genetically susceptible individuals after the ingestion of gluten. The total elimination of gluten from the diet still remains the only treatment available, leading to significant clinical and histological improvement. Small bowel biopsy has been the gold standard diagnosis for CD during many years; however the identification of antibodies involved in the autoimmune response led to the development of new and non-invasive diagnostic tests. Serum antibodies generated against gliadin and tissue transglutaminase (tTG) are specific serological markers of this autoimmune condition.

Disposable electrochemical immunosensors for the detection of IgA and IgG anti-gliadin and anti-tTG autoantibodies in real patients' samples were developed. Screen-printed carbon electrodes modified with carbon nanotubes and gold nanoparticles were used as the transducer surface. The use of nanohybrid systems such as carbon nanostructures/metal nanoparticles allows a synergic effect of each material property, providing an excellent transducer platform for the amplified transduction of the biological events. The immunosensor is based on the immobilization of the antigens (i.e. gliadins or tTG) onto nanostructured screen-printed carbon electrodes. After the incubation with real serum samples, the antigen-antibody interaction is recorded using alkaline phosphatase labelled anti-human antibodies and a mixture of 3-indoxyl phosphate with silver ions was used as the substrate. The analytical signal obtained is due to the anodic redissolution, by cyclic voltammetry, of enzymatically generated metallic silver.

The electrochemical behaviour of these immunosensors was carefully evaluated, assessing aspects like sensitivity, non-specific binding, detection limit, and reproducibility. The results obtained were corroborated with commercial ELISA kits, indicating that the developed electrochemical immunosensors are trustful analytical screening tools.

***Acknowledgments:** This work has been financially supported by the “Fundação para a Ciência e a Tecnologia (FCT)” and “Fundo Social Europeu (FSE)” through project PEst-C/EQB/LA0006/2011 and a PhD grant (SFRH/BD/46351/2008) attributed to Marta M.P.S. Neves. Additional funding was obtained from the “Instituto Politécnico do Porto (IPP) through the “PAPRE – Programa de Apoio a Publicações em Revistas Científicas de Elevada Qualidade”.*

Codeposited antimony-bismuth film carbon paste electrodes for electrochemical stripping determination of trace heavy metals

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Considering toxicity of mercury and its salts, new alternative electrode materials, suitable for trace metal measurement are very desirable in progressive area of contemporary electroanalysis. In 2000, a new type of electrode, the BiFE (bismuth film electrode), was proposed as an alternative to MFES (mercury film electrode) [1]. The most significant advantage of BFEs is that they are environmentally friendly, since the toxicity of bismuth and its salts is negligible. The advantageous analytical properties of BiFEs in voltammetric analysis, roughly comparable to those of MFES, are attributed to the property of bismuth to form “fused alloys” with heavy metals, which is analogous to the amalgams that mercury forms [2].

Recently, antimony film electrode (SbFE) [3,4] was suggested as another alternative that approaches the electroanalytical performance of mercury- and bismuth-based electrodes featuring some interesting characteristics, such as favourably negative overvoltage of hydrogen evolution, wide operational potential window, convenient operation in relatively strong acidic medium ($\text{pH} \leq 2$).

Since the conditions and the deposition potentials for bismuth and antimony are approximately the same and also considering ability of antimony to form alloys with different metals, it seemed possible to codeposit both metals on the electrode surface. This has been investigated and high enhancement in current was observed for both lead and cadmium as samples of heavy metals.

Acknowledgments: Support of Ministry of Education, Youth and Sports of the Czech Republic (projects MSM0021627502 and LC06035) is gratefully acknowledged.

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PB 6

Stability of polypyrrole/polyethylene glycol composite films in aqueous solution for uric acid determination

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Due to their conductivity or semiconductivity and other interesting properties, conducting polymers have played important roles in many industrial applications in spite to their relatively short history. The major aspect useful for most applications is the combination of electrical conductivity and polymeric properties such as flexibility, low density, ease structural modification and deposition.

Among the conducting polymers, PPy has attracted great attention because of its high electrical conductivity and good environmental stability.

The heteroatomic and extended π -structure of PPy provide it with chemical stability and electrical conductivity respectively. In order to improve the poor mechanical stability, adherence or chemical permeability of polypyrrole deposited films, a polypyrrole/polyethylene glycol (PPy-PEG) composite films [1] were proposed for uric acid determination. A significant enhancement of the conductivity by using PEG as an additive during the polymerization was also reported [2].

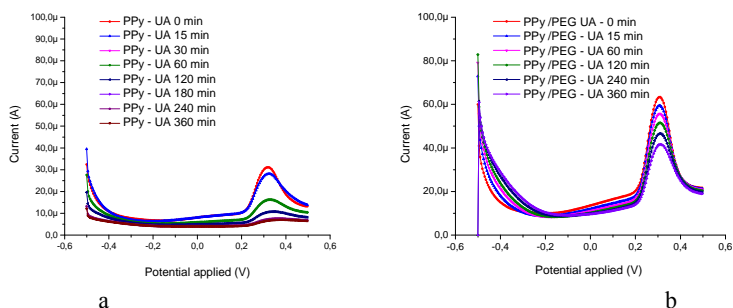


Figure 1. DPV voltammograms for PPy (a) and PPy-PEG (b) films in uric aqueous solution for different immersion times.

The presence of PEG in the polymer film structure improves signal detection of uric acid and stabilizes the electrode for large immersion times in test solution.

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Electrochemical aspects on wettability changes during PPy/PEG film deposition on Ti surface

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Conducting polymers represent a class of materials that are intensively studied for their application in energy storage, sensors, membranes, protective coatings, biomedical devices [1,2]. Polypyrrole has attracted the attention due to its high electrical conductivity, stability in air, its easily synthesis both chemically and electrochemically [3,4].

This study is an electrochemical approach on the influence of PPy-PEG films composition, deposition methods and parameters, on the surface wettability. The relationship between the doping level, charge carrier density and contact angle were evidenced.

Potentiostatic and potentiodynamic polymerization using different voltage domain and different Py/PEG ratio were performed. CV, EIS and Mott Schotky analysis were used to highlight the electrochemical changes that occur during the films deposition and films characterization in buffer solution, related to undoping-doping process, and the correlation between charge carrier density and the variation of contact angle values.

