

#### XXIII Meeting of the Portuguese Electrochemical Society Abstract Book

#### XXIII Encontro da Sociedade Portuguesa de Eletroquímica Livro de Resumos



Municipal Library Almeida Garrett, Porto, Portugal 2<sup>nd</sup> – 4<sup>th</sup> May 2018

## 23<sup>rd</sup> Meeting of the Portuguese Electrochemical Society

Sociedade Portuguesa de Electroquímica

Departamento de Química e Bioquímica Faculdade de Ciências da Universidade do Porto Porto Portugal

2<sup>nd</sup> to 4<sup>th</sup> May 2018





#### Title

23<sup>rd</sup> Meeting of the Portuguese Electrochemical Society

#### **Event Abbreviation**

SPE2018

#### Coordination

Diana Fernandes

#### Edition

Faculdade de Ciência da Universidade do Porto Rua do Campo Alegre, s/n, 4169-007 Porto, Portugal

#### Date

April of 2018

#### **Previous Meetings**

1<sup>st</sup> Meeting of the Portuguese Electrochemical Society Coimbra, 1984

2<sup>nd</sup> Meeting of the Portuguese Electrochemical Society Ofir, 1986

**3<sup>rd</sup> Meeting of the Portuguese Electrochemical Society** Faro, 1987

4<sup>th</sup> Meeting of the Portuguese Electrochemical Society Sintra, 1989

5<sup>th</sup> Meeting of the Portuguese Electrochemical Society Aveiro, 1991

6<sup>th</sup> Meeting of the Portuguese Electrochemical Society Vila Real, 1992

**7<sup>th</sup> Meeting of the Portuguese Electrochemical Society** Faro, 1995

8<sup>th</sup> Meeting of the Portuguese Electrochemical Society Covilhã, 1996

**9<sup>th</sup> Meeting of the Portuguese Electrochemical Society** Braga, 1997

**10<sup>th</sup> Meeting of the Portuguese Electrochemical Society** Évora, 1999

**11<sup>th</sup> Meeting of the Portuguese Electrochemical Society** Porto, 2001

**12<sup>th</sup> Meeting of the Portuguese Electrochemical Society** Lisboa, 2003

**13<sup>th</sup> Meeting of the Portuguese Electrochemical Society** Covilhã, 2005

**14<sup>th</sup> Meeting of the Portuguese Electrochemical Society** Coimbra, 2007

**15<sup>th</sup> Meeting of the Portuguese Electrochemical Society** Lisboa, 2008

**16<sup>th</sup> Meeting of the Portuguese Electrochemical Society** Lisboa, 2011

**17<sup>th</sup> Meeting of the Portuguese Electrochemical Society** Funchal, 2012

**18<sup>th</sup> Meeting of the Portuguese Electrochemical Society** Porto, 2013

**19<sup>th</sup> Meeting of the Portuguese Electrochemical Society** Aveiro, 2014

**20<sup>th</sup> Meeting of the Portuguese Electrochemical Society** Braga, 2015

**21<sup>st</sup> Meeting of the Portuguese Electrochemical Society** Bragança, 2016

**22<sup>nd</sup> Meeting of the Portuguese Electrochemical Society** Açores, 2017

#### Welcome to the 23<sup>rd</sup> Meeting of the Portuguese Electrochemical Society

On behalf of the Organizing Committee we would like to welcome you to the 23rd Meeting of the Portuguese Electrochemical Society held at the Municipal Library Almeida Garrett in Porto, from Wednesday 2<sup>nd</sup> to Friday 4<sup>th</sup>, May, 2018. This meeting was organized on the behalf of the Portuguese Electrochemical Society (SPE), following other meetings in previous years.

The Meeting focuses on various aspects of Electrochemistry, such as:

- Analytical Electrochemistry and Sensing
- Bioelectrochemistry
- Corrosion and Passivity
- Electrocatalysis
- Electrochemical Energy Storage and Conversion
- Electrochemical Engineering
- Electrochemistry in Biomedical Science and Technology
- Electrochemistry of Functional Materials
- Environmental Electrochemistry
- Molecular Electrochemistry
- Nanoscale Electrochemistry
- Photoelectrochemistry
- Theoretical and Computational Electrochemistry

This meeting is inserted in the activities of the Portuguese Electrochemical Society (SPE), which has a long-standing tradition in the organization of these meetings as a valuable exchange platform for all aspects of Electrochemistry and as a tool to highlight the importance of Electrochemistry in the development of an innovative and sustainable future.

The scientific program of the conference includes plenary, keynote, oral and poster communications.

Finally, we would like to thank all of you for attending the meeting. We wish a fruitful conference and stay in Porto.

Cristina Freire & Diana Fernandes

#### **Conference Venue**



The XXIII SPE Meeting will be held at the Municipal Library Almeida Garrett in Porto, from Wednesday 2<sup>nd</sup> to Friday 4<sup>th</sup>, May, 2018.

#### **Organizing Committee**

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## Programme

9:00 - 9:30	Registration
9:30 - 10:00	Opening Session
10:00 - 11:00	José Solla-Gullón, Universidad de Alicante, Spain PL 1 - Electrocatalysis on shape-controlled metal nanoparticles: advances and challenges
11:00 - 11:30	Coffee Break
11:30 - 12:00	Simone Morais, Instituto Superior de Engenharia do Porto, Portugal KN 1 - Electrochemical Biosensors: Principles, Design and Applications
12:00 - 12:20	Mariana Campaniço, Universidade Nova de Lisboa, Portugal OC 1 - Direct Electrochemistry of Formate Dehydrogenase
12:20 - 12:40	Ana Rita Pereira, Faculdade de Farmácia do Porto, Portugal OC 2 - Construction and evaluation of a histamine potentiometric sensor
12:40 - 14:15	Lunch
14:15 - 14:45	Jorge Correia, Universidade de Lisboa, Portugal KN 2 - Mass Transfer Process in Conducting Polymers; a Mirage Effect Approach
14:45 - 15:05	Ana Brandão, Universidade do Porto, Portugal OC 3 - Electrodeposition of Sn and Sn/carbon materials composites using choline chloride-based ionic liquids – Preliminary results
15:05 - 15:25	Inês J. Pereira, Universidade de Lisboa, Portugal OC 4 - New Insights on Electroless Precipitation of Noble Metals on Polyaniline
15:25 – 15:45	<b>Gonçalo Tiago</b> , Instituto Superior Técnico, Portugal OC 5 - Cyclic voltammetry of ionic liquids and copper(II) complexes in ionic medium
15:45 – 16:05	Manuel Melle-Franco, Universidade de Aveiro, Portugal OC 6 - Electrochemistry, Modelling and Nanomaterials
16:05 - 16:35	Coffee Break
16:35 - 17:05	Poster Session.

## Thursday, 3<sup>rd</sup> May 2018

9:00 - 10:00	Hubert Girault, EPFL, Switzerland PL 2 - Soft probes SECM imaging of cells and tissues
10:00 - 10:30	<b>Lifeng Liu</b> , INL, Portugal KN 3 - Improving electrocatalytic performance of water splitting through materials composition engineering
10:30 - 11:00	Coffee Break
11:00 - 11:30	Poster Session
11:30 - 11:50	Víctor Abdelkader Fernández, Faculdade de Ciências do Porto, Portugal OC 7 - Simultaneous carbonization/doping treatments: a versatile tool to enhance the OER/ORR electrocatalytic activity of MOF-74
11:50 - 12:10	<b>Rafael Morais</b> , Faculdade de Engenharia do Porto, Portugal OC 8 - Hybrids of glucose-derived carbons and CNTs for the Oxygen Reduction Reaction
12:10 - 12:30	Junyuan Xu, INL, Portugal OC 9 - Hollow Porous Cobalt Phosphide Octahedron with Exceptionally High Water and Methanol Oxidation Performance
12:30 - 14:30	Lunch
14:30 - 17:30	Social Program
20:00	Dinner at Casa da Música

## Friday, 4<sup>th</sup> May 2018

9:00 - 10:00	Adélio Mendes, Faculdade de Engenharia do Porto, Portugal PL 3 - <i>Towards energy sustainable buildings</i>
10:00 - 10:30	João Tedim, Universidade de Aveiro, Portugal KN 4 - <i>The design of functional additives for smart coatings</i>
10:30 - 10:50	<b>Teresa Centeno</b> , CSIC, Spain OC 10 - On the need for specific protocols for the characterization of carbon porosity in supercapacitors
10:50 - 11:20	Coffee Break
11:20 - 11:40	Nan Zhang, INL, Portugal OC 11 - High Performance Asymmetrical Supercapacitors Based on Bi- Metallic Transition Metal Phosphide Nanocrystals
11:40 - 12:00	<b>Orayech Brahim</b> , CIC Energigune, Spain OC 12 - An optimized PVC-based soft carbon as the negative electrode of sodium-ion batteries
12:00 - 12:30	Maksim Starykevich, Universidade de Aveiro, Portugal Prémio Jovem Electroquímico KN 5 - Electrosynthesis of ordered TiO <sub>2</sub> nanotubular layers in deep eutectic solvents
12:30 - 14:30	Lunch
14:30 - 16:00	General SPE Assembly

## **Sponsorship**

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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.

Link: http://www.ise-online.org/



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## **Partners**





# U. PORTO

**Plenary Lectures** 



## PL1. Electrocatalysis on shape-controlled metal nanoparticles: advances and challenges

#### José Solla-Gullón\*

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**Keywords:** Electrocatalysis, nanoparticles, shape-controlled, surface structure.

Shape-controlled metal nanoparticles have indisputably enhanced the Electrocatalysis of several electrochemical reactions of interest both from fundamental and applied points of view [1-4]. Interestingly, this type of nanoparticles has also contributed to a better understanding of the correlations between surface structure and electrochemical reactivity at the nanoscale. In this communication, I will discuss about the requirements to properly use these shaped metal nanoparticles for different electrochemical reactions of interest. Finally, some examples of Electrocatalysis with shaped metal nanoparticles will be presented and discussed.



