



**XXI Encontro
Sociedade Portuguesa
de Eletroquímica**

**XVIII Encontro
Ibérico
de Eletroquímica**

**XXI Meeting of the Portuguese Electrochemistry Society
&
XVIII Iberian Electrochemistry Meeting
Abstract Book**

**XXI Encontro da Sociedade Portuguesa de Eletroquímica
&
XVIII Encontro Ibérico de Eletroquímica
Livro de Resumos**

Bragança, Portugal ◊ 14-17 setembro 2016



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XXI Meeting of the Portuguese Electrochemistry Society &
XVIII Iberian Electrochemistry Meeting

Título

XXI Encontro da Sociedade Portuguesa de Eletroquímica &
XVIII Encontro Ibérico de Eletroquímica

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O XXI Encontro da Sociedade Portuguesa de Eletroquímica & XVIII Encontro Ibérico de Eletroquímica decorreu no Instituto Politécnico de Bragança, Portugal, de 14 a 17 de setembro de 2016. O Encontro permitiu aos participantes apresentar e discutir as suas linhas de trabalho em Eletroquímica bem como, desenvolver parcerias estratégicas com objetivos comuns, pensando também nos desafios que se avizinham no âmbito das políticas Europeias.



El XXI Encontro da Sociedade Portuguesa de Eletroquímica & XVIII Encontro Ibérico de Eletroquímica ocurrió en el Instituto Politécnico de Braganza, Portugal, durante los días 14-17 de septiembre de 2016. El Encontro fue una plataforma de debate entre los participantes y un lugar privilegiado para presentar y discutir las líneas de trabajo en Electroquímica así como, establecer colaboraciones estratégicas con objetivos comunes, pensando, también, en los desafíos que se avecinan en el ámbito de las políticas europeas.



The XXI Meeting of the Portuguese Electrochemistry Society & XVIII Iberian Electrochemistry Meeting took place at Instituto Politécnico de Bragança, Portugal, from 14 to 17 of September of 2016. The Meeting was a forum for researchers' debate and a privileged platform for presenting and discussing work lines in Electrochemistry as well as, to develop strategic partnerships with common objectives, taking into account the challenges that lie ahead in the context of European policies.



Sociedade Portuguesa de Eletroquímica



Luísa M. Martins
Presidente da SPE

A Sociedade Portuguesa de Eletroquímica (SPE) é uma associação científica, criada a 23 de Novembro de 1983, sem fins lucrativos, para o desenvolvimento da eletroquímica a nível nacional e internacional. A SPE tem cerca de 100 membros, englobando sócios a nível individual (professores, investigadores e estudantes de doutoramento) e sócios coletivos (empresas comerciais e indústrias). Atua na área de Investigação & Desenvolvimento no domínio da Eletroquímica promovendo a organização de reuniões científicas, cursos de formação, seminários e sessões de divulgação.

O XXI Encontro da Sociedade Portuguesa de Eletroquímica é um evento anual organizado pela SPE, com o objetivo de aumentar a divulgação da atividade científica nas diferentes vertentes da Eletroquímica. O XVIII Encontro Ibérico de Eletroquímica resulta da cooperação com o “Grupo de Electroquímica” da Real Sociedad Española de Química, realizando-se periodicamente.

A SPE atribui, anualmente, o Prémio Sociedade Portuguesa de Eletroquímica a um investigador de reconhecido mérito científico em Eletroquímica que tenha contribuído para o desenvolvimento desta Sociedade; e o Prémio Jovem Investigador em Eletroquímica da SPE, a atividades relevantes de um jovem investigador em Eletroquímica que contribuíram para a publicação de artigos em revistas internacionais de reconhecido mérito, na revista da SPE - *Portugaliae Electrochimica Acta* e de patentes.

O projeto editorial *Portugaliae Electrochimica Acta*, uma publicação periódica, “open access”, sem custos para os autores, que permite a publicação de artigos científicos originais englobando aspetos teóricos e práticos da eletroquímica. Esta publicação está indexada a várias bases de dados internacionais (Elsevier Database / SCOPUS, Chemical Abstracts, SciELO Citation Index, ISI Thomson Reuters, SCIMAGO, entre outras).



Social Program / Programa Social



- Visita à cidade de Miranda do Douro: Receção de boas-vindas aos participantes pela Câmara Municipal de Miranda do Douro - Capa de Honras; Passeio de Barco pelas arribas do Parque Natural do Douro Internacional; Visita guiada pelo centro histórico da cidade, com passagem pelo Museu da Terra de Miranda; Jantar do Encontro.
- Visita à cidade de Bragança para acompanhantes dos participantes no Encontro: visita guiada pelo centro histórico e museus da cidade de Bragança.



- Visita a la ciudad de Miranda do Douro: Recepción de Bienvenida a los participantes por el Ayuntamiento de Miranda do Douro – “Capa de Honras”; Crucero Ambiental por las Arribas del Parque Natural del Duero Internacional; Visita guiada por el centro histórico de la ciudad, con entrada en el Museo de la Tierra de Miranda; Cena del Encontro.
- Visita a la ciudad de Bragança de compañeros de participantes en encuentro: visita guiada por el centro histórico de la ciudad y museos de Bragança.



- Visit to the city of Miranda do Douro: Welcome reception to the participants by the Municipality of Miranda do Douro - “Capa de Honras”; Boat trip in Douro River at the Douro International Natural Park; Guided visit through the historic city center, including a visit to the Museum of “Terra de Miranda”; Meeting dinner.
- Visit to the city of Bragança for accompanying persons of participants of the Meeting: guided visit through the historic city center and museums of Bragança.



Sponsorships / Patrocínios



The **International Society of Electrochemistry** was founded in 1949 by leading European and American Electrochemists to serve the growing needs of electrochemistry in becoming a modern scientific discipline. At that time only a handful of experts were assembled in the original CITCE (Comité International de Thermodynamique et Cinétique Electrochimiques). Since then the association has evolved and now comprises about 3000 individual members and more than 20 Corporate Members (teaching institutions, non-profit-making research organizations and learned societies) and Corporate Sustaining Members (industrial and commercial organizations). Its membership comes from more than 70 countries and is organized in over 40 regional sections. Both industrialized and developing countries from all five continents are represented. ISE is, therefore, a truly world-wide organization. ISE is a non-profit-making organization with its seat in Lausanne, Switzerland.

ISE is an Associated Organisation of IUPAC. Website of the IUPAC Electrochemistry Commission

ISE's objectives

- to advance electrochemical science and technology;
- to disseminate scientific and technological knowledge;
- to promote international cooperation in electrochemistry;
- to maintain a high professional standard among its members.

Reference: <http://www.ise-online.org/geninfo/index.php>



Bio-Logic Science Instruments SAS is a French designer and manufacturer of high performance laboratory research instruments and software. The headquarters are based in Seyssinet Pariset, France (close to Grenoble in the French Alps).

Founded in 1983 by a CNRS researcher Yves Dupont and an industrial partner, Bio-Logic SAS has designed instruments for a variety of domains and applications:

- Electrochemistry
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Sponsorships / Patrocínios



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Program / Programa SPE2016

Time	Wednesday - September 14	
16:00-18:00		• <i>Registration</i>
18:15-20:00		• <i>Meeting reception</i>
Time	Thursday - September 15	
8:30-9:30		• <i>Registration</i>
9:30-9:50		• <i>Opening session</i>
9:50-10:35	P1	La conductividad electrolítica. Una herramienta sencilla para conocer la estructura de la disolución. Miguel A. Estesó
10:35-11:00		• <i>Coffee Break</i>
11:00-11:30	IOC1	Electrochemical (bio)sensors: tools for environmental, food and health analysis. Cristina Delerue-Matos
11:30-11:50	OC1	Electrochemical genoassay with gold-coated magnetic nanoparticles as new approach to detect the soybean GTS40-3-2 event in food and feed. Alexandra Plácido
11:50-12:10	OC2	POM@graphene hybrids as highly efficient electrocatalysts for the hydrogen evolution reaction. Diana M. Fernandes
12:10-12:30	OC3	Self-assembled monolayer-based immunosensor for the determination of thyroxine (T4). Rosa A.S. Couto
12:30-14:00		• <i>Lunch</i>
14:00-14:45	P2	Potentiometry and electrolyte solutions. M. Isabel Ferra
14:45-15:05	OC4	Electrochemical tools for the evaluation of bioactive compounds in bee products. Soraia I. Falcão
15:05-15:25	OC5	Sucrose-derived activated carbons as electrocatalysts for the oxygen reduction reaction. Marta Nunes
15:25-15:55	OC6	Development of sulfur based polymers for rechargeable lithium batteries. Carlos M.F. Almeida
15:55-16:10		• <i>Coffee Break</i>
16:10-16:40	IOC2	Water Splitting for Renewable Energy Storage. Lifeng Liu

16:40-17:00	OC7	A representação matemática do desempenho eletroanalítico do material radicalmente pré-tratado, modificado por safranina, na detecção de compostos hidroquinônicos. Volodymyr V. Tkach
17:00-17:20	OC	Bio-logic, your electrochemical partner. Joel Carballo
17:20-18:30		• <i>Coffee Break + Poster session</i>
Time Friday - September 16		
9:00-9:45	P3	From corrosion to biology. A tour with microelectrode applications. Alexandre C. Bastos
9:45-10:05	OC8	Ti/Pt/TiO ₂ electrodes prepared by DC Magnetron Sputtering: Environmental application on the degradation of the Acid Orange 7. Lurdes Ciríaco
10:05-10:25	OC9	Optimización de los parámetros de funcionamiento de un proceso de electrocoagulación para el tratamiento de efluentes de curtiduría. Mario H. López Araiza
10:25-11:15		• <i>Coffee Break + Poster session</i>
11:15-11:45	IOC3	Arrays of voltammetric sensors using combinations of electrocatalytic materials for the analysis of foods. M.L. Rodríguez-Méndez
11:45-12:05	OC10	Cyclic voltammetry of ionic liquids and of copper complexes therein. Gonçalo Tiago
12:05-12:30		General Assembly of the "Sociedade Portuguesa de Eletroquímica"
12:30-13:30		• <i>Lunch</i>
		• <i>Visit to Douro River</i>
		• <i>Meeting Dinner</i>
Time Saturday - September 17		
10:00-10:30	IOC4	The intrinsic and intriguing electrochemical properties of carbon-based solutions generated from graphite. M. Cristina F. Oliveira
10:30-11:30	IOC5	Multisensor devices and chemometrics. Luís G. Dias
11:30-11:45		• <i>Coffee Break + Poster session</i>
11:30-11:50	OC11	Electrochemical aptasensor array for multiple detection of human osteopontin. Sofia Meirinho

11:50-12:10 **OC12** Application of an electronic tongue for evaluating basic gustatory attributes perceived in table olives: qualitative and quantitative approaches
António M. Peres

12:10-12:30 • *Closing session*

P Plenary communication

IOC Oral communication by invitation

OC Oral communication





P

PLENARY SESSIONS

SESSÕES PLENÁRIAS

P1

La conductividad electrolítica.

Una herramienta sencilla para conocer la estructura de la disolución.