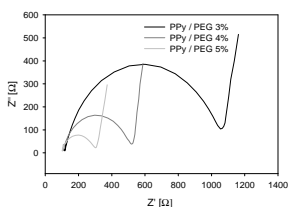


Figure 1. Nyquist plot for PPy/PEG films for different PEG concentration

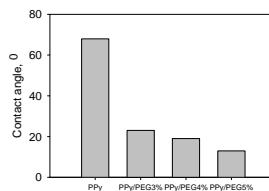


Figure 2. Variation of contact angle, in function of PEG concentration

The liquid AFM analysis sustains electrochemical behaviour and was helpful in understanding some contact angle values, in those cases where the roughness is the determinant factor.

Acknowledgments: Authors recognize financial support from the European Social Fund through POSDRU/89/1.5/S/54785 project: "Postdoctoral Program for Advanced Research in the field of nanomaterials".

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PB 8

This abstract was removed because it was not presented in the meeting;
Participant did not attend the meeting.

Platinum instability in PEM fuel cells catalyst layers

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PEM Fuel cells membrane-electrode assembly (MEA) ageing and degradation mechanisms are not well understood, being affected by the unavoidable degradation of materials in the context of load cycling and/or the influence of operating conditions such as temperature and humidity. Intended for the passive management of water, the cell was operated integrating a range of relative humidity (RH) from ~30 to 80% and temperatures from 5 to 55 °C.

In this work, cathode catalyst migration anomalies was favored by the presence of chloride contamination that induced platinum particles dissolution allowing them to break free from their carbon backing and migrate toward the polymer electrolyte. Migration of platinum resulted in precipitation with larger mean particle size distribution within the solid electrolyte, when compared to the original catalyst layer, rendering a very significant loss of thickness in the cathode material. Coarsening of platinum particles occurs at nano and micro-scale. The mechanism for the lost of catalyst by dissolution and growth is discussed on the basis of a joint electrochemical and SEM/TEM study.

The loss of performance with temperature increase was related to an increase in the membrane resistance which may correspond to loss of water on the anode side.

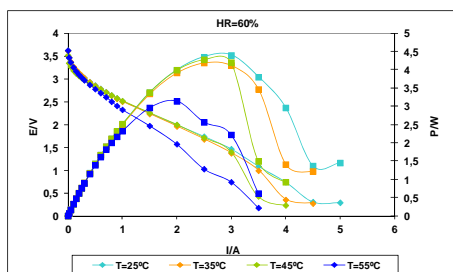


Figure 1. Voltage and power vs current curves for PEM low power stack fed with pure hydrogen at 0.25 bar, 0.5 Lmin⁻¹, for a relative humidity of 60%. The cathode is under excess air stoichiometry condition. Temperature varied from 25 to 55°C.

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PC 2

Development of silver-based gas diffusion electrodes for the oxygen reduction reaction

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The rather inexpensive and abundant Ag is a top candidate to replace Pt on oxygen reduction reactions (ORRs) due to its high activity in the alkaline medium [1,2]. Research works have shown that Ag and Ag-alloy catalysts have comparable overvoltages and similar activities to Pt-alloys [3]. The kinetics of the ORR depends on a multitude of factors including catalyst loading, particles size, morphology and catalyst supporting material.

In this work, Ag catalysts supported on a gas diffusion electrode (GDE) were prepared by electrodeposition using two different Ag-based solutions, with and without EDTANa₂. The catalyst structure, morphology and electrochemical properties were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and voltammetry. The electrocatalytic activity of prepared Ag/GDE electrodes was determined in terms of mass activity. The number of exchanged electrons for the ORR was evaluated from RDE experiments. It was observed that the complex agent does not affect morphology and ORR kinetic parameters.

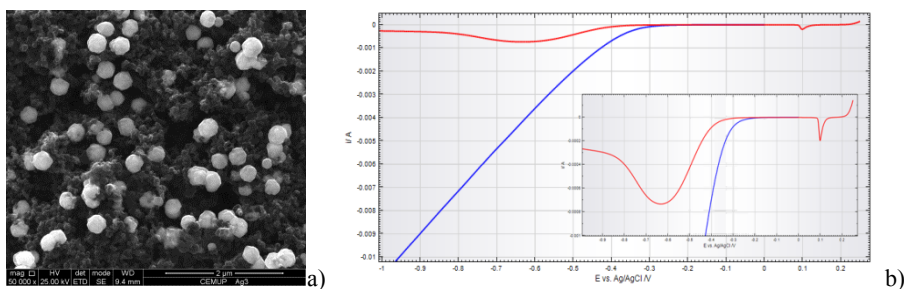


Figure 1. a) SEM image of a Ag-based gas diffusion electrode; b) Voltammetric curves for Ag-based gas diffusion electrode in 0.1M NaOH (red line) and in O₂-saturated solutions (blue line).

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Implant dental alloys stability as a function of oral environment

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In the point of view of corrosion, Ti has very good behaviour in bioliquids, but only acceptable mechanical properties [1]. Alloying is the way to have better mechanical properties and in this idea TiAlNb [2] and recently TiAlZr were investigated.

The present study is focussed on corrosion of Ti6Al7Nb and Ti6Al4Zr, in two different artificial saliva (Fusayama, Afnor)[3] at various pH and various immersion times. Electrochemical behaviour analysis comprising Tafel plots, cyclic voltammetry and electrochemical impedance spectroscopy is completed with corrosion rates computed from ICP-MS measurements. Surface characterization which supports electrochemical data include roughness and contact angle measurements.

Surface features (2D AFM images of TiAlNb and TiAlZr alloys), average roughness (R_a) computed with the Gwyddion software and the corresponding contact angle values for these samples are shown in Table 1 and Figure 1.

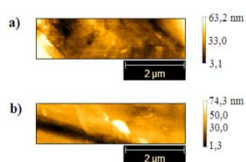


Figure 1. 2D AFM images of a) Ti6Al7Nb and b) Ti6Al4Zr

Table 1. R_a and CA values for Ti6Al7Nb and Ti6Al4Zr

	R_a / nm	CA / °
TiAlNb	8.1	68
TiAlZr	12.9	65

After immersion in Fusayama and Afnor saliva, the roughness increases and the contact angle values decrease for both alloys.

EIS data showed that as a function of the immersion time, for both tested alloys, the more hydrophilic surface barrier layer R_{bl} increases significantly while n_{bl} suffers no significant change. Corrosion rates from Tafel plots are pretty close to corrosion rate from ions release computed from ICP-MS data.