#### References

[1] J. Solla-Gullon, F. J. Vidal-Iglesias, J. M. Feliu, Annu. Rep. Prog. Chem., Sect. C: Phys. Chem., 2011, 107, 263.

[2] H. You, S. Yang, B. Ding, H. Yang, Chem. Soc. Rev., 2013, 42, 2880.

[3] S. E. F. Kleijn, S. C. S. Lai, M. T. M. Koper, P. R. Unwin, *Angew. Chem. Int. Ed.*, 2014, *53*, 3558.

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#### PL2. Soft probes SECM imaging of cells and tissues

Tzu-En Lin, Sorour Darvishi, Milica Jović, Andreas Lesch and Hubert Girault\*

<sup>a</sup> École Polytechnique Fédérale de Lausanne (EPFL), Laboratory of Physical and Analytical Electrochemistry (LEPA), Rue de l'Industrie 17, CH-1950 Sion, Switzerland \*e-mail: hubert.girault@epfl.ch

Keywords: SECM, Melanoma, Bacteria detection

Electrochemical bioimaging of cells and tissues with micrometric electrodes or pipettes and microelectrode arrays gains in importance. These tools can record for instance the respiratory activity of alive biological samples or detect the release of metabolic compounds from such into the extracellular environment. By reducing the size of the probes to the nanoscale, intracellular measurements have been realized through the insertion of the probe tips into the alive cells. Fixation and permeabilization of cells or the biopsy of tissues enable the immunolabelling of proteins for the specific detection of intracellular enzymatic activity. The investigation of tissues is attractive towards diagnostic applications.

Herein, we will present first the recording of maps of the biodistribution of the diagnostic melanoma biomarker tyrosinase (TyR) in human excised skin tissue sections using scanning electrochemical microscopy with soft probes (Soft-Probe-SECM). A constant working distance is realized while the delicate tissue remains intact. Using arrays of microelectrodes and a restricted density of data points in the SECM image results in shorter experimental times and allows the identification of melanoma and its progression stage.

We will further demonstrate how Soft probes SECM can be used to record maps of the biodistribution of graphene oxide nanoribbons (GONRs), injected as potential nano-drug carriers into mice, in excised liver tissue using the feedback mode of SECM. The accumulation of the GONRs in hepatic lobules was clearly revealed with micrometre resolution. Finally, we will show the electrochemical bioimaging of an entire mouse heart section by the label-free visualization of redox active proteins, *e.g.* hemoglobin, using the SECM feedback mode.

To complete, the presentation we shall present some recent work on electrochemical bacteria detection.



#### PL3. Solar energy harvesting and storage - an integrated approach

A. Mendes\*

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**Keywords:** Photovoltaic, Perovskite solar cells, Redox flow battery, Solar redox flow cell

In the 16th century Thomas More described an ideal and sustainable city in his book Utopia. Today's an ideal city should comply with the Near Zero Energy Building directive (nick name for the Energy Performance of Buildings Directive (2010/31/EU)) and going beyond. PV electricity is already today the cheapest if produced in countries with high solar irradiance; the world's cheapest price for electricity of 2017 was for a PV farm in Saudi Arabia [1].

PV electricity is, however, only generated during the daylight time and then just partially dispatchable. To make it fully dispatchable it is necessary to store and batteries is a technology of choice. Among electricity storage technologies redox flow batteries (RFB) emerged as promising offering very low storage costs [2], expected price of 3  $\notin$ /kWh/cycle by 2050 [3], independent power from storage capacity, very reliable and robust operation. The all vanadium RFBs display an energy density of ca. 50 Wh/L but the use of non-aqueous solvents for dissolving the redox pairs promises to bring soon this energy density to values which ideally can reach 1 kWh/L. The storage of electricity in an electrochemical fluid instead of a solid such as in conventional batteries opens the doors to the electrochemical fuels that can be easily stored and transported.

More recently, it was proposed the direct conversion of sunlight into storable electrochemical fuels and heat using photoelectrochemical panels. The solar redox flow cells promise to bring the cost of stored electricity to even lower values making the dream of self-energy sustainable cities, in terms of electricity and heat, a closer reality. But other technologies are emerging and the use of microbial cells for charging the electrolytes of a redox flow battery is proposed for the first time.

References

[1] https://www.thenational.ae/business/energy/world-s-cheapest-prices-submitted-for-saudi-arabia-s-first-solar-project-1.663842 – consulted in February 2018.

[2] http://energystoragereport.info/study-flow-batteries-beat-lithium-

ion/#sthash.lfBTEoYs.dpbs - consulted in February 2018.

[3] European Energy Storage Technology Development Roadmap, 2017.

## **Keynote Lectures**



#### KN1. Electrochemical Biosensors: Principles, Design and Applications

#### S. Morais

#### <sup>a</sup> REQUIMTE–LAQV, Instituto Superior de Engenharia do Porto, Rua Dr. António Bernardino de Almeida, 4249-015 Porto, Portugal. \* sbm@isep.ipp.pt

**Keywords:** Enzymatic biosensors, Immunosensors, Nanomaterials, Immobilization strategies, Electrochemical techniques.

Electrochemical biosensors integrate the sensitivity of electrochemical transducers with the high selectivity of biological recognition. The biological element recognizes its analyte causing a biocatalytic or binding reaction, which yields an electrochemical signal (registered by a transducer), that is related with the analyte concentration. Biocatalytic devices incorporate enzymes, whole cells, or tissue slices that identify the target analyte and originate electroactive species [1-3]. Affinity devices are based on a selective binding interaction among the analyte and the biological component such as an antibody, nucleic acid, or a receptor [3]. The past and recent accomplishments of nanotechnology assure that good (immobilization) stability, ultrahigh sensitivity, good selectivity, low detection limit, fast response time, and miniaturization of the biosensing platform can be reached. Among the several types of biosensors, enzymatic biosensors and immunosensors are those that have been increasingly important in food quality and safety, pharmaceutical and clinical analysis but also in other fields such as environmental pollution control [2-3]. Several case studies will be discussed.

#### Acknowledgements

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#### References

[1]. N. J. Ronkainen, H. B.Halsall, W. R. Heineman, Chem. Soc. Rev., 2010, 39, 1747.

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#### KN2. Mass Transfer Process in Conducting Polymers; a Mirage Effect Approach

#### Jorge P. Correia

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Keywords: Probe Beam Deflection, EQCM, Mass transfer, Conducting polymers

The unique properties of conducting polymers have been explored for a variety of applications and these materials have been well succeeded in many fields. One of the characteristics that largely contributed to the establishment of such versatile materials in our society is the fast and quite reversible switching between the high and low conducting forms of the polymer. This is accomplished by redox conversion between its reduced and oxidised states, being the polymer charge balanced by counterions incorporation(expulsion) into(from) the matrix. The change of its electrochemical state results in mechanical deformations of the polymer (swelling/shrinking) forcing the solvent to move into and out of the organic film. The nature and magnitude of the mass transfer phenomena taking place during the polymer redox conversion is absolutely necessary to better understand these materials and of upmost importance for several applications.

Microgravimetry experiments carried out by Electrochemical Quartz Crystal Microbalance (EQCM) provide valuable information about the overall mass transferred during the electrochemical changes. Unfortunately it is unable to distinguish from solvent and electroactive species when opposite flows occur. Moreover it is poorly sensitive to light ions such as  $H^+$  or  $Li^+$ . Probe Beam Deflection (PBD) experiments, based on the mirage effect, is, in turn, quite responsive to the fluxes towards and from the electrode, but "blind" to the solvent. Being so, by cooperatively using the information gathered by these two techniques, it becomes possible to individually resolve the several contributions for the whole mass transfer process. This is achieved through the mathematical tool of temporal convolution of PBD data, as demonstrated by the verification of cation participation in the synthesis and redox process of an anion-doping polymer. The mass fluxes tanking place during the redox process of a *pseudo* cation-doping polymer were also addressed revealing a quite fast non-ideal conversion, being the perchlorate anion participation lower than 40% of the overall ionic transfer when Li<sup>+</sup> is the cation.

Acknowledgments: This work is funded by FCT (Fundação para a Ciência e a Tecnologia) through the Project UID/MULTI/00612/2013



#### KN3. Improving Electrocatalytic Performance of Water Splitting Through Materials Composition Engineering

Lifeng Liu<sup>*a*,</sup>\*, Junyuan Xu<sup>*a*</sup>, Junjie Li<sup>*a*</sup>

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**Keywords:** electrocatalysis, water splitting, oxygen evolution reaction, transition metal phosphide, composition engineering

Transition metal phosphides (TMPs) have recently emerged as a new class of catalysts that can efficiently catalyze the hydrogen and oxygen evolution reactions (HER & OER) in water splitting. While mono-metallic TMPs have been extensively investigated, recent studies indicate that tuning the catalyst's composition by introducing a secondary metal(s) may improve the catalytic performance of TMPs. We recently have synthesize a series of TMP nanoparticle catalysts containing different equimolar metal (M = Fe, Co, Ni) components and investigate their electrocatalytic performance for the OER [1]. Notable trends in OER activity are observed, following the order of FeP < NiP < CoP < FeNiP < FeCoP < CoNiP < FeCoNiP, demonstrating that the introduction of a secondary metal(s) to a mono-metallic TMP indeed boosts the OER performance. The promotional effect can be ascribed to the enhanced oxidizing power of bi- and trimetallic TMPs that can facilitate the formation of MOH and chemical adsorption of OH<sup>-</sup> groups, which are the rate-determining steps for these catalysts. In addition, we also developed a novel ruthenium cobalt phosphide hybrid catalyst by phosphorizing ruthenium cobalt alloy clusters obtained through wet chemical reduction [2]. Compared to pristine ruthenium clusters, the hybrid ruthenium catalysts composited with cobalt and phosphorus show exceptionally high catalytic performance for the HER, with a turnover frequency of 10.95  $s^{-1}$  at an overpotential of 100 mV in 0.5 M  $H_2SO_4$  and of 7.26 s<sup>-1</sup> at the same potential in 1.0 M KOH, outperforming many stateof-the-art HER catalysts reported in the literature.