Miguel A. Esteso

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Muchas disoluciones de electrólitos exhiben comportamientos anómalos en sus propiedades fisicoquímicas, cuando éstas dependen de manera directa de la concentración total de electrólito disuelto. Tales anomalías pueden explicarse en base a la formación de “especies iónicas complejas” en la disolución que, en muchas ocasiones, no presentan estequiometrias sencillas. El estudio de estos sistemas complejos se ha acometido a través del análisis del comportamiento de sus diferentes magnitudes fisicoquímicas, utilizando para su determinación diversas técnicas experimentales.

Una de las más sencillas pero que, al mismo tiempo, facilita gran información acerca del sistema disuelto, es la medida de la conductividad electrolítica. A partir de datos precisos de conductividades, haciendo uso de ecuaciones de conductividad adecuadas y superando las dificultades matemáticas que se derivan de los problemas de convergencia en los procesos de optimización, es posible obtener información muy precisa acerca de la formación de pares iónicos y otras estructuras complejas (moléculas neutras e, incluso, iones complejos con carga de signo opuesto a la que corresponde al ión simple) que tienen lugar en la disolución. Hasta finales de los años 70 del pasado siglo, la mayor parte de los estudios de conductividad estuvieron dirigidos hacia los electrólitos simétricos (para los que, con rigor, es aplicable la teoría de Debye-Hückel-Onsager). Sin embargo, con la aparición de las ecuaciones de conductividad de Lee-Wheaton y de Quint-Viallard, en 1978, ha sido posible extender dichos estudios rigurosos a los electrólitos asimétricos, dentro del marco de un modelo de asociación.

P2

Potentiometry and electrolyte solutions.

M. Isabel Ferra

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The electrolyte solutions properties depend on both solute and solvent and it is the solvent which enables the electrolyte to display its peculiarities. Although there is much work done on non-aqueous solvents, water is by far the most important of the ionizing solvents and the most part of the knowledge about electrolytes refers to aqueous solutions due to their importance in biological, geological and industrial systems.

By the beginning of the 20th century, it was recognized that the behaviour of electrolytes, even in the dilute range, differed from that of non-ionic solutions. In 1923 Debye and Hückel presented a simple mathematical expression considering ionic forces and later several theories led to expressions for the behaviour of more concentrated electrolyte solutions. More recently, advances in this field were in the area of mixed electrolyte solutions of relatively high concentrations at high temperatures and pressures.

For the evaluation of activity coefficients, the Pitzer theory, which takes into account specific ionic interactions, has been widely used in studying electrolyte solutions behaviour. It arbitrarily separates electrostatic and specific short-range interactions and enables these, expressed as virial coefficients, to be evaluated for single electrolyte solutions and these values can then applied to the analysis of mixtures. It has been successfully applied to many single and mixed electrolytes in both aqueous and non-aqueous solutions with ionic strengths up to saturation.

Among various experimental methods for the measurement of the activity coefficients of electrolytes in mixed solutions, a very accurate one involves the use of galvanic cells without liquid junction. Potentiometric titrations have also been used for this purpose. A few examples of those determinations will be presented. The measurement of single ionic activities will be discussed as well as its implications on the pH definition.

Acknowledgements:

The author wishes to thank Fundação para a Ciência e a Tecnologia, FCT, for funding the FibEnTech Research Unit, project PEst-OE/CTM/UI0195/2014.

P3

From corrosion to biology. A tour with microelectrode applications.

A.C. Bastos

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This communication gives an overview of some lines of research being conducted at the Department of Materials and Ceramic Engineering of University of Aveiro with electrochemistry in the background and microelectrode techniques as the connecting link.

The talk starts with metallic corrosion, its impact in our metals-based society and the localised nature of the phenomenon. Being corrosion an electrochemical process, electrochemical methods are well suited for its investigation. However, the traditional techniques provide the average response of the sample and miss the localised features. These can be resolved with the help of microelectrodes. A few localised electrochemical techniques are described with emphasis laid on three types of sensor that operate close to the corroding surface. One is a small vibrating probe that senses the electrical field in solution and maps the ionic currents flowing therein. The others are simply micropotentiometric and microamperometric sensors, which, long before the ascension of the scanning electrochemical microscope, were already being used to sense the chemical species involved in electrophysiological processes, in living tissues or inside biological cells. In corrosion these techniques provide information about the localisation of anodes and cathodes in the active electrode, their rates and also the local concentration of important species like dissolved O₂, pH, metal cations from the corroding surface and ions from the testing medium. General information is given on how these microelectrodes are constructed, how they work, their capabilities and limitations, together with selected examples in corrosion research.

These techniques are also being used to probe the self-healing properties of protective coatings which has become a hot topic in recent years. Results of self-healing materials for corrosion protection developed by the group, their synthesis, their characterisation, their modes of action and the corrosion testing are presented. A new area for the group is the application of the microelectrodes to analyse the degradation of biomaterials, in collaboration with research groups from the Materials department.

The talk ends with illustrative examples of these microelectrodes in biology, which is the area where they were developed and used for the first time. Hopefully, this sort of studies will be performed in Aveiro as well, in collaboration with the Biology department.



IOC

ORAL COMMUNICATIONS BY INVITATION

COMUNICAÇÕES ORAIS POR CONVITE

IOC1

Electrochemical (bio)sensors: tools for environmental, food and health analysis.

Cristina Delerue-Matos

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Electrochemical methods are highly-sensitive, convenient and effective tools for the analysis of important substances in the environment, foods and biological samples. The development of disposable (bio)sensors for in situ mono- and multi-parametric control is a constant challenge. For this purpose, different transducers must be tested to develop innovative (bio)sensors (e.g. immuno-, geno- and enzymatic sensors; molecular imprinted polymers (MIPs)). The possibility to integrate nanomaterials in the sensors allowed the introduction of novel strategies in (bio)sensor research by exploring their unique characteristics (such as increased strength, chemical reactivity, conductivity, ...) compared to the same material with larger (micro/macro) dimensions.

The Grupo de Reação e Análises Químicas (GRAQ) [1] is a research group that is part of the Laboratório Associado para a Química Verde (LAQV) from REQUIMTE [2], and has a strategic research plan in which the development of (bio)sensors as alternative analytical methodologies is a topic of major significance, including the development of screening methods and/or the improvement of existing confirmatory methods for analytes determination based on the principles of Green Chemistry. Electrochemical methods contribute to the minimization of environmental problems since: (a) electrons are intrinsically clean reagents; (b) most of the reactions may take place at room temperature which reduces energy consumption; (c) the volume of solvents is low and in many cases aqueous buffers can be used; (d) electrochemistry is flexible in the sense that it can be used to analyze inorganic, organic, or biochemical substances; (e) the amount of waste produced is small; (f) cost-effectiveness can be raised because the necessary equipment and operations are usually simple [3].

Highlighting some of the projects that have been developed in GRAQ over the last years, different (bio)sensors for the analysis of (bio)molecules to assess the environment [4, 5], human health [6], and food quality and safety [7, 8] will be presented.

References:

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IOC2

Water Splitting for Renewable Energy Storage.

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Increasing the share of renewable energies in global energy supply has become a pressing need to reach the target of the 2015 Paris Climate Conference (COP21). However, given the intermittent nature and the mismatch between energy demand and supply, large-scale deployment of renewable energies such as solar and wind requires us to develop advanced energy storage solutions. Converting renewable energies into storable and dispensable hydrogen fuel through water splitting represents one of the most promising and important means to store renewable energies.

In this communication, recent progress in developing efficient, inexpensive and durable water splitting devices at the International Iberian Nanotechnology Laboratory (INL) will be presented. Focus will be placed on the following two topics: (1) electrochemical water splitting. Many efforts have been made to fabricate self-supported monolithic electrodes comprising transition metal phosphides – a remarkably new class of electrocatalysts emerged since 2013. The electrocatalytic performance of the as-fabricated transition metal phosphide electrodes towards both the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) has been investigated in detail. (2) photoelectrochemical water splitting. Nanostructured semiconductor photocathodes and photoanodes have been developed. Non-precious, earth-abundant electrocatalysts are used to couple with these semiconductor photoelectrodes to achieve photoelectrochemical water splitting.

IOC3

Arrays of voltammetric sensors using combinations of electrocatalytic materials for the analysis of foods.

M.L. Rodríguez-Méndez

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Electrochemical sensors have been prepared using a range of materials and using a variety of methods. The selection of phthalocyanines or nanoparticles as sensing materials in electrochemical sensors was inspired in their electrocatalytic properties¹. In turn, nanostructured sensors prepared using the Langmuir-Blodgett (LB) or the electrostatic Layer-by-Layer (LbL) techniques have the advantage of the enhanced number of active sites that has a reflect in the increase in the intensity. The control of molecular architectures afforded by these techniques can led to the development of a variety of devices where synergy is achieved by combining distinct materials, including organic-inorganic hybrids².

In this work combinations of phthalocyanines or conducting polymers with nanoparticles have been used as voltammetric sensors for the detection of compounds of interest in the food industry (i.e. phenols or organic acids). The role of the molecular interactions in the electrocatalytic properties has been studied and the existence of synergistic effects has been evidenced. For instance, the combination of phthalocyanines with gold nanoparticles in LB films produced an increase in the sensitivity towards phenols and detection limits of 10^{-7} mol.L⁻¹ were attained.

Biosensors have also been developed by introducing enzymes in the sensing layer. For instance LB films combining phthalocyanines and amphiphilic molecules provided biomimetic environments where enzymes could preserve their functionality. Detection limits as low as 10^{-8} mol.L⁻¹ towards phenols were attained.

Finally, the performance can be further improved by constructing arrays formed by sensors with complementary activity. The signals provided by the array analyzed by means of chemometric methods have allowed detecting antioxidants present in complex mixtures such as wines or musts.

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¹M.L. Rodríguez-Méndez, C. Medina, J.A. de Saja, C. Apetrei, R. Muñoz, *Sensor arrays based on phthalocyanines: New developments on nanostructured and biomimetic electrochemical sensors*. In *Multisensor systems for chemical analysis: materials and sensors*. Eds. L. Lvova, D. Kirsanov, C. Di Natale, and A. Legin. PAN STANFORD PUBLISHING. Chapter 4, 70-109 (2012)

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IOC4

The intrinsic and intriguing electrochemical properties of carbon-based solutions generated from graphite.

M. Cristina F. Oliveira

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Graphite has been the starting platform for the top-down preparation of a wide spectrum of graphene-based materials with different sizes and shapes, like sheets, nanoribbons and flakes. Among the many applications of these nanomaterials, there has been a particular interest in their use as electrode materials in electrochemical devices, such as biosensors, supercapacitors, solar cells and fuel cells. In this context, there has been a significant interest in studying the electron transfer kinetics and capacitance of these graphene-based materials in the solid state¹, which contrasts to the incredible lack of studies concerning the electrochemical properties of the solutions containing hydrophilic graphene-based materials.

Actually, apart from the nanostructures mentioned above, there is a class of carbon-based nanomaterials, highly soluble in water, which is concomitantly formed upon the oxidation of graphite. This class comprises carbon clusters, often referred as carbonaceous fragments or oxidation debris. Although these materials are often treated as an undesired by-product, remaining strongly adsorbed to graphene-based materials, several authors have called the attention to their important role in the electrochemical properties of graphene oxide (GO)² and carbon nanotubes (CNT)³, underlying that some of the properties exhibited by GO and CNT should be assigned to the carbonaceous impurity itself. It is thus most urgent to gain an effective insight on the properties of this type of material.

