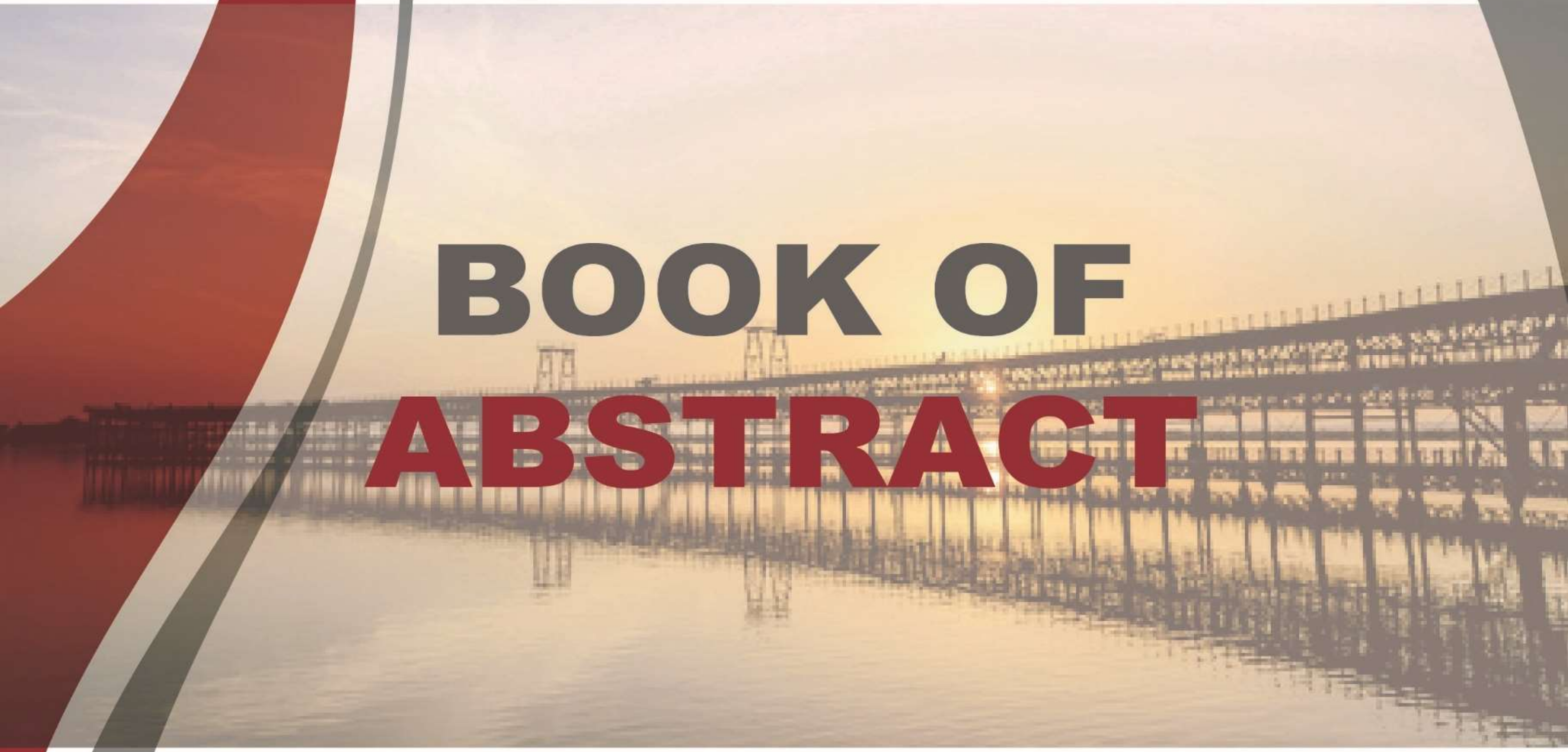
XL MEETING OF THE SPECIALIZED GROUP OF ELECTROCHEMISTRY OF THE ROYAL SPANISH SOCIETY OF CHEMISTRY

XX IBERIAN MEETING OF ELECTROCHEMISTRY



BOOK OF ABSTRACT

XL GE-RSEQ
XX EIB

HUELVA, JULY 9th TO 12th, 2019

XL Meeting of the Specialized Group of Electrochemistry of the Royal Spanish Society of Chemistry

XX Iberian Meeting of Electrochemistry

Huelva, from 9th to 12th of July 2019

Scientific Committee

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SIMPOSIA ABBREVIATION

Analytical Electrochemistry	(AEC)
Bioelectrochemistry	(BEC)
Electrochemical Energy Storage & Conversion	(ECE)
Material Electrochemistry	(MEC)
Electrochemical Process Technology & Engineering	(ECP)
Molecular Electrochemistry	(MOE)
Fundamental Electrochemistry	(FEC)

Extended Programme

JULY 9TH

16.00 – 21.00	Registration & Documentation delivery
16.00 – 19.00	Dropsens-Metrohm Workshop on Spectroelectrochemistry
17.00 – 19.00	EC&T Master and Doctoral programmes Commission Meeting
19.00 – 21.00	Welcome party

JULY 10TH

9.00 – 9.15	Welcome Act	
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10.00 – 10.30	Coffee Break + Visit to Posters & Exhibition Area	
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12.30 – 13.00	GE Young researcher Award: D. Martín-Yerga; KTH Royal Institute of Technology *"A Holistic Approach to Enhanced Electroanalytical Applications using Disposable Electrochemical Devices"*	*Chairman: I. Gallardo*
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20.00 – 00.00	Social Activities	

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JULY 11TH

9.00 – 9.45

Plenary Session
Aula Magna
Chairman: J.D. Mozo
G. Ríos; Atlantic Copper
"Electrochemistry and Copper Industry"

10.00 – 10.30 Coffee Break + Visit to Posters & Exhibition Area

Oral Contributions

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11.35 – 11.55	E. Sánchez-Tirado (UCM)	J. González (UM)	M. E. Lorenzo (UAM)	M. Borràs (LEITAT)
11.55 – 12.15	C. Gutiérrez-Sánchez (UAM)	J. M. Gómez-Gil (UM)	S. Hernández (UBU)	

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Aula Magna
Chairman: A. Heras
J. Garoz; Universidad de Burgos
"Multipurpose Spectroelectrochemistry: Paving the Way for In Vivo Measurements"

13.30 – 14.45 Lunch

15.00 – 15.45

Plenary Session
Aula Magna
Chairman: J. Solla
C. F. Oliveira; Universidad Tras-os-Montes e Alto Douro
"Hydrophilic Carbon Nanomaterials – A platform for Electrocatalysis and Nanomedicine"

Oral Contributions

	GE Room (BEC)	AC Room (MEC)	UH Room (AEC)	AE Room (ECE)
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16.45 – 17.05	C. Busó-Rogero (IMDEA)	F. Vicente (UV)	G. Martínez-García (UCM)	P. Ocón (UAM)
17.05 – 17.25	I. Márquez (US)	E. García (CSIC)	M. Pérez-Estébanez (UBU)	
17.25 – 17.45	T. Fernández-Otero (UPCT)	I. López (UDA)	P. López-Cornejo (US)	

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GE Room Programme

Sponsored by Group of Electrochemistry

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Sponsored by Group of Electrochemistry

JULY 11TH

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GE Room Programme (*Cont.*)

Sponsored by Group of Electrochemistry

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AC Room Programme

Sponsored by Atlantic Copper

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Sponsored by University of Huelva

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UH Room Programme *(Cont.)*

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10.30 – 11.15	Oral Contributions (AEC) *Chairman: P. Yáñez-Sedeño* R. Jiménez-Pérez ; Universidad de Castilla-La Mancha *"Highly Sensitive H_2O_2 Sensor Based on Poly(Azure A)-Platinum Nanoparticles Deposited on Activated Screen Printed Carbon Electrodes"*
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12.20 – 13.20	Awards and Closing Ceremony

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Sponsored by Applied Electrochemistry Research Group

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10.00 – 10.30	Coffee Break + Visit to Posters & Exhibition Area
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11.15 – 11.35	E. Gyenge; University of British Columbia *"Efficient Bifunctional Oxygen Reduction and Evolution Reaction (ORR/OER) Electrocatalysts for Alkaline Rechargeable Metal-Air Batteries: Doped Mixed Oxides"*
11.35 – 11.55	M. Borràs; LEITAT *"Green and Printed High Performant Supercapacitors"*
11.55 – 12.15	
12.30 – 13.00	IV Antonio Aldaz Award: *Chairman: A. Heras* J. Garoz; Universidad de Burgos *"Multipurpose Spectroelectrochemistry: Paving the Way for In Vivo Measurements"*
13.30 – 14.45	Lunch
15.00 – 15.45	Plenary Session *Chairman J. Solla* C. F. Oliveira; Universidad Tras-os-Montes e Alto Douro *"Hydrophilic Carbon Nanomaterials – A platform for Electrocatalysis and Nanomedicine"*
16.00 – 16.45	Oral Contributions (ECE) *Chairman: C.M. Sánchez-Sánchez* E. Pastor ; Universidad de La Laguna *"Cobalt Supported on N and S Dual-Doped Reduced Graphene Oxide as Highly Active Cathode Catalyst for DEFC"*
16.45 – 17.05	P. Ocón; Universidad Autónoma de Madrid *"Manganese Oxide Catalysts for Oxygen Reaction Reduction in Sea Water and Alkaline Al-Air Batteries"*
17.05 – 17.25	
17.25 – 17.45	
17.50 – 18.20	Coffee Break + Visit to Posters & Exhibition Area
20.45 – 3.00	Official Dinner

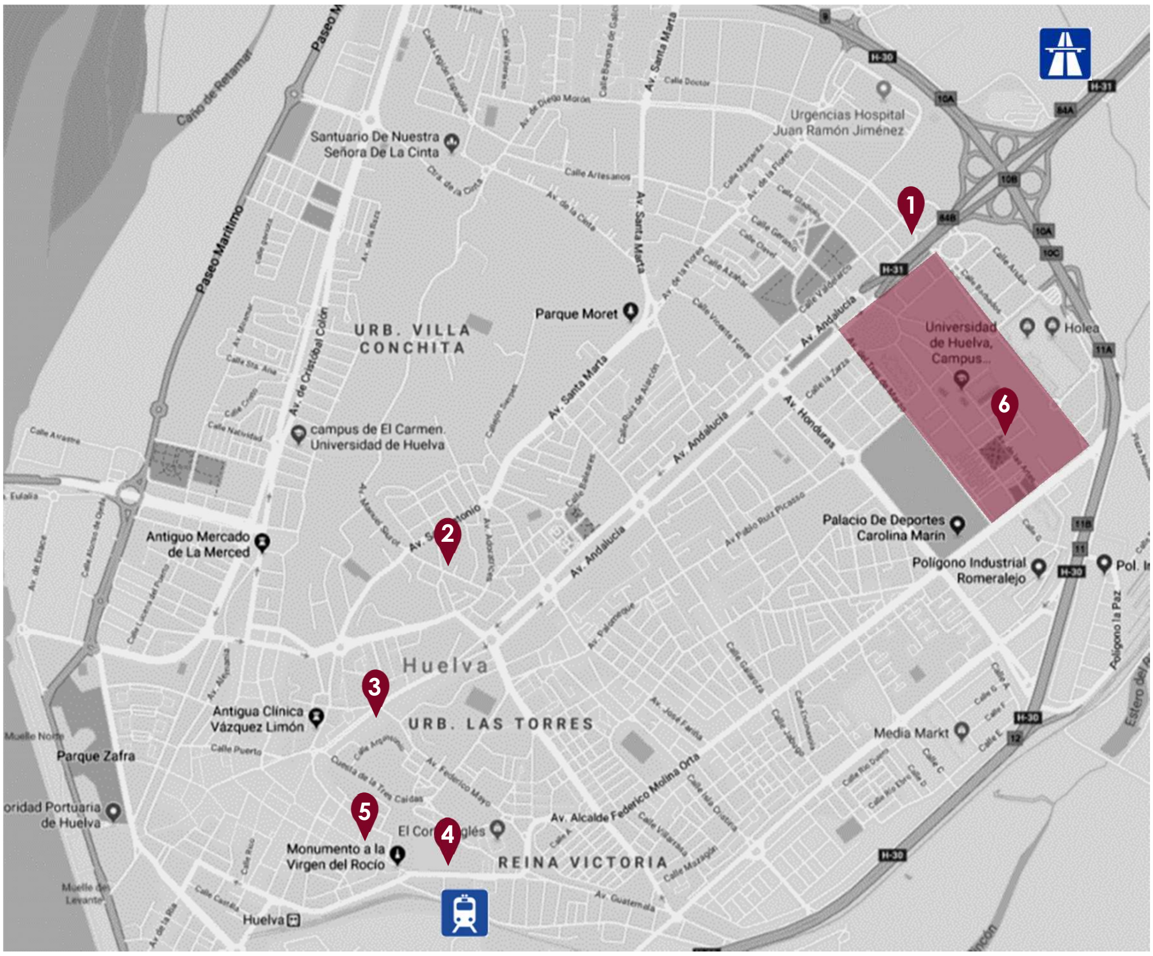
AE Room Programme (*Cont.*)

Sponsored by Applied Electrochemistry Research Group

JULY 12TH

9.00 – 9.45	Plenary Session: J. A. Squella; Universidad de Chile *"Electrochemistry of Nitroaromatic Compounds: From Mercury to Carbon Nanotubes"*	*Chairman: J. Carbajo*
10.00 – 10.30	Coffee Break + Visit to Posters & Exhibition Area	
10.30 – 11.15	Oral Contributions (MOE/FEC) A. Heras; Universidad de Burgos *"UV/Vis Absorption Spectroelectrochemistry for Studying Antioxidant Properties"*	*Chairman: A. Colina*
11.15 – 11.35	L. E. Botello; Universidad de Alicante *"Activation Energy of Hydrogen Adsorption on Platinum (111) from Impedance Spectroscopy in Alkaline Media"*	
11.35 – 11.55	M. Chávez-Peraza; Universidad de Córdoba *"Efficient Formation of Polymer Brushes from Mixed Self-Assembled Monolayers using the eATRP Technique"*	
11.55 – 12.15	J. J. García-Jareño; Universidad de Valencia *"Kinetics of Surface Processes from Colour Standard Deviation"*	
12.20 – 13.20	Awards and Closing Ceremony	

Huelva Map



1. AC Hotel by Marriott Huelva
2. Albergue Inturjoven Huelva
3. Senator Huelva Hotel
4. Hotel NH Luz Huelva
5. Hotel Exe Tartessos
6. Jacobo del Barco Pavilion

Jacobo del Barco Pavilion Plane

1. Magna Classroom
2. AC Conference Room
   Sponsored by Atlantic Copper
3. UH Conference Room
   Sponsored by University of Huelva
4. GE Conference Room
   Sponsored by Group of Electrochemistry
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   Sponsored by Applied Electrochemistry G
6. Registration
7. Information
8. Posters exhibition
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11. Lunch Area
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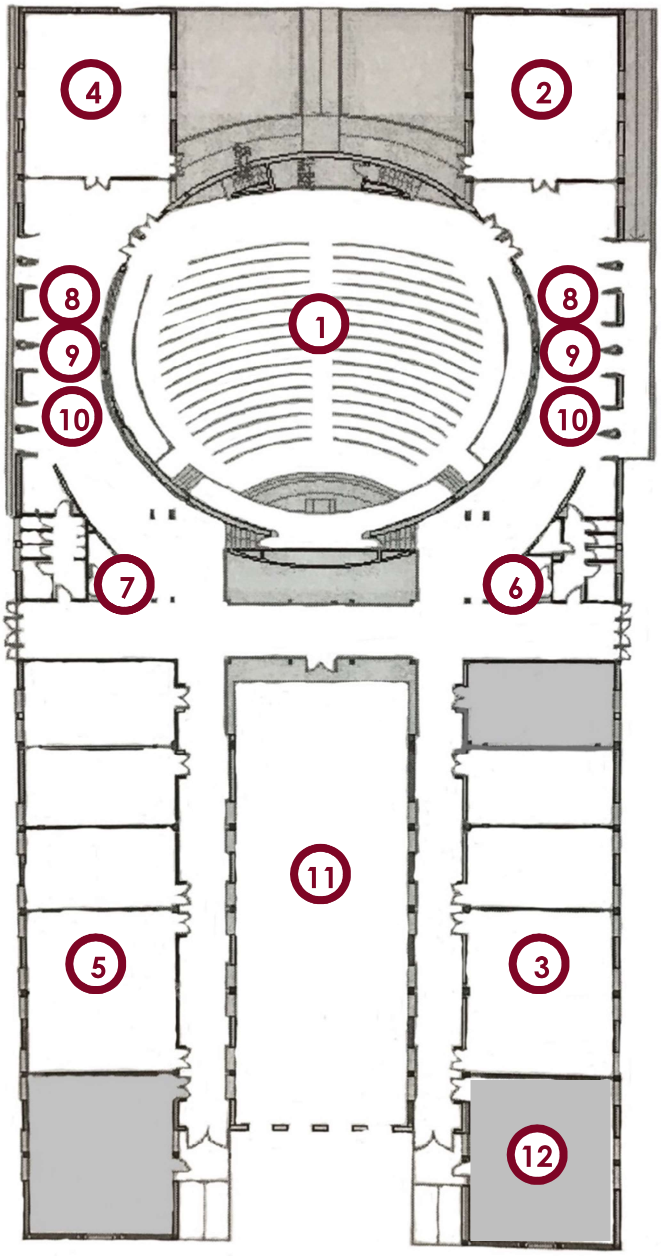
    Workshop



Plenary Sessions
& Awards

C-MEC01

FUNCTIONALIZATION OF METALIC SURFACES FOR APPLICATIONS IN NANOMEDICINE

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Keywords: *nanomaterial; surface modification; protein corona; polymer brushes.*

The use of nanomaterials (NM) in health and medicine has generated an important new discipline known as Nanomedicine. One of the main objectives in this field is the combination of diagnostic and therapeutic functions in a single platform that allows reaching the tissue target and delivering of specific drugs avoiding the different obstacles that can be found in the biological systems. The sequestration of NMs upon entering the biological system involves the adsorption of plasma proteins onto the circulating NMs, that is, the formation of a *protein corona*. The protein corona is formed instantaneously and change the chemical properties of the NM surfaces [1].

The protein *corona* depends on several factors that include NM size, surface charge and chemistry and its stability and structure depend on the charge and conformation of the proteins upon *corona* formation [2]. It is very well known that the *protein corona*-NMs attach to the surface of specific receptors of phagocytes and they do not arrive to the target. To solve this problem, the nanoparticles are covered by polyethylene glycol (EGn) that are grafted to the gold surface via ligand exchange (PEGylation). It has been shown that PEGylation prolongs circulation time from minutes to hours [3].

The bottom-up strategy to build nanostructures from individual molecular components is one of the most attractive protocols due to the flexibility and versatility in the design. The self-assembly of this building blocks and the intermolecular forces play a role in the final structure because of a competitive balance. EGn-SAMs built with EGn of different chain lengths have been shown low organization due to the high conformational freedom of the molecules. Only for the shorter chains, a *helicoidal* conformation of the EGn chain has been found that becomes *all-trans* when the substrate allows for the higher packing density. When using polymeric chains, the *brush* preferred structures are difficult to be found. The approaches used for film formation include the *grafting to* and *grafting from* strategies [4].

Acknowledgments.
Ministerio de Economía y Competitividad (MINECO) (Proyectos CTQ2014-60227-R and CTQ-2015-71955-REDT Red de Excelencia Sensores y Biosensores Electroquímicos) y Universidad de Córdoba.

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C-ECP02

ELECTROCHEMISTRY AND COPPER INDUSTRY

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Keywords: electrorefining*; copper; cathode; tankhouse; operations*

Electrochemistry has always been defined as the science describing the chemical changes caused by an electrical current and the production of electricity by chemical reactions. These two areas of electrochemistry are of equal importance, but it could be said the use of electricity, as a chemical reagent, has played an important role in the development of the extractive metallurgy of copper, and hence in the history of Mankind.

Pyrometallurgy of copper is an ancient art dating to the Copper Age (5000 BC to 3000 BC) and the hydrometallurgy of copper can be traced to the Middle Ages, for example the cementation of copper from an aqueous solution of copper sulphate was practiced in China in the 10th century. On the contrary, it can be said that electrometallurgy is a “recent technology” that dates back to the end of the 18th century and the discoveries of great scientists such as Volta, Ampère and Faraday. In 1800 Cruikshank found out that metallic copper may be precipitated from a solution by means of the electricity supplied by a “Voltaic pile” and years later Faraday formulated his very well-known “laws of electrolysis” in 1831. The electrolytic refining of copper was invented by a British electroplater, James Elkington, in 1865 and the first refinery was constructed in 1869 in Pembrey, near Swansea in Wales, where electricity was supplied by Voltaic cells [1].

Nevertheless, it should be pointed out that it was another finding made by Faraday, and formulated in his “law of induction”, that made possible the subsequent development of industrial copper electrochemistry. In 1831, Faraday showed that a rotating copper disc in a magnetic field could generate a constant flow of electricity. This led to the invention of the electric dynamo by Werner von Siemens in 1866. This invention enabled the production of electricity at large scale and with the reliability required by the industry to produce a high purity copper cathode with excellent conductivity.

After the invention of the dynamo, the first continuous working tankhouse for the electrolytic refining of an “anode copper”, coming from a copper smelter, was commissioned in 1876. This took place at Norddeusche Affinerie (nowadays Aurubis) in Hamburg with a capacity of 6 t/d of copper [2]. This first industrial production of copper cathodes gave rise to the extensive use of electricity and hence the to the World as it is known today. Nevertheless, none of this would have been possible without the invention of the dynamo.

Another milestone in the electrolytic production of copper was the implementation of solvent extraction technology, in the 70’s and 80’s of the last century, which made possible the production of copper cathodes by electrowinning from the leaching of oxidic ores. Nowadays, of the 28 million tonnes of copper consumed each year worldwide, 20 % are being produced by electrowinning and the remaining 80 % by electrorefining. This paper describes the fundamentals of these electrolytic copper production processes as well as the operational practices and further developments that have made possible the reaching of these production figures in modern tankhouses.

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C-MEC03

HYDROPHILIC CARBON NANOMATERIALS – A PLATFORM FOR ELECTROCATALYSIS AND NANOMEDICINE

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Keywords: *Oxygen reduction; peroxide reduction; antioxidant; redox active; biomolecules*

Graphite provides a cheap source of obtaining a wide range of carbon nanomaterials, ranging in size from 0-D to semi-infinite 2D structures. Typically, these materials are insoluble or difficult to dissolve in water. However, a very simple methodology to produce amorphous hydro-soluble carbon nanomaterials from graphite was recently found [1,2]. This material was named Electrogenerated Hydrophilic Carbon (EHC) due to its outstanding solubility in water.

The EHC nanomaterial is a carbonaceous material dominated by sp^2 carbons and possessing a significant amount of oxygen. This material is endowed by two remarkable properties: ability to form two-dimensional nanostructured layers with conductive properties and an anomalous ability to retain cations (e.g. Na^+). Taken together, this means that this material can be explored by electrochemists in two different ways, as an electrolyte and as an electrode material.

As an electrolyte, it was found that these materials can exhibit electro-donating or electro-accepting properties. These qualities can be particularly useful for nanomedicine, to restore and/or to assure the normal redox state of cells and, in this way, treat, delay and/or prevent pathologies caused by oxidative stress.
Actually it was shown that EHC can exhibit a high radical scavenging activity and a concentration-dependent capability to protect the mitochondrial lipids and intracellular thiol groups from strong oxidant agents (*t*-BHP and hydroxyl radicals) [3].

As an electrode material, this material has shown interesting properties in the electrocatalysis field. Examples will be given concerning oxygen and peroxide reduction reactions and dopamine oxidation. The overall results will show that Hydrophilic Carbon Nanomaterials are a most promising and exciting material, whose electrochemical properties can be easily modulated by the experimental synthesis conditions.

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C-FEC04

ELECTROCHEMISTRY OF NITROAROMATIC COMPOUNDS: FROM MERCURY TO CARBON NANOTUBES

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Keywords: *Nitroaromatics; cyclic voltammetry; nitro radical anion; MWCNT.*

The strong electronegativity of the nitro group comes from the combined action of the two electron-deficient oxygen atoms bonded to the partially positive nitrogen atom. When attached to an aromatic ring, the nitro group is able to delocalize π-electrons of the ring to satisfy its own charge deficiency. This characteristic gives these compounds an extraordinary ability to be reducible. The electrochemistry of these nitro compounds has been reviewed by several authors [1] and it is possible to conclude that the reduction involves a series of one-electron additions and chemical steps wherein the differences are mainly in the chemical follow up reactions rather than in the electrochemical steps. The mechanisms are very complex with a multifactor dependency, but in this work, we will focus in some applications related on the influence of the reaction medium and the electrode material.

By means of voltammetry on conventional mercury or carbon electrodes it is possible to obtain a signal due to the 4-electrons 4-protons reduction due to the reduction of the nitro derivative to the hydroxylamine derivative. The advantages of this signal are both the high quantity of current produced per mol of electroactive compound and the relatively low energy requirements for the nitro reduction. Consequently, this signal is very useful for the electroanalytical point of view allowing the implementation of analytical methods for several nitroaromatic compounds of pharmacological interest such as: Nifedipine, Nimodipine, Nitrendipine, Nimesulide, Ranitidine, Loratadine, Nitrofurantoin, Metronidazole, Nitrofurazone, and several others [2].

On the other hand, under suitable conditions of the medium on mercury electrodes, reduction of nitroaromatics can occur in separate steps wherein the one electron reduction can be isolated producing well resolved cyclic voltammograms due to the nitro/nitro radical anion redox pair ($RNO_2/RNO_2^{\cdot-}$). By using appropriately the wide versatility of the cyclic voltammetric technique, it is possible to study the feasibility of formation of nitro radical anions, their prototropic behavior, their natural lifetimes and their reactivity with other molecules.

More recently, with the introduction of NTCs as electrode materials, it has been possible to study the behavior of nitroaromatic compounds in electrodes modified with multi walled carbon nanotubes [3]. A new, non-conventional voltammetric experiment was developed, which involves firstly trapping a nitroaromatic electroactive species on the surface of a modified MWCNT electrode, then washing the electrode and finally applying a potential scan in a fresh buffer solution. Using the above approach, it is possible to trap the nitroaromatics in the porous network of the MWCNTs on the electrode, prioritizing thin layer-type mass transport, and leading to larger peak currents and smaller concentration overpotentials. In addition, using this methodology it is possible to activate the nitroaromatic derivative trapped in the electrode and generate the redox active pair ArNHOH / ArNO feasible to use as an electrocatalytic redox mediator.

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A-SR01

DECONTAMINATION AND DISINFECTION OF URBAN AND INDUSTRIAL WASTEWATERS BY ELECTROCHEMICAL ADVANCED OXIDATION PROCESSES

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Keywords: *anodic oxidation; electro-Fenton; photoelectro-Fenton; pig slurry; pilot plant*

Over the last 4 years, our research group has applied several electrochemical advanced oxidation processes (EAOPs) like anodic oxidation (AO), electro-Fenton (EF) and photoelectro-Fenton with UVA light (PEF) or sunlight (SPEF) to the decontamination and disinfection of urban and industrial wastewater to establish their viability at industrial scale. Four main activities have been undertaken:

A. Study of synthetic matrices. Sulfate, chloride or nitrate solutions were used to remove dyes, herbicides and chemicals in cells with a boron-doped diamond (BDD), Pt, RuO_2 or IrO_2 anode, coupled to an air-diffusion cathode for H_2O_2 electrogeneration. At pH 3.0, the oxidation power of the processes grew in the order: AO < EF < PEF, with 0.50 mM Fe^{2+} as catalyst in EF and PEF. In sulfate or nitrate medium the oxidizing agent was $^{\bullet}OH$; in chloride medium, active chlorine (Cl_2/HClO) was more effective but led the formation of chloroderivatives that slowed down the mineralization. The BDD anode was the most powerful and an almost complete mineralization was achieved using PEF.

B. Decontamination of urban wastewater. The treatment of several organics, such as the antibiotic trimethoprim, spiked into urban wastewater was studied by AO, PEF and SPEF with Pt and BDD. A mixture of parabens was treated by SPEF with BDD, Pt, RuO_2 and IrO_2. It was found that: (i) the natural organic matter was gradually mineralized, decelerating the pollutant removal; (ii) low currents were required to avoid hazardous products; and (iii) the most efficient process was SPEF with BDD, yielding almost total mineralization. Intermediates were identified for each contaminant, allowing the proposal of the reaction sequences.