References:

[1] J. Y. Xu, J. J. Li, D. H. Xiong, B. S. Zhang, Y. F. Liu, K. H. Wu, I. Amorim, W. Li, L. F. Liu, *Chem. Sci.* 2018, *9*, 3470.

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#### KN4. The design of functional additives for smart coatings

#### <u>J. Tedim</u>

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**Keywords:** smart coatings, controlled release, corrosion, sensing, fouling.

Man-made materials used in infrastructures, vehicles or even biomedical implants are subjected to extreme conditions during service-life, which can lead to their degradation, impairing the role for which they were initially designed.

From the different strategies used to improve durability of materials, engineering of surfaces through development of protective coatings and films with feedback responsive ability, has been addressed in recent years [1].

In this work, the development of additives for smart coatings used in corrosion protection will be discussed, and the way this approach can be extended to impart other functionalities presented [2, 3].

References:

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## KN5. Electrosynthesis of ordered TiO<sub>2</sub> nanotubular layers in deep eutectic solvents

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**Keywords:** Titanium dioxide, Deep eutectic solvents, Ionic liquids, Choline chloride, Ordered nanotubular layers.

Preparation of anodic titania with porous nanotubular (TNT) structure was firstly reported by Zwilling et al. in 1999 [1]. Using a chromic acid electrolyte with hydrofluoric acid, a porous film of about 0.5  $\mu$ m thick was obtained. They also showed the importance of the presence of fluoride ions in the electrolyte for manufacturing the porous layer. In the following years, several electrolytes for TNT preparation were proposed, such as the water-based ones with sulphate, phosphate and acetate ions or organic electrolytes based upon glycerol and dimethyl sulfoxide. While titania nanotubes produced from water-based electrolytes had sidewall inhomogeneity (ripples) and low aspect ratio, anodizing in organic electrolyte systems such as ethylene glycol [2] resulted in the formation of high-ordered and long (more than 250  $\mu$ m [2]) tubes with smooth walls. In spite of widespread application of ethylene glycol based electrolytes, the study of other organic solvents for TNT synthesis is still an important point due to significant effects of synthetic mode on morphologic parameters and performance of TNT electrodes.

The successful preparation of the titania nanotubular layers in different deep eutectic solvent based electrolytes is reported for the first time. Choline chloride based deep eutectic solvents with various hydrogen bond donors, such as ethylene glycol, urea and malonic acid were used. All results were compared with standard ethylene glycol based electrolyte. The influence of the electrolyte temperature, fluoride ion concentration, applied voltage and anodization time on morphology of the titania nanotubular layers were explored. General trends for deep eutectic solvent based electrolytes and optimum anodization parameters for each system were developed.

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## **Oral Communications**



#### **OC1.** Direct Electrochemistry of Formate Dehydrogenase

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Keywords: Carbon Dioxide, Bioelectrochemistry, Formate, Enzymes

Formate dehydrogenases (FDHs) are enzymes that catalyse the reversible two-electron oxidation of formate to  $CO_2$ . The class of metal-dependent FDHs comprises only prokaryotic enzymes that hold different redox-active centres and whose active site harbours one molybdenum or one tungsten atom that mediates the formate oxidation or the  $CO_2$  reduction [1, 2]. The reduction of  $CO_2$  to formate is of high interest, because it constitutes a promising route for atmospheric  $CO_2$  mitigation, with the additional advantage of producing valuable chemical feedstocks and fuels (formate-derived compounds).

Recently, we demonstrated that the periplasmatic FDH from *Desulfovibrio* desulfuricans (DdFDH), a molybdenum-containing FDH, is one of the most efficient enzymes for the reduction of CO<sub>2</sub> to formate, with a high  $k_{cat}$  (47/s) and very low  $K_m^{CO2}$  (16µM) [3]. In this work, the immobilized DdFDH direct electrochemical response was attained. The Mo(IV)/Mo(VI) center reduction potential was determined and the global electrochemical behaviour of the enzyme in non-turnover conditions was characterized. The electrocatalytic activity of DdFDH towards CO<sub>2</sub> was also preliminarily characterised.

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#### OC2. Construction and evaluation of a histamine potentiometric sensor

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Keywords: Histamine, Potentiometry, Ion-selective electrodes.

Histamine (HS) is a biogenic amine that results from enzymatic decarboxylation of the amino acid histidine. It is synthetized and released from many cells (mast cells, basophils, platelets, histaminergic neurons, etc.). A strongly potential therapeutic exploitation in allergy, inflammation, autoimmune disorders and possibly cancer has been reported in preclinical data for HS<sup>[2]</sup>. Histamine is the most important inflammatory mediator during an allergic reaction and plays a significant role in anaphylaxis cases<sup>[3]</sup>. Furthermore, it is regarded as one of the biomarkers for quality control during the food production and transportation<sup>[4]</sup>.

Different methods have been applied into determination of HS, namely GC, HPLC, capillary electrophoresis and biochemical assays. However, potentiometric sensors have been described as an alternative due to being simpler, faster, portable and cheaper than the other analytical methods referred above <sup>[4]</sup>.

In the present work, the HS sensor is optimized by using different membrane polymers, ionophores, solvent mediators in the presence of anionic additive. The effect of multiwalled carbon nanotube (MWCNTs) was also considered. The sensor with the best analytical response is composed of 1.0% (w/w) of cucurbit[6]uril, 66.8% (w/w) of 2-nitrophenyl phenyl ether as plasticizer, 29.8% (w/w) of polyvinylchloride, 0.3% (w/w) of potassium tetrakis(4-chlorophenyl) borate and 2.0% (w/w) of MWCNT. The HS sensor's performance is characterized by a slope of  $30.9\pm1.2 \text{ mV dec}^{-1}$ , a detection limit of  $(3.01\pm0.61) \times 10^{-7} \text{ mol L}^{-1}$  and a lower limit of linear range of  $(2.99\pm0.00) \times 10^{-7} \text{ mol L}^{-1}$ . This sensor has been used and optimized under flow conditions, to carry out sequential injection chromatography.

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## OC3. Electrodeposition of Sn and Sn/carbon materials composites using choline chloride-based ionic liquids – Preliminary results

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**Keywords:** Tin, Multi-walled carbon nanotubes, reduced-Graphene oxide, Ionic liquids, Deep Eutectic Solvents.

The electrodeposition of metals and alloys from aqueous electrolytes is limited by the narrow electrochemical window and hydrogen evolution. To surpass these disadvantages, in recent years ionic liquids (ILs) and deep eutectic solvents (DES) based on choline chloride have been successfully applied for electrodeposition of different metals [1]. In the past few years, the attention regarding metal composites, namely Sn-carbon materials composites, has increased due to its possible application as anode for lithium-ion batteries due to the great characteristics of carbon [2].

Nano carbons, such as graphene and carbon nanotubes show very interesting electrochemical properties.

The aim of this study was to study the incorporation of carbon materials in tin chloride (SnCl<sub>2</sub>) electrodeposited matrix in DES based on choline chloride, ethaline. The studied carbon materials for comparison are oxidized multi-walled carbon nanotubes (ox-MWCNT), pristine multi-walled carbon nanotubes (P-MWCNT) and reduced graphene oxide (rGO). Sn and Sn-carbon materials composites were studied by cyclic voltammetry, chronoamperometry, conductive atomic force microscopy (c-AFM) analysis and scanning electron microscope (SEM) analysis. Surface characterization performed by SEM analysis indicates a good incorporation of P-MWCNTs in the Sn matrix.





SEM – Surface characterization P-MWCNTs

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## OC4. New Insights on Electroless Precipitation of Noble Metals on Polyaniline

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Keywords: Electroless Precipitation, Polyaniline, Structural modifications, Silver, EQCM

Polyaniline (PAni) spontaneously reduces and oxidizes in acidic medium at open circuit potential. It is established that when metallic ions are present in solution, they act as an oxidizing agent to polymers, especially those containing nitrogen atoms [1]. Electroless Precipitation consists on the sustained reduction of metal ions onto a polymeric matrix of proper electrochemical activity. Since the state transitions of PAni (Protonated Emeraldine - Pernigraniline) occur between 300mV and 800mV vs. SCE, metal ions undergoing electroless precipitation should have a reduction potential in this potential window, limiting this reduction process to noble metals [2]. Although this process has been known for more than two decades, the structural modifications in the polymer undergoing this process at open circuit potential are still unknown.

In this work the chemical and electrochemical changes imparted by the metal reduction in the polymer matrix are investigated, being the Electroless Precipitation process fully characterized using silver as model of noble metal ion. The synthesis process and the redox conversion of the modified electrodes were monitored by Electrochemical Quartz Cristal Microbalance (EQCM). It is demonstrated that the amount of incorporated silver in the PAni film is quantitatively assessed by its oxidation charge in the voltammetric response of the modified electrodes. The ability of the polymer to be employed in multiple extraction runs was studied by cyclic voltametry and UV-Vis spectroscopy. The determination of the formal potential of the redox conversions of PAni and those of the metal couples (of Ag, Au, Hg and Cu) at different pH, allowed the construction of Pourbaix's type diagram.

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## OC5. Cyclic voltammetry of ionic liquids and copper(II) complexes in ionic medium

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Keywords: cyclic voltammetry, copper, electrochemical window, ionic liquids

In this work, the redox properties of some copper(II) complexes of arylhydrazone and some ionic (of imidazolium, phosphonium or ammonium) liquids were tested by cyclic voltammetry, a very useful electrochemical technique.[1]

Copper(II) complexes,  $[CuL(H_2O)_2].H_2O(1)$ ,  $[CuL(H_3L^1)](2)$ ,  $[{Cu(\mu-1\kappa N,OO':2\kappa O''-L)}_2(\mu-1\kappa N:2\kappa N'-hmt)]_n$  (3) and  $[{Cu(\kappa N,OO'-L)}_2(\mu-1\kappa N:2\kappa N'-bpy)]_n$  (4) whose synthesis have been already reported [2-3], have shown being redox active (Figure 1).