Recently we developed an electrochemical methodology to generate hydrophilic carbon clusters as the main product released from graphite⁴. This finding provided us the raw material to investigate their intrinsic electrochemical properties, including their redox behaviour in solution and effect on the capacitive properties of the electrode-solution interface.

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IOC5

Multisensor devices and chemometrics.

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Multisensor systems are sensor arrays that allow to perform analysis of various physical and chemical parameters in liquids with complex matrices. The sensor types most used are potentiometric and voltammetric:

- in voltammetric systems (typically, a three-electrode system), the sensor array has a reference, counter and several working electrodes, usually metals and/or metals with its surface chemically modified, allowing high sensitive electrochemical determination of organic molecules, as well as ions [1,2].
- in potentiometric systems, the sensor array has a reference electrode and several indicator electrodes, usually ion selective electrodes and/or nonspecific, low-selective chemical electrodes with partial specificity (cross-sensitivity) to different compounds in solution. These last electrodes are sensitive to salty, acid, sweet, bitter and astringent compounds, among others, and therefore analytical systems with these sensors are called of Electronic Tongues (chemical sensor arrays that attempt to mimic the human chemical senses) [3].

The main advantage of multisensor systems based on chemical sensor arrays is to give a signal profile that can be also used as a unique fingerprint of each matrix under evaluation, rather than only consider the individual information about the nature of the studied compounds [4,5]. Chemometrics has direct application in multisensor chemical analysis since it allows to establish: experimental design of the assays, prediction models for qualitative and quantitative analysis, selection the best subset of sensors, identify extreme values, extract the most possible information from the results and, as well, interpret the results correctly with a maximum of relevant information [6].

As an example, a potentiometric multisensor device, having two sensor arrays with the same 20 cross-selectivity polymeric sensors, was used to analyze mixed solutions of glucose, fructose and sucrose, with different concentration levels established by an orthogonal experimental design [7]. Data processing for the quantification of a sugar is shown.

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OC

ORAL COMMUNICATIONS

COMUNICAÇÕES ORAIS

OC1

Electrochemical genoassay with gold-coated magnetic nanoparticles as new approach to detect the soybean GTS40-3-2 event in food and feed.

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Genetically modified organisms (GMOs) are, long time, the subject of intense debate in Europe. The long term effects of the intake of food containing GMOs are not known and has contributed to a concern by consumers. Currently, the legislation makes it mandatory to label foods containing a percentage of GMOs above 0.9% [1]. Accordingly, it becomes increasingly important to develop fast, sensitive, selective and low cost analytical methods to detect the presence of unapproved GMO and compliance with the labelling regulations.

Methods based on amplification of a specific DNA sequence and its subsequent hybridization with complementary probes (genoassays) are currently a promising strategy as alternatives to techniques based on polymerase chain reaction (PCR) as the reference method. These assays enable detection of GMOs through 3 steps: immobilization of the DNA probe; (2) hybridization with the amplified target sequence; (3) detection using tags or labels. In this sense, the electrochemical readout is very convenient because of its sensitivity and amenability to miniaturization. In this work, we used as immobilization platform gold-coated magnetic nanoparticles (Fe₃O₄@Au MNPs) combined with enzyme-amplified electrochemical detection for the determination of soybean GTS40-3-2 event. The optimization of the process is critical to improve the performance of these devices. Thus, we proceeded to optimization of some of these steps, namely: the influence of concentration and ratio of the thiols used in the surface of MNPs (6-mercapto-1-hexanol: 6-mercaptohexanoic acid), the relationship between the amount of MNPs and the concentration of thiols, the influence of heat and the presence of BSA during hybridization. The results showed the assay allows the determination of the analyte in a concentration range of 0.1 to 10 nM. This work opens prospects for application this genoassay in the detection of GMOs in feed and food.

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OC2

POM@graphene hybrids as highly efficient electrocatalysts for the hydrogen evolution reaction.

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Hydrogen (H₂), as a renewable and environment-friendly energy, has triggered broad attention to replace the fossil fuels because of the increasingly serious energy crisis and environmental contamination[1]. Producing H₂ from electrocatalytic splitting of water by the hydrogen-evolution reaction (HER) has become a research focus because of the high efficiency of energy conversion[2]. Pt group metals are the state-of-the-art electrocatalysts to generate H₂ with high current density at low overpotential (η) in acidic media. However, the scarcity, high costs, and the instability of Pt limits the widespread application for the HER[3]. Recently, non-noble electrocatalysts have been widely studied showing promising results but much work remains necessary to decrease the overpotentials required to drive efficiently the HER[4,5].

Our strategy to achieve this goal was to prepare a new electrocatalyst combining carbon materials and a polyoxometalate (POM). POMs are a unique class of materials with different properties and application depending on their versatile structures. One of the more important is their good proton and electron reservoir abilities. The novel nanocomposite was fully characterized by several solid state techniques which confirmed its successful preparation. More importantly, modified electrodes showed promising results towards HER in acidic solution with an overpotential of 58 mV at 10 mA cm⁻².

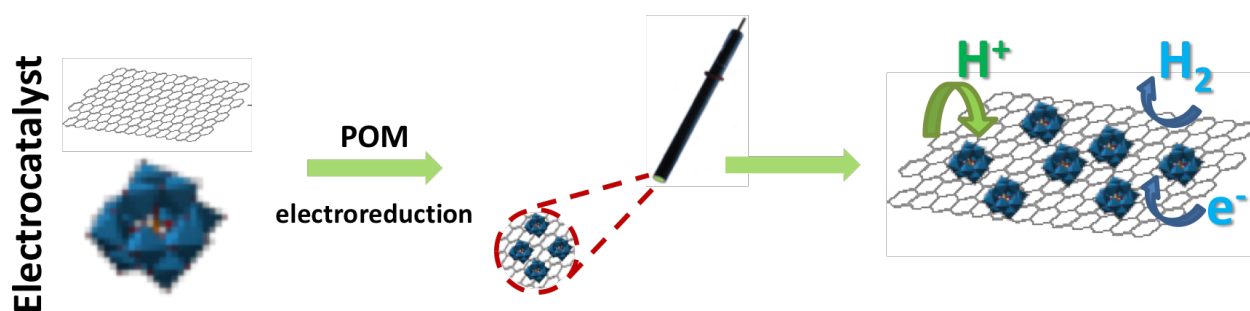


Figure 1. Scheme of the single-step electrochemical reduction synthesis of the POM/graphene hybrid.

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OC3

Self-assembled monolayer-based immunosensor for the determination of thyroxine (T₄).

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Over the past few years, there has been an increasing interest in developing miniaturized electrochemical sensors for the in-situ quantification of a wide range of analytes^{1,2}. Particularly, the exploitation of screen-printed electrodes (SPEs) characteristics and their application in the production of high versatile and portable sensors is currently undergoing a widespread growth. Indeed, SPEs surface can be easily modified in order to improve their selectivity, reproducibility, stability and their potential for mass production, being considered excellent platforms for the development of novel biosensors. This work focuses on the construction of an electrochemical immunosensor for the quantification of thyroxine (T₄), a thyroid hormone with a key role in metabolism regulation. Both an excess and a deficiency of T₄ levels are related with several diseases, such as Graves disease, neurodevelopmental disorders and depression, being its quantification in the human body essential. Here, we developed a T₄ biosensor based on the use of a mixed self-assembled monolayer (SAM) for the immobilization of the anti-T₄ antibody onto a gold SPE (Figure 1). 6-mercaptohexanol and 11-mercaptoundecanoic acid were applied for the covalent binding of the antibody, creating the appropriate linker between the golden surface and the anti-T₄. Electrochemical impedance spectroscopy and cyclic voltammetry techniques were used for the modification procedure control and characterization of the modified electrodes surface. Furthermore, the analytical application of the developed biosensor was carried out by EIS after incubation of the sensor with different concentrations of T₄ hormone and using ferrocene as redox probe.

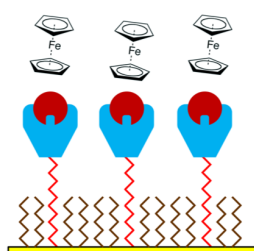


Figure 1: Schematic representation of the developed T₄ biosensor.

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OC4

Electrochemical tools for the evaluation of bioactive compounds in bee products.

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Recent years have seen growing interest from consumers, food, cosmetics and pharmaceutical industries, and researchers into bee products and the ways in which they may help maintain human health. Scientific studies have attested their abundance on nutrients and bioactive compounds, especially antioxidants such as phenolic compounds, so it is important to establish a rapid and reliable analytical method for the evaluation of the nutraceutical value of bee products.

Taking advantage of the electrochemical activity of antioxidants compounds, resulting from the electronic delocalization on the aromatic nucleus, they can be easily oxidized at inert electrodes and therefore be subject of study by electrochemical methods. Its overall reducing power can be evaluated within food and biological samples without the use of specific reagents [1]. An important relationship between electrochemical behavior and antioxidant power as already been established: a low oxidation potential is associated with a high antioxidant power. On the other hand, the intensity of the anodic current is related to the total content of the reducing species present in the sample [2].

In the last years, our research work has been focused in the establishment of a rapid, easy and low-cost tool, for the evaluation of the electroactive species and the antioxidant capacity of some bee products such as propolis and pollen, by using electrochemical methods like cyclic voltammetry and differential pulse voltammetry. The work with propolis allowed the evaluation of the redox profile and the quantification of the total antioxidant capacity in Portuguese propolis from different origins and potential floral sources *Populus x canadensis* Moench and *Cistus ladanifer* L through electrochemical tools [3]. Electrochemical assays were used to distinguish the antioxidant capacity showed by different types of pollen with different colors and floral origins [4]. Also, beebread proved to be a good source of vitamin E, with its quantification achieved through differential pulse voltammetry.

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OC5

Sucrose-derived activated carbons as electrocatalysts for the oxygen reduction reaction.

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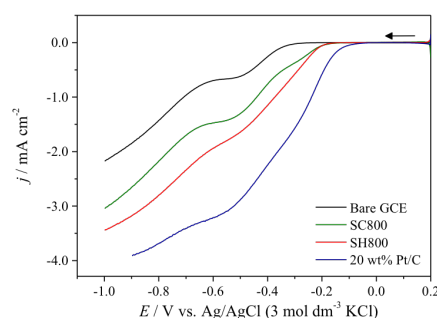
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Nowadays, fuel cells are recognized as an excellent alternative power source [1] and a main tool to counteract the depletion of fossil fuels and the growing threat of environmental pollution. This clean energy conversion technology is based in a series of electrochemical processes that include the occurrence of the oxygen reduction reaction (ORR) at the cathode.[2] The ORR has a strong influence in devices performance, [3] whereby most of the research around fuel cells is focused in finding an efficient ORR electrocatalyst, very stable and cost-effective. In this context, carbon-based materials, with their versatile properties, have been widely applied as ORR electrocatalysts. Activated carbons (ACs), in particular, take advantage of their typical high surface areas, well developed porosity and possibility to be easily obtained from renewable sources, [4] and therefore appear as interesting alternatives ORR electrocatalysts.