C. Disinfection of urban wastewater. AO with BDD caused the total inactivation of the bacteria *Escherichia coli* and *Pseudonomas aeruginosa* in sulfate medium. In sulfate + chloride matrix, the latter microorganism was more rapidly inactivated with IrO_2 due to its larger adsorption and greater formation of active chlorine, which destroys the cell wall more easily than $^{\bullet}OH$. Another EAOP like photoelectrocatalysis with an Ag-decorated TiO_2 photoanode allowed an efficient inactivation of *Pseudonomas aeruginosa.*

D. Decontamination of industrial effluents. Sequential processes involving aerobic treatment followed by AO, EF, PEF or SPEF with BDD were studied for winery wastewater or sanitary landfill leachate. In SPEF, 90% of the organic matter was removed with low energy costs, pointing to their viability for industrial scale-up. Other works were focused on the treatment of olive oil mill wastewater using AO with BDD and electrocoagulation (EC) with Fe/Fe cell followed by EF or PEF with BDD. The best results were obtained with a sequential EC/PEF process yielding a 97% of mineralization.

Finally, *a pilot plant for the integral treatment of pig slurry* was constructed by us in 2017 for the treatment of 1.5 m^3 d^{-1}. It comprises three coupled modules: an initial EC with Fe/Fe cell, an advanced solid-liquid separation and a final AO with BDD. The plant was validated during 9 months (2017-2018) in a farm near Barcelona with 500 pigs. It was found, in average, a reduction of 95% of suspended total solids, 75% of dissolved solids, 80-89% of N and 75-90% of K, with formation of 230 kg sludge m^{-3} with 30% of humidity, along with 98% removal of organic matter, yielding a final water useful for reuse in irrigation.

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A-YR02

A HOLISTIC APPROACH TO ENHANCED ELECTROANALYTICAL APPLICATIONS USING DISPOSABLE ELECTROCHEMICAL DEVICES

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Keywords: *disposable devices; sensing; biosensing; spectroelectrochemistry; zero-cost analysis*

Electrochemical devices such as screen-printed or paper-based electrodes are widely employed for the development of portable user-friendly sensing and biosensing applications. The ideal properties of these devices such as the small size (miniaturization), low cost (mass production), low sample requirement and disposable character (single-use) make them very appropriate for Point-of-Care or decentralized electroanalytical applications. However, improving the physical and chemical properties of these devices and its analytical performance (i.e. selectivity, sensitivity) is still a constant concern in order to achieve universal analytical platforms and expand the scope of their applications.

In this presentation, I will describe a holistic approach considering different fundamental and applied advances using disposable electrochemical devices to enhanced electroanalytical applications such as sensing and biosensing. This includes:

- Understanding the fundamental electrochemical behaviour of these devices to gain valuable information and facilitate the rational design of superior electroanalytical platforms. In this regard, studies of activity-structure relationships in screen-printed electrodes at the sub-microscale using frontier electrochemical imaging will be discussed.
- Adopting cost-effective fabrication materials such as paper or plastic substrates moving towards the goal of “zero-cost” analysis or exploiting particular nanomaterials to enhance the system’s analytical performance.
- Developing innovative strategies for efficient and sensitive detection of nanoparticles [1] widely employed as electrochemical label in biosensing devices.
- Marrying electrochemical and spectroscopic techniques to expand the possibilities of electroanalytical methods using disposable electrodes by increasing the selectivity, sensitivity [2] or opening up new approaches to detect a wider range of analytes.

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A-AA03

MULTIPURPOSE SPECTROELECTROCHEMISTRY

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***Keywords**: spectroelectrochemistry; sensors; carbon nanotubes; optical fibers.*

Spectroelectrochemistry (SEC) is a powerful technique that combines the best of electrochemistry and spectroscopy. In SEC experiments, the optical information is simultaneously recorded throughout the electrochemical measurement, allowing the researcher to obtain information of different nature at the same time and to increase the possibilities to understand reaction mechanisms, to characterize materials or to develop new methods for analysis.

However, it is necessary to realize that SEC was a tedious technique a few years ago, with some disadvantages such as the need to use optically transparent electrodes, the low reproducibility and the difficulty to assemble the existing SEC cells, in particular with respect to the alignment of the light beams. With the aim to overcome these drawbacks, this work has developed new electrodes of carbon nanomaterials and novel SEC devices based on bare optical fibers (Figure 1a) [1].

All the developments performed herein can be applied for different purposes. Nevertheless, the field of analysis is one of the least exploited for SEC. In order to demonstrate the wide variety of advantages that this hybrid technique possesses [2], the main focus of this research has been the quantification of compounds of biological interest such as dopamine, epinephrine and ascorbic acid (Figure 1b) [1], among others, taking advantage of the features of SEC to study real samples and to resolve high complex mixtures.

In our humble opinion, this work has laid the groundwork to increase the use of SEC in many different fields, particularly for sensing applications. It makes sense to do much more work in the near future to give SEC the importance it deserves in quantitative analysis.

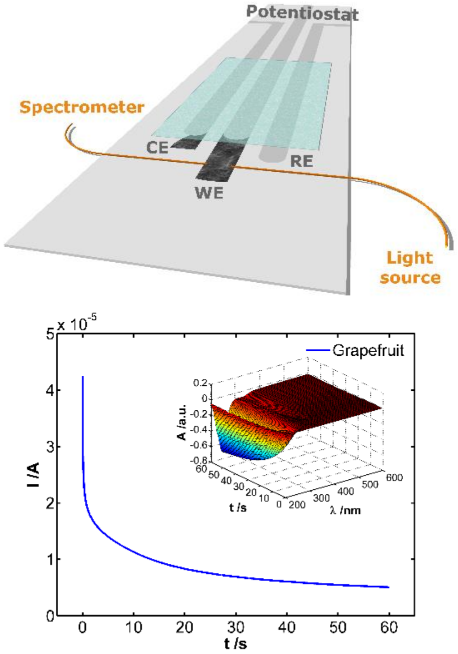

Figure 1. (a) SEC device based on carbon nanotubes and bare optical fibers. (b) SEC experiment inside a grapefruit. Reprinted with permission from Ref. [1]. Copyright 2017 American Chemical Society.

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Acknowledgements

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Oral

Contributions

O-BEC11

ELECTROCLICK CHEMISTRY, A NEW PATH FOR IMMUNOSENSING BIOMARKERS OF AUTOIMMUNE DISEASES

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Keywords: *autoimmune diseases; biomarker; immunosensors; electroclick chemistry; IL-1β*

Autoimmune diseases constitute a social problem affecting many people around the world. These diseases, whose cause is not known, tend to be chronic and find no cure so far. Moreover, their wide variety makes diagnosis and adequate treatment difficult. However, various biomarkers indicative of some autoimmune disorders have been discovered. For example, IL-1β proinflammatory cytokine is overexpressed in rheumatoid arthritis (RA), and it has revealed as a good therapeutic target for this autoimmune disease. Levels of IL-1β in serum of healthy individuals are around units pg mL^{-1}, whereas reported values in serum and synovial fluid of patients with RA reach up to a few cents pg mL^{-1} [1,2]. Sensitive methods are therefore needed for accurate and precise determination of such concentrations in these kind of samples.

Following the research line of our team on development of electrochemical immunosensors, we have prepared a novel design using electroclick chemistry involving IgG-alkyne-azide-MWCNTs conjugates prepared by means of copper (I) catalyzed azide-alkyne cycloaddition reaction as an efficient strategy for the covalent immobilization of immuno-reagents without altering their configurations and preserving their biological activity [3]. As a relevant novelty, it is worth highlighting the electrochemical generation of catalyst, which provides a considerable time saving (5 min vs 16 h) also avoiding the need to use reducing reagents. As it can be seen (Fig. 1), a sandwich-type immunosensor was prepared onto the modified screen-printed carbon electrode (SPCE), the affinity reaction being monitored by means of alkaline phosphatase - labeled streptavidin (AP-Strept) with 1-naphthyl phosphate (1-NPP) as the enzyme substrate. Once optimized the variables involved in the preparation and functioning of the immuno-sensor, a calibration by differential pulse voltammetry was obtained in the 250 to 1000 pg mL^{-1} IL-1β with a high precision (RSD = 4.3 %, n=10) and a 5:1 specific-to-non specific current ratio at the 1 ng mL^{-1} level.

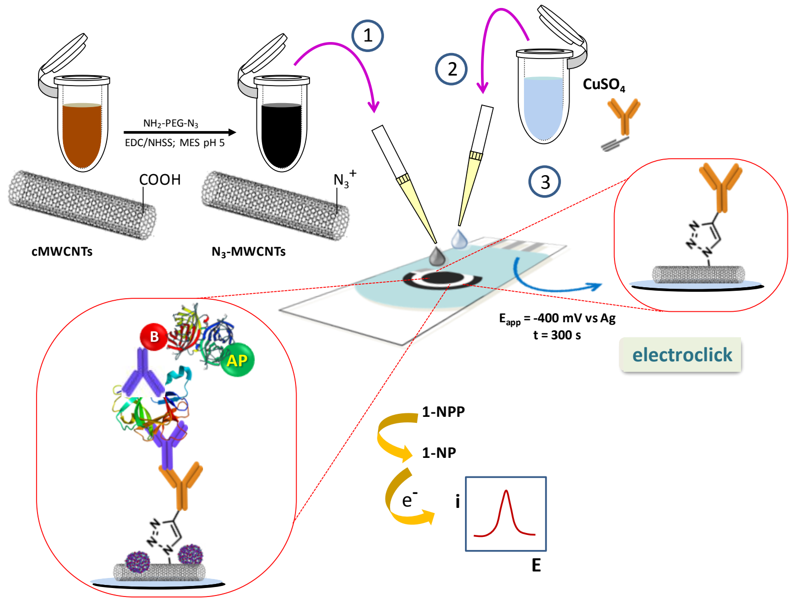

Figure 1. Scheme of the Immunosensor preparation

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RGB VIDEO ELECTROCHESMITRY OF AZINES-BASED CONDUCTIVE POLYMERS. POLY(NEUTRAL RED) AND POLY(AZURE A)

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Keywords: *phenazine; phenothiazine; conducting polymer; digital video; RGB video electrochemistry*

Azine-based dye molecules, such as phenazines (neutral red), phenothiazines (azure A) and phenoxazines, can be electrochemically radicalized and deposited onto electroactive surfaces as redox and conducting polymers [1]. The electrochemical processes of this kind of polymers, where the proton participation is strongly confirmed, are less known than other N-based polymers, such as polyaniline or polypyrrole [2]. In the present work, we have characterized the electrochemical process of the poly (azure A) film (PAA) (Figure 1) and the poly(Neutral red) film (PNR) on a transparent indium-tin oxide (ITO) electrode by means of cyclic voltammetry and RGB digital video. From each extracted digital images, the red, green and blue (RGB) channels were obtained only for the electrode surface [3]. The information obtained from the mean color intensity and the standard deviation for each channel together with the electrochemical response allows us a better interpretation of the electrochemical processes.

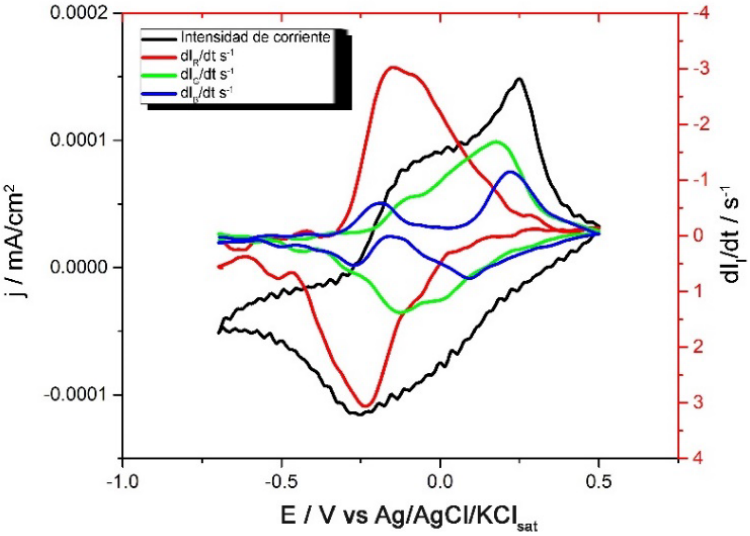

Figure 1: Cyclic voltammetry of PAA in 0.1 M K_2HPO_4 and KH_2PO_4 (pH 7) at 50 mV/s

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Acknowledgments
This work was supported by MINECO-FEDER CTQ2015-71794-R

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MAGNETIC MICROBEADS-BASED IMMUNOSCAFFOLD FOR THE AMPEROMETRIC DETERMINATION OF AN EMERGING METASTASIS CANCER BIOMARKER

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Keywords: *HIF-1α; cancer biomarker; immunosensor; amperometry*

Hypoxia inducible factor 1α (HIF-1α) is a protein which mediates the transcription of numerous genes implicated in cell response to reduced oxygen environments. It is involved in the pathogenesis of cancer, leading to changes in nutrient uptake, glycolysis, waste handling, cell proliferation, migration, apoptosis and angiogenesis, that can promote tumour survival and metastasis. Moreover, in the last years, it has been found that HIF-1α is overexpressed in a variety of human cancers including lung, prostate, breast, colon and oral cancer, being considered as a potent biomarker of these disorders. For this reason, the main objective of this work is the development, up to date, of the first electrochemical immunoplatform for this emerging cancer biomarker determination.

In this context, the development of an electrochemical immunoplatform is proposed consisting of the selective capture of the target by an antibody (AbC) covalently immobilized onto the surface of carboxylic magnetic microbeads (HOOC-MBs), and the subsequent labelling with another specific biotinylated detector antibody (Btn-Ab) further conjugated with a Streptavidin-HRP complex. The extension of the affinity reactions is monitored by amperometric detection at screen-printed carbon electrodes (SPCEs) using the hydroquinone (HQ)/HRP/H_2O_2 system (Figure 1).

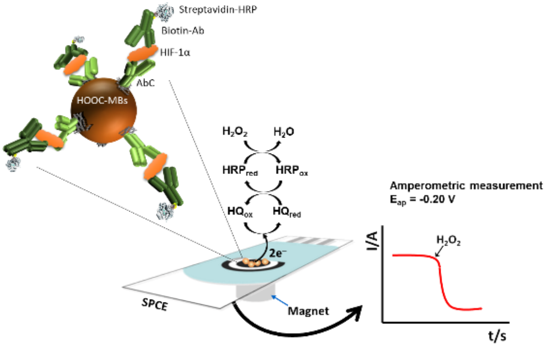

Figure 1. Developed amperometric immunosensor

After all the experimental variables were optimized, the developed immunosensor demonstrated a wide linear concentration range (0.25 – 10 ng mL^{-1}) and a great performance in terms of reproducibility (RSD 4.7 %, n = 10), stability of the AbC-MBs bioconjugates (more than 15 days), analysis time (105 min) and specificity against other proteins commonly found in biological samples. In addition, the obtained limit of detection of 76 pg mL^{-1} is well below the optimal cut-off level established at 460 pg mL^{-1} for HIF-1α protein in serum of patients with oral squamous cell carcinoma [1]. Finally, the applicability of the developed immunoplatform will be checked through the determination of this emerging cancer marker in clinical samples of different nature and complexity (serum, saliva and cell lysates).

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BISMUTH OXIDE (Bi_2O_3) AS A RECHARGEABLE AND HIGH STABILITY POSITIVE ELECTRODE FOR ALKALINE ZINC BATTERIES

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Keywords: Bi_2O_3, Zn Batteries,

Bismuth oxide (Bi_2O_3) is a nontoxic low cost metal oxide that has been applied as catalyst, optical material or gas sensor. Besides, Bi_2O_3 has been used as additive of negative electrodes in different energy storage devices, such as in Zn/air batteries [1]. Recently, due to its high electrochemical stability and high redox reversibility, Bi_2O_3 has been applied as a negative electrode of supercapacitors or NiBi batteries [2]. In this work we have characterized the reversibility of the Bi_2O_3 material by several electrochemical techniques and its application in Zn batteries as the positive electrode.

Figure 1 shows the Cyclic Voltammetry behaviour of Bi_2O_3 material in KOH solution. Cathodic peaks could be ascribed to the formation of a metallic Bi film through the reduction of Bi^{3+} of Bi_2O_3, while anodic peaks are due to oxidation of Bi to Bi^{3+}, following the reaction[1]:

$$Bi_2O_3 + 3H_2O + 6e^- \leftrightarrows 2Bi + 6OH^-$$

We have tested these positive electrodes in a Zn/PVA/Bi_2O_3 battery and the results will be commented in this communication.

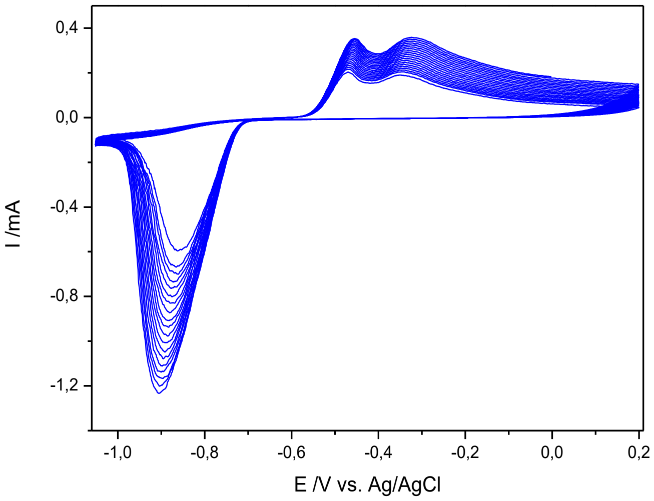

Figure 1. Cyclic Voltammogram of Bi_2O_3 electrode in 0.1M KOH.

Acknowledgments.
Ministerio de Economía y Competitividad and AEI/FEDER/UE (Spain, Refs. ENE2016-79282-C5-5-R and MAT2015-65274-R) and Fundación Séneca (Región de Murcia, Spain; Ref: 20985/PI/18 and 19882-GERM-15)

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O-BEC12

IN-SITU ELECTROCHEMICAL DETERMINATION OF H_2O_2 IN LIVING CELLS IN REAL TIME

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Keywords: *Amperometry, cell cultures, modified electrodes, platinum nanoparticles, polymers.*

H_2O_2, and ROS generally, are a fundamental fact of life in an aerobic environment [1]. Understanding the role of H_2O_2 in plant growth or stress responses requires models that accommodate the large number of ways in which it can be formed and degraded at any given time. In this sense, an electrochemical approach to directly measure the dynamic process of H_2O_2 release from cultures cells is reported. This approach is based on H_2O_2 oxidation on a previously activated screen-printed carbon electrode (SPCE) modified with a conductive polymer (Poly (Azure A)) [2] and electrogenerated platinum nanoparticles. This sensor has remarkable analytical advantages such as low detection limit, wide linear range and fast response time, so it fulfills the requirements for real-time measurement of cellular H_2O_2 in living cells. In addition, this sensor allows to continuously monitor for hours and even days without loss of sensitivity and can be reused after an electrochemical cleaning with sulfuric acid 0.05 M.

The addition of exogenous H_2O_2, as well as other potential stress stimuli [3], was made to freshly weighed grapevine cells diluted in 5 mL of buffered culture medium. Different elicitors (fast and slow actuation) were used in our research to stress living cells and amperometry was chosen to monitor changes in H_2O_2 concentration. This real-time quantitative H_2O_2 analysis is a potential marker for the evaluation of oxidative stress in plant cell cultures.

Therefore, our main goal was to use a simple, rapid, direct and sensitive electrochemical method based on enzyme-free, activated and modified SPCEs for the quantitative determination of H_2O_2 in plant cell suspensions in real-time.

Funding sources: *This work was funded by the Spanish Ministry of Economy and Competitiveness (BFU2016-75609-P) (AEI/FEDER, UE) and by the Junta de Comunidades de Castilla-La Mancha (Spain) (SBPLY/17/180501/000276/2), cofounded with FEDER funds, EU. BGM is a post-doctoral research fellow of the Youth Employment Initiative (JCCM, Spain, cofounded with ESF funds, EU).*

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SIMPLE ANALYTICAL THEORY FOR THE VOLTAMMETRIC RESPONSE OF ELECTRON TRANSFERS WITH NON-UNITY STOICHIOMETRY

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Keywords: *Non-unity stoichiometry; Analytical theory; Concentration profiles; Surface concentrations; Voltammetry*

Key electrochemical processes show non-unity stoichiometry (Scheme I, *a:b E-mechanism*) such as the hydrogen evolution reaction (HER) [1] and the electro-reduction of some mercury complexes [2]:

$$aO + ne^- \rightleftarrows bR \qquad (I)$$

In order to tackle the study of these systems, a general analytical treatment of reversible electron transfer of complex stoichiometry is developed via a simple mathematical procedure that simplifies the diffusion problem to a single independent variable that can be solved rigorously and easily. Thus, a general formulation for the concentration profiles is obtained for any stoichiometry. Moreover, exact solutions are deduced for the profiles, the surface concentrations and the complete current-potential response of the 2:1 E mechanism at macroelectrodes in any voltammetric technique and whatever the diffusion coefficient and bulk concentration of the redox species are. Also, a rigorous demonstration of the relationship between the surface concentrations of the species is carried out, as well of the time independence of the surface concentrations for Nernstian electron transfers regardless of the stoichiometric numbers, which allows for the application of the superposition principle. From the analytical solutions obtained, the particular features of the voltammetry of the 2:1 E mechanism, as compared with the 1:1 case, are analyzed for normal pulse voltammetry (NPV), cyclic voltammetry (CV) and square wave voltammetry (SWV).

It is worth mentioning that, in spite of the 'unsophistication' of the theoretical treatment required, the results presented here mean a significant contribution in the field given that only analytical solutions were available for the half-wave potential of the a:b E mechanism at macroelectrodes [1] and for the current-potential response of the 2:1 E mechanism under transient [3] and steady state [4] conditions. Also, the mathematical relationship between the surface concentrations of species O and R was established only on intuitive basis [5].

Acknowledgments

Fundación Séneca (19887/GERM/15), Ministerio de Economía y Competitividad (CTQ-2015-65243-P), and Ministerio de Educación, Cultura y Deporte (Ayuda FPU-2015).

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STUDY AND RESOLUTION OF TRIPHENYLMETHANE MIXED DYES BY IN-SITU NEAR INFRARED (NIR) SPECTROELECTROCHEMISTRY.

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Keywords: *NIR spectroelectrochemistry; SPELEC NIR; malachite green; crystal violet.*

Over last years near infrared (NIR) spectroscopy has received growing attention for industrial applications [1-3] because is a fast, non-destructive and non-invasive technique. However, the high absorbance of water in NIR spectral range complicates the differentiation of absorption bands and in this way, has limited the development of new applications. In order to overcome the water limitation, this work offers an interesting approach based on using ionic liquids.

NIR spectroelectrochemistry combines electrochemistry and NIR absorption spectroscopy and is a powerful technique not only for monitoring electrochemical reactions, but also, for the resolution of mixtures. As proof of concept, two triphenylmethane dyes, malachite green (MG) and crystal violet (CV), that only differ in one dimethylamino group were selected to demonstrate the usefulness of NIR spectroelectrochemistry. Although MG and CV show similar spectroscopic behaviour since their NIR absorption bands are only separated 54 nm, the evolution of the NIR wavelength is a quick and easy approach to deconvolve mixtures (Figure 1), allowing us to calculate the chemical composition of different samples. Furthermore, analysis of the spectroelectrochemical data with partial least squares (PLS) provides valuable quantitative information for solving dyes mixtures because it enables the determination of the concentration of the two dyes without the previous knowing the total concentration of the mixture.

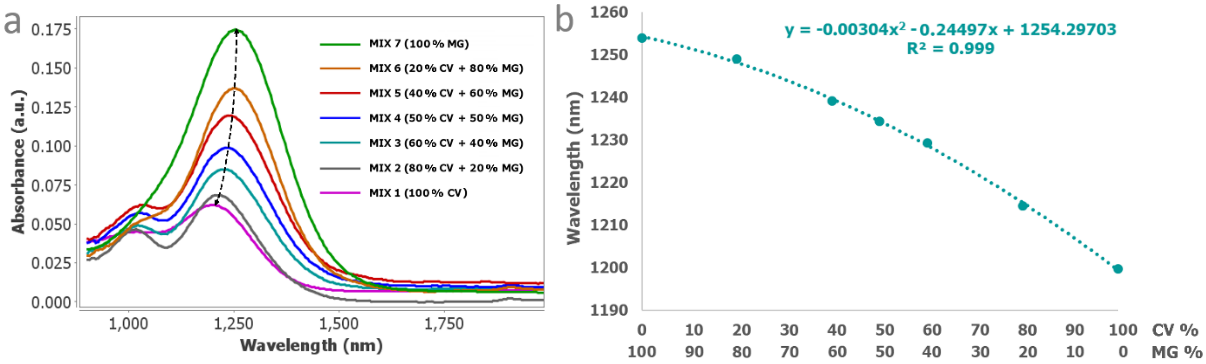

Figure 1. (a) NIR spectra of the maximum absorbance obtained during the electrochemical experiment for CV and MG mixtures. (b) Fitting of the experimental data (wavelength of NIR bands) with second order polynomial regression curve.

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EFFICIENT BIFUNCTIONAL OXYGEN REDUCTION AND EVOLUTION REACTION (ORR/OER) ELECTROCATALYSTS FOR ALKALINE RECHARGEABLE METAL-AIR BATTERIES: DOPED MIXED OXIDES

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Keywords: *oxygen reduction and evolution reaction; electrocatalyst; metal-air battery*

Development of highly active, durable and cost-efficient bifunctional electrocatalysts for the oxygen reduction and evolution reactions (ORR and OER) is of outmost importance for commercialization of rechargeable metal-air batteries (e.g., Zn-air, Al-air, Mg-air, Li-air) and regenerative H_2-O_2 fuel cells. Diverse manganese oxides (MnO_x) have been intensely studied as ORR electrocatalyst in alkaline media. Regarding the bifunctional ORR and OER electrocatalytic activity, however, enhancement of the activity and long-term durability are required for implementation in commercial systems. The purpose of this study is to present novel approaches for tuning the MnO_2 performance with co-catalyst addition, potassium ion doping and support effect (e.g., graphene and carbon nanotube). The combination of MnO_2 with structurally different oxide co-catalysts such as perovskite ($LaCoO_3$) or fluorite-type oxide (Nd_3IrO_7), produces a synergistic catalytic effect improving the bifunctional (ORR and OER) activity compared to the individual oxides. Hybrid catalyst support composed of graphene and carbon nanotubes creating a 3D scaffold-like architecture, enhances the catalyst layer utilization efficiency and durability during accelerated potential deep cycle experiments [1-3].

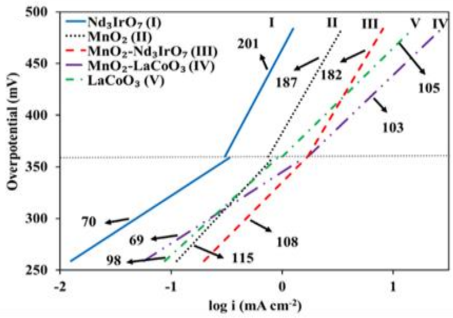

Figure 1. Tafel plots for the oxygen evolution reaction using diverse oxide electrocatalysts. Electrolyte: 6M KOH, 293 K, 1 atm. The numbers indicate the calculated apparent Tafel slopes. [1]

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DEVELOPMENT OF AN ELECTROCHEMICAL IMMUNOSENSOR FOR SENSITIVE DETERMINATION OF INTERFERON GAMMA (IFN-γ) IN CLINICAL SAMPLES

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Keywords: *interferon gamma; IFN-γ; electrochemical immunosensor; clinical sample*

Interferon gamma (IFN-γ), also known as immune interferon, is a pleiotropic cytokine mainly produced by activated T lymphocytes and natural killer cells [1], with a recognized ability to protect cells from viral infections [2]. This protein regulates the immune and inflammatory response, stimulating the action of macrophages, playing also an essential role in the development and severity of systemic autoimmune diseases, particularly lupus erythematosus [3].