Fig.1 Structure and cyclic voltammogram of complex  $[{Cu(\mu-1\kappa N, OO': 2\kappa O''-L)}_2(\mu-1\kappa N: 2\kappa N'-hmt)]_n$  (3).

For imidazolium-based ionic liquids,  $[bmim][NTf_2]$  and  $[hmim][NTf_2]$ , no waves were detected, in contrast with  $[N_{1,8,8,8}][FeCl_4]$  and  $[P_{6,6,6,14}][FeCl_4]$  in which two waves appear (one for oxidation and another for reduction). The effect of the scan rate on the reversibility is also discussed.

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#### OC6. Electrochemistry, Modelling and Nanomaterials

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**Keywords:** Carbon Organic Frameworks, Carbon Nanotubes, Graphene Nanoribbons, (COFs), Computational Chemistry

Computer simulation played a determinant role in the explosive development of carbon nanotechnology. Through the years (and in a more modest scale) we have applied and developed several models to account for electrochemistry experiments. We will discuss how computer models are fundamental to understand the electrochemistry of polydisperse carbon nanomaterials like carbon nanotubes [1]. In addition, we will show electrochemistry, together with spectroscopy and quantum mechanical calculations, can be used to characterize novel, bottom-up, carbon materials for electronics [2-4].



Figure 1. Soluble monodisperse graphene nanoribbon from synthetic chemistry [2].

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## OC7. Simultaneous carbonization/doping treatments: a versatile tool to enhance the OER/ORR electrocatalytic activity of MOF-74

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Keywords: MOFs, carbon materials, energy-related reactions, electrocatalysis.

The worldwide increment of population, climate change and pollution make mandatorily the search of renewable, efficient and less polluting energy conversion/storage systems. In this context, the production of novel electrocatalysts plays a central role in sustainable development. Focusing on fuel cells and batteries, the electrocatalysis of the two coupled O<sub>2</sub>-related reactions, oxygen evolution (ORR) and reduction (ORR) reactions turns out to be a critical factor. Thus, this fact has stimulated the research on the pyrolysis of metal organic frameworks (MOFs) to obtain MOF-derived carbons with very desirable features: electrical conductivity, well dispersed metal-containing nanoparticles (NPs), high surface areas, and possibility of doping.[1]

In this work, we have explored different strategies to enhance the OER/ORR catalytic performance of MOF-74, by producing derived carbon materials containing diverse metal NPs (avoiding noble metals), along with N and S doping heteroatoms.



Examples of OER and ORR catalytic activities for different MOF-74 derived carbons

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#### OC8. Hybrids of glucose-derived carbons and CNTs for the Oxygen Reduction Reaction

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**Keywords:** Fuel Cell, Glucose-derived carbons, Carbon Nanotubes, Oxygen Reduction Reaction

To reduce the environmental impact of fossil fuels, a rising concern over an efficient way to convert chemical energy to electric energy has emerged. Fuel cells appear as outstanding conversion devices, but they are mainly based on the use of platinum electrocatalysts, thereby creating a problem due to the high costs of this metal [1].

The overall reaction kinetics of a fuel cell is limited by the oxygen reduction reaction (ORR), which is a slow process that takes place at the cathode [2]. Therefore, the properties of the electrode materials play a key role in the performance of fuel cells. Among the most studied electrocatalysts for the ORR are carbon nanotubes (CNTs), graphene-based materials and activated carbons.

Recently, it was shown that ball milling could provide beneficial structural properties to CNTs and that N-doping could improve their catalytic activity in the ORR [3].

Therefore, this study has the objective to synthetize hybrid carbon materials from glucose, one of the primary components of biomass (low cost and abundant), and CNTs, as well as to dope those materials with heteroatoms to optimize their properties and consequently their catalytic activity in the ORR.

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#### OC9. Hollow Porous Cobalt Phosphide Octahedron with Exceptionally High Water and Methanol Oxidation Performance

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**Keywords:** oxygen evolution reaction, methanol oxidation reaction, cobalt phosphide, hollow porous octahedron

We for the first time propose a facile strategy to synthesize hollow porous cobalt phosphide (CoP) octahedron. The as-synthesized hollow porous CoP octahedron exhibits excellent electrocatalytic performance for both the oxygen evolution reaction (OER) and the methanol oxidation reaction (MOR) in alkaline media, outperforming porous cobalt phosphide sphere as well as the state-of-the-art commercial ruthenium oxide nanoparticle control catalysts.



**Figure 1.** (a) Schematic illustration of the synthesis procedure for hollow porous CoP octahedron. (b) TEM image, (c) SAED pattern, (d) HRTEM image, (e) HAADF image of CoP octahedron and Elemental maps of Co, O, P and their overlap. (f) OER performance measured in 1.0 M KOH. (g) MOR performance measured in 1.0 M methanol and 1.0 M KOH.



## OC10. On the need for specific protocols for the characterization of carbon porosity in supercapacitors

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Keywords: Electrochemical capacitance, Surface area, Carbon, Supercapacitor

For many years, nanoporous carbons have been widely used as adsorbents for emissions control and host matrices for active materials. In the last two decades, they have also found a niche as electrodes of electrochemical double-layer capacitors, EDLC (also known as supercapacitors, SC). All these applications correspond to very different processes but their description essentially relies on porosity parameters such as pore volume, specific surface area and pores size.

The assessment of a large variety of carbon materials such as activated carbons, nanotemplated carbons, carbide-derived carbons, carbon gels, graphene-related materials, etc. illustrates that the standard approaches for textural characterization of carbons for adsorption or catalysis leads to misleading insights when they are used in EDLC systems [1].

This study shows that the determination of the surface area involved in the formation of the double-layer in carbons is an actual challenge which requires an overall approach taking into account the following issues:



It is pointed out how specific protocols for carbons in supercapacitors allow eliminating inconsistencies between porosity parameters and capacitance [2]. This will certainly benefit the technological development of these devices.

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#### OC11. High Performance Asymmetrical Supercapacitors Based on Bi-Metallic Transition Metal Phosphide Nanocrystals

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**Keywords:** asymmetrical supercapacitor, transition metal phosphide, nickel phosphide, cobalt phosphide, high specific capacitance

Transition metal phosphides (TMPs), as an important class of functional materials, is attracting great interest for use as electrode materials in supercapacitors (SCs) due to their metalloid characteristics and high conductivity.<sup>[1,2]</sup> However, the TMP-based electrodes by far suffer from unsatisfactory specific capacitance and poor cycling stability, impeding their practical use in supercapacitors. In this work, we demonstrate that by introducing a secondary transition metal of Ni in cobalt phosphide nanocrystals, the specific capacitance of the resulting cobalt nickel phosphides (Co<sub>x</sub>Ni<sub>1-x</sub>P) can be significantly enhanced. We have systematically investigated the influence of the Co/Ni ratio on the supercapacitive properties, and found that Co<sub>x</sub>Ni<sub>1-x</sub>P with the optimized Co/Ni ratio reveals a remarkably high specific capacitance of 3093 F g<sup>-1</sup> at a scan rate of 50 mV s<sup>-1</sup>, which is much higher than that of mono-metallic TMPs (CoP and NiP) and other TMPs reported previously.<sup>[3,4]</sup> Furthermore, we have fabricated a free-standing electrode on carbon cloth via the drop-casting method and assembled it with an activated carbon electrode using a gel electrolyte. The as-prepared all-solid supercapacitor achieves both excellent capacitance and high degree of flexibility.

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### OC12. An optimized PVC-based soft carbon as the negative electrode of sodium-ion batteries

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Keywords: Soft Carbons, Hard Carbons, Na-ion batteries, disordered carbons.

The critical role of energy storage is by now self-evident: they are indispensable for an increased share of renewable energy and electric vehicles. Considering the abundance of sodium resources, sodium-ion batteries (NIBs) are poised as an alternative to Li-ion batteries as sustainable electrochemical energy storage (EES) solution. For NIB, a high degree of disorder of the carbon structure is needed to allow sodium insertion at positive voltages.[1-7]

Therefore, alternative anode materials are demanded. One family of candidates is nongraphitic carbon, which comes in the forms of "hard carbon" (HC) or "soft carbon" (SC).[8, 9] The specificity of HC is to present an additional capacity traduced by a low voltage plateau (LVP). However, the LVP is very sensitive to cell polarization increase so that the practical use of this extra capacity at high rates may pose safety issues in regard of sodium plating. For this reason, soft carbons with an extended sloping region constitute an appealing alternative for applications requiring high power capability.

In the present work an optimized PVC-based SC as active material for NIB negative electrode will be underlined. A comparative study of the performance of PVC-C compared to Sugar-HC with similar particle size and electrode preparation will be presented. Although it does not present the typical low voltage plateau of hard carbons, PVC-SC reaches an initial reversible capacity of 230mAh/g and retains 225mAh/g after 150 cycles at 24.8mA/g. At high current density of 1C (372mA/g), the electrode still can achieve a capacity of 175mAh/g with a Coulombic efficiency near 100%.

The microstructure and the morphology of these carbons have been studied and by correlating with their electrochemical performance, had led us to identify key-microstructural features at origin of the performance of PVC—SC and give new insights into the mechanism of sodium insertion into disordered soft and hard carbons. [10]

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### **Poster Communications**



#### P1. Development of Cathode Materials based on Conducting Polymers for Sodium Ion Batteries

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Keywords: Sodium-ion batteries, EQCM, PBD, PEDOT, Pseudo-cationic doping

The batteries of sodium ion (SIBs) appear as an alternative more abundant, in terms of resource, and less expensive than the conventional lithium ion batteries (LIBs), being used for applications where the weight and specific energy are less determinants [1]. However, the delay in marketing is related to the development of materials of anode and cathode with a capacity and potential similar to those achieved by LIBs, since they have to be designed for the exchange of an ion with a larger size [2]. Whereas the anode is based on sodium, the cathodic structure must be sufficiently stable and extremely light [3] to compensate the total mass of the unit and include a wide range of voltages at which the SIBs can operate. For the cathodic matrix to fulfill these requirements, it is proposed a conducting polymer with pseudo-cationic doping.