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PD 2

Increasing antibacterial effect of biomaterials using metallic nanoparticles in hybrid nanoarchitectures

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After the introduction of an implant into the body, bacterial infections may appear. The infections are typically caused by the adherence and colonization of bacteria on the surfaces of the implants. Due to the increasing bacterial resistance to variety of antibiotics, the potential of antibacterial activities of nanoparticles as silver and copper became interesting [1].

An innovative approach to significantly enhance the antimicrobial activity of metallic nanoparticles is to built hybrid nanoarchitecture with such particles.

In this idea we used various types of potential biomaterials able to serve as a support of anchorage for metallic nanoparticles as Ag and Cu. Multiwall carbon nanotubes (MWCNT) functionalized with acids and unfuctionalised was the first choice to serve for this purpose.

Dynamic light scattering (DLS) technique permitted to evaluate dimensions of Ag nanoparticles and to select the critical dimension for enhancing antibacterial effect against *Escherichia Colli* bacteria. Ag nPs adhere preferentially to the surfaces of MWCNTs rather than to other regions without MWCNTs. As can be seen in images of TEM analysis AgnPs appear to have a narrow size distribution, and no free particles are observed in the background of the TEM images, which confirms all formed nanoparticles are durably attached to the nanotubes.

a) b)

Figure1. a) TEM images of Ag nPs and b) of MWCNT-COOAg

Another type of nanoarchitecture with nanoparticles was biomimetic coating with HA (hydroxyapatite) –Ag on Ti alloy surface. Such coating was elaborated via electrochemical methods and electrochemical tests indicated a better stability. The stability was tested in Hank bioliquid, using cyclic polarization and impedance spectroscopy method. All nanoarchitecture were exposed to *Escherichia Colli* and the computed percentage inhibition of bacteria growth indicated the effect of nanoparticles and the relation between this effect and nanoparticles dimension. The mechanism of bacteria action was discussed.

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Electrochemical deposition of nanostructured Fe/carbon nanotubes composites from alkaline media

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Metal/carbon nanotube (CNT) composites have been widely investigated over the last few decades. Owing to unique electrical and mechanical properties, such as high carrier density, high thermal conductivity, low coefficient of thermal expansion, high flexibility, etc., CNTs represent ideal reinforcement agents for metal coatings [1]. Iron and iron alloy plating attract persistent attention for numerous applications due to their magnetic properties and wear resistance. CNTs embedding into Fe films may be promising for improving the mechanical properties, thermal conductivity and corrosion resistance of Fe-based materials. Here we report the synthesis of nanostructured Fe/CNTs composites by electrochemical techniques. Cathodic electrodeposition was performed from alkalised hematite suspensions, in the presence of dispersed CNTs. Triethanolamine (TEA) was used as a stability agent in order to promote the homogeneous dispersion of CNTs in the suspension. Moreover, TEA acted as a complexing agent for Fe(III) and improved the deposit morphology, preventing pillar-like crystal growth, typical for the electrochemical deposition of Fe from strongly alkaline baths. Fe/CNTs electrodeposition was done using two different modes: i) galvanostatic mode and ii) fast pulse potential mode. Both allowed the deposition of films composed of round-like agglomerates of Fe nanoparticles penetrated by a network of CNTs. Acidic leaching of Fe/CNTs coating confirmed uniform distribution of CNTs in Fe matrix (see Figure 1).

Figure 1. SEM image of Fe/CNTs film after treatment in dilute HCl.

Acknowledgments: The Authors acknowledge the support of the EC (Project RFSR-CT-2010-00002/IERO).

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PD 4

Scanning electrochemical microscopy as a highly sensitive tool to evaluate the performance of organic coatings on metals

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Surface modification of metallic materials with polymer coatings constitutes an efficient protection procedure against corrosion as they introduce a physical barrier layer that separate the metal from the corrosive environment. But these organic layers never provide an absolute separation between the underlying substrate and the electrolyte. In fact, the permeation of water and oxygen through the polymer matrix in defect-free coated metals immediately after exposure to aqueous electrolytes is well documented, whereas the development of ionic pathways through the polymer is regarded to occur prior to the transport to the metal-polymer interface of other aggressive species such as the chloride ions. That is, the organic film should have already become defective before the onset of corrosion processes at the buried metal substrate. But these ideas have been shaken by our reports that a specific effect of chloride ions towards swelling of the coating and even early blister initiation in a variety of metal-polymer systems could be observed by SECM operating in the feedback mode [1,2]. This method requires the measurement of a faradaic current at the SECM tip, and topographic changes in an insulating surface such as the defect-free coated metal originate from local hindrance in the diffusion-limited transport of the redox mediator as the tip is moved in close proximity to the surface. In this way, the uptake of reactants from the electrolyte phase through the polymeric matrix to the metal/polymer interface can be investigated even at early exposures. Yet, the method must be carefully checked to discard transport processes from the organic matrix into the solution phase, such as those related to lixiviation. In this later case, the topography of the polymer layer may evolve with time accordingly, not longer exclusively responding to the uptake by the polymer matrix of components from the electrolyte phase. Furthermore, lixiviated species may also react with the SECM tip, eventually leading to the continuous modification of the active surface area of the electrode during the measurements. In this work, the combined effect of reactants uptake from the electrolyte and the lixiviation of components from the polymer film could be distinguished from a coated metal by SECM.

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Influence of Mo in corrosion resistance of stainless steels

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The use of stainless steels (SS) as concrete reinforcement is becoming increasingly popular in coastal and marine constructions in order to prevent corrosion induced by chloride ions penetrating into the concrete [1]. In these highly aggressive situations, stainless steels have been extensively employed due to their high mechanical and corrosion resistances. However, the influence of Mo addition on pitting corrosion resistance of these steels is not fully understood in alkaline chloride conditions although this element is widely associated to an increasing corrosion resistance in acidic and neutral environments. Therefore, understanding Mo role on corrosion resistance in alkaline conditions is hence of major importance for the setting of optimized alloy compositions, particularly for new lean grades with low nickel and molybdenum contents which present a good balance between the properties required in these applications and the final cost of the material [2]. This work aims at studying the effect of Mo addition on pitting corrosion properties of austenitic, ferritic and mainly lean duplex stainless steels in alkaline media, which simulates the concrete environment. For these studies not only several different electrochemical techniques such as open circuit potential (OCP), dynamic polarization, zero resistance ammeter (ZRA) and electrochemical impedance spectroscopy (EIS) were used, but also many materials characterizations techniques such as scanning electron microscopy (SEM), X-ray microanalysis (EDX), and X-ray photoelectron spectroscopy (XPS). The results were discussed with respect to the influence of Mo addition on localized corrosion resistance of both commercial industrial SS (AISI 316L, 304L, 434, 430 and 1.2205 and 1.2304) and highly controlled laboratory ones. These laboratory SS were produced with a well defined chemical composition for which the only difference is the amount of Mo. This allowed us to associate any difference in the corrosion behavior to the Mo content. Finally, as far as the role of Mo is concerned, it will be discussed in terms of pitting corrosion resistance [3,4], repassivation kinetics, and passivation properties from acidic to alkaline conditions.