This work describes the preparation of an electrochemical immunosensor for the sensitive determination of IFN-γ based on the immobilization of the specific capture antibody onto a screen-printed carbon electrode modified with 4-carboxyphenyl groups by electrochemical grafting. Figure 1 shows a scheme of the steps involved in the preparation of the immunosensor wherein the surface of the electrode is activated with a mixture of EDC/NHSS and the capture antibody is covalently immobilized. After blocking the free positions of the electrode with 2% BSA, the electrode is exposed to the analyte. Next, a sandwich immunoassay is established using a biotinylated detection antibody and HRP-Strept. The affinity reaction is monitored amperometrically at –0.2V vs Ag by addition of H_2O_2 solution in the presence of HQ/Q system. A calibration plot within the range and analytical characteristics adequate for the analysis of clinical samples was obtained.

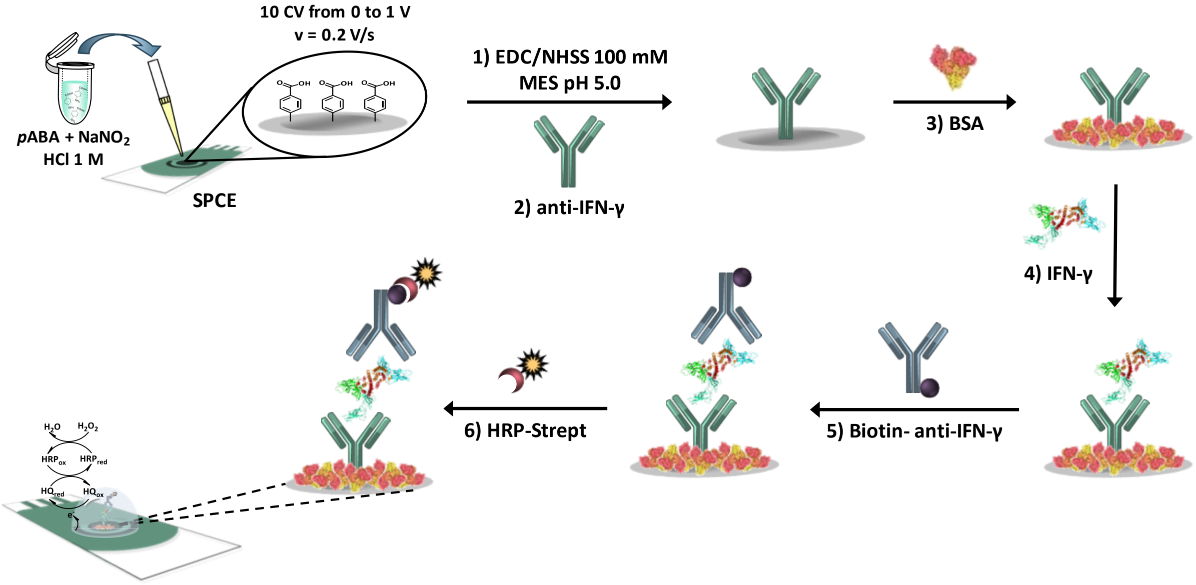

Figure 1. Scheme of the steps involved in the preparation of the immunosensor for IFN-γ

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INFLUENCE OF THE ELECTROSTATIC ENVIROMENT ON THE ELECTROCHEMICAL RESPONSE OF REDOX MONOLAYERS

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Keywords: *electroactive monolayers; square wave voltcoulommetry; intermolecular interactions*

The interest and applications of redox molecular systems confined at conducting interfaces, and electroactive monolayers in particular, has grown remarkably in recent years [1]. In order to improve the performance of these devices it is necessary to get a detailed insight of the processes taking place and, with this aim, several theoretical models have been developed and tested with different electrochemical techniques [2-4].

In this communication, an analysis of the effects of intermolecular interactions on the Square Wave Voltammetric (SWV) and Voltcoulommetric (SWVC) responses of electroactive monolayers under Nernstian and finite redox conditions is presented. Theoretical expressions for the Faradaic and non-Faradaic charge and current potential curves in terms of the potential perturbation variables and of the phenomenological interaction parameters G and S have been deduced [5]. Simple methods are proposed for determining the total excess of electroactive species, the apparent formal potential, the rate constants and the interaction parameters.

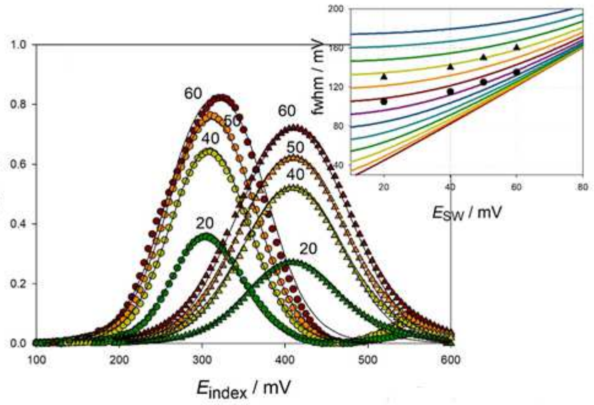

Figure 1. Theoretical and experimental SWVC curves of a binary FcC11SH / C10SH monolayer at gold electrodes in EtOH (circles) and PC (triangles) media for different pulse amplitudes (values in mV)

The results of the application of these methods to the analysis of the electrochemical behaviour of binary monolayers of ferrocenylundecanethiol / decanethiol (FcC11SH/C10SH) at gold and platinum electrodes in two different non-aqueous solvents have allowed us to obtain reliable values of the above parameters that clearly improve those determined by using Cyclic Voltammetry.

Acknowledgements: The authors greatly appreciate the financial support provided by the Fundación SENECA de la Región de Murcia (Project 19887/GERM/15).

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ELECTROCATALYSIS WITH ELECTROCHEMICALLY DRIVEN AZURE A MODIFIED C-NANODOTS

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Keywords: *Carbon nanodots, Azure A, electrografting*

Carbon nanodots (CNDs) are defined as nanoparticles mainly composed of carbon, with a size below 10 nm [1,2]. These materials have attracted intense interest because their photophysical properties resembling in some aspects those commonly found in semiconductor quantum dots (QDs), for example high photostability [1,3]. Besides, the CNDs can be produced easily from a wide range of raw materials and have unique properties. This makes them promising potential substitutes for QDs in biolabeling, bioimaging, drug delivery, analytical sensing and photocatalysis. This lecture will outline our recent research activities for the synthesis and the application as electrocatalytic platforms, after covalent modification with Azure A via electrochemically driven reactions with aryl diazonium salts. The reaction mechanism of diazonium functionalization of CNDs was investigated by Spectroelectrochemistry. The electrocatalytic behavior towards the oxidation of hydrazine is demonstrated.

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O-ECE13

GREEN AND PRINTED HIGH PERFORMANT SUPERCAPACITORS

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Keywords: *supercapacitor; energy storage; printed electronics*

Nowadays by increasing demands of flexible and wearable miniaturized electronic device it is emerged to have a high flexible energy storage such as battery and supercapacitors with high energy. In this context printed electronic has attracted more attention due to its significant advantages including the compatibility with various substrates, low temperature processing, atmospheric pressure, low cost processing, and high throughput production and flexibility.[1]

In the PRESTIGE project an energy-autonomous intelligent wristband base on printed electronics will be developed. This technology allows as to fabricate a wristband with aesthetic feature brought with decorative organic solar cell elements and with energy storage. The unique characteristic of supercapacitors (fast charge-discharge, long cycle life, high power, superior safe, etc [2]) makes that the perfect solution to take the energy from the printed solar cells enhancing the power autonomy of the device.

Figure 1:Smart watch concept.[4]

Hence in this work we develop a high performant and green printed supercapacitors. New formulation of printed inks for carbon base electric double layer capacitors (EDLC) are developed. In order to formulate water-based inks it is necessary to functionalize the carbon used as an active material (commercial active carbon) with hydrophilic groups. In this way we improve its dispersion in water and allow as to use water as solvent. Two type of binders: carboxymethyl cellulose + styrene butadiene rubber (CMC+SBR) and crystalline nanocellulose (CNC) has been used.

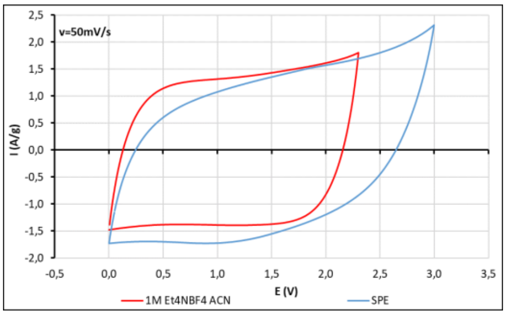

Figure 2: Cyclic voltammetry of 2 supercapacitors using 1M Et4NBF4 in ACN (red) and SPE (blue).

Supercapacitor device at lab scale (in CR2032 cells, electrode area of 1.77 cm^2) by galavonstatic analysis at $2mA/cm^2$ lead to specific capacity of 51F/g or $69mF/cm^2$, specific energy of 9.3 Wh/kg and specific power of 6.8 kW/kg at 2.3V using 1M Et4NBF4 in acetonitrile (ACN) as electrolyte. This results increase significantly using an ionic liquid base SPE [3] obtaining at $2mA/cm^2$ a specific capacity of 90F/kg or $106mF/cm^2$, specific energy of 28.2 kWh/kg and specific power of 68 kW/kg at 3V.

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O-BEC14

NANOSTRUCTURED MODIFIED ELECTRODE FOR TAURINE DETECTION BY ELECTROCHEMILUMINESCENCE

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Keywords: *Taurine, Electrochemiluminiscence (ECL), ZnO nanowires*

Electrochemiluminescence (ECL) is a method characterized by its sensitivity. In this process species generated on the surface of the electrode are subjected electron transfer reactions to form excited states that can produce light when they return to the ground state. Therefore, it is necessary to use luminophore species, such as ruthenium or its derivatives complexes and a co-reactant [1].

A novel electrochemiluminescence (ECL) sensor for the sensitive detection of taurine was developed. Taurine (2-amino ethanesulfonic acid) contains an aliphatic amine that gives it co-reactant properties. The ECL response of the taurine/$[Ru(bpy)_3]^{2+}$ system was analyzed on two different electrodes surfaces, screen-printed graphene and gold electrodes, before and after modification with ZnO nanowires (ZnO NWs). The ZnO NWs modified electrode yielded an enhanced ECL signal, allowing rapid detection of taurine at 5.5 µM detection limit. The ECL signal is stable and reproducible. The sensor has been applied to the determination of taurine in a commercial taurine supplement.

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O-FEC14

HOMOGENEOUS CHEMICAL REGENERATION OF THE REDOX REACTANT FOR GETTING INSIGHT INTO THE ELECTRON TRANSFER KINETICS. APPLICATION TO THE ASSESMENT OF ELECTRODE KINETIC MODELS

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Keywords: *catalytic mechanism; electrode kinetics; Marcus-Hush; Butler-Volmer; reaction layer*

The analytical theory recently developed for the first-order catalytic mechanism (Scheme (I)) [1] reveals that kinetic limitations of the electron transfer are more evident as the homogeneous chemical reaction is faster and so the supply of reactant for the electrode reaction:

$$\begin{gathered} \mathrm{O} + e^{-} \overset{k^0}{\rightleftarrows} \mathrm{R} \\ \mathrm{R}\ (+\mathrm{Z}) \underset{k_2'}{\overset{k_1'}{\rightleftarrows}} \mathrm{O}\ (+\mathrm{Y}) \end{gathered} \qquad \text{(I)}$$

As illustrated in Figure 1, the chief dimensionless parameter that accounts for the apparent electrochemical reversibility of the system is $k^0\delta_r / D$, where k^0 is the standard heterogeneous rate constant, D the diffusion coefficient of the redox species and δ_r the thickness of the linear reaction layer, which depends on the shape and size of the electrode and on the chemical kinetics. Thus, the faster the homogeneous kinetics is, the smaller the δ_r-value becomes and then the more irreversibly the electron transfer behaves.

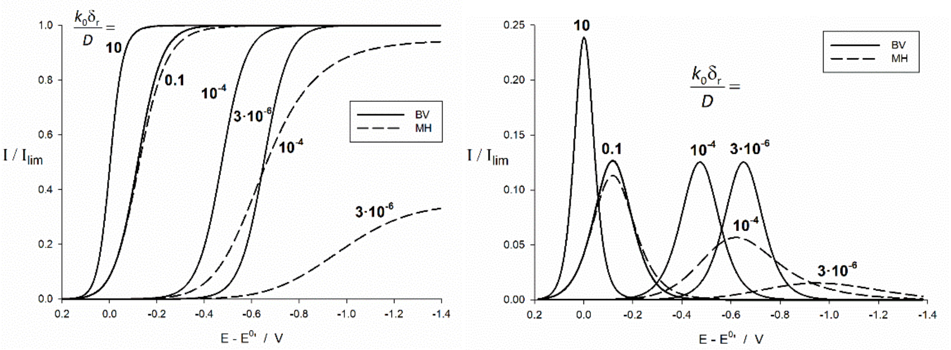

Figure 1. Normal pulse (left) and derivative (right) voltammetries of the catalytic mechanism as a function of the apparent electron transfer reversibility as predicted by Butler-Volmer (BV, α=0.5) and Marcus-Hush (MH, λ=1 eV)

According to the above, it can be concluded that coupling purposely a catalytic reaction to the electron transfer may be useful for the study of (very) fast electrode kinetics, as an alternative to more sophisticated approaches such as the use of nanoelectrodes or ultrafast voltammetry. The feasibility and advantages of this methodology will be discussed in this communication, elaborating on optimum experimental conditions and techniques for quantitative kinetic studies. Moreover, the application to the critical assessment of the most used electrode kinetic formalisms for outer-sphere heterogeneous electron transfers will be investigated. In particular, the voltammetric signals predicted by the Butler-Volmer and Marcus-Hush models will be compared (Figure 1), establishing the catalytic kinetics necessary to effect significant differences between the two formalisms.

Acknowledgements: Fundación Séneca de la Región de Murcia (Project 19887/GERM/15); Ministerio de Educación, Cultura y Deporte for the fellowship ‘Ayuda de Formación de Profesorado Universitario 2015’.

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O-AEC14

RESOLUTION OF COMPONENTS OF VITAMIN B3 USING RAMAN SPECTROELECTROCHEMISTRY

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Keywords: *Raman Spectroelectrochemistry, EC-SERS, EC-SOERS, vitamin B3.*

Raman spectroelectrochemistry (Raman-SEC) is becoming in a powerful analytical technique due to the specificity of the signals that can be considered as real "fingerprints" of the compounds. The main drawback of this technique is the weakness of Raman signal. Nevertheless, this signal can be enhanced by several orders of magnitude by a rational modification of the electrode surface. The most used method to enhance the Raman signal is the well-known Surface Enhanced Raman Scattering (SERS) effect [1]. Plasmonic nanostructures are necessary to obtain a suitable SERS effect, with roughening of a metal electrode (Au, Ag or Cu) being the most easy and classical method to obtain these substrates. In this sense, time-resolved Raman-SEC plays a fundamental role because it allows us to obtain additional information during the roughening procedure.

Our group has recently discovered a phenomenon which is similar to SERS because it enhances the Raman scattering but with some particularities. We denoted it as Electrochemical Surface Oxidation Enhanced Raman Scattering [2] (EC-SOERS), because the enhancement of the Raman signal takes place during the electrochemical oxidation of the electrode surface. Additionally, it has been demonstrated that EC-SOERS can be successfully used for quantitative analysis.

Nicotinic acid and nicotinamide are two forms of vitamin B3. In this work, a new approach based on Raman-SEC is used to determine vitamin B3. The combination of EC-SERS and EC-SOERS in a single experiment allows us to resolve vitamin B3 in its different forms (Figure 1).

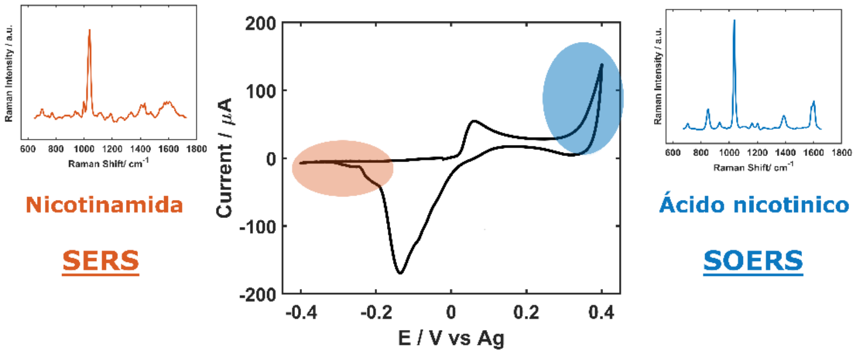

Figure 1. Voltammogram of a silver electrode obtained in a solution containing nicotinic acid and nicotinamide in 0.1 M $HClO_4$ and 0.01 M KCl. Nicotinic acid is observed at anodic potentials (EC-SOERS), whereas nicotinamide at cathodic ones (EC-SERS).

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O-BEC21

THE EFFECT OF HUMAN CYTOCHROME C PHOSPHORYLATION ON ITS REDOX FUNCTIONALITY: A VOLTAMMETRIC STUDY

J. L. Olloqui-Sariego[1,*], A. Guerra-Castellano[2], G. Pérez[2], M. A. De la Rosa[2], M. Molero[1], A. Díaz-Quintana[2], I. Díaz-Moreno[2], J. J. Calvente[1], R. Andreu[1]

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Keywords: Cytochrome C Phosphorylation; Electron Transfer; Thermodynamics; Kinetics

Human cytochrome *c* (hC*c*) stands out as a target for post-translational modifications, such as phosphorylation, which is related to the onset of diseases like ischemia. Previous works with a mimetic phosphorylated hCc, in which tyrosine 48 was replaced by p-carboxy-methyl-L-phenylalanine *(*hC*c-Y48pCMF)*, have demonstrated that phosphorylation provokes significant structural changes that can be related to mitochondrial dysfunction of this protein [1, 2].

In this work, we have carried out a detailed characterization of the direct electron transfer of both hC*c* and hC*c-Y48pCMF* adsorbed onto gold electrodes modified with different carboxylic acid-terminated self-assembled monolayers, by analyzing their voltammetric response as a function of solution pH and temperature.

It is shown that immobilized hC*c-Y48pCMF* displays more negative redox potentials than the wild type, with a steeper variation with temperature. At the same time, the electron transfer rate constant of hC*c-Y48pCMF* is lower than that of the native protein in the entire temperature range tested. Moreover, the pH dependence of both the redox potential and the electron transfer rate constant of hC*c-Y48pCMF* also differ from those of hCc for pHs higher than 6.5.

Overall, the present results point to a key role of phosphorylation into the loss of the mitochondrial function of cytochromes as electron carriers.

Acknowledgements

Authors acknowledge financial support from the Spanish Ministry of Economy and Competitiveness and the European Union FEDER (Funding grants CTQ2014-52641-P and BFU2015-71017-P)

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O-MEC21

ELECTROCHEMICAL STUDY OF THE RESPONSE OF HYDROQUINONE, FERRICYANIDE AND FERROCENEMETHANOL IN GLASS FIBER AND CELLULOSE PAPER

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Keywords: *Paper-based, Electrochemistry*

In the last few decades paper (and paper-related materials) has gained interest in the biomedical community due to the possibility to manufacture easy, rapid and low-costs diagnostic devices known as PADs (Paper-based Analytical Devices)[1]. These devices take the advantage of particular characteristics of paper such as porosity and capillarity to perform microfluidic functions without the need of dedicated instrumentation. Colorimetric detection is the most common method used in this type of platforms. However, despite its inherent simplicity, this technique presents some disadvantages, as for example, the sensitivity dependence on environmental light or subjectivity related to instrument-free observation[2]. In order to increase the sensitivity, selectivity and signal quantification, electrochemical detection is a more suitable method to implement low cost digital PADs. Electrochemical signals coming directly or indirectly from the analyte can be easily driven with instrumentation circuits, which ultimately can be integrated in portable single use platforms. These devices can be manufactured and integrated with rapid prototyping techniques. However, despite the numerous electrochemical paper-based solutions published up to date, the effect of the paper matrix on the electrochemical response of redox pairs has been scarcely studied up to date.

In this work, a study of the effect of the paper matrix on the electrochemical response of different redox species (substrates) has been performed. Redox species commonly used in biosensing such as hydroquinone (HQ), ferricyanide ($K_4[Fe(CN)_6]$) and ferrocenemethanol (FcMeOH) have been characterized by cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS). The paper materials under study have been medical grade papers cellulose (CF3 from Whatman) and glass fiber (Standard 14 from GE).

The work identifies the importance of characterizing the paper matrixes where the PADs are to be fabricated and provides a guideline to select the right paper-chemical compound combination in each particular case.

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Acknowledgments

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O-AEC21

NEW INSIGHTS IN ELECTROCHEMICAL SURFACE OXIDATION ENHANCED RAMAN SCATTERING

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Keywords: *Raman Spectroelectrochemistry, SERS, SOERS.*

Electrochemical Surface Oxidation Enhanced Raman Scattering [1] (EC-SOERS) is a new interesting phenomenon that implies the amplification of the Raman signal of a target molecule during the electrochemical oxidation of a silver electrode. This unexpected behavior cannot be easily explained using the classic models of Surface Enhanced Raman Scattering (SERS), and therefore, makes EC-SOERS an intriguing phenomenon that is worth studying. EC-SOERS could be considered as a new spectroelectrochemical phenomenon since the optical response is only observed when a potential is applied to the electrode (Figure 1). Currently, our group is involved in the study of EC-SOERS process in an attempt to reveal its basic aspects which should help not only to understand the processes taking place at the electrode surface but also to control the phenomenon when it is used for analytical purposes.

In this communication, parameters such as pH, chloride concentration, electrolytic solution, structure of the target molecule, among others, are studied in order to shed more light about EC-SOERS

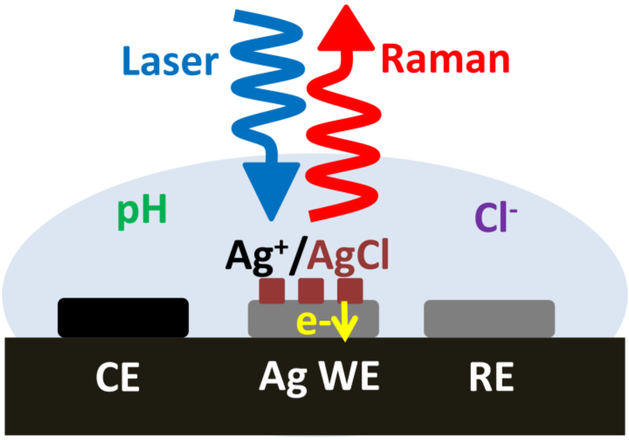

Figure 1. Schematic representation of EC-SOERS effect.

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O-ECE21

COBALT SUPPORTED ON N AND S DUAL-DOPED REDUCED GRAPHENE OXIDE AS HIGHLY ACTIVE CATHODE CATALYST FOR DEFC

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Keywords: cobalto, materiales grafénicos dopados, electrorreducción de oxígeno, DEFC

Polymer electrolyte membrane fuel cells (PEMFCs) are electrochemical systems that convert efficiently chemical energy into electrical energy through electrochemical reactions. There are different suitable fuels for feeding these devices, i.e. H_2 or low molecular weight organic molecules such as methanol, ethanol or glycerol. At standard conditions, liquid fuels reveal higher energy density than hydrogen and do not face the problems of fuel storage and transportation [1].

Despite the significant advantages of PEMFCs as power sources, these devices present several drawbacks which decrease their working performance and increase their cost. One of the most important issues to solve is the slow rate of the oxygen reduction reaction (ORR) occurring at the cathode, usually prepared using platinum-based materials as develop the best catalytic activity; but their elevated cost, low abundance and poor durability appear as important barriers for PEMFC development. Furthermore, a mixed potential occurs at the Pt-based cathode when alcohol is employed as fuel (crossover effect), and consequently, the cell voltage falls. To overcome these issues, alcohol tolerant catalysts have been proposed for the ORR, including carbonaceous materials as carbon nanotubes or reduced graphene oxide [2].

In the current work, cobalt oxide nanoparticles supported on nitrogen and sulphur dual-doped reduced graphene oxide (Co/SN-rGO) are developed and employed as novel cathode for a direct ethanol fuel cell (DEFC). Physicochemical characterization was carried out by X-ray diffraction (XRD), elemental analysis, X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. Meanwhile, the rotating ring-disk electrode (RRDE) and a DEFC test station were used to evaluate the electrocatalytic performance.

Main results indicate higher catalytic activity, stability and ethanol tolerance of Co/SN-rGO in comparison to commercial carbon-supported Pt catalyst.

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Acknowledgment

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O-BEC22

ANTIMONENE: A NEW PROMISING MATERIAL FOR BIOSENSORS AND OXYGEN REDUCTION CATALYSIS

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Keywords*: antimonene; 2D nanomaterials; enzymatic biosensors; oxygen reduction.*

The use of two-dimensional (2D) layered materials like graphene is gaining visibility in the last years due to their wide range of applications in which they can be employed as in biomedicine or energy storage. In the search of new alternatives, antimonene is the 2D nanomaterial chosen to study. It is a resistant, high durability and good conductor material, and presents potential higher electronic gap compared to graphene, opening new possibilities in other fields as optoelectronics purposes [1]. Despite these advantages, there is not many investigations about its possibilities in electrochemical applications.

Previous publications show the ability of antimonene as a supercapacitor [2] or in enzymatic biosensors devices [3]. In this communication, we deepen in this last feature, proposing different options as, for example, the preparation of a biosensor from a co-immobilization of laccase oxidase along with the few layer (FL) antimonene suspension in a carbon screen-printed electrode. This biosensor is tested for different analytes with strong interest in the residual water analysis. Additionally, it is also evaluated the high improvement of the laccase/antimonene system in the electrocatalysis of the oxygen reduction reaction, the main process occurred in the cathode of a fuel cell.

The material is physically characterized by using atomic force microscopy (AFM), scanning electron microscopy (SEM), transmission electron microscopy (TEM) or Raman spectroscopy techniques, whereas the analytic response of the laccase/antimonene system is studied by the currents obtained in electrochemical techniques like cyclic voltammetry or chronoamperometry.

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O-MEC22

ABOUT THE ROLE OF ASCORBIC ACID AS ANTIOXIDANT

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Keywords: *Ascorbic acid; copper; antioxidant; motional resistance.*

The use of ascorbic acid as a food additive is well known in health fields because it is a natural substance that is present in many fruits and vegetables, especially citrus fruits. Its beneficial actions in living beings is frequently associated with its inhibitory action of oxidative biochemical processes. On the other hand, it has also been found to inhibit the corrosion of metal alloys despite the fact that the metals in contact with acidified aqueous media react with the hydrogen ions to give molecular hydrogen and metal derivatives.

When checking in our laboratory that the juice of different citrus fruits and solutions of ascorbic acid and citric acid cause this effect on different technological metals and also check the protective action of ascorbic acid on the superficial atmospheric oxidation of carbonaceous particles, such as those of graphene or graphite, the idea arose to analyze the inhibitory effect of the anodic solution of a known system easy to study using electrochemical techniques that could be model of the inhibitory mechanism caused by ascorbic acid. In this work the inhibitory effect of ascorbic acid on copper anodic dissolution is studied by means of spectrum-electro-gravimetric techniques, since the Cu / acid solution system is a relatively simple model of possible utility to interpret the inhibitory effect of ascorbic acid on other more complicated systems.

The spectro-electro-gravimetric studies are useful to explain the corrosion and electrodeposits kinetics of copper in acid media [1,2]. If we analyze the mass evolution at open circuit potential of copper in sulfuric and ascorbic media, it is showed that in the chase of sulfuric media the mass decreases, but the process is slower at the end attending to the passive layer formation. However, when we analyze the mass evolution for the ascorbic acid dissolution, we can see that the mass grows proportionally to the acid concentration. First, takes place the adsorption on non-charged species over the electrode surface. This fact increases the rigidity over the electrode surface decreasing the values of the motional resistance. When the electrochemical process begins, there is an accumulation of copper ions over the electrode surface. The accumulation of copper ions allows the catalytic oxidation of the ascorbic acid.

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Acknowledgments

This work was supported by MINECO-FEDER CTQ2015-71794-R

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O-AEC22

ELECTROCHEMICAL IMMUNOSENSOR FOR ANTI-CYCLIC CITRUNILLATED PEPTIDE ANTIBODY (ACCP) USING NEUTRAVIDIN MODIFIED MAGNETIC MICROBEADS.