This work presents a systematic and quantitative study of the mass transfer processes involved in redox conversion of Poly(3,4-Ethylenedioxythiophene):Poly(Sodium 4-Styrenesulfonate), PEDOT:PSS. The synthesis of thin films of PEDOT:PSS was performed potenciodynamically and potenciostatically, with simultaneous monitoring by eletromicrogravimetry (EQCM), on platinum electrodes from aqueous solutions containing the monomer EDOT and the PSS polyanion. The characterization was carried out in organic medium (NaClO<sub>4</sub>:CH<sub>3</sub>CN) by cyclic voltammetry (CV), also accompanied by EQCM. The mass transfer processes in polymeric films taking place in their redox conversion were evaluated by EQCM and Probe Beam Deflection (PBD). These techniques are appropriate to quantify the ionic flows that occur between the electrolyte and the electrode; the solvent flows associated with the morphologic changes of the polymeric matrix is obtained only by EQCM. The data provided by these two methodologies allow to individually depict these two mass flows.

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# P2. Development of layered double hydroxides films as coatings for corrosion protection of magnesium alloys

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Keywords: Layered Double Hydroxides (LDH), Conversion Films, Corrosion Protection

Magnesium (Mg) and its alloys are prospective materials for a wide range of applications from a mechanical point of view but extremely susceptible to corrosion. Generically, an adequate corrosion protection can be achieved with a uniform coating well adhered to the substrate, pore-free and with self-healing functionality for applications where physical damages can occur.[1]

The present work focus on the direct growth of LDH films on Mg alloys in order to limit corrosion degradation of these metallic substrates. LDH films can act as a physical barrier and at the same time are able to intercalate and release in a controlled way different active anionic species.

LDH conversion films were produced on different magnesium alloys following a procedure adapted from the literature.[2] Additionally, a set of corrosion inhibitors was tested for protection of Mg alloys directly in solution using electrochemical impedance spectroscopy (EIS). The obtained films were characterized by X-ray diffraction (XRD) scanning electron microscopy (SEM) and atomic force microscopy (AFM) in order to obtain information on LDH phases, morphology and thickness of the films.

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## P3. Electrochemical sensing of the thyroid hormone thyronamine (T<sub>0</sub>AM) via molecular imprinted polymers (MIPs)

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**Keywords:** (Bio)sensor, molecularly imprinted polymer (MIPs), electropolymerization, electroanalysis, thyroid hormone thyronamine

Thyroid hormones play a significant role in several physiological processes related to normal development and metabolic activity in the adult. Besides the known T3 (triiodothyronine) and T4 (tyroxine), T<sub>0</sub>AM (thyronamine) is another relevant thyroid hormone. T<sub>0</sub>AM seems to influence cardiac output, heart rate and it is an important neuroprotectant in acute stroke. However, there is a lack of simple analytical methodologies available that showed its precise importance. Electrochemical (bio)sensors could be excellent choices for the development of point-of-care devices for biological receptors, imitating antibodies. Molecularly imprinted polymers (MIPs) are important tools to improve the selectivity of electrochemical sensors. In this work, an electrochemical MIP sensor for the detection of T<sub>0</sub>AM was developed. The MIP was prepared by electropolymerization in the surface of screen-printed carbon electrodes (SPCEs), using a solution containing 4-aminobenzoic acid (4-ABA), as the building and functional monomer, and T<sub>0</sub>AM as the template. The analysis was performed by square wave voltammetry with a limit of detection (LOD) of 1.9  $\mu$ g dL<sup>-1</sup>, and a repeatability of 3.9%. The sensor showed suitable selectivity in the presence of other thyroid hormones.

#### Acknowledgements

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#### P4. Label-Free Electrochemical Immunosensor for Detection of α-Synuclein Protein

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**Keywords:** Parkinson's disease, Immunosensor, α-Synuclein

Parkinson's disease (PD) is the second most common neurodegenerative disorder and is generally considered a multifactorial disorder that arises owing to a combination of genetic and environmental factors [1]. It has long been characterized by the classical motor features of parkinsonism associated with Lewy bodies and loss of dopaminergic neurons in the substantia nigra [1]. PD is expected to impose an increasing social and economic burden on societies as population ages [1]. Therefore, the development of a laboratory test that enables early diagnosis, even before the onset of motor symptoms is urgently needed. In this work, an electrochemical immunosensor for the detection of  $\alpha$ -synuclein was developed.

The proposed electrochemical immunosensor is based on a glassy carbon electrode (GCE) modified with single walled carbon nanotubes (SWCNTs) that were drop-casted on the GCE surface, electrodeposited gold nanoparticles (AuNPs), antibody against  $\alpha$ -synuclein prepared through chemical modification (thiolation) and albumin from bovine serum (BSA). Square-wave voltammetry, electrochemical impedance spectroscopy and scanning electron microscopy were used to characterize the development of the biosensor. For detection of  $\alpha$ -synuclein, the developed sensor was incubated in several concentrations of  $\alpha$ -synuclein for 20 min at room temperature attaining a linear range of 0.5–50 ng mL<sup>-1</sup>.

#### Acknowledgements

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### P5. Electrochemical immunosensing platforms for breast cancer detection

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**Keywords:** Breast cancer, electrochemical immunoassay, nanomaterials, magnetic beads, SPCEs.

Breast cancer is a worldwide health concern. Screening and early diagnosis are crucial to increase the success of the patient's treatment and improve the survival rate [1]. Tumour biomarkers are specific cancer related biomolecules used in clinical settings for cancer detection. Carcinoembryonic antigen (CEA), cancer antigen 15-3 (CA 15-3) and the human epidermal growth factor receptor 2 (HER2) are some of the reported biomarkers of interest in the development of non-invasive tests. In serum analysis, the biomarkers present on the cell surface and their extracellular domains (ECDs) are commonly used for detection (e.g. HER2-ECD) [2]. Biosensors with rapid, accurate and point of care detection possibilities are prominent alternatives to the traditional methods. In addition, the use of nano- and micro- materials with excellent physicochemical properties can increase the sensors' surface area and the sensitivity of the analysis.

In this work distinct electrochemical immunosensing platforms were successfully developed for early detection of breast cancer through the analysis of HER2-ECD. A sandwich assay was performed using (i) SPCEs modified with gold nanoparticles electrodeposited on carboxylic acid functionalized multiwalled carbon nanotubes or (ii) carboxylic acid functionalized magnetic beads. The antibody-antigen interaction was detected using a secondary detection antibody labelled with alkaline phosphatase and 3-indoxyl phosphate as the enzymatic substrate. The addition of silver nitrate to the enzymatic substrate leads to the deposition of metallic silver which was stripped into solution by linear sweep voltammetry providing the analytical signal. The calibration plot for both sensing platforms was obtained between 7.5 - 50 ng/mL, with limits of detection of 0.15 ng/mL for the immunosensor and 0.86 ng/mL for the magnetic assay.

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Acknowledgments: M. Freitas is grateful to FCT-Fundação para a Ciência e a Tecnologia for her PhD Grant (SFRH/BD/111942/2015).



#### P6. Rechargeable hot water bottles catastrophic burst forensics

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Keywords: Water bottle, Burst, Corrosion, Forensics, Emergency

Scalds are the second most prevalent aetiology in severe burn injury, up to 63% (first in the paediatric age group, up to 75%) [1].

The surge of extremely affordable electric rechargeable hot water bottles turned out into a clear and present danger: a number of seriously injured people was received at the emergency ward of the Unidade de Queimados of the Centro Hospitalar da Universidade de Coimbra (UQ-CHUC), presenting extensive burns in feet and lower legs due to the catastrophic burst of sealed rechargeable hot water bottles in bed.

A team of the UQ-CHUC and the Coimbra Chemistry Center of the University of Coimbra (CCC-UC) set out an investigation.

The use of ferrous electrodes in the hot water bottles compounded by the dangerous design of the samples, was found to be a reasonable and probable cause for the documented accidents.

Following WHO recommendations [2,3], awareness, communication, and effective enforcement of electrical appliances safety policies in this matter should lead governance actions by the national and international authorities.

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### P7. Study of the electrochemical behaviour of drugs using screen-printed electrodes with different working electrodes

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Keywords: analytical chemistry, electrochemistry, screen-printed electrodes

The exploitation of screen-printed electrodes (SPEs) on the analytical determination of pharmaceutical compounds in complex matrixes can provide important advantages, such as no pre-treatment steps, great sensibility, simplicity, disposability, cost effectiveness and potential for mass production [1].

In this work, SPEs with different working electrodes, namely bare-carbon, multi walled carbon nanotubes (MWCNT), graphene and gold electrodes were used to study the electrochemical behaviour of rifampicin.

Rifampicin is a first-line drug used in the treatment of tuberculosis, one of the oldest diseases affecting the humankind, currently being the leading cause of death from infectious disease worldwide.

The drug undergoes on a complex redox process that was studied through electrochemistry, namely cyclic and square wave voltammetry techniques.

SPEs exhibited high stability, reproducibility and repeatability, thus offering a promising alternative for its analysis in micro-volumes of samples. Furthermore, the use of MWCNT greatly enhanced the analytical signal of the analyte, compared with bare-carbon SPEs. Produced electrodes provided excellent biocompatibility, good electrical conductivity, low electrochemical interferences and a high signal-to-noise ratio.

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### P8. Development of voltammetric methodologies towards the detection of benzo(a)pyrene in black tattoo inks.