In this work, two sustainable sucrose-derived activated carbons, denominated SC800 and SH800, were applied as ORR electrocatalysts; the effect of their textural properties – specific surface area, microporosity and morphology - on the electrocatalytic performance was evaluated. [5] Both ACs showed ORR electrocatalytic activity in alkaline medium, with similar onset potentials ($E_{\text{onset}} \approx -0.20$ V vs. Ag/AgCl) but higher current densities for SH800. The electrocatalysts also revealed excellent tolerance to methanol, with SH800 presenting inclusive greater long-term electrochemical stability than the state-of-the-art Pt/C electrocatalyst. In acidic medium, the ACs also showed ORR catalytic activity, although with modest ORR performances, but making them promising for application in proton exchange fuel cells.

Figure 1. ORR results in alkaline medium: linear sweep voltammograms using rotating disk electrode, in O₂-saturated solution.



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Acknowledgments:

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OC6

Development of sulfur based polymers for rechargeable lithium batteries.

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Lithium-ion (Li-ion) batteries are in the front edge of recent achievements concerning energy storage. However, Li-ion devices are reaching their maximum regarding energy density storage which restricts their application in systems with large power needs, such as electric vehicles. Driven by this shortcoming, in the last few years, Lithium-Sulfur (Li-S) batteries are being considered as an alternative for the exploitation of energy storage and conversion systems with improved performance. Indeed, to the S cathodes is associated a theoretical specific capacity of 1672 mA h g⁻¹ and a specific energy of 2600 W h kg⁻¹, which are several times higher than the correspondent to other possible systems. The relative low atomic weight of S in comparison with other elements (e.g. cobalt) and the multi-electron transfer reactions in the pair Li/S are at the source of this superior theoretical performance of Li-S batteries. Nonetheless, different kinds of issues such as the polysulfides formation (causing the shuttle effect in the electrolyte), the poor conductivity of sulfur and the increase of specific volume observed during discharge, lead to a poor stability of the S cathodes with concomitant battery performance degradation after some discharge-charge cycles. Different strategies are being considered in the scientific community to counteract these effects, namely the use of S composite materials, the change of electrolytes to control the shuttle effect or the S encapsulation to avoid the expansion phenomena.[1] Furthermore, a new approach based on the inverse-vulcanization of elemental sulfur was recently proposed to improve the stability of S-based cathodes.[2] Through a ring-opening polymerization, the elemental S is transformed into a polymer network and it was demonstrated that these sulfur-rich copolymers can be used in cathodes of Li-S batteries with enhanced charge capacity and lifetime (e.g 1000 mA h g⁻¹ capacity and 500 charge-discharge cycles).[2]

Very recently, it was shown by our research group that the inverse-vulcanization of S can be carried out with a high degree of control using Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerization and that many new synthesis pathways can be implemented with possible impact in the improvement of the S based cathodes.[3] Here, we present new findings concerning the synthesis, characterization and application of sulfur based polymers in rechargeable Li batteries. Using cyclic voltammetry (CV), it is shown that the synthesized S-networks preserve the fundamental electrochemical activity of the elemental S. Using split test cell type devices, Li-S batteries were assembled with the produced S-networks in the cathodes and submitted to charge-discharge cycling studies (see Figures 1 and 2 below presented). Results thus obtained evidence that the developed S-networks are promising materials to enhance the performance of Li-S batteries concerning their capacity and cycling stability.

Figure 1: Cyclic voltammograms of a Li-S electrochemical cell assembled with a RAFT synthesized sulfur-polymer as active material in the cathode. Testing performed at the scan rate of 20 $\mu\text{V s}^{-1}$.

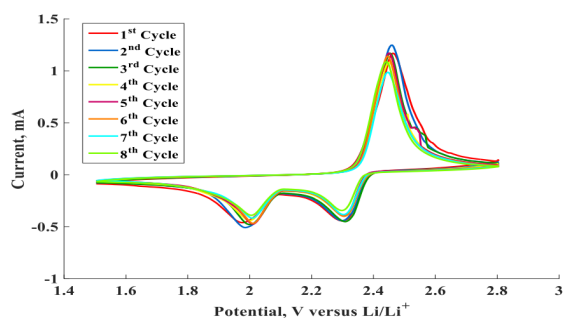
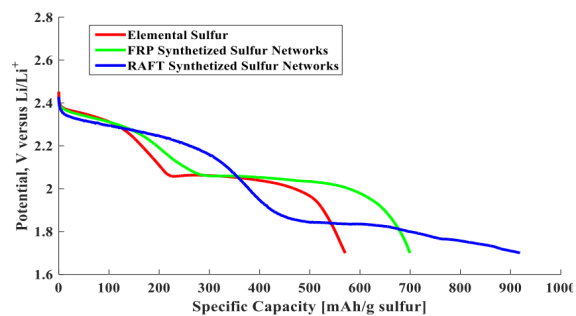


Figure 2: Initial discharge voltage profiles of Li-S cells assembled with cathodes composed of elemental sulfur, FRP and RAFT sulfur-polymers. Testing performed at the C/4 rate.



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OC7

A representação matemática do desempenho eletroanalítico do material polimérico conductor radicalmente pré-tratado, modificado por safranina, na detecção de compostos hidroquinônicos.

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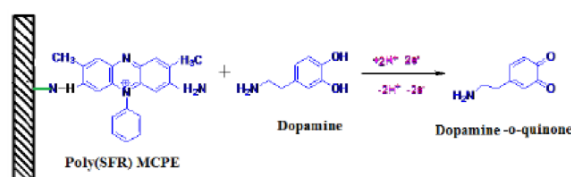
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Os polímeros condutores (PC) constituem uma das classes de materiais orgânicos, mais estudadas ao longo das últimas décadas [1]. O terem as propriedades “afináveis” dá-lhes um espectro vasto e rico de uso. Uma das aplicações mais importantes desse tipo de compostos é o seu uso em eletródios quimicamente modificados. No caso dos PC, a modificação pode ser realizada mediante:

- modificação covalente;
- entrapment;
- dopagem;
- adsorção.

Nos casos mencionados, a escolha do modificador e do tipo de modificação é definida pela natureza do analito. Por exemplo, para os compostos hidroquinônicos, foram elaborados muitos métodos eletroanalíticos, envolvendo os eletródios quimicamente modificados – cada um com suas vantagens e desvantagens [2 – 3]. A elaboração desses métodos enfrenta várias dificuldades, como indecisão sobre o mecanismo mais provável do desempenho do modificador concreto e a presença de instabilidades eletroquímicas (oscilatória e monotônica). Ambos os problemas podem ser resolvidos, com o auxílio de um modelo matemático, capaz de descrever adequadamente o sistema eletroanalítico.

No trabalho [3], foi usado o eletródio de polímero conductor, modificado por safranina, e o mecanismo sugerido do seu desempenho pode ser apresentado como:



Neste trabalho, foi mostrado que o melhor valor do pH para o desempenho do sensor é correspondente ao pH neutro. Os comportamentos oscilatório e monotônico, neste sistema, são possíveis, sendo provocados pelas influências da eletro-oxidação sobre a dupla camada elétrica.

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OC8

Ti/Pt/TiO₂ electrodes prepared by DC Magnetron Sputtering: Environmental application on the degradation of the Acid Orange 7.

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To use titanium oxide as electrocatalyst in environmental applications, it is advisable to immobilize the oxide in the form of a film deposited on a substrate [1]. In this work, a titanium oxide electrode was prepared in three stages: (i) electrodeposition of Pt layer on a Ti substrate that was (ii) covered by a TiO₂ fine film deposited by DC Magnetron Sputtering technique, at constant pressure of 0.8 Pa and oxygen partial pressure of 0.08 Pa, and (iii) annealed at 400 °C. The structural (XRD) characterization of the films was performed, showing a predominant anatase-TiO₂ phase, where some peaks corresponding to the Ti/Pt substrate were also observed. The average crystallite sizes for the films were calculated from the peak width at half peak height of the diffraction peak (101). The obtained value for the average crystallite size was 44 nm, showing the nanocrystalline nature of these anatase-TiO₂ films. The surface morphology (SEM) of the films revealed agglomerates of grains or particulates distributed over the substrate surface with a ‘blooming flower-like’ appearance, of nanosized grains (Figure 1a). The nanosized grains result in an increase in active surface area and also promote the formation of porous TiO₂ films, which is a key parameter in the electrodegradation studies.

The performance of Ti/Pt/TiO₂ as anode was evaluated in the electrodegradation of a model organic pollutant, an azo dye, the acid orange 7 (AO7). Assays were run at 0.1, 0.25 and 1 mA cm⁻², using AO7 concentration of 50 mg L⁻¹, and after 6 h assay an almost complete color removal (at 484 nm) was obtained. The removal of the organic load was evaluated through determinations of chemical oxygen demand (COD) and the results are presented in Figure 1b. The energetic yield decreased with the increase in current density, which is typical of a process controlled by diffusion. When compared to the results obtained for a Ti/TiO₂ anode, it can be concluded that the platinum interlayer reduces the COD removal rate [2]. Despite the Pt layer being covered by TiO₂, the porosity of the titanium oxide film allows the contact between the Pt interlayer and the solution. On the other hand, the platinization of the substrate increases the conductivity of the films, improving the adhesion of the TiO₂ film on the substrate and decreasing the energetic costs of the process.

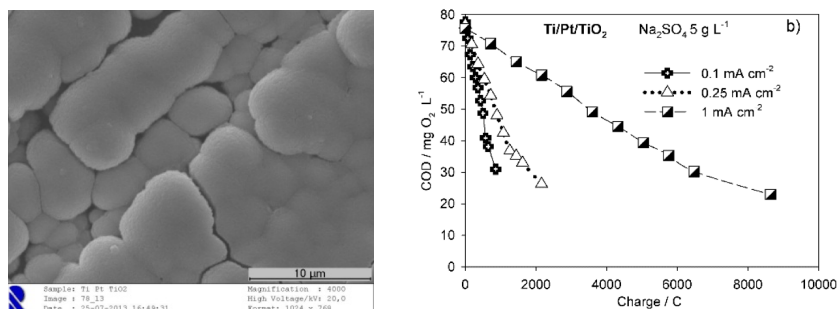


Figure 1. a) SEM micrographs of the Ti/Pt/TiO₂ anode surface (x4000) and b) evolution of COD with the charge, for different applied current densities.



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OC9

Optimización de los parámetros de funcionamiento de un proceso de electrocoagulación para el tratamiento de efluentes de curtiduría.

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La curtiduría es una de las actividades productivas más importantes de la ciudad de León, Guanajuato, aportando un aproximado de las dos terceras partes del total de la cantidad de pieles que se producen en México. (1) En los procesos de curtido, se genera una media de 35 litros de agua residual por cada kg de piel tratada en el procedimiento global (2), lo que impacta de manera importante a los organismos y al medio ambiente. Por su composición, los efluentes son difíciles de tratar y existe una diversa gama de tratamientos probados para su depuración. Debido a la presencia de compuestos y sustancias químicas complejas, los tratamientos biológicos son difíciles de aplicar por la inhibición de la actividad de los microorganismos en el medio, disminuyendo su eficiencia, por lo que son necesarias operaciones terciarias para continuar con el mismo (3). Existen tratamientos químicos como la coagulación, en donde se adicionan reactivos como sulfato de aluminio y cloruro férrico (4), los cuales causan contaminación secundaria debido a las reacciones que presentan en el medio (5); formando en ocasiones lodos tóxicos, generando un problema adicional. Métodos de separación por membranas o de intercambio iónico, suponen un alto costo, por lo que se vuelven poco viables (6). Los tratamientos electroquímicos se han convertido en una opción confiable para este tipo de efluentes (7). Se ha reportado la eficiencia de procesos de electrocoagulación en la remoción de contaminantes orgánicos e inorgánicos, pudiendo reducir significativamente niveles de DQO, turbidez y cromo en un lapso de tiempo reducido y a bajo costo (8).