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Keywords: *autoimmune disease; autoantibodies; electrochemical immunosensor; magnetic beads*

Rheumatoid arthritis is an autoimmune disease characterized by joint, bone or organ damage. In RA, the formation of citrulline residues in proteins is carried out by a post-translational modification of arginine residues catalysed by peptidylarginine deiminases. This citrunillation process can provoke the autoimmune response [1]. Anticitrullinated peptide antibodies (ACCP), that may be detected in the serum of RA patients with a high specificity, are useful biomarkers for the diagnosis of the disease.

In this work, the development of an electrochemical inmunosensor for ACCP determination involving the immobilization of biotinylated cyclic citrunillated peptide (B-CCP) onto neutravidin-modified magnetic microbeads, is reported. As can be seen in Figure 1, a sandwich immunoassay was performed with ACCP and a secondary antibody labeled with peroxidase (HRP-anti-IgG). Then, the electrochemical response was monitored by amperometry at -200 mV vs Ag, after the addition of hydrogen peroxide in the presence of hydroquinone.

Once optimized the experimental variables involved in the preparation and functioning of the immunosensor, a calibration plot for ACCP in the ng mL^{-1} concentration range with useful analytical characteristics for the analysis of clinical samples was obtained. Therefore, successful application of the developed immunosensor to the analysis of real samples was achieved.

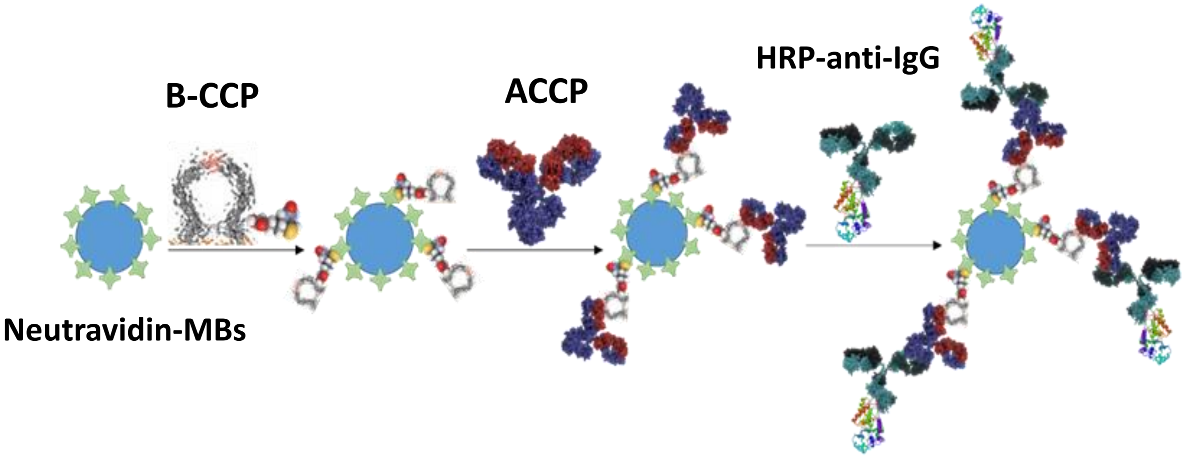

Figure 1. Schematic display of the steps involved in the immunosensor preparation for ACCP determination

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O-ECE22

MANGANESE OXIDE CATALYSTS FOR OXYGEN REACTION REDUCTION IN SEA WATER AND ALKALINE AL-AIR BATTERIES.

G. F. Gimeno[1], C. Martínez-Abascal[1], V. Villalobos[1], L. Sierra[1], D. Vallejo-Sánchez[2], O. Castillo[2], G. Beobide[2], P. Ocón*[1]

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Keywords: *Metal-air; Aluminium-air; Commercial alloys; Manganese Oxide; Gel electroly*te

In the future, the battery market is not going to be dominated by just one type of cell but a mix of different technologies will have their niche markets. Metal-Air batteries have been targeted as a promising technology to meet the energy requirements for energy-demanding devices [1]. They are also promising due to the reduction in costs and their application in large-scale energy storage. Aluminium is a cheap metal, environmentally friendly and a promising power source. Besides, the processing and recycling of aluminium alloys are well-known processes. The theoretical specific capacity is 2.98Ah/g, and against an air cathode in aqueous electrolytes gives a potential around 1.5V. Aluminium possesses high theoretical energy density (4300 Wh g^{-1}). However, the industrial application of Me-air batteries is limited because of low current density and a high overpotential in the cathodic catalyst.

The oxygen reduction reaction (ORR) is the heart of metal–air batteries in combination with the dissolution of the metal in the electrolyte during discharge. The development of catalytic materials for the ORR is one of the major challenges in electrochemical energy conversion and storage technologies such as fuel cells and metal–air batteries [2]. High efficiency is highly desirable for the commercial success of environmentally friendly energy conversion devices. Among the non-precious metal alternatives, manganese oxides have received intensive attention because of their high elemental abundance, low cost and toxicity and appreciable activity, when integrated with a conductive-based support material. However, bulk MnO_2 only delivers moderate catalytic performance because of the lack of open channels for oxygen gas access and transport. The ORR activity is affected by many factors; the particle size, morphology as well as the phase of the Mn oxide. Three-dimensional macroscopic assemblies, such as aerogels and xerogels, represent a category of materials that exhibit favourable features such as low densities, large open pores, high inner surface areas, and superior physical and chemical properties.

In this study, the catalytic activities of both aerogel and xerogel MnO_x materials with different morphologies and composition have been characterized by XRD, FT-IR and Raman spectroscopy. The evaluation of the ORR using Rotating Disk Electrode technique was carried out. The MnO_2 unsupported and supported on Carbon Vulcan and nanotubes and synthesized by hydrothermal way, was evaluated as active material vs ORR reaction. The support was studied in order to evaluate its influence in the ORR. Finally, the Aluminum-Air battery performance in alkaline (gel) and sea water electrolyte under air condition was evaluated.

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O-BEC23

STUDY OF DIRECT ELECTROCATALYSIS OF MULTICOPPER OXIDASES

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Keywords: *multicopper oxidases; electrocatalysis, cyclic voltammetry*

Oxygen reduction is one of the most important reactions in both natural and artificial systems, and it plays a central role in the development of electrochemical biofuel cells (BFC) [1]. BFC are micro-scale energy devices that are built from proteins and enzymes in close contact with the electrode surface. One of the most commonly used biocathodes in BFC is based on the surface immobilization of multicopper oxidases (MCO) [2].

Herein, we report on the electrocatalytic response of *Rhus vernicifera* Laccase (*Rv*Lc) from plants and *Myrothecium verrucaria* Bilirubin oxidase (*Mv*BOx) from fungi, physically and covalently immobilized onto different electrode surfaces. Results show good current densities and stability for both enzymes despite their different *onset* potentials. The catalytic rate constants (k_{cat}) of the enzymes for the oxygen reduction have been determined in both solution and immobilized state. The response of the electrocatalytic signal to the addition of inhibitors and to temperature changes has also been evaluated.

Finally, to explore the biocompatibility of MCO-modified electrodes, for a possible application in electronic body implants, ELISA immunoassay and calorimetry experiments were carried out. It is shown that the biocompatibility of enzymes is improved in the immobilization state.

Acknowledgements

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O-MEC23

ESTUDIO DE CORROSIÓN DE ACEROS EN PROBETAS DE HORMIGÓN EN AUSENCIA DE OXÍGENO MEDIANTE TÉCNICAS DE EIS, MÉTODO DE POLARIZACIÓN LINEAL Y CRONOPOTENCIOMETRÍA.

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Keywords: *concrete; corrosion; anoxic; electrochemical impedance spectroscopy.*

El hormigón armado es uno de los materiales más usados en construcción debido a sus excelentes propiedades y debido también a su gran versatilidad. Uno de los principales deterioros que sufren las estructuras de hormigón armado es la corrosión de las armaduras debido al ingreso de ciertos agentes agresivos como es el caso de los cloruros. El objetivo de este trabajo es estudiar el comportamiento de hormigones armado en condiciones de bajo contenido de oxígeno y en presencia de cloruros simulando el comportamiento de una estructura off-shore.

En este experimento se utilizaron 3 probetas de 10*10*10 cm fabricadas con cemento tipo I 42.5R. El agua de amasado con el que se fabricaron estas probetas contenía un 2%$_{w/w}$ de cloruros en forma de NaCl. En cada una de las probetas fue embebida una barra de acero de 6 mm de diámetro.

Tras un día de curado, dichas probetas fueron desmoldadas e introducidas en una disolución de NaCl 30 g/L. El conjunto entero fue introducido en una cámara de guantes en la que el oxígeno se ha desplazado mediante una corriente de nitrógeno.

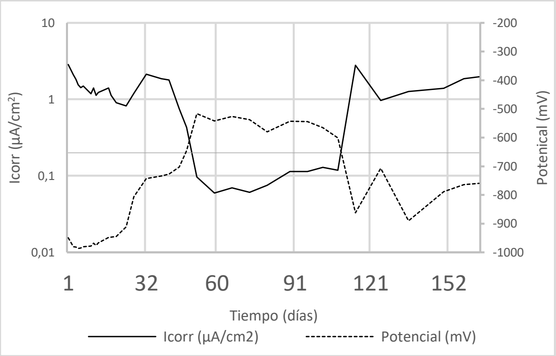

Figura 1. Velocidad de corrosión

La corrosión de dichas probetas es medida mediante los métodos electroquímicos de EIS, resistencia a la polarización lineal (LPR) y cronopotenciometría. Las tres técnicas nos proporcionan los valores de potencial de corrosión, caída óhmica (excepto LPR) y el valor de resistencia a la polarización, de la cual deducimos la velocidad de corrosión [1]. En la Figura 1 se muestra la evolución de la velocidad de corrosión y el potencial para una de las probetas.

De los resultados preliminares de este ensayo se pueden extraer hasta el momento las siguientes conclusiones: i) las tres técnicas coinciden generalmente en la medida de la Rp, excepto en los casos en los que la probeta se encuentra muy activa y los valores obtenidos mediante EIS son netamente inferiores a los obtenidos por los otros métodos, LRP y cronopotenciometría; ii) En ausencia de oxígeno, los potenciales de corrosión durante prácticamente todo el ensayo se han mantenido muy por debajo de -350 mV, potencial umbral para establecer la actividad o pasividad de los aceros en hormigón. Sin embargo, se ha observado que la velocidad de corrosión en unos momentos permanece en valores considerados como activos (Icorr > 0,2 µA/cm^2) y en otros momentos permanecen pasivos (Icorr < 0,2 µA/cm^2).

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O-AEC23

CHEMICAL SELECTIVITY OF EC-SOERS

M. Pérez-Estébanez[1]*, **J.V. Perales-Rondón**[1,2], **S. Hernández**[1], **A. Heras**[1], **A. Colina**[1]

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Keywords: *Spectroelectrochemistry; Raman; EC-SOERS.*

Recently, a new phenomenon able to enhance the Raman signal of certain analytes during a Raman spectroelectrochemistry (Raman-SEC) experiment has been reported [1]. This phenomenon, called EC-SOERS (Electrochemical Surface Oxidation Enhanced Raman Scattering), involves the enhancement of the Raman signal during the electrochemical oxidation of a silver substrate. This phenomenon cannot be easily explained by the classical models for SERS (Surface Enhanced Raman Scattering) effect, which suggests the presence of a nanostructured surface with plasmonic properties that are generally obtained after the silver deposition at cathodic potentials.

Although the origin of the enhancement observed in EC-SOERS is still under discussion, it is known that the presence of a silver precipitant agent, such as chloride, is necessary for observing EC-SOERS. In this sense, the modulation of the concentration of this agent can influence to the intensity of the observed enhancement [2].

Recently, we have discovered that EC-SOERS can be observed in the presence of other precipitant agents such as bromide. Therefore, the change of the halide used allows us to achieve chemical selectivity when using EC-SOERS effect. Herein, we present the results obtained for two molecules, uric acid and benzoic acid, that show different enhancement depending on the halide selected, *i.e.,* bromide or chloride. The EC-SOERS signal suggests the chemical selectivity achieved for these two molecules adding bromide or chloride. Additionally, it has been observed that, under optimal conditions, the Raman enhancement of one molecule can be increased minimizing the Raman signal of the other (Figure 1) and vice versa.

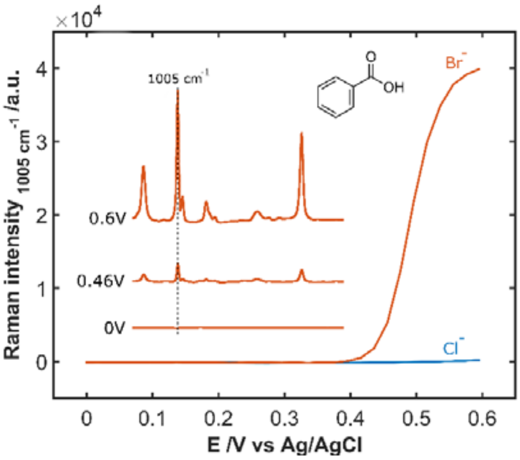

Figure 1. VoltaRamangram for benzoic acid during a Raman-SEC experiment based on a linear sweep voltammetry. EC-SOERS signal of benzoic acid in a chloride (blue) or bromide (orange) solution with electrolyte. Working electrode: silver electrode.

This study reveals a new promising property of EC-SOERS, which could allow us the determination of an analyte in presence of another by tuning the halide contains in a Raman-SEC experiment.

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O-BEC24

THREE-DIMENSIONAL ELECTRODES CONSTITUTED BY MULTIELECTRONIC MOLECULAR MACHINES: REPLICATING BIOLOGICAL MULTIFUNCTIONALITY

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Keywords: *conducting polymers; molecular motors; sensory-motors; muscle fatigue; sensing nervous pulses*

Every polymeric chains of a conducting polymer film electrode, or each carbonaceous structure in a film of carbon nanotubes or graphene, constitutes, under electrochemical reactions in aqueous electrolytes, a reversible molecular machine [1] (2016 Nobel award). Every electron transfer changes the double bond's distribution along the chain (or carbonaceous structure) originating conformational movements replicating similar macromolecular motors producing biological functions at the intracellular matrix (ICM) of living functional cells, i.e. muscular cells. The cooperative actuation of the chains during the film oxidation/reduction originates, or destroys, the electrode free volume required to lodge/expel counterions and solvent required to keep the material charge and osmotic balance: the film electrode becomes a dense reactive gel The electrochemical reactions drive macroscopic structural transformations of the film: swelling, shrinking, closing, conformational compaction and conformational relaxation [2].

Among other properties the reaction drives the Faradaic change of the film polymer/counterion composition, which originates, among other properties, the simultaneous variation of both, the film volume (swelling/shrinking) and the consumed electrical energy[3]. The consumed reaction energy responds to and is a sensor of the reaction physical and chemical conditions. Thus artificial muscles based on reversible volume variations will sense, while working, the working physical and chemical conditions, as natural muscles do (haptic muscles)[4], [5].

The attained sensing equations provide quantitative hypothesis to explain how muscles from coldblooded animals sense the working temperature and extract energy from the ambient. The origin of the sensing signals sent to the brain from muscles to inform about the muscle working conditions and the fatigue state of the muscle can also be described.

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O-MEC24

FINE CONTROL OF THE ELECTROCHEMICAL GRAFTING OF DIAZONIUM SALTS BY AN EXTREMELY SIMPLE METHOD: THE REDOX-CROSS INHIBITION

I. López*[1], L. Pichereau[1], M. Cesbron[1], S. Dabos-Seignon[1], E. Levillain[1], C. Gautier[1], T. Breton*[1]

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***Keywords**: electrode functionalization; diazonium grafting; surface modification; nanomaterials.*

The functionalization of conducting or semiconducting surfaces by electrochemical grafting of diazonium salts is widespread used due to the simplicity and rapidity of the method [1]. However, the reduction of diazonium salts commonly results in the immobilization of a multilayered and disorganized molecular film as a consequence of the uncontrolled polymerization of aryl radicals generated on the electrode surface. This aspect can make difficult the elaboration of molecular coatings with tailored properties.

Several strategies have been developed aiming at controlling the immobilization of a monolayer structure on electrode surfaces. Most of them relies on the synthesis of diazonium salts containing bulky substituents/cleavable groups or the employment of viscous ionic liquid as electrografting medium [2]. In this contribution, we introduce and rationalize an extremely simple and versatile method which allows for controlling the deposition of a monolayer or sub-monolayer of a desired molecule from the electrochemical grafting of the corresponding diazonium salt [3]. The cornerstone of our procedure is a redox-cross reaction between the reduced form of a deliberately added inhibitor and the diazonium salt. The process takes place in the diffusion layer producing aryl radicals which react with solvent molecules before they can reach the electrode. Our approach is straightforward and it does not involve complex synthetic modifications of diazonium salts or the use of non-conventional solvents. Furthermore, the judicious choice of the inhibitor, which can be a commercially available molecule or the dissolved O_2, enables to control the grafting of any diazonium salt. We also provide a rule of thumb for the convenient choice of the inhibitor.

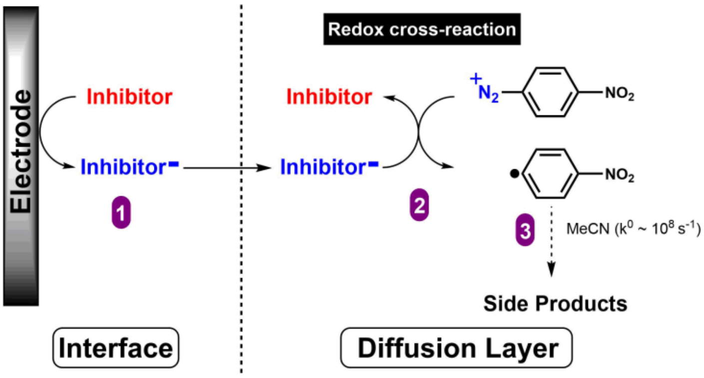

Figure 1. Inhibition mechanism to control the electrochemical grafting of diazonium salts

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O-AEC24

USE OF POTENTIOMETRIC MEASUREMENTS FOR THE DETERMINATION OF SURFACTANT-CNT INTERACTIONS. DRIVING FORCES.

Pilar López-Cornejo*[1], **Manuel López-López**[2], **María Luisa Moyá**[1], **José Antonio Lebrón**[1], **Francisco José Ostos**[1], **Francisco Sánchez**[1]
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Keywords: *Ion-selective electrodes; carbon nanotubes; surfactants; interaction; dispersion.*

Carbon nanotubes, CNTs, are building blocks used in the construction of molecular assemblies [1]. Their walls are formed by curve sheets of graphene. There are two types of CNTs: the single-walled (SWCNTs) and the multi-walled carbon nanotubes (MWCNTs). All these structures show a low solubility in aqueous solution. The presence of attractive Van der Walls and π-π stacking interactions among the tubes provokes their assembly. The dispersion of these tubes can be improved by the addition of chemical species to the solution. Ionic surfactants are frequently used as dispersing agents [2]. Their amphiphilic nature favors their adsorption on the tube walls and decreases the ability of the CNTs to agglomerate by themselves in bundles.

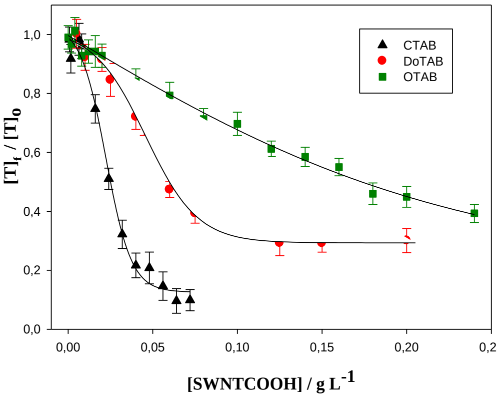

Figure 1. Plot of the relative free surfactant concentration versus the CNT concentration.

The dispersion of anionic, cationic and neutral single- and multiwalled CNTs in aqueous solution has been studied in the presence of several ionic surfactants. The surfactants used were the well-known CTAB, DTAB, OTAB and SDS. Electromotive forces of solutions containing surfactant and CNTs were carried out using ion-selective membrane electrodes. Results showed that the capacity of a surfactant to interact with ionic CNTs and its quality as dispersing agent do not have to coincide. The potentiometric experiments showed a sigmoidal dependence of the free surfactant concentration on the nanotube concentration for all the carbon nanotubes used (Figure 1). This behavior confirms the cooperative character of the surfactant/nanotube interactions. The forces corresponding to the binding of the surfactants with all CNTs studied are driven by hydrophobic interactions between the hydrocarbon tails and the tubes. However, the electrostatic interactions are the driving forces in the dispersion process (Figure 2).

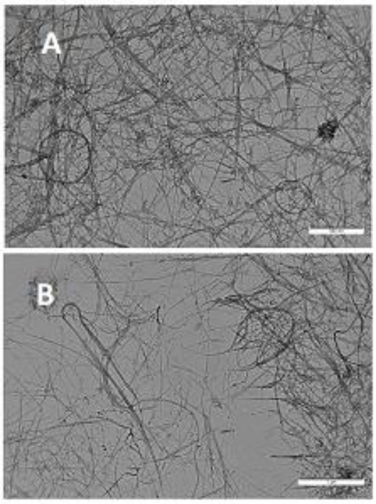

Figure 2. TEM image of SWCNT-COOH in the absence (A) and presence (B) of surfactant.

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O-ECP33

NH_2-MIL-88B-DERIVED MAGNETIC FE@C-N NANOCOMPOSITES AS HETEROGENEOUS ELECTRO-FENTON CATALYSTS FOR THE DEGRADATION OF ORGANIC MICROPOLLUTANTS IN WASTEWATER

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Keywords: *heterogeneous Fenton; metal-organic frameworks; micropollutants; zero-valent iron*

Homogeneous electro-Fenton (EF) has been proven one of the most successful advanced oxidation processes (AOPs) for the destruction of persistent organic micropollutants in wastewater. EF combines the in-situ H_2O_2 generation via cathodic ORR and the production of powerful oxidants ($^{\bullet}OH$) from Fenton's reaction. However, its large-scale application is still limited due to the narrow pH range and gradual loose of catalytic activity. Heterogeneous EF allows overcoming these drawbacks, and many authors have described the use of zero-valent iron (ZVI), iron oxides and iron oxyhydroxides as catalysts. Nonetheless, their performance is lower than required due to short service life [1].

As a relatively new class of crystalline porous organic-inorganic hybrid materials, metal-organic frameworks (MOFs) have recently attracted great attention due to their promising characteristics and versatile functionalities. In this study, immobilized nano zero-valent iron (nZVI) on N-doped porous carbon (Fe@C-N) derived from NH_2-MIL-88B is proposed as EF catalyst for the first time. The target micropollutant gemfibrozil in solutions at near-neutral pH can be completely removed by Fe@C-N-catalyzed EF process after only 1 h at low input current, with very low iron leaching (0.2 mg L^{-1}). Conversely, the Fe@C composite derived from MIL-88B only yielded 52% gemfibrozil removal in 1 h.

Hence, the incorporation of nitrogen into the carbon framework can greatly increase the encapsulation of ZVI, thus improving the structural and chemical properties of the nanocomposite and eventually enhancing its catalytic activity during the treatment. The proportion of encapsulated ZVI grew as the synthesis temperature was increased, reaching the highest at 800 ^{o}C, which was related with the maximum gemfibrozil removal. Electron paramagnetic resonance (EPR) experiments suggested that $^{\bullet}OH$ was the dominant radical responsible for the micropollutant degradation. Furthermore, the catalyst retained good activity after five cycles, and it kept good performance even in urban wastewater since a mixture of four organic micropollutants was successfully degraded.

Acknowledgments
The authors thank financial support from project CTQ2016-78616-R (AEI/FEDER, EU) and the PhD scholarship awarded to Z.H. Ye (State Scholarship Fund, CSC, China).

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O-MEC31

CONTINUOUS PRODUCTION OF FORMIC ACID ON TIN OXIDE NANOPARTICLES BY ELECTROREDUCTION OF CARBON DIOXIDE

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Keywords: *CO_2 reduction; SnO_2 nanoparticles; Electrocatalysis; HCOOH production*

Among the different metals displaying high selectivity towards HCOOH production from CO_2 electroreduction, Sn exhibits the lowest toxicity and represents one of the best options in terms of cost and selectivity [1]. However, small size capping agent free Sn nanoparticles are difficult to be synthesized and present low structural stability due to Ostwald ripening. For this reason, SnO_2 nanoparticles have been recently proposed in the literature as an interesting alternative material for HCOOH production [2], since SnO_2 presents much higher structural stability under electrochemical conditions.

The present communication is devoted to the study of high surface area SnO_2 nanoparticles (2 nm in diameter), synthesized by a facile hydrothermal microwave-assisted method, as an alternative highly efficient and stable electrocatalyst for continuous HCOOH production from CO_2 electroreduction. Our experimental results display high production values using SnO_2 nanoparticles supported on a carbon based gas diffusion cathode (10 cm^2 of geometrical area) in a filter-press reactor configuration. Figure 1 exhibits an almost constant production of HCOOH as a function of time, which demonstrates a long-term stability of SnO_2 nanoparticles during CO_2 electroreduction in aqueous solution.

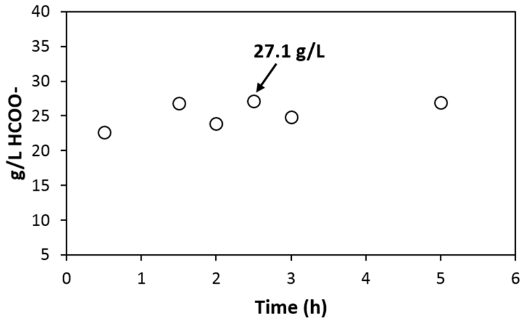

Figure 1. Continuous HCOOH production as a function of CO_2 electrolysis duration at constant current.

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HIGHLY SENSITIVE H_2O_2 SENSOR BASED ON POLY(AZURE A)-PLATINUM NANOPARTICLES DEPOSITED ON ACTIVATED SCREEN PRINTED CARBON ELECTRODES

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Keywords: *Electrochemical sensor; hydrogen peroxide; nanoparticles; modified SPCEs.*

Screen-printed electrodes constitute a relatively recent technology that offers high-volume production of inexpensive electrochemical sensors and biosensors. They offer a number of advantages over conventional electrodes. One of the best known advantages is the easy modification to develop different sensing surfaces. Furthermore, pre-treatments can be performed in order to enhance electro-transfer properties and improve sensitivity to analytes of interest. The electrocatalytic determination of H_2O_2 attending to its reduction or oxidation and using different types of modified electrodes, has been widely studied. In the present work we have developed a highly sensitive electrochemical method for the determination of H_2O_2 taking advantage of the unique properties of conducting polymers (particularly we have used poly(azure A)) [1] combined with the properties of PtNPs [2] by using previously activated screen-printed carbon electrodes [3]. By combining all these processes (activation of the surface, electrochemical polymerization and electrochemical generation of PtNPs) it has been possible to reduce H_2O_2 oxidation potential from ~1-0.7 V to 0.1 V (which will considerably minimize the effect of interfering species), as well as significantly improving sensitivity (2.047 ± 0.0413 $\mu A \cdot \mu M^{-1} \cdot cm^{-2}$) compared to other electrochemical sensors found in the literature. Therefore the fabricated electrodes showed excellent electrocatalytic activity towards H_2O_2 oxidation, making its detection possible at 0.1 V. The PtNPs/PAA/aSPCEs were characterized by scanning electron microscope, linear scan voltammetry and electrochemical impedance spectroscopy. The detection limit was 51.6 nM, which is relevantly low, and the linear range was from 0 to 300 μM. Additional experiments against common interfering agents showed no increase in the current signal, which indicates high specificity of the sensor. The proposed modified electrode has also been used as a sensor for H_2O_2 determination in real samples.

Funding sources: *This work was funded by the Spanish Ministry of Economy and Competitiveness (BFU2016-75609-P) (AEI/FEDER, UE) and by the Junta de Comunidades de Castilla-La Mancha (Spain) (SBPLY/17/180501/000276/2), cofounded with FEDER funds, EU. BGM is a post-doctoral research fellow of the Youth Employment Initiative (JCCM, Spain, cofounded with ESF funds, EU).*

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O-MOE31

UV/VIS ABSORPTION SPECTROELECTROCHEMISTRY FOR STUDYING ANTIOXIDANT PROPERTIES

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Keywords: *UV-Vis Spectroelectrochemistry, o-vanillin, antioxidant.*

UV/Vis Absorption Spectroelectrochemistry (UV/Vis-SEC) is a multi-response technique that has been widely used to study complex electrochemical reaction mechanisms [1]. Antioxidants are molecules that try to inhibit the oxidation of other compounds. Particularly, these types of compounds react with free radicals avoiding reactions that can damage cells. Therefore, the development of analytical techniques to study these processes is of great importance.