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**Keywords:** Benzo[a]pyrene, Nonaqueous media, Differential pulse voltammetry, Boron doped diamond electrode, Black tattoo inks

Nowadays, it's well known that the use of tattoos and permanent make-up has grown in popularity all over the world, particularly amongst the young population. Naturally that the direct and permanent contact of these products with the skin of an individual raises some questions on the health risks involved, due to the presence of chemicals with adverse effects towards the humans. At the same time, the possibility to acquire online tattoo inks, without the proper risk assessment on the chemicals contained therein, has substantially increased [1,2]. Among the various chemicals found in tattoo inks with adverse health effects are the polycyclic aromatic hydrocarbons (PAH), being one of the most representative of this class, the benzo[a]pyrene (BaP). This compound can be found, especially, in black tattoo inks [1]. To detect and assess the presence of this compound in the materials, it is necessary to use very sensitive analytical methods. Knowing that the electroanalytical methods offer this possibility, and that this approach has not been yet duly explored, it is proposed a simple voltammetric method to detect BaP in black tattoo inks.

The developed method is based on the anodic voltammetric response of BaP at a boron doped diamond electrode (BDDE), in 0.1 M LiClO<sub>4</sub> acetonitrile solution. In the present method it is used a voltammetric cell, in which less than 250  $\mu$ L of electrolyte solution are used. The proposed method presents a good performance for the detection of BaP and its applicability is demonstrated in spiked samples of black tattoo inks.

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#### P9. Development of hybrid AC/MnO<sub>2</sub> cotton fabric electrodes for solidstate supercapacitors

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Keywords: Supercapacitor, Carbon Nanofiber, Manganese Oxide

In this work, positive electrodes, based on manganese oxide  $(MnO_2)$ , and negative electrodes, based on activated carbon (AC) slurries, deposited directly onto cotton fabric, were produced to assemble flexible solid-state asymmetric supercapacitor (SC) with a sodium exchanged Nafion 115 membrane. This SC was then investigated through cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) in the operational voltage range from 0 to 1.6 V. Furthermore, electrochemical impedance spectroscopy (EIS), long-term cycling-floating stability and self-discharge tests, were also performed. The solid-state hybrid SC showed a remarkable long-term durability and an increase in its specific capacitance from 105 to 125 F g<sup>-1</sup>, after simultaneously cycling and floating tests [1] during 10 k cycles and 140 h with a voltage holding condition at 1.6 V.

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### P10. Novel electrochemical methodology for dye identification in historical textile fibres with multiple-walled carbon nanotubes immobilizing layer

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Keywords: Voltammetry, Heritage Science, Organic dyes, Textile fibres.

The identification of dyes in historical textiles is an important topic in heritage science as it can help in elucidating questions about the materials used, the textile's place of origin, and the period of time of its production [1].

Important studies suggest voltammetry as an alternative for organic dyes identification [2,3]. As an advantage over chromatography, this technique does not require the extraction or dissolution of a solid sample, in addition to the possibility of been carried out *on situ*.

This study presents a methodology to obtain a direct response from cochineal in a wool fibre [1] with Voltammetry of Immobilized Microparticles analysis, using a portable potentiostat  $\mu$ Stat 200 (DropSens) and a low-cost disposable screen-printed electrode (DRP 110). The electrode surface was modified with gold nanoparticles and a micro sample of the textile fibre was immobilized with a multiple-walled carbon nanotubes layer, allowing us to obtain excellent results. The analytical response was compared with commercial cochineal samples and different red dyes.

The results show that the voltammetric methodology developed constitutes a viable and simple analytical approach for direct identification of dyes in historical textile fibres, and therefore, a promising tool in the field of heritage science.

Acknowledgments: Specials thanks are addressed to Ana Manhita, PhD (HERCULES Laboratory, University of Évora), for providing us the textile fibers samples.

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## P11. Application of a characterized graphene PGE to the electrocatalytic reduction of O<sub>2</sub> using immobilized laccase

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Keywords: Pencil graphite electrode, graphene, biosensor, laccase

Pencil graphite electrodes (PGEs) are another new form of carbon electrodes. They have been successfully applied in the voltammetric studies since they display good mechanical strength and comparable electrical properties. Moreover, their ubiquity and low cost makes them a good alternative to more conventional electrodes especially in disposable applications. In these type of electrodes the hardness of the pencil lead (from H to B, where HB is the medium one) dictates the more or less content of graphite, influencing directly the outcome of the analysis. Nanostructuration of the electrode surface is a viable option to enhance the electrical performance of the sensor. Therefore, application of graphene, a 2D carbon structure material, provides high surface area and conductivity to the electrode however promoting also an elevated capacitance.

In the present work, different pencil lead hardness were evaluated in the performance of the PGE as well as its modification with reduced graphene. Additionally, a PGE biosensor comprising immobilized laccase was applied for the biocatalytic reduction of oxygen.

Homemade PGEs with different hardness (4H, HB and 4B) and diameter of 2 mm were mechanically polished with alumina and evaluated using redox probe  $K_3Fe(CN)_6/K_4Fe(CN)_6$ . The PGE was further modified with 1 mg/ml of graphene oxide and reduced electrochemically in  $Na_2SO_4$  from -1.2 V to 0.8 V at 50 mV/s for 50 scans and evaluated using the same redox probe. The laccase immobilized biosensor was implemented in a 2B, 2 mm PGE and the procedure was based on a literature study [1]. Voltammetric analysis showed higher redox peaks for the softer (4B) PGE followed by HB and lastly 4H. Theoretically, more graphite content translates in a higher conductivity. The modification with graphene conferred much higher redox peaks (3.6 times) when compared with bare PGE. The immobilization of laccase was confirmed by cyclic voltammetry in the presence of soluble mediator, ABTS, in oxygenated and N<sub>2</sub> purged buffer. Amperometric measurements of O<sub>2</sub> at a reducing potential of +0.34 V showed linearity up to 0.36 mM and sensitivity of about 130  $\mu$ A/(mM.cm<sup>2</sup>) to O<sub>2</sub>.

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### P12. Ionic strength effect on the second ionization constant of phosphoric acid

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Keywords: Phosphoric acid, pH standard, ionic strength

The ionic strength of the seven primary standard buffer solutions for pH measurement [1] does not exceed 0.1 mol kg<sup>-1</sup> due to the limit of applicability of the Bates-Guggenheim convention [2] in the calculation of the chloride ion activity coefficient. Two standards are phosphate buffer solutions based on the equilibrium between the ions  $H_2PO_4^-$  and  $HPO_4^{2-}$  which corresponds to the phosphoric acid second ionization.

In this work, stoichiometric ionization constants of this acid (K<sub>2</sub>\*) in potassium chloride solutions were determined from potentiometric titrations of 0.005 mol dm<sup>-3</sup> potassium dihydrogen phosphate with 0.5 mol dm<sup>-3</sup> potassium hydroxide and 0.005 mol dm<sup>-3</sup> potassium hydrogen phosphate with 0.5 mol dm<sup>-3</sup> hydrochloric acid, at 25 °C. The ionic strength varied from 0.1 to 3.0 mol dm<sup>-3</sup>. The SUPERQUAD programme [3] was used for the calculations. The ionic strength dependence of pK<sub>2</sub>\* (pK<sub>2</sub>\*= -log K<sub>2</sub>\*) is shown for both sets of measurements. The curves are identical and those values are useful for the evaluation of each chemical species concentration at equilibrium. From those results, the quantity log ( $\gamma_{HPO_4} \gamma_{H} / \gamma_{H_2PO_4}$ ) can also be easily evaluated ( $\gamma$  refers to activity coefficient of the indicated species).

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#### P13. Treatment of olive mill wastewaters trough electro-Fenton process

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Keywords: Olive mill wastewater, Electro-Fenton, BDD, Heterogeneous catalyst

Wastewaters from olive processing industry are characterized by high organic load due to the presence of high concentrations in organic acids, sugars, tannins and phenolic compounds [1]. They represent a serious environmental contamination source, since they are often discharged untreated into water streams and soil, or stored in evaporation ponds. Although several studies have tried to develop efficient treatments [2,3], more research is necessary to improve the quality of the treated effluent and to decrease treatment costs.

In this work, the application of an electro-Fenton (EF) process, using a boron-doped diamond anode and a carbon-felt cathode, was carried out to treat a Portuguese and a Tunisian olive mill wastewater (OMW). The catalytic activity of mined pyrite (FeS<sub>2</sub>) and chalcopyrite (CuFeS<sub>2</sub>), as iron supplier, for EF oxidation of OMW was investigated.

Results showed that, at the best experimental conditions applied, after 8 h assay, EF process accomplished a chemical oxygen demand removal of 22.7 g L<sup>-1</sup>. Furthermore, the use of iron containing solid catalysts, mined pyrite and chalcopyrite, when compared with traditional iron sulfate and iron chloride, showed to promote identical treatment results. Additionally, the use of these heterogeneous catalysts resulted in lower iron amounts in solution and increased formation of  $H_2O_2$ , with the advantage that they can be recovered and reutilized. Thus, the results indicate that mined pyrite and chalcopyrite can be effectively used as heterogeneous EF catalysts for the degradation of OMW.

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## P14. TiO<sub>2</sub> nanotubes: Preparation, characterization and photoelectrocatalytic environmental applications

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Keywords: Nanotube, TiO<sub>2</sub>, Acid Orange 7(AO7), Photoelectrodegradation

The objective of this study was to prepare and characterize  $TiO_2$  nanotubes over a titanium foil (Ti/TiO\_2NT), and utilize the prepared material for the photoelectrocatalytic degradation of the model dye Acid Orange 7(AO7).

The electrode was prepared by electrochemical anodization [1,2], and the presence of nanotubes was confirmed by FESEM (Fig. 1a). AO7 degradation tests were performed by photolysis, photocatalysis, electrocatalysis and photoelectrocatalysis. AO7 degradation was evaluated by absorbance removal in the visible region as a function of the treatment time. The best colour removal, 95 %, was obtained in the photoelectrocatalytic assay of a 25 ppm dye initial concentration, using as electrolyte Na<sub>2</sub>SO<sub>4</sub>, 5 g L<sup>-1</sup>, after applying a current intensity of 1 mA cm<sup>-2</sup> and UV light (254 nm, 7 W), for 6 h.