En este trabajo, se llevó a cabo el tratamiento de un efluente real de curtiduría del laboratorio del cuero del CIATEC por electrocoagulación con electrodos de hierro y aluminio, con el fin de encontrar los parámetros óptimos para su operación en una planta a escala piloto de tratamiento para cumplir con los ordenamientos jurídicos competentes en materia de descargas de aguas residuales a la red de alcantarillado municipal. Las pruebas se efectuaron a distintas densidades de corriente, realizándose con un volumen de 1 litro a pH 7, a densidades de corriente de 28 y 111 mA/cm² durante 1 hora. Se evaluó el efecto del tratamiento en la disminución de la demanda química de oxígeno (DQO), carbono orgánico total (COT), turbidez, cromo total, sólidos, conductividad y pH. La remoción de DQO y COT fue mayor a 111 mA/cm², siendo más efectivo el tratamiento con electrodos de hierro con 56% de remoción de DQO y 34% de COT. La turbidez alcanzó una disminución del 99% con los electrodos de aluminio a 111 mA/cm². De igual forma se evaluaron los costos de los métodos, siendo el de aluminio a 28 mA/cm² el de menor costo, sin embargo, la remoción de DQO y COT fue la menor de todos los tratamientos. Por lo anterior, se tiene un precedente para la implementación del tratamiento de manera accesible y efectiva en la planta de depuración del CIATEC, por lo que los parámetros de la prueba con hierro a 111 mA/cm², son los más óptimos para su aplicación.

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OC10

Cyclic voltammetry of ionic liquids and of copper complexes therein.

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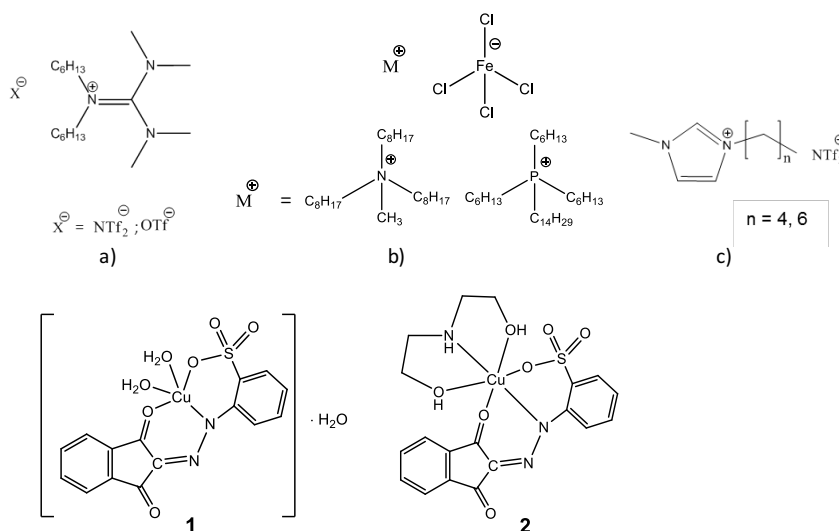
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Cyclic voltammetry provides an useful technique to study the redox properties of substances, what can be useful e. g. to preview the catalytic behavior of some systems. In this work, different types of ionic liquids (a-c) and a couple of copper (II) complexes of arylhydrazone of indandione (1 and 2) were studied and the electrochemical window of the ILs was evaluated. It was found out that the guanidine-based ionic liquids have the shortest electrochemical window of all ILs studied, thus being more redox active and less conveniente to be applied as a medium for electrochemical studies. The results also show that the ILs of the same family have similar windows. [1]

The electrochemistry of the copper(II) complexes dissolved in the ionic liquids was also evaluated, to try to assess their viability as catalysts in alkane and alcohol oxidations. Results will be discussed in light of the yields obtained in the catalytic studies and a comparison between the two catalysts is presented.



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OC11

Electrochemical aptasensor array for multiple detection of human osteopontin .

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Most cancer diseases are associated with the presence of several biomarkers, as the proteins. The proteins, when overexpressed in biological fluids could be used as potential diagnostic or prognostic markers indicative of disease states [1,2]. Osteopontin (OPN) is a phosphorylated glycoprotein and has been reported as a potential breast cancer biomarker, its overexpression may be indicative of tumor formation, cancer progression, metastasis and poor prognosis [3–6]. An early diagnosis of the disease is of utmost importance to improve the patient's survival rate and therapeutic efficacy, as well as to monitor the disease recurrence. In this sense, it is essential to develop new, simple and cost-effective methods holding a high sensitivity and reliability for the simultaneous detection of multiple protein disease biomarkers in biological fluids [7]. The electrochemical multi-aptasensors arrays has recently attracted attention for the detection of various proteins disease biomarkers, due to their advantages, such as high sensitivity, specificity, fast detection, easier experimental procedures, lower cost preparation and the potential for miniaturization, as well as advantages of aptamers as bioreceptors elements such as high affinity and specificity towards a specific target, easy to produce and synthesize, good stability and amenable to chemical modification [8–10]. This study describes the development of an electrochemical multi-aptasensor array for the simultaneous detection of human OPN using two specific aptamers. To enable multiplexed protein assay, the RNA and DNA aptamers were immobilized in the working electrodes of the dual-screen-printed gold working electrodes (dual-SPGEs) via streptavidin-biotin interaction and using the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ as the redox probe for cyclic voltammetry (CV) measurements. The preliminary results herein report showed a good response of the multi-aptasensor array for the detection of human OPN. Moreover, the DNA/RNA multi-aptasensor array was able to selectively detect human OPN in the presence of other interfering proteins such as thrombin, bovine serum albumin, bovine osteopontin and lysozyme. Considering these preliminary results, the multi-aptasensor array holding the two aptamers could be a good alternative for the specific detection of human OPN and for cancer diagnosis overall.

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OC12

Application of an electronic tongue for evaluating basic gustatory attributes perceived in table olives: qualitative and quantitative approaches.

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The organoleptic evaluation of table olives aiming their commercial classification according to sensory trade categories, although not being legally required, is recommended by the International Olive Council. This classification is based on the organoleptic evaluation of negative attributes usually found in table olives (and their respective brine solutions), performed by trained sensory panels. However, the training and implementation of such panels is time-consuming, costly and has some drawbacks like the low number of samples that can be assessed per day as well as the intrinsic degree of subjectivity of the evaluations carried out by the trained panelists. Besides the perception of sensory defects (type and intensity), panelists are usually asked, among other characteristics, to assess the intensity of basic gustatory attributes (e.g., acid, bitter and salty), which knowledge is useful for table olives quality control. In this work, and for the first time, the potential use of a home-made electronic tongue for discriminating standard aqueous solutions of chemical compounds (obtained with mineral water and in the concentration ranges used during sensory panels training sessions) that mimic the 3 basic tastes is evaluated: tartaric and citric acids (0.01 to 2 g/L; for acid taste); caffeine and anhydrous quinine (0.01 to 3 g/L; for bitter taste); and, sodium and potassium chloride (0.5 to 25 g/L; for salty taste). The results showed that a linear discriminant model based on the potentiometric signals recorded by a sub-set of 5 sensors (composed by cross-sensitivity lipidic membranes) could correctly classify the standard solutions according to the basic taste mimicked with sensitivities of: (i) 98% for the leave-one-out cross-validation; and (ii) $98\% \pm 3\%$ (ranging from 91% to 100%) for the repeated K-folds cross-validation (K = 4 folds with 10 repeats, guaranteeing that 25% of the original data was kept for internal-validation purposes). Furthermore, the potentiometric signal profiles recorded by the electronic tongue during the analysis of table olives and respective brine solutions (40 different samples) were used, for the first time, to quantitatively estimate the median intensity of the same gustatory attributes (acid, bitter and salty) perceived by a sensory panel (composed by 8 trained panelists) during the simultaneous analysis of table olives and brine solutions. The results showed that it was possible to establish satisfactory multiple linear regression models based on sub-sets of signals gathered during the analysis of the table olives and/or brine solutions (varying from 21 to 25 depending on the basic taste), also selected by applying the simulated annealing variable selection algorithm: (i) $R^2 \geq 0.968$ for leave- one-out cross-validation; and (ii) $R^2 \geq 0.97 \pm 0.02$ for the repeated K-folds cross-validation (K=4 folds with 10 repeats). These preliminary



qualitative and quantitative results allow foreseen the practical application of the electronic tongue for assessing gustatory basic tastes on table olive real samples, which could be used as a helpful tool for the hard task required to sensory panelists.



PC

POSTER COMMUNICATIONS

COMUNICAÇÕES EM POSTER

PC1

Re-synthesis of LiCoO_2 extracted from low and high SOH discarded batteries and its structural and electrochemical characterization.

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Re-synthesis of the LiCoO_2 electroactive material extracted from the cathode of discarded batteries was performed as a recycling strategy. LiCoO_2 powder extracted from the cathodes of a low (L) and high (H) state of health (SOH) discarded cell phone batteries, identified respectively as $\text{Li}_{0.73}\text{CoO}_2$ and $\text{Li}_{0.96}\text{CoO}_2$ compounds by Rietveld x-ray refinements, were submitted to a re-synthesis process composed by a thermal decomposition followed by a solid-state reaction.

The thermal decomposition of the $\text{Li}_{0.73}\text{CoO}_2$ and $\text{Li}_{0.96}\text{CoO}_2$ compounds at 700 °C produced Li_1CoO_2 and Co_3O_4 as reaction products, at Co_3O_4 concentration equals to 33.5% and 11.8% in wt, respectively [1]. Further solid-state re-synthesis reaction with Li_2CO_3 at 750 °C, transformed the Co_3O_4 into the stoichiometric Li_1CoO_2 compound. All reactions were performed in controlled O_2 atmosphere.

Figure 1a shows the changes in the LiCoO_2 hexagonal lattice parameters with the processing temperatures. The measured c parameter, higher for $\text{Li}_{0.73}\text{CoO}_2$ than for $\text{Li}_{0.96}\text{CoO}_2$ as-extracted compounds, and the inverse behaviour for the a parameter, is an effect of the electrostatic repulsion between the O-Co-O layers upon Li removal [2]. The a and c parameters for the Li_1CoO_2 originated from the thermal decomposition of the L and H as-extracted cathodes converges to their standard values. After the re-synthesis, a single Li_1CoO_2 phase was obtained with $c=14.04965 \pm 59 \times 10^{-5}$ Å and $a=b=2.814125 \pm 17 \times 10^{-5}$ Å. The $c/a = 4.99$ and the x-ray peak intensity ratio $I_{(003)}/I_{(104)} > 2.6$ indicates a well ordered Li_1CoO_2 layered structure, with few or none cationic exchange.