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PE 1

The Electrolytic Dissociation of Alkanepolycarboxylic Acids**Elene Kvaratskhelia**,¹ Ramaz Kvaratskhelia¹ R. Agladze Institute of Inorganic Chemistry and Electrochemistry,
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Alkanepolycarboxylic acids: propanetricarboxylic (PTCA) and butanetetracarboxylic (BTCA) acids are widely used in various fields of industry. PTCA is an inhibitor of the enzyme aconitase and interferes with the Krebs cycle. BTCA is a starting material to produce aromatic polyimide resins having high resistance to thermal stresses. It is a metal chelator and is used as a corrosion inhibitor and a metal-cleaning composition. BTCA is used as non-formaldehyde durable press finishing agent. Fabrics such as cotton and silk, proceed by BTCA, can achieve properties including anti-crease, permanent pre and keeping shape and are of high tenacity. The derivatives and polymers of BTCA are excellent electricity insulators and are widely used in manufacturing various corresponding insulator materials.

In this communication the complex regularities of dissociation of tribasic PTCA and tetrabasic BTCA are investigated with the aid of suggested by authors original method for calculation the parameters of dissociation of weak multibasic organic acids with the “overlapping” equilibria.

The general mass action equation suggested by us for the m dissociation step of weak multibasic organic acid H_nA with the close values of dissociation constants of various steps is written as follows:

$$K_m = \frac{c(\alpha_m - \alpha_{m+1}) \sum_{m=1}^n \alpha_m}{\alpha_{m-1} - \alpha_m} F_m = \frac{c\alpha'_m (1 - \alpha'_{m+1}) \sum_{m=1}^n \alpha'_m \alpha_{m-1}}{1 - \alpha'_m} F_m \quad (1)$$

where K_m is the thermodynamic dissociation constant of m step, c is a total concentration of acid, α_m , α_{m+1} and α_{m-1} are the usual degrees of dissociation of corresponding steps, α'_m , α'_{m+1} and α'_{m-1} are the “partial” degrees of dissociation for these steps (the term of “partial” degree of dissociation was first suggested by authors), F_m is the quotient of the activity coefficients for m step (the latter may be calculated with the aid of the Debye-Huckel equation).

With the aid of equations for an accurate determination of the values of degrees of dissociation for separate steps (which follow from equation (1)) the α_1 , α_2 , α_3 , α'_2 and α'_3 values for PTCA and α_1 , α_2 , α_3 , α_4 , α'_2 , α'_3 and α'_4 values for BTCA in the dilute (0.0001-0.01M) solutions of both acids were determined. With the aid of these values were also calculated the concentrations of all anions and undissociated acid molecules and pH values. The simple empirical equations for fast approximate determination of all α_m , α'_m and pH values were also suggested.

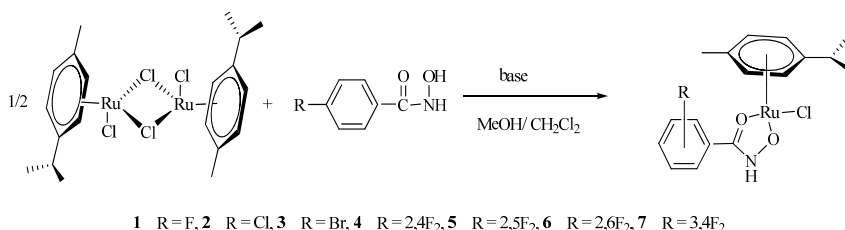
Electrochemical behaviour of halogenobenzohydroxamate ruthenium(II) *p*-cymene compounds

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Inspired by the promising results of ruthenium anticancer drugs[1,2] and the knowledge that they are potentially suitable as electron-transfer activated pro-drugs, the objective of this work was to study the electrochemical behaviour of the ruthenium(II) halogenobenzohydroxamate compounds $[\text{RuCl}(\eta^6\text{-}p\text{-cymene})\{\text{R-C}_6\text{H}_{(5-n)}\text{C(O)NHO}\}]$ (R = F, Cl, Br, 2,4F₂, 2,5 F₂, 2,6F₂, 3,4F₂, n = 1 or 2) **1-7** as well as to explore the influence of the nature, number and position of the halo ring substituent on the redox potential, of significance toward the establishment of possible structure-activity relationships.



The redox properties of **1-7** have been investigated by cyclic voltammetry, using a platinum electrode, in a 0.2 M [ⁿBu₄N][BF₄]/CH₂Cl₂ solution, at 25 °C. They exhibit a single-electron irreversible oxidation, assigned to the Ru^{II/III} oxidation, at the oxidation potential values in the range of 1.51 - 2.05 V vs. SCE and a single-electron irreversible reduction, assigned to the Ru^{III/II} reduction, in the range of -1.51 to -0.51 V vs. SCE, as confirmed by exhaustive controlled potential electrolysis.

The values of the Ru^{II/III} oxidation potential of the complexes allowed to compare the electron-donor characters of the halogenobenzohydroxamate ligands, and to estimate, for the first time, the values of the Lever E_L electrochemical ligand parameter for the halogenobenzohydroxamates R-C₆H_(5-n)C(O)NHOH (R = 4F, 4Cl, 4Br, 2,4F₂, 2,5F₂, 2,6F₂, 3,4F₂, n = 1 or 2).

Acknowledgments: This work has been partially supported by the Fundação para a Ciência e Tecnologia (FCT), Portugal, and its PTDC/QUI-QUI/102150/2008 and PEst-OE/QUI/UI0100/2011 projects. TFSS is grateful to FCT for her PhD (SFRH/BD/48087/2008) fellowship.