Figure 1. a) FESEM micrographs of the  $TiO_2$  nanotubes on the anode surface; b) Absorbance variation with time, measured at 484 nm, of the AO7 solutions submitted to photoelectrodegradation assays.

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## P15. Carbon-Based Hybrid Nanomaterials as Electrocatalysts for the Detection of Carbamazepine

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Keywords: Polyoxometalates, carbon materials, carbamazepine, electrocatalysis

In the last decades, the abrupt growth of world population and industrial processes has had a profound impact on the environment. The presence of drugs, hormones and their metabolites in the aquatic environment has been systematically reported in environmental monitoring studies. The search for innovative technologies that ensure a sustainable and secure water supply system has thrived at a high rate and is one of the main objectives of the 21st century[1]. Carbon nanomaterials, such as graphene (GFx) and single-walled carbon nanotubes (SWCNT), have emerged as important platforms for the development of nano-electrocatalysts[2,3]. More recently, graphite carbon nitride (g- $C_3N_4$ ) has been extensively studied because of its planar structure, electron density and thermal stability[4]. The nanostructures obtained from the joining of graphene flakes, carbon nanotubes or  $g-C_3N_4$  with polyoxometalates (POMs), are presented as new materials with catalytic properties for the efficient detection of emerging pollutants in waters[4]. The materials prepared were characterized by FTIR and XPS. The hybrid nanomaterials were characterized by voltammetric techniques and applied in the electrochemical detection of carbamazepine in a buffer solution  $Na_2HPO_4/KH_2PO_4$  of pH 6.89. It was verified an increase in the current intensity of the electrochemical process associated to carbamazepine compared to the clean electrode, and in some cases, a decrease of the peak potential values, showing that these have an electrocatalytic activity for the oxidation of carbamazepine.

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# P16. Development of functional coatings containing natural occurring materials for the corrosion protection of Mg alloys.

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**Keywords:** encapsulation; natural-based materials; active species; controlled release; corrosion control.

When considering biodegradable biomedical applications, magnesium alloys major advantage is, unfortunately, also their biggest disadvantage: its degradation [1,2]. More specifically, its uncontrolled degradation by corrosion [3], often accompanied by hydrogen formation can cause complications when using these alloys within the human body [1].

In this work, we propose the development of a functional coating, containing naturalbased capsules for the controlled release of relevant species, namely biocompatible corrosion inhibitors. Capsules were characterized by SEM, FTIR and DSC, subsequently incorporated into polyetherimide (PEI) coatings and tested using electrochemical impedance spectroscopy (EIS) to evaluate their corrosion protection properties. These results will be crucial to determine the suitability of the developed materials for future incorporation into polymeric matrices for biomedical applications.

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## P17. Photoelectrocatalytic activity of SrFeO<sub>3</sub> electrodes in the degradation of the dye Acid Orange 7

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Keywords: Perovskites, SrFeO<sub>3</sub>, Photoelectrocatalysis, Visible Light, Acid Orange 7

Strontium ferrite, SrFeO<sub>3</sub>, is a perovskite-like oxide. These oxides are a family of ceramic compounds with general formula ABO<sub>3</sub>, well-known for their versatile and flexible structure and easily tailored properties [1,2].

The aim of this work was to synthesize and immobilize the strontium ferrite powder into electrodes, and test their photo, electro and photoelectro catalytic activity in the degradation of the dye Acid Orange 7 (AO7).

SrFeO<sub>3</sub> powder was synthesized by solid state reaction process and structurally confirmed by XRD. The oxide electrodes were prepared by pressing the obtained powders into 1 cm<sup>2</sup> geometric area pellets and the ohmic contacts were achieved as described elsewhere [3]. 8-hour degradation assays were carried in a one-compartment three-electrode cell with a SrFeO<sub>3</sub> disc pellet work electrode, a platinum foil counter-electrode and Ag/AgCl, KCl, saturated commercial reference electrode, under a controlled temperature of 25  $^{\circ}$ C. Assays were run with an AO7 initial concentration of 25 mg L<sup>-1</sup>, and 5 g L<sup>-1</sup> of Na<sub>2</sub>SO<sub>4</sub> as support electrolyte, and irradiated with a 300 W visible radiation lamp. In the electrocatalytic assays the applied current density was 1 mA cm<sup>-2</sup>. The AO7 degradation was monitored by UV-Visible absorption spectrophotometry.

The best dye removal, 74 %, was achieved by photoelectrocatalytic assay, under visible light, showing the synergistic effect between photo and electro catalysis.

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#### P18. Direct Electrochemical Characterization of Nitric Oxide Reductase and Interactions with its Physiological Partner

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**Keywords:** Enzymes, Nitric Oxide, Cytochrome c<sub>552</sub>, Bioelectrochemistry

Nitric oxide reductase (NOR), from *M. hydrocarbonoclasticus*, is a membrane protein with two subunits, NorC (electron transfer) and NorB (catalytic site). It receives electrons from cyt  $c_{552}$ , catalysing the nitric oxide reduction to nitrous oxide, a denitrification pathway's key step. Also, it presents catalytic activity towards oxygen reduction. NOR has been extensively studied and its properties and catalytic mechanisms unveiled [1, 2]. Its solvent-exposed domain, NorC, and its physiological electron donor, were heterologously produced and from its interactions it was possible to infer that NorC redox potential is modulated by the presence of the second subunit, NorB, tuning the electron transfer properties [3].

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#### P19. Electrochemical oxidation of cotton textile dye-bath effluent

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Keywords: Dye-bath textile wastewater, Anodic oxidation, BDD, Reuse

Textile and Clothing industry is one of the most important sectors in the Portuguese economy. The production processes in the textile industry, mainly in the dyeing and finishing processes, require intensive use of water, with the consequent rejection of large volumes of wastewaters. Cotton and other cellulosics comprise over 40% of world textile consumption. Reactive dyes are the most utilized in the dyeing process of these fibers because of their excellent wash fastness, which arises from a covalent bond formed between the dye and the fiber. However, the reactive dyeing process can be expensive and time-consuming, needing significantly high salt and alkali concentrations that causes a high level of pollution [1], since only 50 to 80% of the dye is fixed to the cotton fabric during the dyeing process [2]; the rest appears in the wastewater, causing high chemical oxygen demand (COD) and color to the effluent. It is therefore essential to develop treatments to allow the wastewater reuse.

The aim of this work was to study the application of anodic oxidation, using a BDD anode, to evaluate the feasibility to treat a cotton dye-bath textile wastewater to, posteriorly, reuse it in new dyeing baths, thus reducing water and salts consumption. The cotton dye-bath containing Brillant Red Levafix E-4B reactive dye, sodium sulfate and sodium carbonate was used. It was studied the influence of applied current density and the presence of the carbonate. After 20 min of treatment the complete colour removal was obtained at the highest applied current density of 60 mA/cm<sup>2</sup> and for the lowest current density it took 60 min. The presence of carbonate increases the COD removal but decreases the mineralization of the organics present in the wastewater: at 20 mA/cm<sup>2</sup>, TOC removal in the absence of the carbonate is 66% and in the presence of this salt decreases to 39%. It was also concluded that after 6 h of electrolysis, sulfate and carbonate concentrations did not vary significantly, which allows the reuse of the treated effluent without the necessity of adding these salts to the cotton dye-bath.

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## P20. Coal Char as cathode material for the electrochemical production of hydrogen peroxide

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Keywords: Coal Char, Hydrogen Peroxide production, Electrocatalysis.

Hydrogen peroxide is a potential energy carrier and an environmentally friendly oxidant for chemical industries and environmental remediation. Its electrochemical production through the selective reduction of oxygen has been subject of particular interest, once allow the safe *in situ* generation of  $H_2O_2$ .[1] Carbon-based electrocatalysts (ECs) with high selectivity and durability have been pursued for this purpose,[2] but the efforts can be compromised by the high supply risk of natural graphite in a near future. The coal combustion carbon-rich solid residues (Char) are promising materials for substitute the carbon-based ECs, allowing simultaneously the recycle of coal combustions ashes for high-tech applications and the reduction of their environmental impact.

In this work, several char samples derived from coal combustion (PEGOP, Portugal) were tested as cathode ECs for the production of  $H_2O_2$  via the reduction of oxygen. The samples were pre-treated in order to have different (i) particle sizes and (ii) carbon concentrations. The influence of these parameters in the 2-electron oxygen reduction was evaluated in alkaline medium, and the results were correlated with the X-ray Photoelectron Spectroscopy (XPS) data.

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#### P21. Paper-based Potentiometric Immunosensor for Salmonella Thyphimurium Detection

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Keywords: paper-based, immunosensor, potentiometry, Salmonella, label-free

*Salmonella (S.)* is still one of the most frequently occurring pathogens worldwide, originating large number of hospitalizations and millions of deaths every year. Accordingly, a rapid, sensitive, low-cost and user-friendly detection method that can be used onsite in different matrices is still needed [1].

In this work, a flexible, simple and affordable analytical device for *S. Thyphimurium* detection was developed. Paper was chosen as support for electrode construction and potentiometry as sensing technique. Herein, a thin flexible polymeric membrane, which serves as platform for biorecognition element loading [2,3], was drop on a paper filter strip impregnated with poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS). Usually, the detection of biomolecules or larger analytes using paper-based potentiometric devices resorts to enzyme labeling [4]. In proposed work, to avoid expensive and unstable labels, a label-free biosensor was assembled. Two different immunosensing interfaces were implemented. The simplest interface relied on direct conjugation of the antibody to the polymer membrane and the second one resorted to an intermediate layer of polyamidoamine (PAMAM)-NH<sub>2</sub> G4 dendrimer. The results show that both interfaces can accurately predict low levels of *S. thyphimurium*.