Electrochemistry can be used to generate radicals while UV/Vis spectroscopy is widely used to follow the reaction of antioxidants with free radicals. Thus, UV/Vis-SEC should be a very useful technique to study this type of processes because joins in a single experiment these two measurements.

To illustrate the capabilities of UV/Vis-SEC to study antioxidant properties of specific molecules, we have selected in this work the study of 3-methoxysalicylaldehyde (*o*-vanillin), an antioxidant compound that exhibits good properties as free-radical quencher. Figure 1 shows the UV/Vis-SEC responses registered for this molecule in dimethyl-sulfoxide (DMSO) in presence of oxygen, in the potential region where superoxide anion ($O_2^{\cdot -}$) is generated.

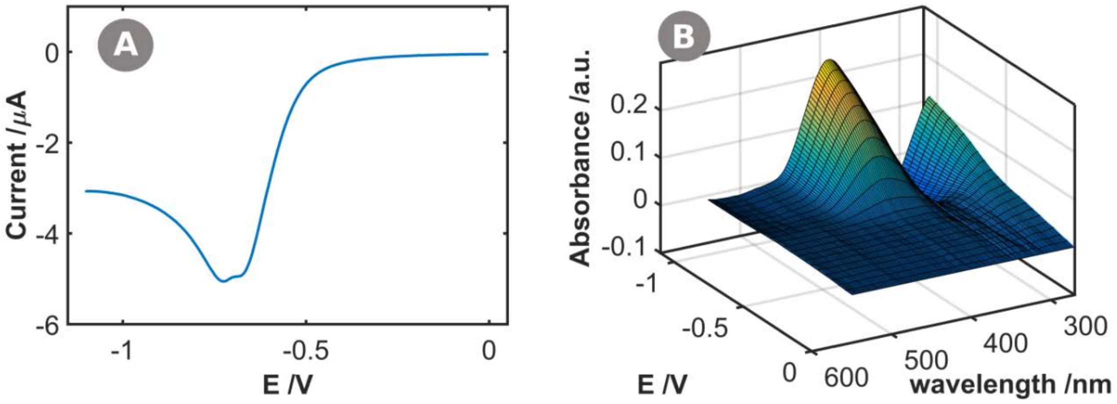

Figure 1. (A) Linear sweep voltammogram and (B) 3-D plot of evolution of UV/Vis spectra during the cathodic scan of o-vanillin in DMSO in presence of O_2.

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O-ECP32

REMOVAL OF ORGANOCHLORINATED COMPOUNDS FROM POLLUTED SOILS USING ELECTROOXIDATION TECHNOLOGIES COMBINED WITH ZVI PARTICLES

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Keywords: *soil washing, clopyralid, ZVI, combined treatment, electrooxidation*

During lots of decades the study of different electrochemical advanced oxidation process (EAOPs) to remove chlorinated hydrocarbons from soils have been widely assessed with promising results. They were evaluated in the treatment of a wide variety of compounds as pesticides [1], to avoid the further magnification of the problem with the later pollution of water reservoirs.

Lately, in some works were determined the efficiency of soil treatment technologies using ex-situ techniques as the electrolysis combined with ultrasounds [2] or adding a surfactant to promote a high efficient extraction. Also the electrokinetic soil flushing is as example of an in-situ technique used with remarked results in polar and non-polar compounds.

However, many these research works require lots of reagents and long treatment times with low efficiencies that make unreliable the process, so in order to improve the remediation of soil with the electrooxidation process it has been developed a combined treatment that evaluate the further use of microorganism. To do this, it is necessary the determination of important parameters of effluents as the toxicity or biodegradability after the electrochemical treatment time. To start with, clopyralid, an example of a chlorinated hydrocarbon, is extracted from soil without applying any surfactant due to the polarity in an ex-situ treatment, but zero valent iron particles (ZVI) that it could promote the dehalogenation process are added with different contact times during the soil washing. Then, it was evaluated the efficiency of the electrochemical technologies as photolysis or electrooxidation with Boron-Doped Diamond (BDD) and dimensional stable anodes (DSA) to remove the dehalogenated pollutants obtained. Finally, it was monitored the changes into the toxicity and biodegradability of the fluids after the treatments proposed in order to conclude about the viability of applying further conventional and economic treatments to diluted wastes of persistent pollutants if the samples are less toxic and more biodegradable.

Results shown that the contact time with ZVI particles has a reduce influence in the full treatment time but a reduction in the toxicity is obtained after full treatment in all the cases studied. The process is more efficient with BDD electrodes in terms of removal of clopyralid and just a slightly increase in terms of biodegradability is detected.

Financial support from the Spanish Ministry of Economy, Industry and Competitiveness through project CTM2016-76197-R (AEI/FEDER, UE) and from CTQ2017-90659-REDT are gratefully acknowledged.

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MICROSCALE INVESTIGATION OF THE HETEROGENEOUS ADSORPTION KINETICS OF NEW GREEN CORROSION INHIBITORS

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Keywords: *SECM; Corrosion protection; Green inhibitors; Adsorption kinetics*

The recent trends towards the use of green corrosion inhibitors for the protection of structural metallic materials has motivated the investigation of novel compounds, extracted from natural products, as cheap and environmentally friendly promising substances for corrosion protection [1]. Their inhibitive action is typically investigated taking advantage of the alteration of the electrochemical properties of the metal substrates. The kinetic study of their adsorption has already been proposed using the electrochemical quartz microbalance (EQCM) [2], supported by multiscale electrochemical techniques. However, heterogeneous blockage is expected within the early stages of the formation of inhibitive films, hence surface analysis is mandatory for the monitoring of the inhibitive effects.

The Scanning Electrochemical Microscopy (SECM) has shown to be powerful for the investigation of the surface activity of metals when exposed to corrosion inhibitors [3]. The analysis of the probe current sensed with the SECM operated in the feedback mode allows the determination of the constant rate of the electron exchange occurring between the metal surface and a given redox mediator. This phenomenon, dynamically and heterogeneously evolving throughout the substrate surface, actually reflects the remaining active sites still available for electron donation during their deactivation upon interaction with the inhibitor.

This contribution focuses on the electrochemical monitoring of the adsorption and protective effect of a green corrosion inhibitor, extracted from horse-chestnut, on bronze surfaces in simulated acid rain. SECM was used to determine the electron exchange rate constants by recording probe approach curves at desired locations. The probe current values sensed during the acquisition of 2-D scans served to investigate the heterogeneous surface activity. A kinetic evaluation of the distribution of these current data recorded during scan acquisition is proposed for the study of the blockage of the active sites that is promoted by this inhibitor. Results correlate well with the provided corrosion protection as studied using conventional electrochemical techniques. The applied methodology is regarded as particularly promising for the investigation of the heterogeneous protective effects provided by green corrosion inhibitors.

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O-AEC32

NOVEL ELECTROCHEMICAL IMMUNOPLATFORMS USING HYBRIDS OF GOLD NANOPARTICLES AND CARBON NANOTUBES AS NANOCARRIERS FOR THE DETERMINATION OF EMERGING CLINICAL BIOMARKERS

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Keywords: *Rank-L, amplification, gold nanoparticles, rheumatoid arthritis, carbon nanotubes*

Bone loss and bone erosions are the main unresolved problems in rheumatoid arthritis (RA), a common inflammatory autoimmune disease characterized by chronic synovitis in joints. Overexpression of osteoclasts, are one of the pivotal effector cells in the pathogenesis of osteoporosis, might correlate with joint cartilage and bone destruction in RA. Function of osteoclasts is mainly controlled by receptor activator of the nuclear factor κB ligand (RANK-L).

This factor, originates from the surface of osteoblasts, plays a key role in the promotion of osteoclastogenesis, osteoclast maturation, activation and prevention of the apoptosis of osteoclastic cells. Furthermore, activity of RANK-L is the essential factor in the progression of bone damage in inflammatory joint diseases and determines extent of bone destruction mediated by osteoclasts. It has been found that soluble receptor (sRANK-L) concentration in serum is elevated in RA patients compared to controls, establishing a cut-off value of 50 pg mL^{-1} [1]. All these findings highlight the relevance of sRANK-L determination in serum. In this context, we have developed the first electrochemical immunosensor for determination of the RANK-L based on the use of a hybrid nanomaterial composed of multiwalled carbon nanotubes (MWCNTs) and gold nanoparticles (AuNPs) as nanocarriers of antibodies and HRP for signal amplification. The biotinylated capture antibody is immobilized onto the streptavidin-modified electrode through grafting with *p*-aminobenzoic acid (*p*-ABA) and further activation using EDC/Sulfo-NHS chemistry. Then, a sandwich configuration involving MWCNTs-AuNPs (-HRP)-antibody as carrier nanotags for detection was prepared. The extension of the affinity reactions was monitored amperometrically using the H_2O_2/HQ system.

Once optimized the variables involved in the preparation and performance of the immunosensor. Analytical characteristics of the method were established, and the immunosensor was applied to the determination of RANK-L in serum samples.

The financial support of projects: Ministry of Economy and Competitivity CTQ2015-70023-R, CTQ2015-64402-C2-1-R (MINECO Research Projects) and the TRANSNANOAVANSENS-CM Program from the Community of Madrid (Grant P2018/NMT-4349) are gratefully acknowledged. R.B. acknowledges the financial support of the PI17CIII/00045 grant from the AES-ISCIII program.

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ACTIVATION ENERGY OF HYDROGEN ADSORPTION ON PLATINUM (111) FROM IMPEDANCE SPECTROSCOPY IN ALKALINE MEDIA

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Keywords: *single crystal; platinum; hydrogen adsorption; EIS*

The study of hydrogen reactions (adsorption, evolution and oxidation) has implications in many different fields of significant applied importance such as hydrogen storage, fuel cell development and water electrolysis. The theoretical understanding of these reactions often implies the use of model surfaces to obtain adsorption and activation energies from theoretical calculations, but there is still a lack of experimental data. The determination of energetic parameters for the hydrogen adsorption reaction on highly oriented single crystal platinum surfaces can provide valuable experimental data to test such theoretical calculations.

The adsorption of hydrogen onto platinum is a very fast reaction, making electrochemical impedance spectroscopy (EIS) an appropriate technique to obtain direct kinetic information [1]. However, while the rate of this reaction is too fast in acid solution, the charge transfer resistance for this reaction in alkaline solution is high enough to obtain accurate results [2].

Direct charge transfer resistance results are obtained by EIS measurements, after fitting to a physically valid equivalent circuit. These are represented in Nyquist plots of admittance that show clear evidence of a change in the admittance response with temperature. This change would be difficult to measure by conventional cyclic voltammetry because of the absence of a clear peak and the similarity of the voltammetric profiles across temperatures.

The results will be analysed according to a Frumkin isotherm to extract values of the activation energy and other relevant thermodynamic parameters.

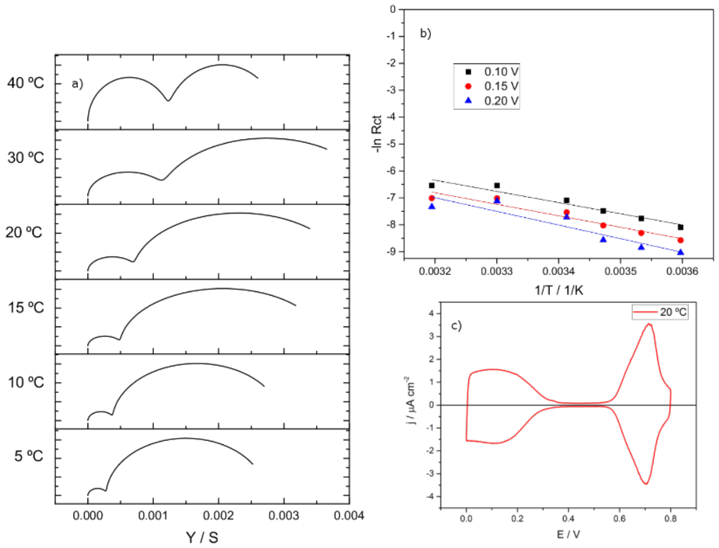

Figure 1. a) Admittance plot at different temperatures, E=0.15 vs. SHE, b) natural logarithm of charge transfer resistance vs. temperature plot, c) cyclic voltammetry of a Pt(111) electrode in NaOH.

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DEGRADATION OF TRICLOPYR IN WATER AT PH 7.0 BY PHOTOELECTRO-FENTON USING FE(III)-EDDS COMPLEX AND UVA LIGHT OR SUNLIGHT

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Keywords: *homogeneous catalysis; pesticide; photoelectro-Fenton; water treatment*

In recent years, several advanced electrochemical technologies have been developed for the removal of organic pollutants from water under the action of different types of hydroxyl radical ($^\bullet$OH). In electrochemical oxidation (EO), the combination of air-diffusion cathodes and DSA® or boron-doped diamond (BDD) as anodes has yielded good results when the produced H_2O_2 is decomposed with a catalytic amount of Fe^{2+} via Fenton's reaction. Based on this concept, electro-Fenton (EF), photoelectro-Fenton (PEF) and solar photoelectro-Fenton (SPEF) processes have appeared as promising technologies, showing high mineralization rates during the treatment of industrial wastewater. The main requirement is that the effluent to be treated has a pH around 3.0, constituting an important limitation because it does not allow treating many aqueous samples like groundwater or industrial wastewater at neutral/alkaline pH. The main strategies to increase the viability of Fenton-based technologies involve the use of: (i) heterogeneous catalysts, or (ii) alternative structures that are able to solubilize the iron catalyst at high pH.

This work describes the successful removal of triclopyr (3,5,6-trichloro-2-pyridinyloxyacetic acid), a pyridinic organochloride that is used as a systemic foliar herbicide and fungicide and presents high ecotoxicity. The degradation trials have been carried either by PEF with a 6-W UVA lamp or SPEF under natural sunlight, using a DSA® or BDD anode. The pollutant was spiked at 0.12 mM (10 mg L^{-1} of total organic carbon (TOC)) in ultrapure water, in the presence of sulfate or sulfate/chloride ions at pH 7.0 in both, using ethylenediamine-N,N'-disuccinic acid (EDDS) as an iron-chelating agent to improve its solubility. This ligand has a good biodegradability, and it may offer a more sustainable and eco-friendly alternative to other chelating compounds, which may have higher environmental issues. Fixed or varying current densities (j) have been used during the treatments. Triclopyr concentration has been monitored by reversed-phase HPLC, showing a complete removal in PEF and SPEF after ca. 60-120 min, working at $j < 67$ mA cm^{-2}. EDDS was also gradually destroyed, as revealed by HPLC and TOC measurements. The largest mineralization was attained in SPEF, reaching up to 80% at 300 min. The main oxidation by-products have been identified.

Acknowledgments
The authors thank financial support from project CTQ2016-78616-R (AEI/FEDER, EU) and the PhD scholarship awarded to Z.H. Ye (State Scholarship Fund, CSC, China) and R. Oriol (MINECO, Spain).

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O-AEC33

A FAST AND EFFICIENT WAY TO ACTIVATE SCREEN PRINTED CARBON ELECTRODES BY OZONE TREATMENT

María Isabel González-Sánchez*[1], María Isabel Romero-Llapa[1], Beatriz Gómez-Monedero[1], Rebeca Jímenez-Pérez[1], Jesús Iniesta[2], Edelmira Valero[1].

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Keywords: *screen printed carbon electrodes, electrochemical activation, ozone, phenols.*

Screen printed carbon electrodes (SPCEs) have been employed for many years in screen printing technology for a variety of sensor/biosensor applications. Over the years researchers have developed different methods to activate carbon electrode surfaces in order to improve their electrochemical properties. In this sense, our group has recently reported some works, such as an electrochemical activation treatment using H_2O_2 [1] and a combined electrochemical activation protocol using H_2SO_4 and H_2O_2 [2]. These treatments are highly effective in the activation of SPCEs, but they take relatively long times. Encouraged by the search of a reduction of the activation time, we propose herein a facile electrochemical method using ozone gas in alkaline solution for the activation of SPCEs.

The voltammetric protocol was optimized by changing the experimental conditions such as number of cycles, scan rate, potential windows, pH, etc. The optimized protocol activation method consisted in the performance of a voltammetric cycle between -2 and 2 V at 10 mVs^{-1} in a 0.1 M NaOH solution with a constant ozone gas flux into the electrochemical cell. The resulting activated electrodes (aSPCEs) showed important enhancement in the analytical outcome towards hydrogen peroxide, acetaminophen, hydroquinone and dopamine. This ozone based electrochemical treatment only lasts 12 minutes, therefore, it could be used routinely previously to any modification for different analytical applications. The main causes of these improved electroanalytical properties were attributed to the increase of electroactive surface area and the functionalization of the electrode surface with carbon-oxygen groups onto working electrode inks.

Funding sources: *This work was funded by the Spanish Ministry of Economy and Competitiveness (BFU2016-75609-P) (AEI/FEDER, UE) and by the Junta de Comunidades de Castilla-La Mancha (Spain) (SBPLY/17/180501/000276/2), cofounded with FEDER funds, EU. BGM is a post-doctoral research fellow of the Youth Employment Initiative (JCCM, Spain, cofounded with ESF funds, EU).*

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O-MOE33

EFFICIENT FORMATION OF POLYMER BRUSHES FROM MIXED SELF-ASSEMBLED MONOLAYERS USING THE eATRP TECHNIQUE

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Keywords: *polymer brush; grafting from; gold surfaces; biocompatibility; polyethylene glycol (PEG)*

The use of controlled drug delivery systems that can be serve in theragnostic applications (diagnostic and therapeutic) require the development of multifunctional hybrid materials that are crucial for Nanomedicine advances. Organic-inorganic hybrid materials formed from 2-D and 3-D gold surfaces and polymers compact layers *(brush polymers)* are of great interest for a variety of biomedical applications [1]. In particular, the use of oligo-ethylene glycol terminated molecules bring to the nanomaterials interesting features, as biocompatibility and protection against nonspecific adsorption in biological medium.

In order to obtain well-defined, high-density polymer brushes we employ a grafting from approach, in which the controlled radical polymerization (CRP) techniques are used [2]. More specifically, we have employed the electrochemically mediated atom transfer radical polymerization (eATRP), in which the chain-growth is made connecting the monomers one-by-one using electrochemical parameters to control the activator/deactivator ratio of catalyst by a redox process [3]. In this work, we present the formation of polyethylene glycol-based polymer brushes on 2-D gold surfaces. The initiator surface is based on a mixed self-assembly monolayer made of bis[2-(2-bromoisobutyryloxy)undecyl] disulphide (DTBU) and 6-mercaptopurine (6MP).

The obtained polymer brushes have been characterized by using electrochemical techniques such as cyclic voltammetry, electrochemical impedance spectroscopy and electrochemical quartz crystal microbalance, Fourier transform infrared and X-ray photoelectron spectroscopies, as well as, by contact angle measurements.

Acknowledgements

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O-MEC33

AN ELECTROCHEMICAL INSIGHT INTO GOLD NANOPARTICLES SYNTHESIS: THE SHAPING-ROLE OF SURFACTANTS

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Keywords: *AuNPs; citrate; glutamate; single crystal gold electrodes.*

Citrate is by far one of the most used agents for nanoparticles synthesis. Mainly because of its easy-removal capabilities as well as being non-cytotoxic in human serum originated citrate to be a cornerstone of a wide number of nanoparticles synthesis processes. Furthermore, gold nanoparticles (AuNPs) have being widely studied showing up to be a good candidate for drugs delivery. Due to this facts, it is crucial to understand the shaping mechanisms of AuNPs, which are still poorly understood. On the other hand, we chose glutamic acid as a potential AuNPs synthesis actor, due to its biocompatibility because of being an amino acids of human serum as well as the lack of AuNPs synthesis using it as both capping and reducing agent.

Concerning this, we carried out thermodynamic analysis of the adsorption properties of solvated citrate by using a combination of electrochemical experiments (CVs), FTIR spectra (IRRAS spectroscopy) and DFT calculations, on well-defined surfaces. Thank to this, the adsorption behaviour of solvated citrate on the basal planes of gold (Au(111), Au(100), Au(110)) in water have being done to determine where citrate bonds preferentially. In the case of glutamate, our results indicate it to be not only being adsorbed, but reacting during the adsorption process. So FTIR spectra may point out the products that originate. Besides, the UPD of lead technique will allow us to identify the crystallographic facets AuNPs have preferentially under glutamic acid control during the synthesis growth.

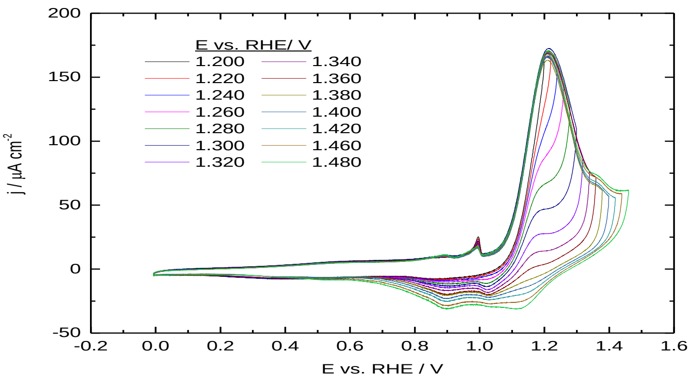

Figure 1:Voltammetric profiles of Au(100) electrode in solution at 0.1 M NaOH r + 10^{-3} M glutamic acid under different maximum potential limits. Scan rate: 20 mV s^{-1}

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O-ECP34

TOWARDS THE REDUCTION OF ENVIRONMENTAL AND SANITARY IMPACT OF HOSPITAL URINES USING ELECTROCHEMICAL TECHNOLOGY

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Keywords: *electrolysis; disinfection; urine; diamond*

The presence of pharmaceuticals and pathogens in wastewater poses a risk to the environment and human health. Currently, conventional treatment technologies that are placed in Wastewater Treatment Facilities (WWTFs) are not able to completely degrade these chemical and biological pollutants. Hence, they can be found in downstream areas where humans may be brought into contact with them. One of the effluents that represents a major risk are hospital wastewater because their concentrations of pharmaceuticals and pathogens are very high. Specifically, the urine of polymedicated patients can be considered as the main source of these pollutants. Hospital effluents are commonly treated in urban WWTFs and, consequently, they are not properly managed. For this reason, it is necessary to develop clean and efficient technologies that allow the removal of both pharmaceuticals and pathogens in this type of effluents.

Electrolysis with diamond anodes has been proven efficient for the removal of several organic pollutants and disinfection of urban treated wastewater. This technology consists of the production of large amounts of hydroxyl radicals from water oxidation that are the main responsible species for the degradation process. Likewise, other powerful oxidants can be electrogenerated during the treatment by means of the oxidation of the ions naturally contained in wastewater over diamond surface. These species also contribute to the removal of organics and/or disinfection, improving the process efficiency.

With this background, the main aim of this work consists of testing the electrolysis with diamond anodes for the reduction of environmental and sanitary impact of hospital urines. To do this, the removal of an antibiotic model and a bacteria model typically found in urine has been evaluated using different reactor configurations and operating conditions. Results show that it is possible to completely remove both antibiotic and bacteria from synthetic urine at moderate current densities. In the case of antibiotic removal, powerful oxidants electrogenerated such as peroxodisulfate or peroxodiphosphate seem to be the main responsible species for the degradation process whereas free and combined chlorine species (hypochlorite and chloramines) are the compounds directly involved in the disinfection process.

Acknowledgements
This work has been supported by Junta de Comunidades de Castilla-La Mancha (JCCM) and European Union through the project SBPLY/17/180501/000396 and the grants SBPLY/16/180501/000404 (Dr. S. Cotillas) and SBPLY/18/180501/000009 (M. Herraiz). UCLM-Excma. Diputación de Albacete (Apoyo a la actividad investigadora en el campus de Albacete) is also acknowledged.

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O-AEC34

SIMULTANEOUS DETERMINATION OF THE COLORECTAL METASTATIC BIOMARKERS IL-13Rα2 AND CDH-17 USING INTEGRATED ELECTROCHEMICAL IMMUNOSENSORS INVOLVING GQDs/MWCNTs AS HYBRID CARRIERS TAGS

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Keywords: *dual immunosensor, metastatic biomarkers, colorectal cancer cells, tumor tissues.*

The ability to disseminate to distant organs during metastatic processes has become the leading cause of death in patients diagnosed with cancer. These processes depend on extensive interactions through several protein families on the tumor microenvironment and, within this context, recent findings have demonstrated that hyperexpression of extracellular IL-13 receptor α2 (IL-13Rα2) and cadherin-17 (CDH-17) proteins may be reliable biomarkers in late-stage and metastatic colorectal tumors [1,2]. The clinical methods commonly used for the determination of these emerging biomarkers require multiple steps, time-consuming analysis and have limited applicability in decentralized settings. Therefore, the development of new methodologies for their fast, simple, cost-effective and accurate determination is highly demanded for early diagnosis, disease follow-up and identification of metastatic processes.

This work describes the development of a dual electrochemical immunoplatform for the simultaneous determination of IL-13Rα2 and CDH-17 involving the formation of sandwich immunocomplexes comprising specific antibodies integrated onto dual screen-printed carbon electrodes modified by 4-aminobenzoic acid (*p*-ABA) electrochemical grafting, and the use of the hybrid nanomaterials for signal amplification based on graphene quantum dots/multi-walled carbon nanotubes (GQDs/MWCNTs) as nanocarriers of the detector antibodies and HRP molecules [3] for the amperometric detection using the H_2O_2/hydroquinone (HQ) system.

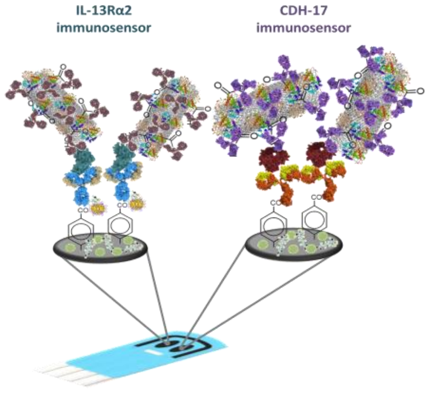

Figure 1. Dual immunosensor

The results obtained demonstrate that the developed dual bioplatform allows the selective determination of both biomarkers with analytical characteristics compatible with the required clinical ranges (LOD of 1.44 and 0.03 ng mL^{-1} for IL-13Rα2 and CDH-17, respectively) and are advantageous compared with commercial methodologies in terms of simplicity, assay time, cost and feasibility to on-site determinations in resource-limited settings. Their successful applicability using very simple protocols, shorter time assays (3 h) and small amounts (0.5 µg) of raw lysates of colorectal cancer cells with different metastatic potential and extracts of paraffin-embedded colon cancer tissues of different metastatic grade will allow further advancing in the clinical validation of these emerging relevance metastatic biomarkers to perform rapid routine screening of colorectal cancer, offering the opportunity of improving the patient management and getting an efficient therapeutic intervention and therefore a better cancer outcomes.

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O-FEC34

KINETICS OF SURFACE PROCESSES FROM COLOR STANDARD DEVIATION.

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Keywords: *surface processes, standard deviation, kinetics, RGB video electrochemistry*

Kinetics of processes taking place on the electrode surface are of especial interest in Electrochemistry. The evolution of chemical species on the electrode surface can be followed by different techniques. Among these possibilities, spectroscopy gives a quasi-instantaneous estimation of the amount of different species on the electrode surface. However, this response usually corresponds only to a small region of the electrode or a global response. In recent years we have developed the possibility to follow electrochemical advance by digital video[1]–[3]. This way of working allows recovering valuable information on the complete electrode surface and therefore, obtaining information about the homogeneity of the electrochemical reaction advance. Color standard deviation or variance are excellent parameters measuring this homogeneity, but also it proves useful for kinetic purposes.