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PE 3

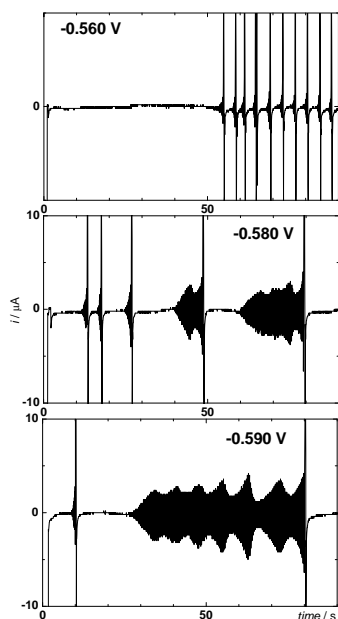
Coupling of Heterogeneous and Homogeneous Electron Transfer: Transition from Stability to Chaotic Behavior.

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This communication describes redox behavior of a series of extended viologen molecules, whose electrical response is characterized by a negative differential resistance (NDR) or a hidden NDR [1]. These molecules contain multiple identical redox centers with reversible electron transfers [2]. According to the applied bias voltage current–time transients of their representative members show stability, bistability, periodicity and chaotic behavior [1,3].

Figure 1



The analysis of periodic current–time series and bifurcation points gives the experimental estimate of the Feigenbaum universality constant $\delta = 4.68$, whereas the theoretical value is $\delta = 4.6692\dots$. The Feigenbaum constant characterizes functions approaching chaos through period doubling.

Careful choice of the controlling parameters yields also sustained sinusoidal current oscillations with characteristic frequency of 4 Hz. This type of electrochemical oscillator does not require any additional external impedance, whereas the oscillatory behavior is achieved by a mutual interplay of the heterogeneous supply of electrons and the homogeneous redox (disproportionation) reactions between the transient redox forms. Selected examples of the current–time transients are shown in Figure 1 at different applied potentials.

The system dynamics was also analyzed using theoretical approaches of deterministic chaos theory. For selected current–time measurements (not shown) a positive value of Ljapunov exponent equal to $\lambda = 0.41 \pm 0.05$ was obtained.

Acknowledgments: Financial support from GAAV (IAA400400802), GAČR (203/09/0705) and CNR-AVCR Chem 12 is greatly acknowledged.

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SERS spectroscopy applied to nanoparticulate electrodes

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Recent years have witnessed a strong increase of interest in the use of nanoparticles as electrocatalytic materials. In addition, the application of spectroscopic techniques to electrodes opens new prospects in the investigation of their adsorptive and electrocatalytic behavior, especially regarding the detection and identification of surface poisons and adsorbed intermediates. The study of adsorbed monolayers on electrodes can be carried out by taking advantage of the surface enhanced Raman scattering effect (SERS). One feasible approach of preparing SERS active substrates consists in depositing transition-metal nanoparticles (spontaneous deposition) on a support inactive for SERS (non-roughened metal, graphite, etc.). It is sometimes known as the nanoparticles-on-electrode approach [1]. This method supplies a substrate with high sensitivity, stability and reproducibility. In addition, the substrate is clean enough so that it can be employed in the study both of strongly and weakly adsorbed species.

In situ Raman spectra have been obtained for different species (CN⁻, CO, C₂H₄, C₃H₆, CO₂,...) [2] adsorbed on nanostructured electrodes prepared by spontaneous deposition of pure Pt and Pd nanoparticles (around 4 nm in size) on either gold or platinum electrodes. On the other hand, the SERS spectroscopy applied to in-situ characterization of interfaces metal electrode / solution, is particularly suitable for studying processes taking place on nanostructured metallic thin layers due to enhancement that occurs when working with these thin layers (adsorption on gold thin films of glycolate and glyoxylate, acetate and trifluoroacetate, ...)[3]. Finally, it is also possible to obtain SERS information by using electrodes composed of Pt nanoparticles with preferential surface crystallographic orientation as shows in the study of the selective reduction of aldoximes on (111) sites present at the surface of Pt nanoparticles [4].

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PE 5

Electrochemistry of polyaniline deposited on graphite electrodes modified with self-assembled monolayers

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The use of self-assembled layers (SAM) provides a number of advantages, among which is included the easy preparation on various substrates, and the achievement of highly organized structures [1]. Their versatility can be improved, in particular, by immobilization on them of various chemical structures including conducting polymers [2]. In this regard, polyaniline (PANI) stands out in terms of several properties (*e.g.* redox conversion, high conductivity, mechanical flexibility) [3-5].

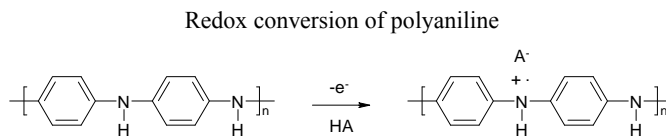


Figure 1. Represents the oxidation of polyaniline (Adapted from 5).

With the aim of obtaining further information about the electrochemical behaviour of polyaniline deposited on self-assembled layers, we performed a series of electrochemical studies, with electrodes prepared by deposition of the conducting polymer polyaniline on graphite (C_{gr}) alone and on graphite modified with self-assembled layers of 3-mercaptopropylsulfonic acid sodium salt (MPS) and 4-aminothiophenol (4-ATP). Therefore, we resorted to the electrochemical techniques of cyclic voltammetry and electrochemical impedance spectroscopy to study the electrochemical behaviour of the modified electrodes thus obtained.

The electrochemical analysis allowed us to obtain valuable information about the redox processes of the conducting polymer and its dependence of the substrate for the deposition, C_{gr} or C_{gr}/SAM .

Acknowledgments: We acknowledge the Portuguese National NMR Network (RNRMN, REDE/1517/RMN/2005), supported with funds from Fundação para a Ciência e a Tecnologia (FCT). The support from FCT through the Pluriannual base funding of CQM (PEst-OE/QUI/UI0674/2011) and CS Madeira is also gratefully acknowledged.