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## P22. Electrochemical biosensor for histamine detection in fishery products

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Keywords: electrochemical biosensor, food safety, biogenic amines, fishery products

Histamine is a biogenic amine and is one of the freshness indicators of fishery products [1]. This biogenic amine is considered the worst problem associated with food poisoning and can cause many symptoms such as flushing, vomiting, diarrhea, among others. Hence, the level of histamine is an important parameter included in the routine analysis in the fishing industry. According to European Legislation, the level of histamine in fishery products from fish species cannot exceed 200 mg/kg [2]. Therefore, it is important to develop analytical devices that are robust and easy to handle and allow cheap, fast and sensitive histamine analysis.

In this work we developed an electrochemical enzymatic sensor to address the industry's current demands. The basis of this biosensor consisted of the immobilization of the enzyme (diamine oxidase) by cross-linking on the surface of a screen-printed carbon electrode. All relevant experimental variables were studied and optimized, achieving a biosensor able to rapidly detect histamine in the range of 4 - 800 mg/kg, which is useful in the fish industry's safety control.

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### P23. Electrogenerated polydopamine films as platforms for enzyme immobilization

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Keywords: Electropolymerization, covalent binding, Laccase, biosensors

The chemical immobilization of stable and functional enzymes is one of the most crucial steps when developing a biosensing interface [1]. Bio-inspired materials such as polydopamine films (PDA) are being explored to covalently bind target biomolecules through the reactivity between quinones moieties and amine functions [2]. Most of PDA studies involve the chemical polymerization of dopamine in alkaline aerated solutions. Nevertheless, it is widely accepted that chemical synthesis yields poorly conductive and heterogeneous films, with physico-chemical properties that are difficult to reproduce. The electrosynthesis of dopamine arises as an alternative [3], although polymerization mechanisms and the final film properties are yet to be explored.

In this work, we use potentiodynamic and potentiostatic methods to generate reproducible PDA polymeric films with controlled thickness and electroactivity. It is undoubtedly proved that electrogenerated films display higher surface density of quinone groups, required for the covalent immobilization of proteins, when compared to spontaneously formed PDA films with similar thickness. The catalytic performance of Laccase immobilized on electrochemical synthesized PDA was assessed by chronoamperometry and cyclic voltammetry towards the oxidation of 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic) acid diammonium salt (ABTS). The results disclose the enormous potential of the electrochemical routes in the development of biocompatible polymeric matrixes for biosensing devices.

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### P24. Potentiometric determination of potassium ion in coffee extracts using a FIA system.

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Keywords: potassium selective electrode, coffee extract, flow injection analysis (FIA).

Potassium is the main inorganic ion naturally occurring in coffee representing ca. 1.5% w/w of the coffee bean content. Potassium concentration in coffee beans has impact upon the bean development and also upon the final bean's sugar concentration [1], the latter being important for the beverage final quality.

The determination of potassium is generally performed using ICP-AES [2], ICP-OES [3] or flame photometry [4] and, to the best of our knowledge, the use of a potassium selective electrode to this aim has not been exploited. Preliminary results using a potassium selective electrode (based in valinomycin ionophore) in batch analysis showed a deep matrix effect, jeopardizing this determination. To overcome this scenario, the potassium selective electrode was used in a FIA system, taking advantage of the recognized benefits of this strategy, namely, automatic sample pretreatment, efficient electrode surface cleaning and high repeatability in samples measurement.

The results obtained will be further assessed with a comparison methodology based on previous digestion of the samples and AES.

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#### P25. Electric Impedance spectroscopy characterization of tea and coffee

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Keywords: Tea, Coffee, Electrical Impedance Spectroscopy (EIS), Chemical analysis

Electrical Impedance Spectroscopy (EIS) is a non-destructive technique that can provide quantitative measurements and characterize different samples [1]. The EIS is used to characterize 6 tea infusions ( $Ch_1$ - $Ch_6$ ) and 8 coffee brews ( $C_1$ - $C_8$ ) leading to a representation of the impedance Z(j $\omega$ ) in the frequency domain. The EIS series of values constitutes an alternative description of chemical analysis based on the total antioxidant capacity, total sugars, proteins, total solids, organic matter and ashes. Multidimensional scaling (MDS) technique is adopted for reducing dimension and visualizing the relationships between the measures. Figure 1 a) illustrates the Nichols diagram of Z(j $\omega$ ) of 2 coffee samples ( $C_1$  and  $C_2$ ) and 2 tea infusions ( $Ch_1$  and  $Ch_2$ ). Fig 1 b) and c) present the MDS maps for the ESI and the chemical analysis, respectively. In both cases the MDS plots include identical tea infusions ( $Ch_1$ - $Ch_6$ ) and coffee brews ( $C_1$ - $C_8$ ) samples. The results show a positive correlation between the two descriptions.



Figure 1. Nichols diagram a) of  $Z(j\omega)$  (0.01 < f < 10<sup>4</sup> Hz) of 2 coffee samples (C<sub>1</sub> and C<sub>2</sub>) and 2 tea infusions (Ch<sub>1</sub> and Ch<sub>2</sub>). MDS plots of tea infusions (Ch<sub>1</sub>-Ch<sub>6</sub>) and coffee brews (C<sub>1</sub>-C<sub>8</sub>) samples b) ESI and c) chemical analysis.

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### P26. Electrochemical studies of aquasoluble iron(III)-arylhydrazone-βdiketone complexes

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Keywords: iron(III), arylhydrazone, β-diketones

The aquasoluble  $Fe^{III}$  complexes  $[Fe(H_2O)_3(L^1)]\cdot 4H_2O$  and  $[Fe(H_2O)_3(L^2)]\cdot 3H_2O$ , bearing the basic forms of 5-chloro-3-(2-(4,4-dimethyl-2,6-dioxocyclohexylidene)hydrazinyl)-2hydroxy-benzenesulfonic acid  $(H_3L^1)$  and 3-(2-(2,4-dioxopentan-3-ylidene)hydrazinyl)-2-hydroxy-5-nitrobenzenesulfonic acid  $(H_3L^2)$ , were synthesized and fully characterized including by X-ray crystal structural analysis.<sup>[1]</sup>



We now report the redox properties of the aquasoluble  $Fe^{III}$  complexes, 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 [<sup>n</sup>Bu<sub>4</sub>N][BF<sub>4</sub>]/CH<sub>2</sub>Cl<sub>2</sub> 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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# P27. Room temperature ionic liquids: comparison of electrochemical windows

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**Keywords:** electrochemical window, cyclic voltammetry, room-temperature ionic liquids (RTILs)

To date, most of the reactions have been carried out in molecular solvents. Recently, however, a new class of solvent has emerged – ionic liquids. These are often fluid at room temperature and consist entirely of ionic species. They have many fascinating properties, which make them of fundamental interest to electrochemists [1].

Herein the cathodic and anodic limits of room-temperature ionic liquids (RILs), formed from a combination of 1-butyl-3-methylimidazolium (BMIM) and three common anions  $-[PF_6]^-$ ,  $[BF_4]^-$  and bis(trifluoromethylsulfonyl)imide  $[TFSI]^-$  – (Figure 1), investigated by cyclic voltammetry, are presented and discussed. The anion, in particular, was found to affect the level of water uptake. The hydrophobicity of the anions adhered to the following trend:  $[TFSI]^- > [PF_6]^- > [BF_4]^-$ .

Cyclic voltammetry has shown that an increase in water content significantly narrows the electrochemical window of each ionic liquid.



Figure 1: Ionic liquids ions investigated. Cation: (a) 1-butyl-3-methylimidazolium. Anions: (b) hexafluorophosphate, (c) tetrafluoroborate, and (d) bis(trifluoromethylsulfonyl)imide.

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## P28. Cyclic voltammetry of a C-scorpionate nickel(II) complex in ionic liquid media

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Keywords: electrochemical window, cyclic voltammetry, C-scorpionate

The electrochemical behaviour of the C-scorpionate nickel(II) complex  $[NiCl_2{\kappa^2 - HC(pz)_3}]$  (pz = pyrazol-1-yl, Figure 1a) dissolved in the ionic liquids 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [EMIM][TFSI] (Figure 1b) or 1-butyl-3-methylimidazolium bromide [BMIM][Br] (Figure 1b) was evaluated, to assess its viability as catalyst in CO<sub>2</sub> hydrogenation.



Figure 1

The electrochemical results are discussed in light of the uptake, as function of time, of  $CO_2$  in the both ionic liquids.

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## P29. ZnO<sub>2</sub> based nanofluids parameters for electrochemical applications

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Keywords: nanofluids, zirconia, electrocatalysis

Nanofluids are liquids that are engineered by stably dispersing functional nanomaterials in base fluids. They have been historically investigated for their superior thermal properties such as thermal conductivity and heat transfer ability, and typically considered for use in industrial and automotive cooling applications.

Complex behaviours exhibited by nanofluids [1] have resulted in multiple theories attempting to explain the experimental viscosity and thermal conductivity enhancements. However, no universal theory has been proposed to date, to explain the behaviour of the whole family of nanofluids.

In this work, nanofluid parameters (particle concentration, size, loading and surfactant) will be discussed for the development of nanofluids with highest possible loading of zirconia (ZnO<sub>2</sub>) nanoparticles in aqueous electrolytes, which are of interest as new media for electrochemical energy storage, photo- and electro-catalysis.

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# P30. Electrochemical study as a function of the ionicity of hydrophobic ionic liquids

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Keywords: Ionic liquids, heat transfer fluids, ionicity

Ionic liquids (ILs), which are liquids comprised totally of ions, can potentially be applied as heat transfer fluids (HTFs) due to their characteristic properties including low vapour pressure, wide liquid range and high thermal stability.

However, not all of the ions present at an IL appear to be available to participate in conduction processes, to a degree that is dependent on the nature and structure of the ionic liquid. Therefore, there is much interest in quantifying and understanding this "degree of iconicity" phenomenon.

As a continuation of work developed [1] in the evaluation of the potential of some ILs as HTFs and considering that most of them already have their physicochemical properties available for comparison with commonly used materials, herein we present an electrochemical study as a function of the ionicity of the IL, for a range of hydrophobic ILs bearing large cations.

The aim of this work was to increase the knowledge of the IL characteristics, as highly promising materials as HTFs that may be a solution for several engineering issues.

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