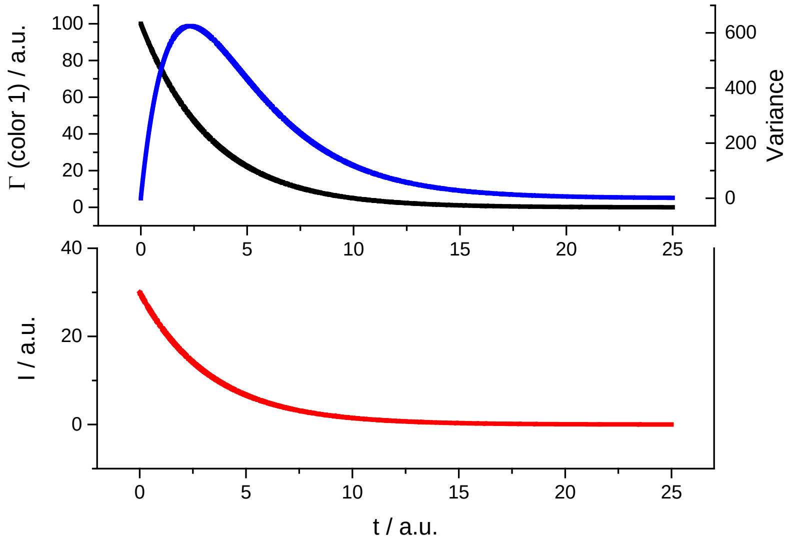

Figure 1: Variance, surface concentration and current against time simulated for a 1st order kinetic process

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O-MEC34

SMART CONDUCTING POLYMERS MICRODEVICES

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Keywords: *Conducting polymers, Smart polymers actuators, Micro devices, PC´s microrobotics*

Conducting Polymers are Reactive Redox Materials Any of those CP (as films coating metals or as self-supported material) follows reversible oxidation/reduction processes in electrolytes. The reactions can be driven under electrochemical control. Under electrochemical (faradaic) control the consumed charge (Q) drives the counterion content, mol L^{-1}, evolution (Q/FV, F is the Faraday's constant and V the film volume) of the oxidized or reduced material. The reaction induces macroscopic (relaxation, swelling, shrinking, compaction) and molecular (conformations) structural changes; which are very important for the design of micro devices designed with conducting polymers (CPs).

Reversible breaking and rearrangement of double bonds along chains in CPs constitute the basic conformational molecular motors (artificial muscles) mimicking actin and myosin macromolecules in muscles. The microscopic dimensional variations were transferred to macroscopic movements by the reversible generation of stress at a polymer/tape interface. The Construction of a bilayer (polypyrrole/tape) or three-layer (polypyrrole/tape/polypyrrole) artificial muscle has been characterized in order to show angular displacement movements under faradaic control, the applied current controls the speed of movement and the electric charge the angular displacement of the artificial muscle, here now we present some challenges and problems encountered to be able to design small mechanical electrochemical devices controlled electrochemically, the way in which these should be synthesized to have greater homegeneity in their characterization: physical-chemical and electrochemical. Mobility results of these devices are shown, showing their correlation in functionality with the electrical energy consumed, in order to assemble new linear and angular devices assembled multiple to perform specific tasks: as is the lifting of objects, the dragging of objects and others. Showing new application potentials to different areas of knowledge.

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EC&T Master & Doctoral Students

D-NSM01

SUSTAINABLE BATTERIES FOR DISPOSABLE ELECTRONIC DEVICES

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***Keywords**: biodegradable batteries, flow batteries, paper microfluidics, hydrogel, circular economy*

The proliferation of electronic devices has caused an increasing demand of batteries. This fact, coupled with a trade model based on lineal economy results in the proportional generation of electronic compounds and battery waste (*e-waste*). The unsustainable e-waste generation has raised an alarm due to the hazardous consequences to human health and environmental damage. Despite the efforts to implement regulations and social awareness to encourage safe disposal and e-waste recycling [1], during 2017, only 45.7% of batteries sold in European Union were collected for recycling, with the remaining ones being disposed of in an uncontrolled way.

The work herein aims to develop alternatives to the current batteries and electronic devices production. Taking advantage from the intrinsic capabilities of non-damaging natural materials as cellulose, chitosan, quinones, carbon or vitamins, different batteries and electronic compounds are under development.[2] In this regard, the PhD goals have been completely conceived under circular economy principles (Figure 1B). Being the starting point the development of an Eco-Friendly Cellulose-Chitosan Hydrogel Battery in a standard coin cell format (Figure 1A) and the potential applications of an Evaporation Flow Paper-Based Microfluidic Battery (Figure 1C). The electrochemical cells characterization and evaluation will be carried out using well-known electroanalysis techniques, as well as biodegradability tests and climate chamber studies that ensure their implementation in future sustainable electronic devices.

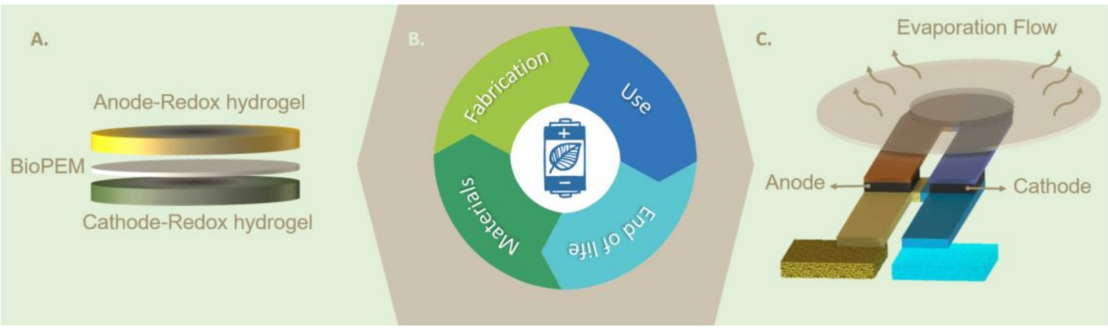

Figure 1. A. *Cellulose-Chitosan Hydrogel Battery Diagram,* B. *Circular economy battery life cycle,* C. *Evaporation Flow Paper-Based Microfluidic Battery.*

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D-GCJ02

SYNTHESIS AND CHARACTERIZATION OF NANOPARTICULATED SUPPORTED CATALYSTS FOR POROUS ELECTRODES AND ENVIRONMENTAL APPLICATIONS

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Keywords: *Pt-based electrocatalysts; core-shell nanoparticles; fuel cells; water depollution.*

The development of environmentally friendly energy sources is a present need because the use of fossil fuels causes negative effects on the environment, such as climate change. Hydrogen is a clean energy vector that can be satisfactorily used in fuel cells, which have higher efficiency than other competing devices [1]. The hydrogen synthesis has then a special interest, for example from water electrolysis, in which high purity H_2 can be obtained. Pt is the best catalyst for the hydrogen oxidation and the hydrogen evolution reactions and, therefore, it is the preferred one in polymer electrolyte fuel cells and water electrolyzers, respectively. However, Pt is expensive, scarce and susceptible to poisoning. Therefore, reducing the cost and improving the catalyst activity and stability are active research areas at present. It has been shown that multi-metallic catalysts such as Pt(Cu) core-shell nanoparticles can contribute to the reduction of the cost and to the CO poisoning in fuel cells [2].

One of the main objectives of this project is to synthesize and characterize core-shell nanoparticles containing a sacrificial metal as the core, Cu for example, coated with a Pt shell, dispersed on different supports, such as carbon blacks and mesoporous materials. Characterization by means of structural and electrochemical techniques will be carried out in order to study the performance of the obtained catalysts. Application in fuel cells will be assessed. In addition, the core-shell nanostructures will be used for water treatment by means of electrochemical advanced oxidation processes, in which Pt can be used as the anode to contribute to the oxidation of organic pollutants. This strategy opens the way to explore new catalysts for water treatment and would also allow reducing the cost and improving the performance of the catalysts. Furthermore, a good anode catalyst could be combined with a hydrogen producing cathode in an electrolysis cell and, in this form, water treatment with H_2 co-generation could be performed. The H_2 produced could then be used in a fuel cell and hence, the energy consumed during the electrolysis could be partially recovered. A step forward is also planned in the case of obtaining good anode catalysts for the oxidation of organic pollutants, since its combination with a gas-diffusion cathode would yield a fuel cell for water decontamination. Using a specialty electrode as gas-diffusion electrode for hydrogen peroxide generation, the addition of Fe^{2+} or purpose-made Fe-based heterogeneous catalysts to the solution in catalytic amounts could promote Fenton's reaction, thus enhancing the degradation of contaminants.

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D-ABB03

CO_2 ELECTROREDUCTION ON ADVANCED NANOMATERIALS: TOWARDS MORE SELECTIVE AND STABLE ELECTROCATALYSTS

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Keywords: *electrocatalysis; CO_2 reduction; nanomaterials; selectivity; durability.*

Carbon dioxide (CO_2) is a very alarming greenhouse gas released from the excessive use of fossil fuels. Recently, the CO_2 emission problems have drawn intensive attention and especially, how to reduce the accumulation of CO_2 in atmosphere. Among the different options, the electrochemical reduction of CO_2 offers a promising means of storing electricity in chemical form and very relevant efforts have been performed about this topic in the last years [1,2]. The products of this reaction as formate/formic acid, methanol, ethanol or methane can be used in fuel cells to generate electricity and this would allow the creation of a carbon-neutral cycle. The reduction of CO_2 with electric power is an important transformation method with high possibility of finding application, owing to its high environmental compatibility and good combination with other renewable energy sources, such as solar energy and wind energy.

The key research area in this field is to find more efficient, selective and stable electrocatalysts. It must work at low overpotentials, reducing CO_2 in the presence of water, selectively converting CO_2 to desirable chemicals and being sufficiently stable. The main objective of this Doctoral Thesis is to study the process of electrochemical reduction of CO_2 to different interesting products with electrodes constituted by metal nanomaterials of different nature. The synthesized nanomaterials will be conveniently characterized and subsequently used to build electrodes. Different electrode-electrochemical reactor configurations will be evaluated [2].

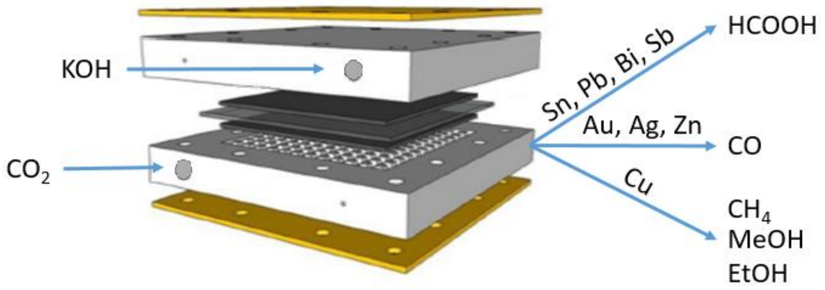

Figure 1. PEMER configuration and a scheme of different desirable products.

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D-BOL04

TEMPERATURE EFFECTS ON FUEL CELL ELECTROCATALYTIC REACTIONS USING HIGHLY ORDERED SURFACES

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Keywords: *fuel cells; oxygen reduction; hydrogen adsorption; impedance; single crystals*

One of the most promising technologies for clean energy is that of hydrogen fuel cells, which makes it one of the most researched topics in electrochemistry. The oxygen reduction reaction (ORR) still needs to be optimized to decrease or even avoid the use of precious metals as electroactive materials. On the other side of the cell, the fundamental study of the hydrogen oxidation represents a challenge since most techniques do not allow to obtain kinetic results for such fast process. To obtain information on the mechanisms of these reactions, this work will mainly use temperature perturbations, which are underreported in the literature.

The study of the ORR will focus on the use of biosimilar molecules supported on single crystal gold electrodes. The ORR is catalysed by natural enzymes, but they have serious disadvantages, such as low activity and stability. A similar catalytic activity has been detected on molecules that mimic the active centre of the enzyme, involving coordinated metal ions. For these studies, carbon substrates have been used [1]. If single crystal surfaces are used instead, the reaction mechanism can be probed with *in situ* microscopy techniques (STM, AFM) in addition to (spectro)electrochemical analysis, offering additional insights. Temperature studies in this area are extremely important since they could result in changes of electrocatalytic activity.

The electrochemical impedance spectroscopy (EIS) technique can be used to study the rate of hydrogen adsorption [2]. In addition, a laser induced temperature jump method [3] provides kinetic information by studying the coulostatic response of the potential to a sudden change of temperature in the submicrosecond time scale. Obtaining the rate constant for the H adsorption reaction at different temperatures in highly ordered platinum surfaces can provide information on the activation energy of the adsorption mechanism and its dependence on the surface structure. Thermodynamic analysis of the data collected at different temperatures provide additional information on Gibbs energies, enthalpies and entropies of adsorption. Such results will constitute very valuable reference data to be used in computational electrochemistry.

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D-MGE05

DEVELOPMENT OF AN ACID-BASE ELECTROCHEMICAL FLOW BATTERY

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Keywords: *hydrogen; energy storage system; redox flow battery; acid; base.*

The efficient storage of energy is a key issue for a sustainable electric energy supply from sources such as photovoltaic devices. The most common energy storage systems suited for this application are so-called flow batteries, which convert chemical energy into electrical energy through reversible oxidation and reduction of working fluids. However, those developed until now are expensive and not environmentally friendly [1].

An interesting alternative to the classic redox batteries is a pseudo-redox flow battery based on the neutralization of acids and bases due to the oxidation and evolution of hydrogen. The main advantage of this concept is that the electrolytes to be used such as HCl, NaOH and NaCl are abundant and inexpensive, and hydrogen is a clean, renewable and efficient resource.

The Acid-Base Electrochemical Flow Battery (ABEFB) is composed of acidic and alkaline solutions, both with a high supporting electrolyte concentration, which are separated by a cationic exchange membrane. Fig. 1 illustrates the processes taking place. During the charging process water is reduced to hydrogen at the negative electrode, whereas hydronium ions are formed from hydrogen oxidation at the positive electrode. On the other hand, during the discharging process hydrogen oxidation to water takes place at the negative electrode, while at the positive electrode hydronium ions are reduced to hydrogen. The neutralization energy obtained from these solutions is used as electromotive force.

The ABEFB is still at a very early stage of development since it has first been mentioned [2], so this work will be focused on the optimization of all elements involved (electrodes, membrane, solutions), as well as the battery operating parameters.

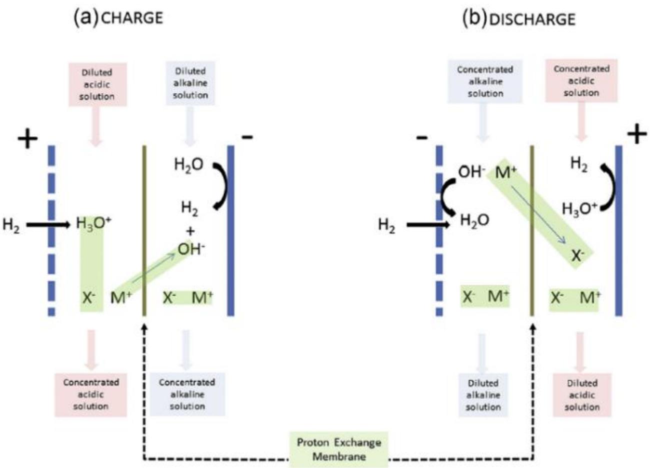

Fig. 1. Scheme of a) charging and b) discharging processes from ABEFB

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D-SDJ06

MEASURING THE AVAILABILITY OF METALS IN LARGE MIXTURES WITH DIFFUSIVE GRADIENTS IN THIN FILMS (DGT) DEVICES.

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Keywords: *DGT; diffusive gel; binding layer; Finite Element Method; availability*

The availability of contaminants or nutrients in natural media are relevant issues for the understanding of the ecotoxicity or nutritive properties of this media. The thesis will combine mathematical and numerical tools to understand metal availability measurements in natural waters with DGT passive samplers. With these devices, metal is forced to diffuse trough a diffusive gel disc before it is accumulated in situ in a resin disc that contains a strong binding agent [1]. Both, the resin and the diffusive discs are mounted in a plastic holder which can be disassembled for the metal accumulation measurement with ICP-MS after elution.

The mathematical formulation of this problem is similar to that of the electrochemical techniques where the electroactive species are transported by diffusion towards an electrode where, under limit diffusion conditions, its concentration drops to zero. The influence of the complexes present in the system will be studied in the thesis similarly to the CE mechanism in the electrochemical processes.

At high salt background, reaction-diffusion equations have to be used in the mathematical formulation of the relevant processes. However, at low ionic strength, migration can also influence transport phenomena [2]. A general simulation tool based on Finite Element methods will be developed to solve these problems. Limiting conditions allowing analytical solutions will also be considered.

DGT devices with a stack of resin and/or diffusive gels with filters of different pore size will be used to measure accumulation of metals in mixtures. Numerical treatment of these data is expected to allow the determination of the contribution of the different species or pools in the availability of metals in mixtures.

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D-MMM07

NEW ELECTROCHEMICAL TECHNIQUES FOR THE DETERMINATION OF ANTIOXIDANT CAPACITY IN FOOD EXTRACTS BASED ON THE CUPRAC METHOD

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Keywords: *Antioxidant Capacity; Carbon Modified Electrodes; CUPRAC; Antioxidants.*

In last years, a great effort is being devoted to the development of methods to evaluate the antioxidant capacity, since antioxidants are often used in the conservation of foods and cosmetics. Electrochemical methods have been recently reported [1], but they present limitations dealing with the stability in non-aqueous media and the complexity of their preparations. Spectrophotometric methods present limitations dealing with the turbidity and the colour of samples and/or reaction products (which originates errors by excess or default) and the non-physiological conditions used (for example, the working pH of Cupric Reducing Antioxidant Capacity, CUPRAC, is 5.5; for DPPH the reaction medium is non-aqueous). The aim of this study is establish if known antioxidants as Ascorbic and Gallic acids react with the intermediates produced in the Cu(II) reduction, to establish the optimal conditions to relate such interaction with the antioxidant capacity and to apply the proposed modified CUPRAC method with electrochemical detection to coloured samples and unstable chemicals.

The CUPRAC assay is based in the Cu(II)−Cu(I) reduction in the presence of the selective Cu(I)-stabilizing ligand neocuproine. The kinetics of this assay is relatively fast, the incubation time being typically one hour which prevents the AOC determination for unstable compounds and the antioxidant capacity being related to the absorbance measured at 450 nm, which is proportional to the amount of complex formed between Cu(I) and Neocuproine in the incubation time. Carbon electrodes modified with copper nanoparticles (0.01M $CuCl_2$) can replace the Neocuproine as indicator focusing on the signal provided by the passage from Cu(II) to Cu(I) (reduction sweep).

In this study the square wave voltammetry technique has been used which has a high sensitivity and presents a great reproducibility of the signals obtained by monitoring the signal provided by the Cu(II) to Cu(I). The antioxidant-probe reactions take place in the diffusion layer near to the electrode surface, being much faster than the same reactions in the bulk of solution. The capacity of the different antioxidants was studied in order to reduce this pair, so that the greater the reducing capacity of an antioxidant, the more Cu(II) it reduced, and the application of a potential sweep , the signal provided by the reduction of Cu(II) to Cu(I) was smaller, since there was less free Cu(II) in the solution to be reduced.

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M-EGA01

ELECTROCHEMISTRY AND SCANNING PROBE MICROSCOPY TO STUDY ELECTRON TRANSPORT OF REDOX PROTEINS.

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Keywords: *Ferredoxin; Cyclic voltammetry; Redox protein; Scanning tunnel microscopy*

Following the main objective of the project of elucidating the mechanisms of long distance charge transport in respiratory and photosynthetic complexes recently observed in our laboratory [1][2]. The present work particularly focuses on the study of the electron conduction of the redox protein ferredoxin. Ferredoxins are proteins with center type [2Fe-2S], type [4Fe-4S] or type [3Fe-4S]. They are mainly found in in bacteria, plants, algae and animals and they function as electron carriers in respiration and photosynthesis systems. For the study, mutated spinach ferredoxin [2Fe-2S] was used, introducing a cysteine (Cys) with the goal of improving the protein immobilization to the structure of gold surfaces without the need for a self-assembled monolayer (SAM). The surface used, which acts as substrate and electrode, is a gold <1,1,1> monocrystal.

Two different versions of the mutated protein were characterized, one of them conserving a histidine tag (His-tag) residue introduced for the purification steps, and the other one with the His-tag removed. The evaluation of how the conservation of the His-tag influences the protein was part of the present work. We characterized the protein distribution and immobilization using atomic force microscopy and spectroscopy (AFM-FS), and the electrochemical behaviour and charge transport at the nanoscale using electrochemical tunnelling microscopy and spectroscopy (ECSTM).

We observed a different behaviour for both samples. We verified when making images with AFM and ECSTM that their attaching to the substrate is different, even following the same incubation process. The protein with the Cys (noHis-tag) was successfully individually immobilized. We have also observed different behaviour when using the cyclic voltammetry. Possibly, the stability of the protein was altered by the procedure used to remove the histidine tag, affecting the [2Fe-2S] center integrity, as suggested from reported studies [3] on the comparison between the potentials of ferredoxin and the soluble fragments of the Rieske protein that demonstrated remarkably different oxidoreduction potentials for the protein with a functional center [2Fe-2S] and without this same center

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M-FMN02

CHARACTERIZATION OF ENZYME INHIBITION IN A LACCASE IMMOBILIZED ON GRAPHENE VOLTAMMETRIC BIOSENSOR

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Keywords: *Biosensor, Laccase, Voltammetry, Graphene*

Laccases are an interesting group of multicopper-containing oxidases enzymes found in a great variety of plants and fungi; they are characterized by having different active sites set apart by specific properties that play an important role in their catalytic mechanism. Given the prolonged exposure we have today to diverse pollutants present in wastewater, electrochemical inhibition biosensors involving laccase are under study, as the former can affect the enzyme activity altering its electron system and leading to a decrease of substrate conversion.

This study shows the construction of an enzymatic laccase biosensor based on a graphene platform for evaluating its activity and inhibition degree by the presence of selected organic and inorganic substances. Among others, some compounds that have demonstrated interesting inhibition were EDTA and benzoic acid.

It is known that most of these compounds can be detected easily via direct electrochemistry. The building of the desired biosensor was based on the carbodiimide reaction between residual carboxylic moieties on graphene and the amino lateral group of the enzyme, using as linkage the N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) coupling agent. The selected enzyme used was laccase which catalyzes the oxidation reaction of phenolic compounds such as cathecol, thus improving the sensitivity of the signal provided with respect to its ERGO and bare electrode analogues. On the contrary, the presence of enzyme inhibitors caused a significant decrease of the signal to be observed. To prove this, different biosensor combinations (Enzyme-ERGO-GEC, ERGO-GEC and GEC) were tested with cyclic voltammetry (CV).

This research reports a simple, low cost and fast operation device that present an alternative to analytical methods used up to now. It can be assumed that through the measurement of the enzymatic activity and the inhibiting mechanism of laccase, knowledge of the biologic catalyst and its possible applications in the near future is improved and would allow a fast monitoring of these compounds in polluted waters and wastewater.

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M-FMA03

EVALUATION OF THE PHYSICOCHEMICAL PROPERTIES OF A CU COMPLEX USED IN AQUEOUS ELECTROCHEMICAL-ATRP

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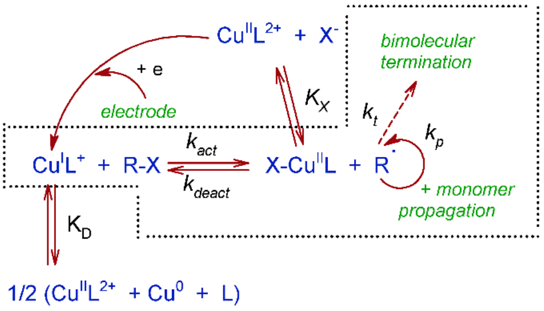
Keywords: *Copper; ATRP; Electrocatalysis; complexes* Cu^{II}*(TPMA)/* Cu^{I}*(TPMA)*

Electrochemical atom transfer radical polymerization (eATRP) is a recently reported controlled radical polymerization methodology that can be used to synthetize polymers in aqueous media [1]. The ATRP process is catalysed by a Cu^{II}/Cu^{I} system that enables a rapid and reversible activation/deactivation step. The system is in a dynamic equilibrium where activators ($Cu^{I}L^{+}$) react with dormant species (RX) to produce propagating radicals ($R^{\bullet}$) and deactivators ($X\text{-}Cu^{II}L$) (Scheme 1).



Scheme 1. Mechanism of ATRP (inside dashed line) and eATRP.

The limits in control in aqueous solutions have been recently addressed focusing on the electrochemical behaviour of the different catalysts in aqueous media [2]. In the present work we report a systematic study on the characterization of the Cu^{II}(TPMA)/Cu^{I}(TPMA) complexes, with TPMA being tris(2-pyridylmethyl)amine by using spectroscopic and electrochemical techniques. The characterization includes studies carried out in different background electrolytes and the determination of the kinetics and stability constants for the different processes.

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M-FRL04

ELECTROCHEMICAL STUDY OF SELF-ASSEMBLED MONOLAYERS OF DTBU, RADICAL INITIATOR IN SURFACE-INICIATED ATOM TRANSFER RADICAL POLYMERIZATION (SI-ATRP), ON POLYCRYSTALLINE GOLD ELECTRODE

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Keywords: *SI-ATRP; DTBU-SAM; mixed monolayer, cyclic voltammetry and impedance spectroscopy*

Electrochemically mediated Atomic Transfer Radical Polymerization has the advantage of tailoring polymers, since the polydispersity of the polymers can be controlled, and also, the manufacture of copolymers on demand [1]. The goal of the work is the generation of surfaces suitable for polymerization.

Bis[2-(2-bromoisobutyryloxy)undecyl] disulphide (DTBU) is a polymerization initiator capable of functionalizing metal surfaces, since it forms self-assembled monolayers (SAM). These SAMs are assemblies formed by spontaneous adsorption of molecules on surfaces. Monolayers are formed because the thiol groups in the molecule have a strong affinity with the substrate, which is a polycrystalline gold electrode.

For the characterization of this SAM, cyclic voltammograms have been recorded after different modification times, both for reductive and oxidative desorption. Capacity-potential curves offer information of the permeability of the monolayers. Studies of integrity of the monolayer and the blocking effect with different probes using cyclic voltammetry and impedance were also carried out. As a complementary measure, a contact angle experiment has been performed.

Mixed monolayers with 6-mercaptopurine have also been studied, since it has been demonstrated that the presence of this thiol facilitates electronic transmission through the monolayers [2]. Different proportions DTBU:6MP have been investigated (90/10, 70/30, 50/50, 30/70), obtaining information by the reductive desorption by cyclic voltammetry, and the integrity and blocking effect of the SAMs through impedance measurements. The experiments were carried out with a modification time equivalent to overnight.

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M-GBE05

SPECTROELECTROGRAVIMETRY STUDY OF POLY(3,4-ETHYLENDIOXYTHIOPHENE)

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Keywords: *PEDOT; Supercapacitors; Video Digital RGB; Ac-Electrogravimetry*

Poly (3,4-ethylenedioxythiophene) has been widely studied up to now due to its good electrical conductivity, low density and its use in sensors and electrical supercapacitors. Polymerization of 3,4-ethylenedioxythiophene (EDOT) was carried out in a solution 0.1 M $LiClO_4$ and 0.01 M EDOT in aqueous medium by chronoamperometry using as a reference electrode Ag | AgCl | KCl (sat), as a counter-electrode, a platinum mesh and an indium tin oxide (ITO) transparent electrode as working electrode. The characterization of the polymer was carried out by coupling the video analysis to conventional electrochemical techniques (chronoamperometry and cyclic voltammetry), obtaining significant results such as the supercapacitor behaviour and the oxidation savings and the reduction of the species. In addition, it has been possible to verify that the analysis allows RGB to separate the faradic and non-faradic contributions, as well as the effect of the ohmic drop along the electrode. Time derivate color intensity d (I_R,I_G,I_B) /dt showed a good correlation with the current peaks and shoulders of the cyclic voltammogram identifying intermediate forms of PEDOT. The standard desviation of colour (stdR, stdB, stdR) can be related to the color homogeneity of the surface [1].

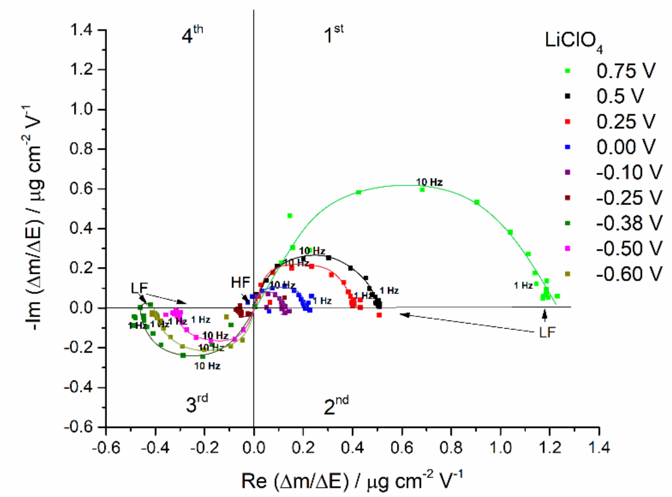

Figure 1.Experimental (symbols) and theoretical (lines) mass/potential transfer function, $\Delta m/\Delta E\ (w)$ of a thin PEDOT in 0.1M $LiClO_4$ aqueous solution.