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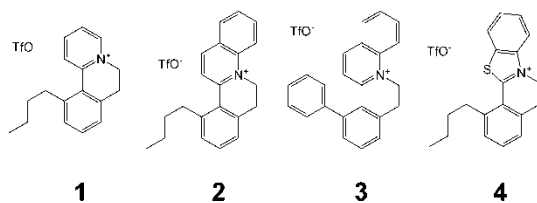
Dimer/monomer switching of pyridinium and quinolinium cations by electron transfer

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Radicals of organic compounds play an important part in many processes. Radical-radical dimerization often determines the lifetime of these very reactive species. In this work the electron transfer mechanism of four novel compounds [1] containing pyridinium, quinolinium, and benzothiazolium moiety has been investigated by voltammetric, impedance, spectroscopic and quantum chemical techniques [2]. The reduction of pyridinium and quinolinium derivatives **1** to **3** by



one electron yields radicals that very rapidly form σ -dimers. Dimers can be converted to parent cations by oxidation, which proceeds at considerably higher potentials. Hence the dimerization can be reversibly switched by application of the appropriate electrode potential. Theoretical models indicate the

γ -position as the most probable dimerization sites in reduced pyridinium and quinolinium species. Indeed, the introduction of the second heteroatom, sulfur, eliminates the dimerization. Compound **4** yields reversible features observed by all applied techniques and gives the EPR signal of a radical formed by one-electron reduction. Properties of **4** oppose short lifetimes of radicals derived from pyridinium **1** and quinolinium **2** or **3**, which rapidly form dimers and cannot be detected by EPR. Quantum chemical calculations elucidate the role of the charge delocalization for the observed coupled chemical step in species **1-3** and its absence in species **4**. The evaluation of kinetic parameters by simulation of cyclic voltammograms was conveniently facilitated by the estimation of adsorption and heterogeneous electron transfer rates using the AC techniques. Relation between molecular structure and redox potentials E^0 for the reduction and the dimer oxidation will be discussed.

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PE 7

Catalytic activity of the novel palladium-aminocarbene species in Suzuki–Miyaura cross-coupling forecasted by the electrochemistry tools

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A series of seven aminocarbene complexes [Pd{C(N=C(C₆H₄CNHN))=N(H)R¹}]₂ (R¹ = cyclohexyl (Cy) 82% isolated yield), [PdCl{C(N=C(C₆H₄CNHN))=N(H)R¹}(CNR¹)] (R¹ = Bu^t 78%, Xyl 84%, CMe₂CH₂CMe₃ 79%) and *cis*-[PdCl{C(N=C(C₆H₄CNHN))=N(H)R¹}(PPh₃)] (R¹ = Cy 84%, Bu^t 76%, CMe₂CH₂CMe₃ 75%) derived from the integration between two or one equivs 1,3-diiminoisindoline and starting *cis*-[PdCl₂(CNR¹)₂] or *cis*-[PdCl₂(CNR¹)(PPh₃)], were prepared. All thus obtained species were fully characterized by elemental analyses (C, H, N), ESI⁺-MS, IR, 1D (¹H, ¹³C{¹H}) and 2D (¹H,¹H-COSY, ¹H,¹³C-HMQC/¹H,¹³C-HSQC, ¹H,¹³C-HMBC) NMR spectroscopies, as well as by X-ray diffraction (for two compounds) [1].

The redox properties of the compounds, as well as, for comparative purposes, of the ligands, have been investigated by cyclic voltammetry (CV), at a Pt electrode (*d* = 1 mm) in 0.2 M [ⁿBu₄N][BF₄]/THF solution, at 25 °C. The Pd(II) complexes show two reduction process (¹E_p^{red} from *ca.* -0.38 to -0.88 V *vs.* SCE and ¹¹E_p^{red} in the range from *ca.* -0.63 to -1.25 V *vs.* SCE) and one oxidation process at ¹E_p^{ox} in the range from *ca.* 1.13 to 1.64 V *vs.* SCE. Within the aminocarbenes, the complexes containing one phosphine and one aminocarbene are easiest to reduce (least cathodic reduction potentials), while the *bis*-aminocarbene derivatives are the most difficult to reduce.

Catalytic properties of the prepared carbene species in the Suzuki–Miyaura cross-coupling of aryl bromides with phenylboronic acid (in EtOH as solvent, K₂CO₃ or Cs₂CO₃ as base, 80 °C) yielding biaryls, were evaluated [1], demonstrating that the (one aminocarbene/one phosphine)-type complexes (easiest to reduce) behave as better catalysts (yields up to 98%, TONs up to 9.8×10⁴, TOFs up to 3.9×10⁴) as compared to the other understudied compounds.

Acknowledgments: This work has been partially supported by the Fundação para a Ciência e a Tecnologia (FCT), Portugal (including FCT projects PTDC/QUI-QUI/098760/2008, PTDC/QUI-QUI/109846/2009 and PEst-OE/QUI/UI0100/2011).

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Electrochemical behaviour of C-scorpionate gold(III) compounds

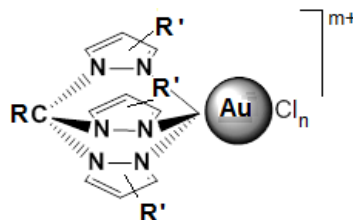
Luísa M.D.R.S. Martins,¹ M. Peixoto de Almeida, S.A.C. Carabineiro, Armando J.L. Pombeiro

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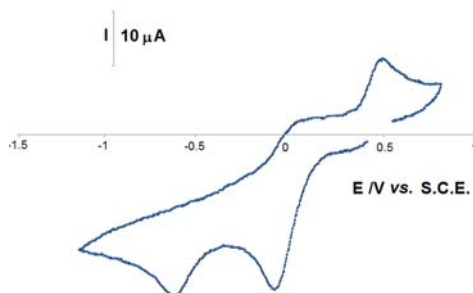
Tris(pyrazol-1-yl)methane-type scorpionates $RC(R'pz)_3$ (pz = pyrazol-1-yl; R = H or substituent; R' = H or substituent at the pz ring), which are much less studied than the related tris(pyrazol-1-yl)borates, constitute an emerging field of research [1].

In pursuit of our recent work on the coordination chemistry of $HC(Rpz)_3$ and derivatives at several transition metals, we have now extended these studies to a gold(III) centre, leading to C-scorpionate complexes of general formula $[AuCl_n\{RC(R'pz)_3\}]^{m+}$ (R = H, CH_2OH or SO_3 ; R' = H, 3,5- Me_2 , or 3-Ph; n = 1 - 3; m = 3-n).



The redox properties of our compounds have been investigated by cyclic voltammetry and controlled potential electrolysis at a platinum electrode, in a 0.2 M $[^nBu_4N][BF_4]$ / CH_3CN solution, at room temperature.

Their reduction behaviour allowed us to get an insight into the net electron-donor ability of the C-scorpionate ligands, in the redox $Au(III)/Au(I)$ and $Au(I)/Au(0)$ interplay, essential to account for their versatility as potential catalysts for reactions of industrial interest.