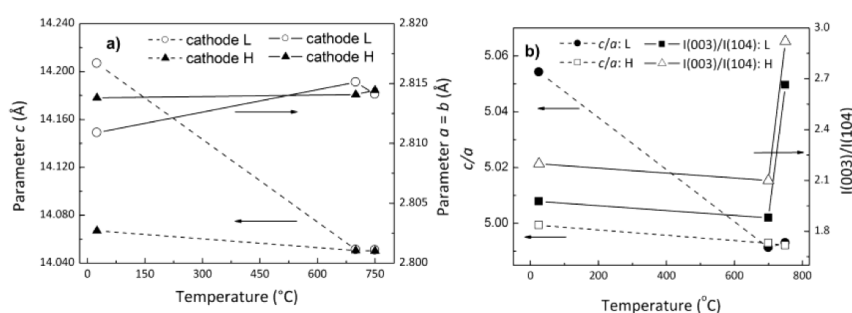


Fig.1. Lattice parameters for the as-extracted (25 °C), thermal decomposed (700 °C) and re-synthesized (750 °C) LiCoO_2 compound from the L and H cathodes (a), the corresponding c/a and x-ray intensity $I_{(003)}/I_{(104)}$ ratios (b).

Figure 2a shows the voltage profiles for the two re-synthesized Li_1CoO_2 electrodes, measured against a metallic Li anode in a $\text{LiClO}_4/\text{EC}:\text{DMC}$ electrolyte, as a function of the specific discharge capacity. Higher specific charge capacities were measured for the electrode manufactured from the re-synthesized L cathode than from the re-synthesized H cathode, Figure 2b. Under charge-discharge cycles capacities equals to 130.0 and 125.0 mA h g^{-1} were measured in the twentieth cycle for the re-synthesized L and H cathodes, respectively. These values are very close to those obtained from pristine commercial LiCoO_2 electrodes. We argue that the small size of the re-synthesized particles from the L cathode (as observed from SEM images) can explain the best performance of the corresponding $\text{Li}_1\text{CoO}_2/\text{Li}$ cell, due the higher specific surface area of this electrode.

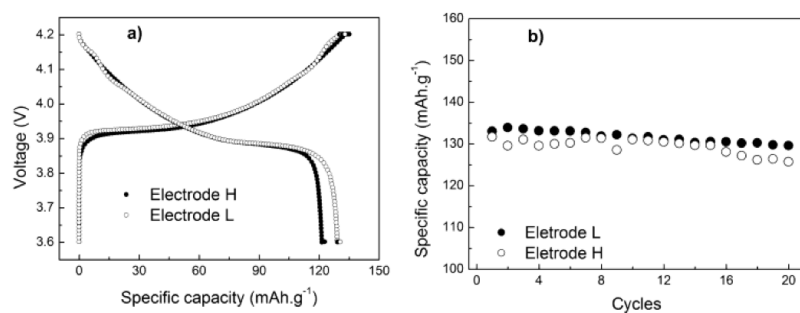


Fig.2. Voltage profiles as a function of the specific charge capacity for the L and H re-synthesized LiCoO₂ cathodes, in the twentieth charge-discharge cycle (a), cycling discharge capacities measured at 0.2C rate for the re-synthesized L and H cathodes. (b).

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PC2

A label-free potentiometric biosensor for the detection of *Salmonella typhimurium*.

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Foodborne illnesses are a worldwide public health issue and *Salmonella* is one of the most frequently occurring pathogens in food. The consumption of contaminated food and water by pathogenic microorganisms, according to World Health Organization (WHO), causes 1.8 million of deaths per year worldwide [1].

Analysis of *Salmonella* is usually based on culture and colony counting, Polymerase Chain Reaction (PCR) and immunological methods, which sometimes are combined in an attempt to obtain more consistent results. These methods have some disadvantages such as the need for intensive work by experts and it takes up to 7-10 days for confirmation of positive results [2]. Because of alarming statistics, it is still necessary to develop new applications, methods and technologies for food safety, mainly in the time consumption to have definitive results, to avoid massive contamination.

Immunoassays, exploring the selectivity arising from the use of immunochemical interactions, are the largest group of rapid methods used for this purpose. Important advances have been accomplished using functionalized magnetic nanoparticles and nanoparticle labels coupled to electrochemical detection [2, 3]. Apart of these, in last years label-free biosensors to detect *Salmonella* have attracted large attention [4-9], because these sensors give real-time measurements, with no requirement of labels or intermediaries, making the detection procedure more simple, with less variables to control and resources needs. The simplicity, portability and ease of miniaturization of potentiometric instrumentation makes this an attractive electrochemical technique to develop label-free immunosensors with enhanced potentialities for application in rapid microbial analysis.

In this work, a label-free potentiometric immunosensor for *Salmonella typhimurium* was designed and evaluated. The antigen-antibody binding event induces changes in the diffusion layer close to the sensor membrane and triggers a membrane potential change, which can be measured by a simple potentiometer in a small sample volume. To maximize the sensibility of the biosensor, were tested several support membrane configurations both to ensure a homogenous distribution and high concentration of antibody on the membrane surface, so as to amplify the electrochemical signal related to antigen-antibody binding. To achieved these, we used a conjugation of a dendrimer G4 to membrane structural grown, and gold nanoparticles to amplify the signal and due their well-known biocompatibility.

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PC3

Electrochemical treatment of tannery wastewater: Two different approaches.

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Tanning operations consist of transforming the raw hide/skin, a highly putrescible material, into leather, a stable product with a commercial value [1]. The leather production process includes different steps, in which large quantities of water and chemicals are applied to the skins and the characteristics of the resulting effluents vary with the applied process. Although conventional biological processes are the most used in the treatment of tannery wastewater, they are unable to perform the complete removal of the hazardous compounds [2]. This study proposes an electrochemical solution for this problem: anodic degradation using different electrode materials.

The samples utilized in this study were collected in a Portuguese tannery industry. The anodic oxidation of the real tannery effluents was performed in setups utilizing different anode materials: Setup A – two electrochemical cells, working in batch mode with recirculation, and having as anodes Ti/PtSnO₂-Sb₂O₄ in the first cell and Ti/Pt/PbO₂ in the second cell; Setup B - one electrochemical cell, working in batch mode with recirculation, and having as anode a boron-doped diamond (BDD) electrode. The effluent was first clarified by chemical coagulation with Fe³⁺ ions, 0.25 g L⁻¹, and submitted to anodic oxidation, in setups A or B, for a period of 8 hours. The charge passed in both setups was identical. The efficiencies of the sets were tested by evaluating temporal variations of chemical oxygen demand (COD), total and dissolved organic carbon (TC, DOC), nitrogen-containing compounds, sulfide, sulfate and Cr(VI).

Although chemical coagulation is effective for the clarification of tannery effluents, the pH of the solution was found to be a crucial parameter to attain good removal of the organic and inorganic loads. In the electrochemical treatment, both setups present similar behavior in the COD, TC, DOC, total Kjeldahl nitrogen (TKN) and ammonium nitrogen removal, showing the possibility of using metal oxides instead of BDD, which decreases the capital costs of the electrochemical process. In both setups, the COD concentration worked as an important inhibiting factor for TKN removal. The setup B presented a performance slightly superior in the production of SO₄²⁻ from sulfur species. Regarding energy consumption, in general, the setup B presents the lowest specific energy consumption due to the higher conductivity of the metal oxides than BDD.

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PC4

Reuse of cotton dyeing effluent treated by anodic oxidation with BDD anodes.

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The Textile and Clothing industry is one of the most important sectors in the Portuguese economy, accounting for 10% of total exports, 19% of employment in manufacturing and 8% of turnover and manufacturing production [1]. The production processes in the textile industry require intensive use of water, which is used in different steps of the production process, with the consequent rejection of large volumes of wastewaters. According to a study performed in Portugal [2] companies finalization processes can achieve water consumption ranging between 42,000 and 750,000 m³ / year. Thus, these industries have been confronted with issues relating to the efficient management of water and energy, and consequently there has been a growing need to implement environmental policies and sustainability. The effluent from the dyeing process and finishing of textiles contain synthetic organic dyes and other refractory products. Although they do not contribute significantly to the organic load, they are poorly biodegradable. It is therefore essential to develop treatments, which can allow the wastewater reuse. The electrochemical oxidation, with boron-doped diamond anode (BDD), has been used with success for the treatment of textile effluents leading to complete removals of color and to high removals of organic load and ammoniacal nitrogen [3,4].

The aim of this work was to study the application of anodic oxidation, using a BDD anode, to treat a textile wastewater from cotton dyeing process and to reuse the treated effluent in new dyeing baths, in successive cycles, by repeating the sequence electrochemical treatment+reutilization in new dyeing process. In this context, it was studied the influence of the electrolysis operational conditions, namely the applied current density (2.5-20 mA cm⁻²), on the treated effluent characteristic and, consequently, its influence on the dyeing quality of the cotton when the treated effluent is reused in the dyeing bath. The cotton fabrics dyeing process was conducted using as dye exhausted bath an aqueous solution containing Brilliant Red Levafix reactive dye, sodium sulfate and sodium carbonate, at a pH of 10.5. The electrochemical treatments were performed with 400 mL of the effluent from the dyeing bath. The experiments were conducted in a batch, with stirring, undivided cell, using as anode a BDD electrode (10 cm²) and as cathode stainless steel plate (10 cm²), with an inter-electrode gap of 1 cm.

Complete decolorization of the effluent was achieved after 12 h of treatment, with COD removal between 60 and 83%, being the highest removal obtained for the highest applied current density. After the electrochemical treatment, the inorganic ions, such as carbonate and sulfate, used in the cotton dyeing baths remain in the treated effluent. Consequently, it is not necessary to add them to the new dyeing bath. The results from the reusability studies of the electrochemical treated effluent showed that the dyeing quality depends on the current density applied to the effluent during the electrochemical treatment. The compositions of the treated effluents vary with this operational condition. The best results for the cotton dyeing was obtained for the lowest applied current densities, which are 2.5 and 5 mA cm⁻². In these cases, no significant color differences were observed between reference dyeing and the cotton dyed with the treated exhausted effluents. It can be concluded that there is a good possibility of using anodic oxidation to

treat textile effluents and reuse them, thus reducing the fresh water and salts consumption in the textile industry.

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PC5

Electrochemistry of dibutyltin(IV) compounds which induce apoptosis: a preliminary study.

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Early accomplishment of platinum chemotherapeutic metallopharmaceuticals has shifted to non-platinum compounds with the objective of minimizing side effects. This has motivated inorganic and organometallic chemists to search for other platinum and non-platinum metallodrugs (e.g., Sn, Ti, Au, Cu, Ru, Pd) that might exhibit a different pattern of antitumor specificities and a more promising pharmacological and toxicological profile, preferably against tumors that are responsible for high cancer mortality. Several organotin(IV) complexes, particularly the carboxylate derivatives, have demonstrated interesting anticancer activities.

Metal based drugs can be activated by reduction, a matter particularly relevant for platinum(IV) and ruthenium(III) metal-based drugs which can exist in inert high oxidation states and become more labile in their lower Pt(II) and Ru(II) oxidation states.^[1] A similar behavior has been proposed for diorganotin(IV) compounds.^[2]

The study we now report presents the electrochemical behavior of dibutyltin(IV) complexes of general formula $\{[\text{Bu}_2\text{Sn}(\text{L}^n\text{H})]_2\text{O}\}_2$ ($\text{L}^n =$ (phenyldiazenyl)benzoic acid derivatives) which were investigated by cyclic voltammetry at a Pt disc electrode in 0.2 M $[\text{nBu}_4\text{N}][\text{BF}_4]/\text{DMSO}$ solutions and at room temperature. They exhibit two well defined irreversible reduction waves which, upon reversing the potential scan direction, lead to novel species that are irreversibly oxidized at higher potential values, thus featuring the aforementioned activation by reduction.