Finally, PEDOT films were investigated by using Ac-Electrogravimetry, impedance and electrogravimetry spectroscopies in $LiClO_4$ aqueous solution. Electrochemical impedance spectroscopy combined with mass impedance spectroscopy proves useful for species identification. Information about the movement of anions, cations, and solvent during the switching of PEDOT between oxidation states obtained [2].

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M-HRL06

PREPARATION OF SEMICONDUCTOR NANOESTRUCTURED LAYERS FOR THE PHOTOCATODIC PROTECTION OF METALS

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Keywords: *corrosion; semiconductor; photocatotodic protection; nanostructured layers*

Cathodic protection is a technique to control the galvanic corrosion of a metallic surface converting it into the cathode of an electrochemical cell. This is achieved by making the electrical potential of the metal to be protected more electronegative by applying a direct current or joining it to a sacrificial anode. Although cathodic protection has been widely applied in the field of metal protection against corrosion, it has some drawbacks such as electrical consumption or sacrificial anodes and associated contamination. In this context, the use of new non-polluting technologies based on the use of renewable energies is attractive. The cathodic photoelectrochemical protection has these characteristics.

The objective of this work has been the preparation, characterization and subsequent modification of nanostructured layers of n-type semiconductor oxides deposited mainly on stainless steel. The layers may be prepared from pre-synthesized (or commercial) nanoparticles or directly by electrochemical (anodized) or chemical (chemical bath tank) methods.

In the first place, a structural, morphological and compositional characterization of the oxide layers was carried out. Next, its electrochemical response has been explored in darkness and under illumination in the ultraviolet-visible(1) range. In this way, fundamental information on the load transfer processes has been obtained and the applicability of the layer for the cathodic photoprotection of the substrate will be evaluated.

Finally the modification of the nanostructured layer is proposed by depositing a second semiconductor, such as tungsten oxide or adsorbing species so that the protection can be effective even during short periods in darkness.

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M-LRF07

CHARACTERIZATION OF FERROCENE-TERMINATED SELF-ASSEMBLED MONOLAYERS ON GOLD ELECTRODES.

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Keywords: Electroactive *SAMs/alkanethiols/ferrocene/mixed monolayers*

Self-assembled monolayers (SAMs) attract much interest because of their unprecedented simplicity and versatility to tune the interfacial properties at surfaces by mimicking intermolecular interactions similarly to what occurs in membranes and biological systems. The most widely studied SAMs are mercapto-derivatives with alkyl chains of different length and terminal groups that adsorb on metal substrates. The energy balance between the S-Au bond formation and intermolecular interactions leads to the spontaneous organization of SAMs into different structures depending on the conditions employed during the assembly process (e.g. type of substrate, solvent, thiol concentration in the modification solution or temperature). The final SAM organization may reach semi- or crystalline structures with alkyl chains well-packed and functional groups exposed at the interface. [1]

This works aims to characterize alkanethiol SAMs of different chain length with redox-active terminal groups formed on a polycrystalline gold electrode. In particular, ferrocene moieties (Fc) grafted to hexane- (SHC_6Fc) and undecanethiol ($SHC_{11}Fc$) molecules have been used as the electroactive element. [1] The surface-confined redox reaction due to the ferrocene-terminated SAMs deposited on Au is studied by means of cyclic voltammetry (CV) at different scan rates in a 0.1 M $NaClO_4$ solution. Two overlapped voltammetric signals were clearly discernible at the SHC_6Fc and $SHC_{11}FC$ SAMs with their redox potentials displaced at higher values upon increasing the alkyl chain length. The surface charge density and coverage of the Fc groups were determined from the integrated area under the CV peaks, and the electron transfer rate (ET) constants calculated for each type of Fc population at the SAMs upon peak deconvolution by applying the Laviron´s formalism.

Redox SAMs are of especial interest because they are considered a model system to study interfacial ET. ET rate is affected by the dielectric medium, distance and orientation of the redox groups relative to the electrode and between neighbouring moieties. Thus, the majority of the applications of these systems are based on the formation of mixed SAMs with two or more components (i.e. binary or ternary monolayers) in order to control the distance between neighbouring groups and proper orientation to the surface. [2] Then, the surface ratio of diluent molecules to redox-active ones SAMs is a key aspect to control ET that can be tuned by changing the molar fraction of each component at the modification solution. In this work, mixed alkanethiol and ferrocene-terminated SAMs were formed for different molar fractions of each component in solution. These SAMs were electrochemically characterized as described above for the pure SAMs.

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M-MAA08

ELECTROCHEMICAL SYNTHESIS OF CARBON-SUPPORTED Pd(Zn) AND Pd(Cu) CORE-SHELL NANOPARTICLES AS CATALYSTS FOR OXYGEN REDUCTION

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Keywords: *core-shell nanoparticles; electrodeposition; galvanic exchange; oxygen reduction reaction.*

Recent adverse events regarding energy sources made us realize the importance and imperative need to find and enhance alternative ways that would allow countries to have an independent energy policy and face the fossil fuel problems. Fuel cells are potentially suitable devices due to their scarce environmental impact. The problem of fuel cells lies in the kinetics of the reactions involved. Pt appears to be the best catalyst for the oxygen reduction reaction (ORR). However, it is expensive and scarce on the Earth and therefore, alternative catalysts are being studied. Previous computational studies have shown that palladium-metal (Pd@M) core-shell nanostructures could have a high performance due to the displacement of the d-band of Pd due to the electronic effect of the core metal, which appears to be one of the most determining factors in the catalytic activity [1]. In this work, carbon supported Pd(Zn) and Pd(Cu) core-shell nanoparticles were synthesized by two-step process (electrodeposition of the non-noble metal on supporting carbon and consecutive galvanic exchange to build up the Pd shell). The characterization of the nanoparticles was carried out by transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX). A TEM image of the Pd@Zn sample is shown in Fig. 1. The activity of the different electrocatalysts in front of the ORR was studied by linear sweep voltammetry using the rotating disk electrode (RDE) technique. Figure 2 compares the results obtained using different core-shell structures. A limiting current density of 3.5 mA·cm^{-2} for the Pd@Cu/C core-shell structure was determined in O_2-saturated 0.5 M H_2SO_4, which is smaller than that for Pt (5.5 mA·cm^{-2}). The experimental work is being continued to establish the lines for its further improvement.

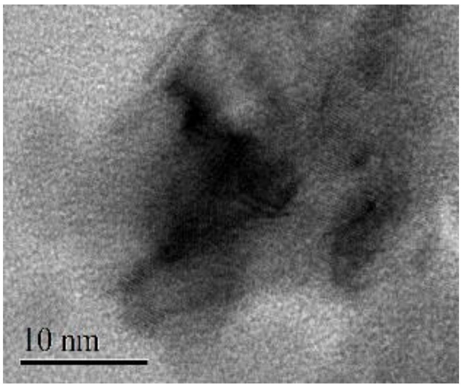

Figure 1. TEM image of Pd@Zn/C.

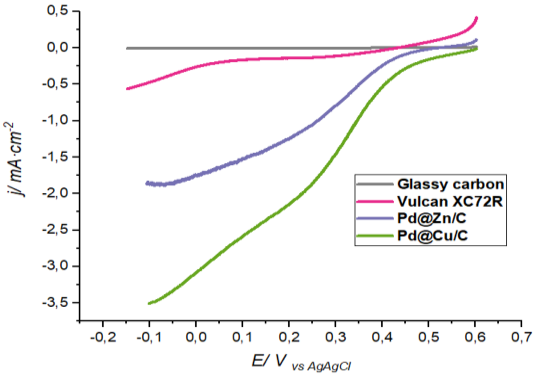

Figure 2. Linear sweep voltammograms for the ORR on the RDE at 500 rpm and 5 mV·s^{-1} in O_2-saturated 0.5M H_2SO_4.

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M-MGA09

A PRELIMINARY ELECTROCHEMICAL STUDY OF QUINONES AND LYSOZYME AS A MODEL SYSTEM IN CONFORMATIONAL DISEASES

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Keywords: *protein electrochemistry, lysozyme, hydroquinone, 1,4-benzoquinone*

Neurodegenerative amyloid disorders (e.g. Alzheimer and Parkinson diseases) are driven by protein misfolding. The hallmark of such diseases is the formation of soluble toxic oligomers or insoluble fibrils with a cross β-sheet structure that accumulate intra- or extracellularly. [1] A wide range of analytical techniques has been used to clarify the amyloidogenic mechanisms and the transient pre-fibrillar oligomers involved to find therapies. Although protein electrochemistry is well stablished, electrochemical methods have emerged for the redox-mediated or label-free detection of proteins/biomarkers at the early stages of aggregation, which might help to point-of-care detection and personalized healthcare.[2] Lysozyme is amyloidogenic and a model protein for investigation of the misfolding events underlying conformational diseases. [3] Thus, a preliminary study of the electrochemical behaviour of native hen egg white lysozyme (HEWL) is performed in glycine (pH=2) and phosphate (pH=7) saline buffers, since fibrillation may be triggered under such conditions upon increasing the temperature. The irreversible oxidation signal of the HEWL will be used to optimize the potential and time of accumulation for its detection using a glassy carbon electrode (GCE).

Polyphenols and quinones have been reported to inhibit protein amyloidogenesis and reduce toxicity both in vitro and in vivo. [4] Although the inhibition process has been mainly monitored by spectroscopic techniques, the electrochemical characterization of these redox compounds and their protein adducts is scarcely reported. Hydroquinone (HQ) and 1,4 benzoquinone (BQ) are used here as the simplest redox molecules of both family of compounds. They will be studied at a GCE in glycine and phosphate solutions under buffered and unbuffered conditions at different pH and concentration. Thus, experimental conditions will be set-up to study the electrochemical response of HQ or BQ and HEWL mixed at different molar ratios. Finally, a signal amplification strategy based on the design of electrosynthesized molecular imprinted polymers[5] on GCE to bind HEWL will be attempted and the results will be presented if accomplished.

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M-MJA11

BIOELECTROCHEMICAL REDUCTION OF INORGANIC NITROGENOUS COMPOUNDS USING ELECTROACTIVE MICROORGANISMS

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Keywords: *water pollution; biorremediation; bioelectrochemistry; nitrate; biocathode.*

Water pollution and toxic brines production are one of the biggest problems caused by the progressive industrialization of society that demands low cost-efficient solutions. Particularly, the treatment of toxic brines is especially difficult because of its high salinity and the presence of polluting, harmful compounds such as nitrates, nitrites, oxychlorides, heavy metals, ammonium and some aromatic compounds and their derivatives. Conventional chemical and biological water treatments are both expensive and little efficient, so they are unable to be used in the remediation of brines or containing toxic chemicals brines. Bioelectrochemical systems are quite the opposite of the conventional approaches and they are becoming a promising technological alternative for an inexpensive, sustainable elimination of those toxic compounds present in industrial wastewater. In a deeper view, the bioremediation (elimination of pollutants using microorganism) coupled to electrochemical methods is effective enough to be successfully applied to wastewater treatment containing high amounts of salts [1].

In the present work, the denitrifying activity (nitrate and nitrite reductase) of *Haloferax Mediterranei* (HM) haloarchaea has been explored in order to develop a bioelectrochemical system which can be applied to wastewater bioremediation. In the first place, a freshly HM strain was cultivated. Then, different strategies for the immobilization of HM onto platinum, gold and carbonaceous materials (such as glassy carbon) were studied and optimized. The electrochemical response of the biocathode was characterized using several electrochemical techniques like cyclic voltammetry, chronoamperometry and electrochemical impedance spectroscopy, allowing us to find a different behaviour of the biocathode in the presence and absence of HM [2], [3]. UV-vis spectroscopy technique was also used to characterise the adsorption rate of HM at the cathode. Finally, the bioelectrochemical response of the HM immobilised on the optimum electrode substrate was explored using a nitrate fortified sample by analysing the time dependent electrical response in order to determine the ratio of nitrate depletion.

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M-MJA12

DEVELOPMENT AND CHARACTERIZATION OF GLASSY CARBON ELECTRODES MODIFIED WITH POLYANILINE AND COPPER NANOPARTICLES

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Keywords: *antioxidant; glassy carbon electrode; polyaniline; copper nanoparticles*

Antioxidants are widely used in food industry and play a major role in the protection of our organism from the oxidative stress caused by reactive oxygen species [1]. Therefore, it is important to be able to measure the antioxidant capacity of the different antioxidant compounds we may found in our food, in order to know how well protected is our food from oxidation and spoilage.

There are a few methods used in the determination of antioxidant capacity based on spectrophotometric measurements, such as FRAP, CUPRAC and DPPH. However, these traditionally used methods present some inconvenience. Since they are based on spectrophotometric measurements, a bigger error is obtained if working with coloured samples. Electrochemical methods are presented as a solution to this problem, since they don't present this kind of inconvenience.

The aim of this work is to investigate, develop and characterize electrodes which can be used as sensors for the antioxidant capacity of a wide range of samples.

To develop these electrodes, a glassy carbon electrode has been modified on its surface with a polymer, polyaniline, using cyclic voltammetry. Once the polyaniline has been placed on the GCE, Cu nanoparticles are placed on our electrode by a method of electrodeposition.

This modified electrode has been used to carry out the determination of the antioxidant capacity of different antioxidants, based on the measurement of the reduction peak intensity and its decrease when the antioxidant compound is added. The antioxidants used in this work were ascorbic acid, galic acid and trolox. The electrodes were characterized by SEM in the different stages of the development.

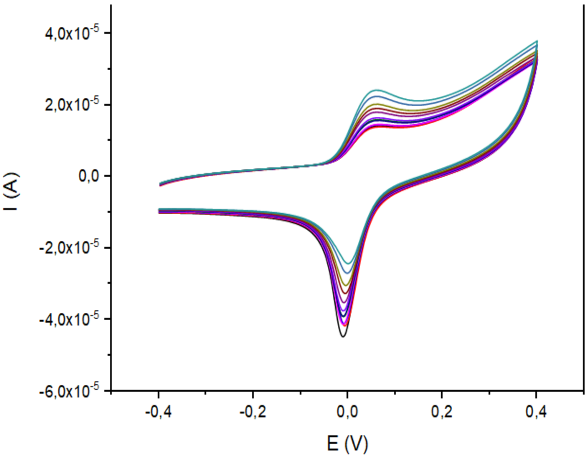

Figure 1. GCE cyclic voltammograms when added different quantities of ascorbic acid

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M-MCM13

CARACTERIZATION OF CONDUCTING POLYMERS AS SOLID CONTACT MATERIAL FOR pH POTENCIOMETRIC SENSORS

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Keywords: *Solid-contact ion selective electrode; Conducting polymers; Ion-selective membrane; Potenciometry; pH electrode*

In this work, the fabrication of single-use, low-cost and robust solid-contact pH-sensitive electrodes (pH-SCISEs) based on conducting polymers was carried out due to the great interest to replace the traditional glass electrode in several applications such as clinical analysis, water treatment, etc. The pH-SCISEs are based on a conductive polymer (CP) film deposited on a plastic / gold support [1] and a photocurable membrane selective to hydrogen ions. As the electroactive material, polypyrrole – block – poly (caprolactone) (PPY-PCL), poly (3,4-ethylenedioxythiophene) – poly (styrene sulfonate) (PEDOT:PSS) high conductivity, poly (3,4-ethylenedioxythiophene) – tetremethacrylate (PEDOT-TMA), poly (3,4-ethylenedioxythiophene) – bis – poly (ethyleneglycol) (PEDOT-PEG) and a Graphene / PEDOT:PSS hybrid ink were used and characterized by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and potenciometry. The response to pH, stability, lifetime, linear range, reproducibility of the different electrodes were studied by potenciometry. Among all the electrodes, pH-SCISEs based on PEDOT-PEG as solid-contact exhibited greater sensitivity and stability values.

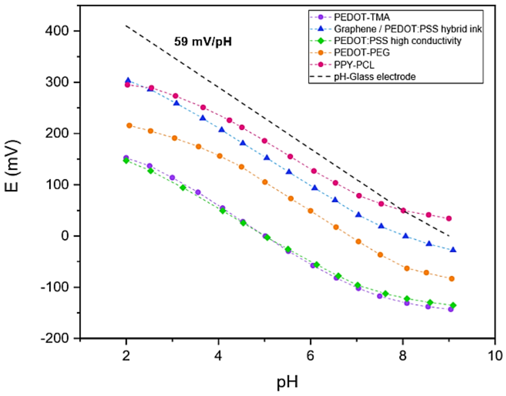

Figure 1. Potenciometric response of the different pH-SCISEs.

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M-OLY14

SURFACE MODIFICATION BY DOPAMINE-ELECTROPOLIMERIZATION ON GLASSY CARBON AND GOLD ELECTRODES. CHARACTERIZATION OF SOME ELECTRODE PROCESSES

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Keywords: *surface modification; dopamine; polydopamine; cyclic voltammetry.*

The electropolymerization of dopamine (DA) for surface modification has been proven to be a simple and effective method in preparing biomaterials [1]. This method is an alternative to DA self-polymerization under alkaline conditions that shows a lower control and efficiency. The film presents adhesion and biocompatibility properties that makes this material useful for adsorption of different compounds and recognition systems with potential applications as membrane interfaces.

Polymer growth at gold electrodes has been investigated as a function of DA concentration, pH, and scan rate by using the electrochemical quartz crystal microbalance (EQCM) and it has been found that the polymer deposition can be significantly inhibited by the solution electrolyte at high concentrations. This film exhibits attractive cationic permselectivity [2].

The present study deals with the preparation and characterization of modified surfaces at both glassy carbon and polycrystalline gold electrodes. A comparative study of electro- and self-polymerization under different experimental conditions is carried out.

Electrochemical processes are used through the work to check the performance of these films. The electropolymerization is performed by cycling the electrode in the appropriate potential window in Tris buffer. Upon increasing the number of cycles, the film growths correspondingly. The presence of these films inhibits the response of ferricyanide redox probe in a fashion proportional to the film thickness (Figure).

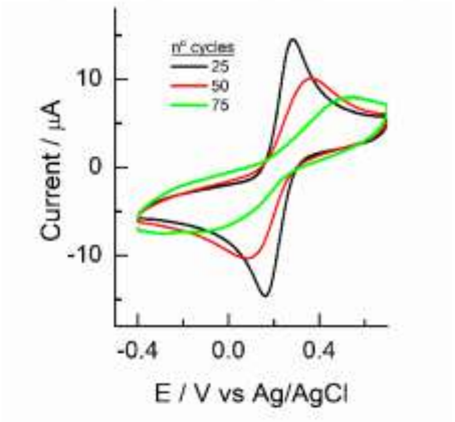

Figure. Typical cyclic voltammograms of ferricyanide recorded with a DA-polymer film-GC electrode.

The study is focused in obtaining a reproducible and stable modified surface for selecting the appropriate strategies for application in selective determination of substances and to be used as biocompatible interface.

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M-RMA15

ELECTRODES BASED ON ORGANIC-INORGANIC PEROVSKITES AS ANODES FOR LITHIUM-ION BATTERIES.

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Keywords: perovskites; mechanochemical synthesis; anode; Li-ion battery.

Currently, rechargeable Lithium-ion battery (LIB) is the main source of energy for many electronic devices (smartphones, tablets, laptops). This type of batteries provides high specific capacity, the low density of lithium makes them light and relatively safe. However, being a booming sector, LIB technology is unable to cope with the dizzying pace of demand for increasingly powerful applications, such as the electric car, making it necessary to research materials in this technology to increase its performance [1].

Recently, perovskites have attracted the interest of the scientific community due to offer efficiencies of approximately 20% in the conversion of solar energy to electricity in photovoltaic cells [2]. It is thus a material with a semiconductor behavior like that of silicon, which, due to its applications in processors and electrical circuits, is scarce and expensive. Recently, it has been suggested that it could be used as an electrode in lithium batteries [3].

This communication presents the mechanochemical synthesis of organic-inorganic hybrid perovskites, from their precursors in solid state, by planetary ball milling. Subsequently, the resulting powder was characterized by various techniques and used for the preparation of electrodes. The $MAPbI_3$, $MAPbBr_3$, $Cs2AgBiBr_6$ and $Cs_2AgSbBr_6$ phases have been obtained with high purity. The proportion of perovskite and electrode additives was optimized to achieve the best results.

Electrochemical measurements for Li-ion batteries have been carried out to evaluate the behavior of these perovskites as anodic active material. The cyclic voltammetries show the sequence of reversible reactions in the electrodes, obtaining values of specific capacity of relative stability along the prolonged cycling, comparable to those previously reported [3].

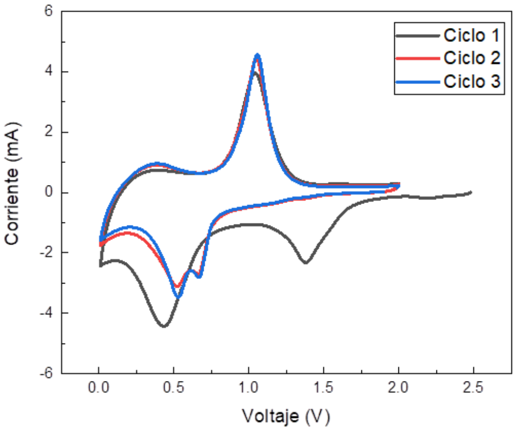

Figure 1. Cyclic voltammetry of perovskite-based electrode as anode in LIB

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M-SSI16

TOWARDS INTERPHASED CALCIUM METAL ANODE BATTERIES

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Keywords: *Calcium batteries; plating; stripping; interface; solid electrolyte interphase.*

Lithium-ion batteries (LIBs) have been considered prospective candidates for new technologies due to its properties and benefits.[1] During first charge of the Li-ion battery the electrolyte undergoes reduction at the negative electrode surface. Upon accumulation of insoluble decomposition products at the electrode surface a passivation layer is formed comprising of inorganic and organic compounds. The passivation layer formed on the electrode surface is named Solid Electrolyte Interphase (SEI) layer and its properties affect the cyclability, life-time, power, and even the safety of the battery.[2] Therefore, the comprehension of the formation of the SEI layer is essential for optimizing the LIB systems. The role of the SEI layer is to prevent further decomposition of the electrolyte during the charge/discharge cycles. Therefore, the SEI layer should present good adhesion, low solubility in the electrolyte and be good electronic insulator and cation conductor.[2] Additionally, its formation occurs in a certain potential range and depends on the electrolyte formulation (solvent, salt and additives).

Yet, Li-ion is slowly but surely reaching its limits and controversial debates on lithium supply cannot be ignored. New sustainable battery chemistries must be developed and Ca or Mg metal anodes are very appealing alternatives which could bring a breakthrough in terms of energy density relying on much more abundant elements.[3,4] Pioneering work by Aurbach et al. allowed to conclude that the electrochemical behaviour of Ca and Mg metal anode is conventional organic electrolytes is surface-film controlled, as is the case for Li, but Ca and Mg plating is virtually impossible, which was attributed to the lack of divalent cation transport through the SEI. Nonetheless, the host laboratory recently demonstrated that calcium can be reversibly plated and stripped through a stable SEI layer.[5]

The current study aim at further investigating Ca plating and stripping as well as the SEI formation by means of Electrochemical Quartz Crystal Microbalance (EQCM) and Electrochemical Impedance Spectroscopy (EIS).

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M-STL17

GE ANODE MATERIALS FOR LITHIUM-ION BATTERIES

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Keywords: *batteries; germanium anode; LiBs; capacity.*

In recent years, the demand in portable electronics, electric vehicles and stationary grid storage have raised of energy storage devices. Recently, the great part of the energy storage devices as based on lithium ion batteries (LIBs) due to their feature such as high lifetime and rechargeable.

In this field, the purpose of improve the features of LIBs modifying graphite anode (theoretical capacity 372 mA h g-1) by group IV elements, such as Si, Sn and Ge is carry out. These elements have concerned attention owing to high theoretical capacity, fast charge carrier mobility and safety characteristic.

Ge anodes display theoretical capacity of 1600 mA h g^{-1} and present a high lithium ion diffusivity (400 times higher than Si) and a high electronic conductivity (10^4 times higher than Si). Though the electrochemical lithiation and de-lithiation of Ge sources huge volume changes which results in anode cracking. For this reason, we need a nanostructure material that mitigated the stress caused by volume expansion. [1]

Here we report an α-Ge material as anode for high capacity LIBs. The nanoparticles of Ge (100-150nm) were obtained by a fast and easy method to produce highly stable isopropanol/water (4:1) suspensions by liquid-phase exfoliation of germanium crystals in a process assisted by sonication. The anode was performed by slurry method, with a mixture of 1:1 carboxy methyl cellulose (CMC) as binder and Vapor Grown Carbon Fibers VGCF) (% in weight) as conducting support to therefore spraying the Ge-nanoparticles scattering over the dry slurry. The amount of active material used in the anode electrode was ≈ 0.5 mg. Coin semi-cell 2032 is conformed with Li metal as reference and counter electrode, Ge as working electrode and 1M $LiPF_6$ ethylene carbonate and dimethyl carbonate (EC:DMC) (1/1 V%) and 5% Vinyl carbonate (VC) as electrolyte.

The electrochemical performance of Ge semi-cell was analysed by cyclic voltammetry at different scan rate 0.1-5 mV/s. The first lithiation scans shows three characterises peaks located at (0.28, 0.15, 0.017 V vs Li/Li^+) that described both the lithium insertion and the formation of Ge-alloys.

The reverse scan shows the de-lithiation and characteristic peak about 0.5 V vs Li/Li^+ is shown (Figure 1).[2].

On the other hand, we studied a charge/discharge cycles at a current rate of 0.1C (160 mA g^{-1}). In the first cycles we have obtained specific capacity of 289.6 mA h g^{-1} for discharge and 227.1 mA h g^{-1} for charge. These values are still below of other values that it obtained in the literature.

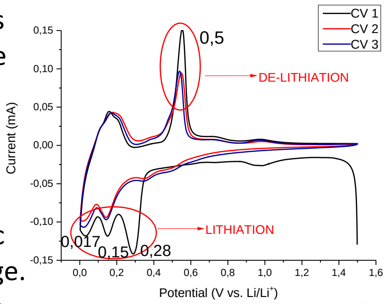

Figure 1. Cyclic voltammetry of Ge scan rate 0.1 mVs^{-1}

In the next step, a different Ge-anode preparation methods will be made and we will be proven to increase the amount of active materials for a better results.

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M-SPF18

STUDY OF NICKEL NANOPARTICLES ENCAPSULATED IN GRAPHITIZED CARBONS AS AN ELECTRODE FOR LI-ION BATTERIES

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***Keywords**: graphite; Ni nanocrystals; anode; Li-ion batteries*

A graphite/Ni composite was prepared via thermal decomposition of a nickel oleate complex at 700 ^{o}C [1], yielding disperse Ni nanocrystals (20 mm average size), encapsulated by a graphite matrix as deduced from transmission electron microscopy and confirmed using X-ray photoelectron spectroscopy. The X-ray diffraction pattern revealed a good ordering of the carbon layers forced by the Ni encapsulation to adopt a bending structure.

Considering the close interaction between the graphitized frameworks and metallic nanoparticles, the properties of the composite as an anode for Li-ion batteries were studied. The discharge/charge profiles of this carbon are more similar to those of graphitized carbons [2] than to those of more disordered carbons like carbon nanotubes [3]. In these carbons, a strong polarization is observed between the discharge and charge curves, and an abnormally high irreversible capacity as a result.

At moderate rate values, 0.25 C, the electrode delivers an average capacity value around 723 mAh g^{1} on cycling.The rate capability measurements confirmed a progressive drop in the capacity of the electrode, more pronounced in the interval ranging from 0.1 to 0.6 C. When the current is restored to 0.1 C, the electrode recovers most of its capacity, around 815 mAhg^{-1}.