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PE 9

Redox properties of organotin (IV) Cycloalkylhydroxamate complexes with different ring sizes: anti-tumor activity and reduction potential

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The potential of organotin(IV) compounds as biologically active metallopharmaceuticals has been recognized [1], but their antitumor action mechanism is still unclear.[2]

Investigations on metal-based drugs ‘activated by reduction’ have become very popular with platinum(IV) and ruthenium(III) compounds [3,4], since various metal-complexes exist in rather inert high oxidation states but are more active in reduced oxidation states.

Encouraged by the reduction mechanism of other metal-based antitumor complexes like Pt(IV) or Ru(III) and by the widely studied [5] anticancer activity of organotin(IV) compounds, and considering that cycloalkyl groups can display better hydrophobic and different electronic properties than aryl groups, we tried to investigate the effect of the cycloalkyl moiety in the antitumor activity.

We now report the electrochemical behaviours, at a Pt electrode and in aprotic media, of new diorganotin(IV) cycloalkylhydroxamate complexes with different ring sizes, formulated as the mononuclear $[R_2Sn(HL)_2]$ (R = ⁿBu and Ph) (1:2) and the polymeric $[R_2SnL]_n$ (R = ⁿBu) (1:1), and relate the reduction potential with their in vitro activities against human tumor cell lines [a human promyelocytic leukemia (HL-60), hepatocellular carcinoma (Bel-7402) and nasopharyngeal carcinoma (KB)]. The electrochemical behavior of two complexes was also investigated using theoretical (DFT) methods.

Acknowledgments: This work has been supported by the Foundation for Science and Technology (FCT) (grant No. SFRH/BPD/44773/2008) and the IPL/41/2003 project.

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Electrochemical studies of novel-type aminocarbene palladium(II) complexes

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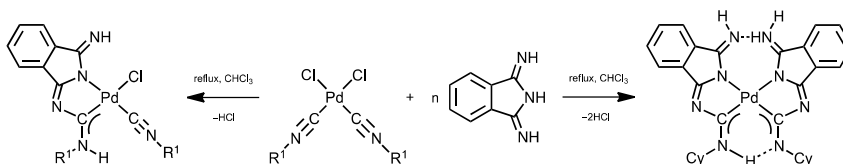
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In pursuit of our interest on the design of novel carbene ligands [1–3], we prepared a series of novel type aminocarbene Pd(II) complexes, *i.e.* $[\text{Pd}\{\underline{\text{C}}(\text{N}=\text{C}(\text{C}_6\text{H}_4\text{CNHN}))=\text{N}(\text{H})\text{R}^1\}_2]$ ($\text{R}^1 = \text{cyclohexyl (Cy)}$), $[\text{PdCl}\{\underline{\text{C}}(\text{N}=\text{C}(\text{C}_6\text{H}_4\text{CNHN}))=\text{N}(\text{H})\text{R}^1\}(\text{CNR}^1)]$ ($\text{R}^1 = \text{Bu}^t, \text{Xyl}, \text{CMe}_2\text{CH}_2\text{CMe}_3$) and *cis*- $[\text{PdCl}\{\underline{\text{C}}(\text{N}=\text{C}(\text{C}_6\text{H}_4\text{CNHN}))=\text{N}(\text{H})\text{R}^1\}(\text{PPh}_3)]$ ($\text{R}^1 = \text{Cy}, \text{Bu}^t, \text{CMe}_2\text{CH}_2\text{CMe}_3$, Scheme 1) derived from the reaction of palladium-bound isonitriles in *cis*- $[\text{PdCl}_2(\text{CNR}^1)_2]$ or *cis*- $[\text{PdCl}_2(\text{CNR}^1)(\text{PPh}_3)]$, with 1,3-diiminoisoindoline $[\text{HN}=\text{CC}_6\text{H}_4\text{C}(\text{=NH})\text{NH}]$ as a nucleophile. Furthermore, complexes derived from the addition of structurally related 3-iminoisoindolin-1-one $[\text{HN}=\text{CC}_6\text{H}_4\text{C}(\text{=O})\text{NH}]$ and 2-aminopyridine in the place of nucleophile were obtained for the comparison purposes.



Scheme 1

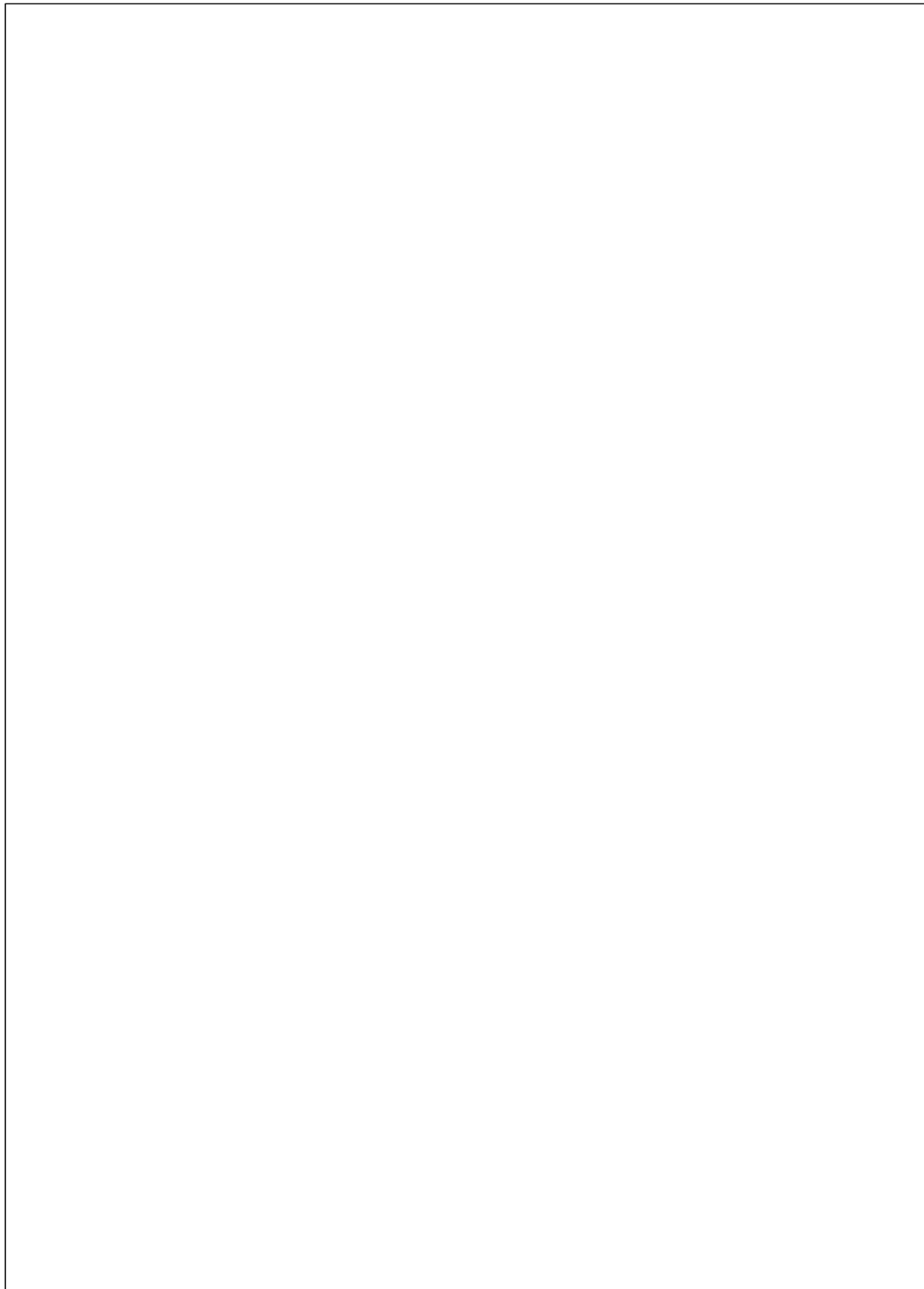
We now report the study of the electrochemical behaviour, by cyclic voltammetry (at a Pt-disc electrode) and by controlled potential electrolysis (at a Pt-gauze electrode), of all abovementioned complexes in aprotic media and at room temperature. The obtained electrochemical results are discussed in terms of electron richness of the metal centre and the electronic properties of the ligands.