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PC6

Determination of sodium chloride activity coefficients in the system NaCl+AlCl₃+H₂O from potentiometric data.

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Although sodium and aluminum chloride activity coefficients are well known at 298.15 K for single salt solutions, the information provided in the literature is still not enough to calculate the activity coefficients of those two salts when dissolved in mixed aqueous solutions [1].

In this work, mean activity coefficients of sodium chloride were determined from potentiometric measurements in galvanic cells without liquid junction, with silver-silver chloride electrodes of the thermo-electrolytic type, prepared in the laboratory as described in the literature [2], and a commercial glass sodium ion selective electrode, Metrohm, ref. 6.0501.100(OD). The temperature was controlled within ± 0.1 K by means of a thermostat, Grant, CB2 5QZ. Potentiometric measurements were taken for NaCl and (NaCl + AlCl₃) solutions, in the ionic strength range 0.2 to 6 mol kg⁻¹. The temperature varied between 283.15 and 313.15 K. The sodium chloride activity coefficients were then evaluated using the Nernst equation.

The Pitzer theory [3,4], which takes into account specific ionic interactions, was here applied to the calculation of aluminium chloride activity coefficients in the mixed solutions. The mixing parameters, $\theta_{Na,Al}$ and $\psi_{Na,Al,Cl}$, according to the Pitzer formalism [4], were evaluated and it was shown that the inclusion of the higher order electrostatic terms in the equations is necessary to obtain a good fit to the experimental data, in the present situation. Those quantities account for binary and ternary interactions, respectively, between ions of like charge, and so they are expected to be quite small.

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PC7

Electrochemical characterization of luminescent carbon nanomaterials from different sources.

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Carbon nanomaterials, in particular those with particle sizes of less than 10 nm, the so-called carbon dots (C-dots) [1], are gathering increasing attention in fluorescent bio-imaging and nanomedicine [2], sensory analysis [3] and as photocatalysts [4]. Top-down and bottom-up approaches are both being used for their synthesis [1]. Herein we report two types of C-dots prepared by a hydrothermal process from two different carbon sources in the presence α,ω -alkyldiamines, namely citric acid (CD 1) and cork industry wastewater (CD 2). Aiming to understand the potentiality of this luminescent nanomaterial as fluorescence sensors, cyclic voltammetry (CV) studies were performed, with emphasis on the LUMO energies and band gaps determination. CV analysis were conducted in a standard three-electrode system with a platinum sheet as the working electrode, a platinum wire as the counter electrode and Ag/AgCl as reference, in DMF with tetrabutylammonium tetrafluoroborate as electrolyte. Fig. 1 shows selected voltammograms and the oxidation and reduction peak potentials are presented in Table 1. For comparison purposes, the optical band gaps for the two nanomaterials were also determined using combined data from UV-Vis, excitation and emission spectra (CD 1 – Fig.2 and CD 2 – Fig.3).

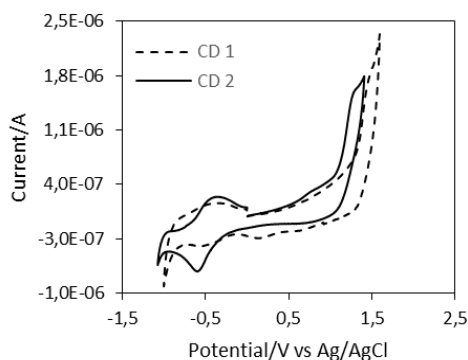


Fig.1 – CV of CD 1 and CD 2, scan rate 100 mV s⁻¹.

Table 1 – Oxidation and reduction peak potentials of CD 1 and CD 2.

	E_{ox} (V vs .SCE)	E_{red} (V vs. SCE)
CD 1	1.057	-0.602
CD 2	1.232	-0.532

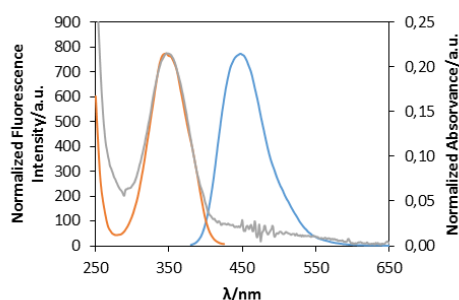


Fig.2 – UV-Vis (gray), excitation (orange, monitored at 460 nm) and fluorescence (gray, λ_{exc} = 380 nm) normalized spectra of CD 1 in aqueous solution (0.1 mg mL⁻¹).

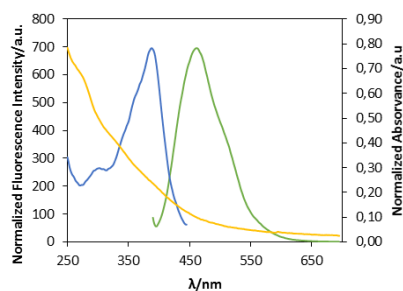


Fig.3 – UV-Vis (yellow), excitation (blue, monitored at 460 nm) and fluorescence (green, λ_{exc} = 380 nm) normalized spectra of CD 2 in aqueous solution (0.1 mg mL⁻¹).

Correlation between optical and electrochemical band gaps and the thus obtained HOMO and LUMO energies will be discussed in connection to the different carbon sources.

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PC8

Produção do gás de síntese através da eletrólise da água, usando biomassa liquefeita.

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O presente trabalho de investigação consiste na produção de gás de síntese através da eletrólise da água, recorrendo ao uso de energia elétrica renovável, e ainda de biomassa liquefeita como fonte de carbono necessária à obtenção de monóxido e dióxido de carbono. Trata-se de um processo inovador, uma vez que a adição dos produtos resultantes da liquefação de resíduos de biomassa ao eletrólito torna o processo menos dispendioso, do ponto de vista económico, que o processo patenteado de produção do gás de síntese usando elétrodos de grafite. O grande desafio deste trabalho passa por aumentar a condutividade elétrica da biomassa liquefeita, identificar eletrólitos com elevada condutividade elétrica e que permitam ultrapassar a barreira da baixa condutividade da biomassa, e os líquidos iónicos surgem como uma alternativa aos eletrólitos comumente utilizados (hidróxido de sódio ou hidróxido de potássio).

O trabalho experimental foi levado a cabo num eletrolisador de 100 W, sem membrana de separação de gases, com elétrodos de aço, usando diversas soluções de eletrólito e otimizando as condições operacionais, tais como: concentração de eletrólito a utilizar, concentração do liquefeito a adicionar ao eletrólito, bem como temperatura, pressão e intensidade corrente aplicada ao eletrolisador. Foram avaliadas as principais saídas do processo, tais como os teores de monóxido de carbono, dióxido de carbono e oxigénio, bem como o caudal total dos gases produzido. Para além da produção de produtos químicos, o gás de síntese (constituído essencialmente por CO, CO₂, H₂ e algum O₂), dependendo das condições operacionais, pode ser convertido em combustíveis sintéticos renováveis, tais como metano, metanol, éter dimetílico, diesel, etc., que possam ser utilizados em transporte rodoviário.

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PC9

Electrochemical characterization of ionanofluids.

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Nanofluids have showed interesting thermo-physical properties, for example, thermal conductivity, thermal diffusivity, viscosity and heat transfer coefficient when compared to their base fluids.[1]

In this study we present the electrochemical study of several ionanofluids comprising an ionic liquid (base fluid) and a nanomaterial. The ionanofluids were prepared from the base fluids 1-butyl-3-methylimidazolium bromide, [Bmim]Br, and 1-butyl-3-methylimidazolium tetrafluoroborate, [Bmim]BF₄, and Ni, Fe and CuO nanoparticles, created in situ.

This allows to evaluate the redox potential and provides a tool for evaluating the ionanofluid catalytic ability.

The electrochemical properties of the ionanofluids are correlated with their catalytic performances in Heck and Sonogashira C-C coupling reactions.

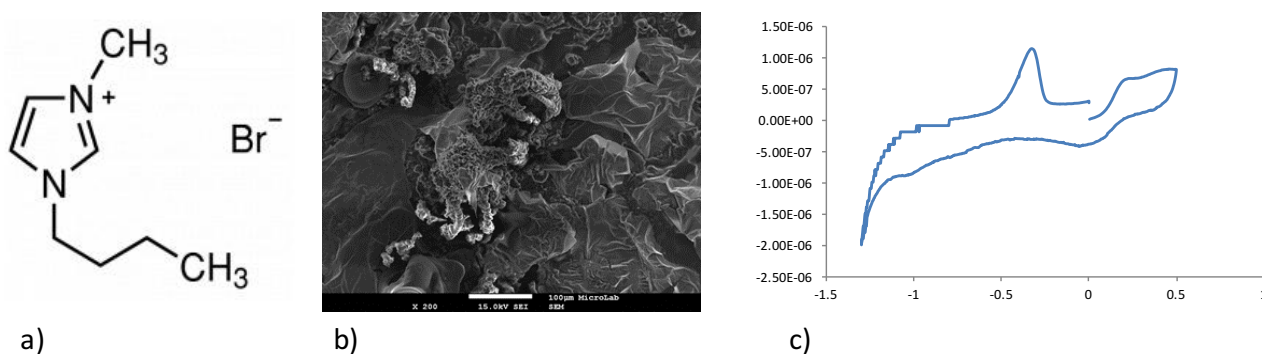


Figure 1 - a) 1-Butyl-3-methylimidazolium Bromide structure; b) SEM image of a ionanofluid formed with CuO and [Bmim]Br; c) cyclic voltammogram for ionanofluid b), using a platinum working electrode, 200 mV/s.

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PC10

Influence of fructose on the diffusion of sodium tetraborate at 25 °C.

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Fructose is a monosaccharide found in natura in fruits and honey. However, exponential growth in the use of high fructose corn syrup (HFCS) as a sweetener in processed foods, appeared on the focus of recent scientific literature as an established cause of the obesity epidemics and a growing number of fructose-correlated diseases and conditions.

Recent research shows that borate complexed with fructose provides an alternative, time-saving, and specific method for serum fructose determination¹. However, studies are still needed in order to better model the ionic behavior in the presence of fructose.

In order to establish new mobility data, mutual diffusion coefficients for sodium borate in aqueous solutions (0.100 mol dm⁻³) containing fructose at various concentrations (from 0.001 to 0.100 mol dm⁻³) have been measured at 25 °C, by using a conductimetric Lobo's cell coupled to an automatic data acquisition system to follow the diffusion.

This apparatus proved itself to be very useful when studying interactions of an electrolyte and non-electrolytes, as it can measure the whole system transient response using a pseudo-binary approach while maintaining the concentration changes of the non-electrolyte component inconsequent to the conductimetric measure.

The analysis of the fructose-limited sodium borate diffusion coefficient values obtained should prove useful in modeling metabolic syndrome mechanisms and other fructose related diseases and conditions recently reported.

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The Authors gratefully acknowledge the support of the Coimbra Chemistry Centre.