Acknowledgments: *This work has been partially supported by the Fundação para a Ciência e a Tecnologia (FCT), Portugal (including FCT projects PTDC/QUI-QUI/098760/2008, PTDC/QUI-QUI/109846/2009 and PEst-OE/QUI/UI0100/2011).*

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PE 11



Electrochemical evaluation of new anticancer drug candidates

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The involvement of oxidative stress in the mode of action of various bioactive substances, including anticancer drugs has been recently reported [1]. There are evidences supporting the participation of electron transfer processes in the mechanism of action of several anticancer drugs [1-3]. Many of these molecules or their metabolites incorporate electron-transfer groups that readily accept electrons from biological sources, therefore generating reactive oxygen species, typically by redox cycling with oxygen [2,4].

Significantly, a large number of physiologically active substances possess redox potential values greater than about -0.74 V vs. SCE so they can accept electrons from biological donors or suffer metabolic changes, providing easily reduced derivatives [4].

A few studies [5,6] established a relationship between the reduction potential of anticancer agents and their cytotoxicity against several tumor cell lines - the more delocalized the electronic system, implying higher reduction potentials, the greater the cytotoxic activity. These results suggest that electrochemical methods can provide valuable insight concerning the mode of action of anticancer drugs and that a preliminary screening of the potential anti-cancer activity of new compounds can be made using their redox potentials.

With this aim the electrochemical behavior of a series of new imidazo[4,5-*d*]pyrrolo [3,2-*f*]diazepines synthesized in our group, was studied. The effect of the nature of the substituents on reduction potentials of the compounds was evaluated.

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PF 1

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Participant did not attend the meeting.

Li_{1.43}[Fe^{II}_{4.43}Fe^{III}_{0.57}(HPO₃)₆] \cdot 1.5H₂O: A New Cathode Material for Li-Ion Batteries?

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Li_{1.43}[Fe^{II}_{4.43}Fe^{III}_{0.57}(HPO₃)₆] \cdot 1.5H₂O has been synthesized by mild hydrothermal techniques. This phase exhibits a crystal structure formed by the [Fe^{II}_{4.43}Fe^{III}_{0.57}(HPO₃)₆]^{-1.43} inorganic framework with the Li⁺ cations as counterions. The anionic inorganic skeleton is based on layers of FeO₆ octahedra linked along the c-axis through (HPO₃)²⁻ oxoanions. The sheets are constructed by twelve membered rings of FeO₆ octahedra that repeat in the ab plane giving rise to channels of ca. 3 Å diameter along the [100] direction in which the water molecules and Li⁺ cations are located showing positional disorder. From the fit of the Mössbauer spectrum, in the paramagnetic state, the simultaneous presence of Fe(II) and (III) cations have been obtained. The existence of mobile lithium cation in the channels of Li_{1.43}[Fe^{II}_{4.43}Fe^{III}_{0.57}(HPO₃)₆] \cdot 1.5H₂O was studied by impedance spectroscopy at different temperatures. The sample shows reversible redox behaviour due to the mixed Fe(II,III) with processes at 2.5 and 3 V vs. Li/Li⁺, coupled with a lithium extraction/insertion capability for more than 100 galvanostatic cycles, equivalent to 12mAh.g⁻¹ of sample. This phase is the first phosphite polyanion based material which shows reversible lithium ion intercalation and iron redox reaction [1].

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PF 3

Preparation and cyclic voltammetry studies of Ru and Pd phenylene ethynylene and thiophenylene ethynylene rods.

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Organometallic rods with robust and redox capable metal centres can offer excellent properties and attractive advantages (either over traditional wires or their purely organic counterparts) when considering potential materials for nanoelectronic applications [1-2]. Higher energy throughput and lower production costs can be serious advantages of these materials over the classical technology [1]. OPE (oligo(phenylene ethynylene)s) and OTE (oligo(thiophenylene ethynylene)s) derivatives [3] can be used to adjust the electronic communication between metal centres.

The preparation and CV studies of a family of *trans*-[M(PP)₂Cl₂] (M = Pt; PP = PEt₃ and M = Ru; PP = dppe) rods using as organic bridges, a family of OPEs or OTEs are presented and discussed in this work.

Figure 1. Cyclic voltammograms of two phenylene ethynylene Ru rods at 100mV s⁻¹ vs Ag/AgCl in CH₂Cl₂ with NBu₄PF₆ 0.1M.

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