PC11

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

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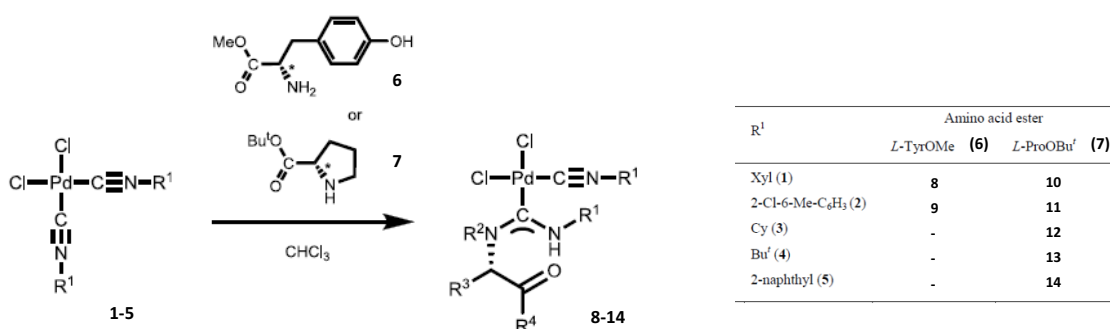
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Metal-mediated coupling between equimolar amounts of *cis*-[PdCl₂(CNR₁)₂] (**1-5**) and the amino acid esters L-HTyrOMe (**6**) or L-HProOtBu (**7**) proceeds at room temperature in chloroform yielding the complexes *cis*-[PdCl₂(CNR₁){C(TyrOMe)=NHR₁}] (R₁ = Xyl **8**, 2-Cl-6-Me-C₆H₃ **9**) or *cis*-[PdCl₂(CNR₁){C(ProOBut)=NHR₁}] (R₁ = Xyl **10**, 2-Cl-6-Me-C₆H₃ **11**, Cy **12**, But **13** and 2-naphthyl **14**) (Scheme 1). The full conversion of the reactants to **8-14** was achieved within ca. 48 h.



Scheme 1

We now report the redox properties of the aminocarbenes Pd(II) compounds **8-14**, by cyclic voltammetry (CV), at a Pt-disc electrode (d = 1 mm) and by controlled potential electrolysis (at a Pt-gauze electrode), in 0.2 M [ⁿBu₄N][BF₄]/CH₂Cl₂ solution, at 25 °C. The obtained electrochemical results are discussed in terms of electron richness of the metal centre and the electronic properties of the ligands.

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PC12

Electrochemical behaviour of new monomeric keto and polymeric enol aroylhydrazone Cu(II) complexes.

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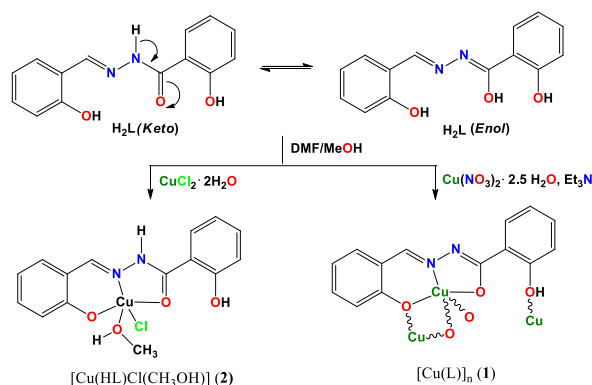
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Cu(II) complexes in two different tautomeric form (keto and enol) derived from the aroylhydrazone Schiff base 2-hydroxy(2-hydroxybenzylidene)benzohydrazide (H_2L) (Scheme 1) have been synthesized and characterized by elemental analysis, IR spectroscopy, ESI-MS and X-ray crystallography. The Cu(II) complex having enol form of the ligand, $[Cu(L)]_n$ (**1**), exists as 1D polymer where the complex with the keto form of the ligand, $[Cu(HL)Cl(CH_3OH)]$ (**2**), exists as monomer.



Scheme 1

The redox properties of the new Cu(II) compounds **1** and **2**, as well as of H_2L have been investigated by cyclic voltammetry (CV), at a Pt electrode ($d = 1$ mm) in 0.2 M $[nBu_4N][BF_4]/DMSO$ solution at 25 °C and related with their catalytic performance towards peroxidative oxidation of toluene and 1-phenylethanol.

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PC13

Qualitative evaluation of Tunisian olive oils using an electronic tongue and chemometric tools: a prospective study.

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Olive oil commercialization has a great impact in the regional economy of several countries including Tunisia. It is a high-value food product, quite prone to frauds. So, it is important to establish analytical techniques that can ensure labeling correctness regarding olive oil quality as well as its origin, namely concerning the olive(s) cultivar(s) used in the production, which is of major importance for monovarietal olive oils. Traditional analytical techniques like those based on chromatography are quite expensive, time-consuming, not portable and difficult to implement in-situ, considering the usual harsh environments of the olive industry. In this work, the feasibility of using an electronic tongue as a classification tool for discriminating Tunisian olive oils according to their quality level (i.e., extra virgin olive oil, virgin olive oil or lampante olive oil) and olive cultivar (i.e., Chetoui, Shali and others, according to the label information) was evaluated for the first time. Olive oil quality was assessed quality parameters (free acidity, peroxide values, K_{232} and K_{270} extinction coefficients) and on the organoleptic evaluation carried out by a sensory panel parameters (according to the International Olive Council directives). The potentiometric signal profiles recorded with the electrochemical multi-sensor device during the electrochemical analysis of olive oils' hydroethanolic extracts (≈ 5 min), coupled with linear discriminant models, established based on the most informative sub-sets of sensors, selected by a simulated annealing algorithm, were able to satisfactorily perform olive oils discrimination according to:

- (i) Olive cultivar: sensitivities of 88% for leave-one-out cross-validation and mean sensitivities of 79% for the repeated K-folds cross-validation (4 folds with 10 repeats), achieved with a multivariate model based on the information gathered by 20 sensors of the electronic tongue; and,
- (ii) Quality level: sensitivities of 91% for leave-one-out cross-validation and mean sensitivities of 84% for the repeated K-folds cross-validation (4 folds with 10 repeats), achieved with a multivariate model based on the information gathered by 26 sensors of the electronic tongue.

Overall, the results show the satisfactory performance of a potentiometric electronic tongue containing cross-sensitivity lipid membranes as sensors, which may be tentatively attributed to the capacity of the electrochemical device in discriminating olive oils with different polar compounds contents, which are related to specific sensory attributes of olive oils such as bitterness and pungency. Furthermore, the present study, concerning Tunisian olive oils analysis using an electronic tongue, confirms the results previously reported in the literature for olive oils from other geographical origins.

PC14

Determination of antioxidant activity in propolis using square wave voltammetry.

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Propolis is a resinous substance obtained by bees (*Apis mellifera* L.), using compounds collected from floral and leaf buds, which are mixed with pollen, and enzymes of bees' saliva [1,2]. This product is considered a "natural antibiotic" which plays an important role in defending the hive, protecting it from fungi and bacteria, embalm dead insects that cannot be removed from the hive, thus preventing its putrefaction and spread of disease within the hive [3,4]. Propolis has a complex composition, depending on its geographical origin and botanical [5]. Among its major components, phenolic acids (hydroxybenzoic and hydroxycinnamic acid) and flavonoids are closely associated to its claimed biological properties such as antioxidant, antimicrobial, anti-inflammatory activities [4,6].

This study shows the preliminary results for the analysis of bioactive compounds, with oxide-reducing properties, in samples of propolis by square wave voltammetry, an antioxidant activity method based on its ability to donate electrons. The advantages of using this method is because includes its simplicity, the low consumption of reagents, its good selectivity and its associates low detection limits [7].

The assays were carried out with miniaturized electrochemical sensors chips of the Micrux Thecnologies, based on metal-based three-electrode (micro) system, having gold thin-film electrodes (working, reference and auxiliary) on a glass substrate. This electrochemical cell enables the use of very small sample volume. The analyses were carried out with a mixture of acetonitrile and phosphate buffer. Gallic acid was used as the standard compound for the method calibration, with concentrations varying between 20 and 280 mg/L. Several propolis samples were analyzed with this methodology and the results obtained were compared with the antioxidant capacity evaluated by several traditional techniques (spectrophotometric methods). In addition, the individual phenolic composition of propolis samples was analyzed through by ultra-high performance liquid chromatography with diode-array detection coupled to electrospray ionization tandem mass spectrometry (UHPLC-DAD-ESI-MSⁿ).

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PC15

Application of the Scanning Vibrating Electrode Technique in Deep Eutectic Solvents. First results.

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Deep eutectic solvents (DESs) are formed from a eutectic mixture of Lewis or Brønsted acids and bases and are considered a new class of ionic liquids. The first paper with DESs was published in 2001 [1]. Since then these solvents have received considerable attention because they are easy to handle (stable in air, cheap and safe) and show good qualities as alternative media for electrochemically difficult or environmentally hazardous processes [2]. The main applications that are being investigated are metal processing and electroplating at very negative potentials (where usually hydrogen evolution makes the processes impossible) and as environmentally benign media for synthesis.

The Scanning Vibrating Electrode Technique (SVET) is a technique used mainly in the life sciences [3] and corrosion research [4] that provides the distribution of ionic currents in solution by the measurement of the electrical field. It permits to map the currents that emerge from the surface of an electrode.

This work presents the first results ever reported using the SVET in DESs. The technique was used to characterize four different electrochemical processes in a eutectic mixture of choline chloride and ethylene glycol (1:2 in molar proportion): i) corrosion of iron and zinc, ii) galvanic coupling of iron and zinc, iii) electrolysis with two platinum electrodes, iv) electrodeposition of zinc in a platinum electrode.

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PC16

Sugars quantification using an Electronic Tongue: multivariate calibration with a genetic algorithm for sensor selection.

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Sugar analysis contributes to the assessment of their impact on the human health and their physiological effects, allowing to better understand their relation with sensory attributes and acting on quality control and authenticity of food products [1,2]. Although, several analytical methods are routinely used in the identification and quantification of sugars in foods, in general, these methods have several disadvantages such as, slowness of the analysis, high consumption of chemicals and the need for destructive pretreatments of samples. The development of new reliable methods have been proposed [3] to avoid these disadvantages and, in this follow-up, it was decided to apply a potentiometric electronic tongue, built with cross-selectivity polymeric sensors that were selected considering the sensitivities towards sugars, previously reported [4]. The analysis of sugars (glucose, fructose and sucrose) in this study aimed to establish an analytical methodology and mathematical framework to quantify these compounds. For this purpose, analyzes were performed using standard solutions of ternary mixtures of these sugars, by applying an orthogonal experimental design to establish different concentration levels [5]. It was then made an exploratory data analysis using principal component analysis to verify data variability. To establish a multiple linear relationship between the concentration of sugars and the potentiometric signals obtained by the electronic tongue, a genetic algorithm was used to select the best subset of sensors and cross-validation with K-folds, to optimize the model in prediction. Satisfactory results were obtained in each sugar analysis. For instance, the multiple linear regression model for fructose analysis allowed to have, by cross-validation using K-folds (dividing analytical data randomly into 7 groups), a R^2_{adjusted} above 0.99 and RMSE less than 0.5. Moreover, the linear relationship between the predicted values by the obtained model and the respective fructose experimental values allowed to obtain a slope of 0.98 ± 0.02 (close to unity) and an intercept value statistically equal to zero.

The multisensor system used proved to be a suitable tool for the analysis of sugars, when present in majority concentrations and alternative to the instrumental reference methods, such as HPLC. It allowed to decrease the time and price of each analysis, and also, to reduce sample preparation work and eliminate pollutants in the analysis procedure.

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