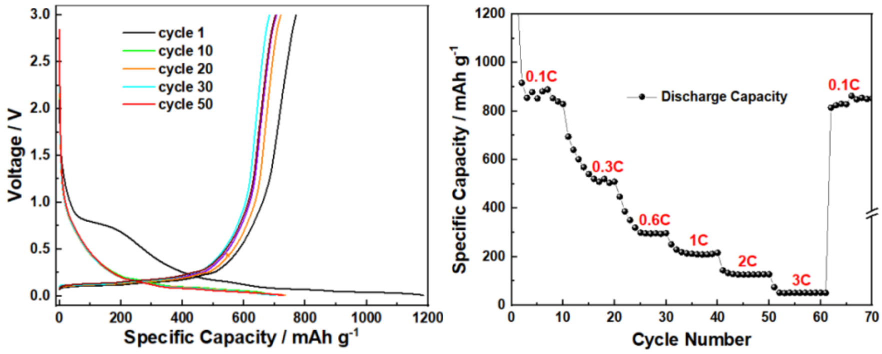

Figure 1. Galvanostatic discharge/charge curves and rate capability test for graphite/Ni composite electrode.

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M-TBA19

LI-S BATTERIES ELECTRODES BASED ON REGENERATED CARBONS USED IN GAS FILTERS.

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Keywords: *active carbons; lithium-sulfur battery; cathode; WWTP*

Li-S battery technology, in terms of capacity and energy density (1675 mAh / kg and 2500 Wh / kg), is really competitive, clearly surpassing other batteries such as Li-ion (≈ 250 Wh / kg) [1, 2] However, it also has drawbacks that limit its practical development, highlighting the conductive electrical behaviour of sulfur; The physical, morphological and volume changes during the electrochemical reactions and the solubility of the polysulfides, which lead to a gradual loss of performance. To address these problems, it's possible to take advantage of the greater conductivity and the surface area, that the active carbons present, using them as a matrix for the insertion of elemental sulfur in their pores. So they can be used as positive electrodes (cathode) in these Li-S batteries [3]. These coals can proceed to the revaluation of industrial agricultural waste, rising in this work the use of filters used for odorous gaseous emissions in a Wastewater Treatment Plant (WWTP).

The regeneration of the active coals has been carried out through a process of controlled pyrolysis in an oxidizing atmosphere up to a temperature not higher than 350 °C. With the regenerated samples, we have proceeded to determine their main physical-chemical properties through the use of material analysis techniques such as X-ray diffraction, isotherms of adsorption-desorption nitrogen and thermogravimetric analysis. The data reveals the possibility of regenerating these filters obtaining coals with the textural properties required for their use as electrodes.

Carbon and sulfur compounds have been produced from these carbons, which are tested as cathodes in Li-S batteries. The cells have been analysed electrochemically with techniques such as cyclic voltammetry, observing processes of high reversibility, as well as charge and discharge cycles at a constant current, demonstrating that the battery releases a specific practice capacity of remarkable values and high stability (Figure 1).

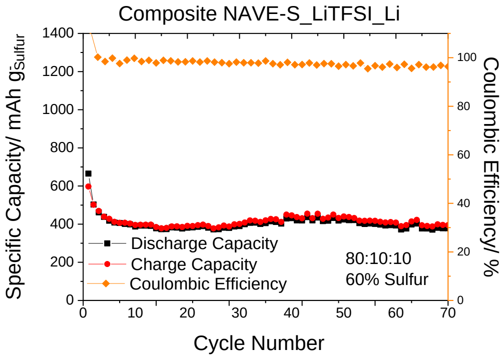

Figure 1. Charge and Discharge cycles at constant current.

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M-ZMC20

ELECTRICAL MODEL TO UNRAVEL DIFUSIONAL PROCESSES FOR THE DESIGN OF INTEGRATED MICROPOTENTIOSTATS

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Keywords: *Impedance Spectroscopy; Warburg impedance; Diffusional processes; Equivalent circuits; Amperometry; Micro-potentiostats;*

In electrochemical sensing, in situ detection requires miniaturization and integration of both electrodes and potentiostats. Micro-potentiostats based on silicon integrated electronics promises great compactness (1 mm x 1 mm) while maintaining all the functionalities needed for electrochemical analysis. Since such circuits are specific for the target application and their monolithic implementation prevents them to be reconfigured against with several decades of variation of the electrochemical parameters (i.e. dynamic potential/current range, sensitivity, etc.) cannot be modified after fabrication. For this reason, it is crucial to know the electrochemical conditions of the system during the design of the micro-potentiostat since, once stablished they cannot be changed. Thus, a reliable electrical model of the electrochemical system is necessary during the design and simulation of the integrated micro-potentiostats.

Impedimetric models of electrochemical systems have been already proposed although still being a subject of discussion. Most of the controversy remains in the modelling of the diffusion of electroactive species by the Warburg element, which cannot be fitted with a simple resistor or capacitor in the electrical model. To solve this issue, different configurations based on parallel RC circuits have been already presented, which adjust to the response of the Warburg element [1].

This communication presents a novel approach for fitting the Warburg element with minimum error and simplicity. Based on previous publications, this theoretical model adjusts the impedance module decay associated to diffusion in the electrical circuit (in dB/decade) by means of a combination of n parallel RC circuits. The modelling is performed with a Python algorithm capable of processing circuits with values of R and C that, added together, adjust to the drop of the Warburg element.

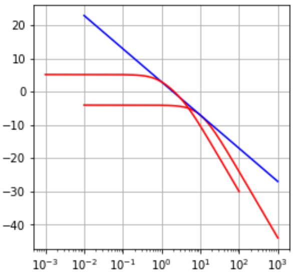

Figure 1. Bode's diagram of Warburg in EIS (blue) and through RC approximants (red)

To validate the model, results are compared with the experimental response of screen-printed microelectrodes measured with a custom-made micro-potientiostat, both of them manufactured at IMB-CNM facilities. Cyclic voltammetry and electrochemical impedance spectroscopy are used in order to analyse the diffusional processes of reduction pattern of ferricyanide.

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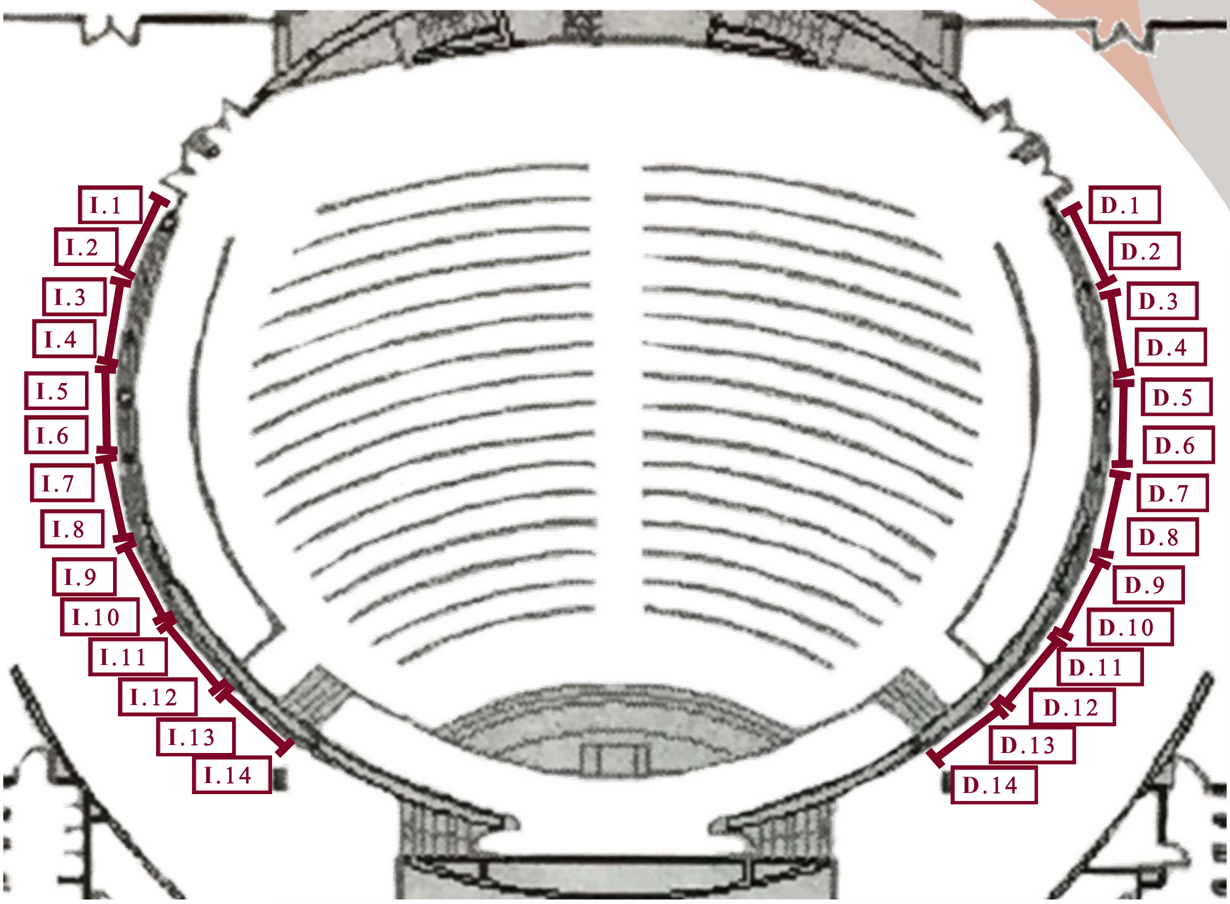

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P-ECE01

THREE-LAYERED FILMS OF CONDUCTING POLYMERS AS ELECTROCHEMICAL SUPERCAPACITORS. ENHANCEMENT OF CHARGE STORAGE CAPACITY BY NANOPHASE-SEGREGATION IN THE DIELECTRIC LAYER

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Keywords: *three-layered films;* poly(3,4-ethylenedioxythiophene)*; N-methylpyrrole; 3,4-ethylenedioxythiophene-co-N-methylpyrrole .*

Properties related with the charge storage capacity have been evaluated for three-layered films made with two sheets of poly(3,4-ethylenedioxythiophene) separated by a sheet of poly(N-methylpyrrole) or poly(3,4-ethylenedioxythiophene-co-N-methylpyrrole).

The most distinctive trend of the copolymer, which shows electrochemical properties intermediate between those of the two homopolymers, is the formation of a biphasic structure, EDOT- and NMPy-rich blocks organizing separately. The ability to exchange charge reversibly is higher for 3l-PEDOT/P(EDOT-co-NMPy) than for 3l-PEDOT/PNMPy, the electroactivity and electrostability of such two 3-layered films being significantly better than that of single-layered PEDOT. Advantages of 3l-PEDOT/P(EDOT-co-NMPy) are mainly based on the nanophase-segregated structure of the copolymer.

Thus, the intermediate layer can be considered as random disposition of ultrathin dielectrics having nanometric length and width. In terms of charge storage, the intermediate layer of 3l-PEDOT/P(EDOT-co-NMPy) can be viewed as a thin reservoir filled of heterogeneously distributed nanometric supercapacitors that are connected in series among them and in parallel to the PEDOT layers.

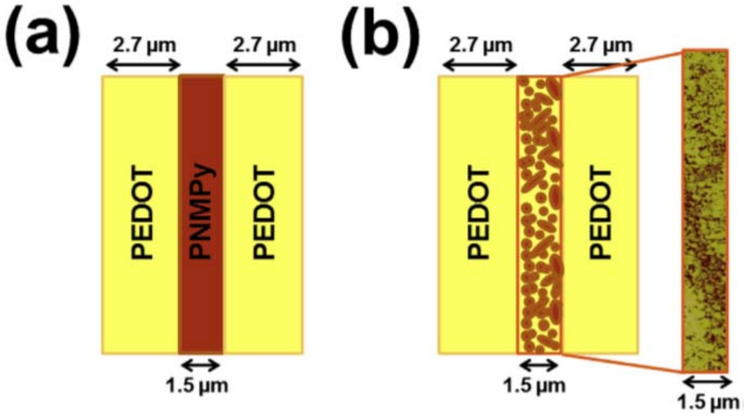

Fig. 1- Scheme illustrating the behavior of (a) 3l-PEDOT/PNMPy and (b) 3l-PEDOT/P(EDOT-co-NMPy) supercapacitors in which the intermediate layer acts as a conventional dielectric layer and a thin reservoir filled of heterogeneously distributed nanometricsupercapacitors, respectively. The AFM phase image (1.5 _ 5 mm2) corresponds to the poly(EDOT-co-NMPy) intermediate layer.

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P-ECE02

RENDIMIENTO ELECTROQUÍMICO MEJORADO EN BATERÍAS LITIO-AZUFRE: USO DE GRAFENO 3D ACTIVADO.

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Palabras clave: *Activación física; grafeno 3D, síntesis hidrotermal; microondas; batería Li-S.*

Hoy en día existe una amplia variedad de baterías comerciales en el mercado. Uno de los tipos más comunes es la batería Litio-ion (LIB), utilizada actualmente en dispositivos electrónicos portátiles. Existe un gran interés en el desarrollo de sistemas de energía de alta densidad de potencia para lograr avances en vehículos eléctricos, así como en energías renovables. Para estas aplicaciones, las baterías de Litio-ion presentan graves deficiencias, debidas principalmente a la limitada energía que suministran los procesos de intercalación química que impulsan la reacción electroquímica [1].

Otras reacciones electroquímicas reversibles, como el proceso de conversión entre Li y S, con una energía específica teórica de 2600 Ah kg^{-1}, pueden llegar a duplicar la energía práctica con respecto a las LIBs comerciales [2]. Sin embargo, las baterías Li-S presentan inconvenientes debido principalmente a problemas de conductividad del material y al “efecto shuttle”. Para abordar este desafío, se han desarrollado varias matrices conductoras para albergar azufre y evitar la disolución del material activo, incluyendo carbones micro/mesoporos, nanotubos de carbono, óxido grafítico y láminas de grafeno como en nuestros estudios previos [3].

En esta comunicación se propone una activación física de grafeno como estrategia para inducir un sistema de microporos en la matriz y mejorar el rendimiento electroquímica de la batería Li-S. Concretamente, se trata de un grafeno tridimensional dopado con nitrógeno sintetizado mediante un proceso hidrotermal asistido por microondas. Seguidamente, se ha activado físicamente con CO_2 en una única etapa; y ha sido utilizado para la preparación de un composite con azufre (A-3DNG/S).

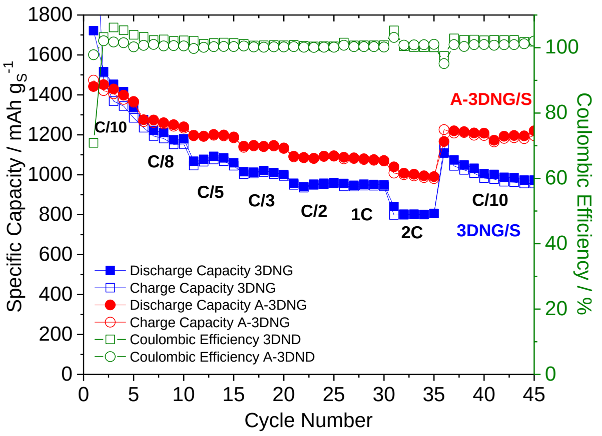

Figura 1. Rate Capability comparativa: 3DNG/S y A-3DNG/S.

En conclusión, la activación física del grafeno es un método simple, limpio y rápido, en particular si se compara con los métodos de activación química, y conduce a un rendimiento mejorado en la batería Li-S. El composite A-3DNG/S exhibió propiedades electroquímicas sobresalientes, como una capacidad de velocidad excelente (1000 mAh g^{-1} a 2C), alta capacidad reversible y estabilidad de ciclos (capacidad promedio ~800 mAh g^{-1} a 1C después de 200 ciclos), valores que superan los medidos en grafeno químicamente activado.

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P-ECE03

BATERÍAS LI-ION DE ALTO VOLTAJE BASADAS EN ESPINELA Y GRAFITO RECICLADO.

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Palabras clave: *espodumeno; espinela; grafito reciclado; full cell; baterías de ion litio*

La creciente preocupación por problemas como el calentamiento global y el efecto invernadero está propiciando una mayor investigación por otras fuentes de energía alternativas a los combustibles fósiles para su uso en vehículos eléctricos. Uno de los dispositivos más prometedores son las baterías ion litio (LIBs) debido a su alta densidad energética y menor impacto ambiental. Las materias primas para su producción están basadas en compuestos de intercalación de Li para el cátodo y grafito en el ánodo. Para el cátodo la principal fuente de de Li es el Li_2CO_3 obtenido a partir de salmueras de los salares, y en menor proporción a partir de fuentes minerales como el espodumeno. Mientras, la producción del ánodo procede principalmente del grafito natural. Por lo tanto, en el presente trabajo se ha estudiado una espinela de composición $LiMn_{1.5}Ni_{0.5}O_4$ como material catódico sintetizada con LiCl producido a partir del espodumeno y grafito reciclado de LIBs como material anódico, analizando su comportamiento electroquímico en LIBs de alto voltaje.

En los resultados electroquímicos, los perfiles galvanostáticos de $LiNi_{0.5}Mn_{1.5}O_4$ vs. Li/Li^+ en el rango de voltaje entre 3.5-4.9 V reflejaron que la mayor parte de la capacidad suministrada procede de la oxidación Ni^{2+} a Ni^{4+}, entre 4.5-4.7 V. Además, se observó una pequeña meseta a 4.0 V, indicando un menor contenido de Mn^{3+} y vacantes de O_2 en la estructura. Los valores iniciales de capacidad de carga y descarga a 0.2 C fueron de 146 y 118 mAh g^{-1}, respectivamente, mostrando una retención de la capacidad del 60 % a los 50 ciclos. Es importante el papel que juega el pequeño contenido de Mn^{3+} y vacantes de oxígeno en la obtención de material de alto rendimiento [1]. Para el grafito reciclado, las capacidades iniciales de carga y descarga a 0.2 C fueron 395 y 315 mAh g^{-1}, respectivamente, con una retención del 98 % a los 50 ciclos. Finalmente, la configuración en *full cell* de ambos materiales mostró altos valores de capacidades iniciales de carga y descarga de 599 y 482 mAh g^{-1}, respectivamente (referidos al ánodo), manteniéndose en 170 mAh g^{-1} después de los 50 ciclos [2].

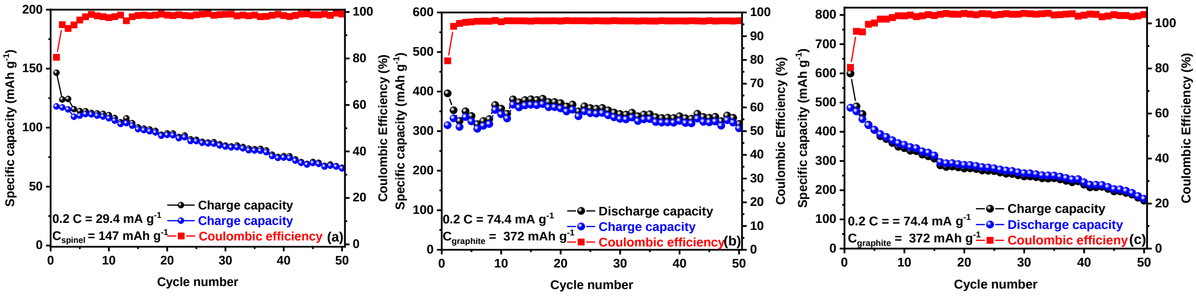

Figura 1. Rendimiento de ciclaje a 0.2 C: a) $Li_2Ni_{0.5}Mn_{1.5}O_4$; b) grafito reciclado; c) configuración en full cell.

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P-ECE04

PERFORMANCE OF LEAD-ACID BATTERIES WITH METALLIC IMPURITIES IN THE ELECTROLYTE

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Keywords: *Impurity; Hydrogen Evolution Reaction; Oxygen Evolution Reaction, Lead Acid Batteries.*

Abstract:

The presence of metallic elements after the production process is one of the difficult points to resolve in the lead acid batteries (LABs). These metallic impurities can be harmful for the performance, since, the theory affirms that the same impurities are electrocatalysts of two important reactions: Hydrogen Evolution Reaction (HER) and Oxygen Evolution Reaction (OER)[1].

During the charge process, the lead (II) sulfate reacts through oxidation (positive plate) or reduction (negative plate)[2], but at high rate charge the mass transport increases and it develops the reactions previously mentioned: HER (negative plate) and OER (positive plate). These last two secondary reactions have a direct relation with the water consumption, being one of the causes of the cycling life reduction of LABs.

Therefore, the objective of this study is to know in deep which impurity catalyses the hydrogen or oxygen gassing or both, and to fix the limit impurity concentration in the electrolyte in order to avoid this problem.

The experimental equipment for the study was a three-electrode cell using a lead rotating disk electrode (RDE) as working electrode, Hg/HgSO4 electrode as reference electrode, a big lead as counter electrode. The electrolyte was 1.28 sg H_2SO_4, recreating the same electrolyte concentration used in commercial batteries. Through cyclic voltammetry and linear voltammetry different tests was carried out and, Tafel parameters and the exchange current density of the reactions were determined.

The information obtained with the study will mark the beginning points for a new one, where it will measure the impurity effect in 2 V/ 1 Ah cells through electrical tests: Capacity (C_{20}), Initial Charge Acceptance (ICA), Tafel and Cycles with 17.5% Depth of Discharge (DOD).

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P-ECE05

CATIONIC MEMBRANE EFFECT ON THE BEHAVIOUR OF AN ACID-BASE ELECTROCHEMICAL FLOW BATTERY

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Keywords: *hydrogen; energy storage system; redox flow battery; acid; base.*

The growing concern about climate change and the increase of global energy demand require the development of new energy generation technologies whose sources are not based on fossil fuels but on inexhaustible resources of nature. Moreover, it is not only necessary to develop accumulators that allow energy to be obtained and stored efficiently from these sources, but also systems where the chemicals used were environmentally friendly.

A redox flow battery is an electrochemical energy storage device that converts chemical energy into electrical energy through reversible oxidation and reduction of working fluids [1]. Based on this concept, an Acid-Base Electrochemical Flow Battery (ABEFB) was developed as a pseudo-redox flow battery [2]. This system is composed of acidic and alkaline solutions, both with a high supporting electrolyte concentration, which are separated by a cationic exchange membrane. Hydrogen oxidation and evolution reactions take place during the charge and discharge processes, which acidifies or basifies the electrolytes. The neutralization energy obtained from these solutions is used as electromotive force [2]. In this case, HCl and NaOH are used as electrolytes, NaCl as supporting electrolyte, a platinised Pt electrode as cathode, a Pt-catalysed gas diffusion electrode as anode (catalyst loading of 0.5 mg cm^{-2}) and a cationic membrane as ionic separator.

In this work, the effect of the cationic membrane on the behaviour of the ABEFB has been systematically studied. Different membranes (Nafion® 112, Nafion® 117, Nafion® 450 and Selemion™ CSO (with different thickness, morphology and structure) have been tested. Polarization and power curves and charging/discharging cycles have been carried out to analyse the influence of the cationic membrane on the electrochemical response.

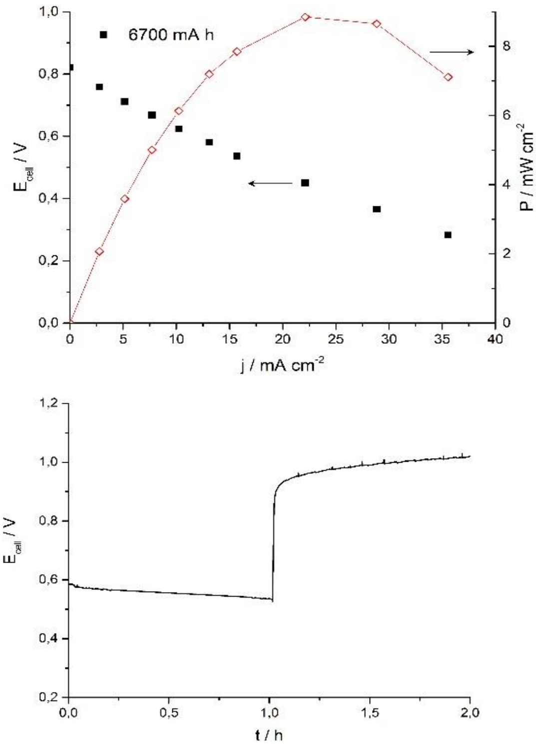

Figure 1. Electrochemical behaviour with Nafion® 117: a) discharging curve (left axis), and power curve (right axis). b) charging/discharging cycles for charge capacity of 6700 mA h at 12,5 mA cm^{-2}

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P-ECE06

MATERIALES GRAFÉNICOS COMO SOPORTE DE ELECTROCATALIZADORES PARA LA REACCIÓN DE REDUCCIÓN DE OXÍGENO

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Keywords: materiales grafénicos, electrorreducción de oxígeno, PEMFC

Los materiales grafénicos (MGs) han recibido especial atención como soportes de catalizadores para pilas de combustible de electrolito polimérico (PEMFC) debido a su elevada área superficial, alta conductividad y resistencia mecánica [1]. La utilización de estos MGs como soporte podría suponer una mejora del rendimiento de estos sistemas electroquímicos favoreciendo la actividad catalítica en el cátodo debido al efecto sinérgico soporte-metal del catalizador [2].

En el presente trabajo, se sintetizaron catalizadores de Pt fueron soportados sobre carbono Vulcan y diferentes MGs empleando el método de reducción con ácido fórmico. Todos los MGs fueron sintetizados mediante el método de Hummers modificado [3], realizando una posterior reducción con citrato sódico y dimetilsulfóxido (DMSO), para sintetizar óxido de grafeno reducido (rGO) y rGO dopado con azufre (S-rGO), respectivamente. La estructura, morfología y propiedades de los materiales sintetizados fueron caracterizadas mediante técnicas de rayos X, como la difracción (XRD) y la energía dispersiva (EDX), microscopía electrónica de transmisión (TEM) y espectroscopía Raman.

Se evaluó la respuesta electroquímica de los catalizadores respecto a la reacción de reducción de oxígeno (ORR) en una estación de prueba para PEMFC. El contenido de Pt en ambos electrodos fue de 0,35 $mg_{Pt}\cdot cm^{-2}$ con una carga metálica del 20 % en peso. El catalizador empleado en el ánodo fue Pt comercial (20 wt. % Pt/C, ETEK) en todos los casos. Se suministraron hidrógeno puro y oxígeno al ánodo y al cátodo, respectivamente, y se emplearon temperaturas de trabajo de 30, 60 y 90 °C.

Los principales resultados indican una alta correlación entre las propiedades fisicoquímicas de los materiales preparados y el rendimiento catalítico desarrollado en la PEMFC.

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Los autores agradecen al Ministerio de Ciencia, Innovación y Universidades (MICINN) por la financiación del proyecto ENE2017-83976 -C2-2-R (FEDER) y al SEGAI por su colaboración. L.M.R. agradece a la Agencia Canaria de Innovación, Investigación y Sociedad de la Información y (ACIISI) y GG al programa Viera y Clavijo (ACIISI & ULL) por los contratos pre- y post-doctoral, respectivamente.

P-ECE07

ELECTROCHEMICAL SYNTHESIS OF PtSn(Cu)/C ELECTROCATALYSTS FOR ALCOHOL ELECTROOXIDATION: EFFECT OF Cu DEPOSITION POTENTIAL AND Sn DEPOSITION TIME.

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Keywords: *PtSn(Cu)/C electrocatalysts; methanol oxidation; ethanol oxidation; Cu deposition; spontaneous deposition.*

PtSn supported catalysts are currently considered as an efficient and economical formulation for the oxidation of alcohol in fuel cells [1]. PtSn (Cu) / C electrocatalysts have been synthesized on Vulcan XC72R in glassy carbon electrode in a three-stage electrochemical process. In the first stage, a controlled amount of Cu was electrodeposited on the substrate and the effect of the deposition potential on the characteristics of the catalyst was studied by cyclic voltammetry. The second and third stage of the synthesis uses spontaneous surface replacement of Cu by Pt resulted in Pt (Cu) / C and later of Sn species on Pt (Cu) / C, obtaining PtSn (Cu) / C. The characteristic features of Pt surface electrochemistry (hydrogen adsorption/desorption peaks and oxide formation/stripping wave/peak are clearly observed at the Pt(Cu)/C catalysts.

The PtSn (Cu) / C catalysts obtained by immersion in 1.0 mM $SnCl_2$ + 0.5 M H_2SO_4 presented voltammograms that show widening of the double layer region which increases with the time of spontaneous deposition. In addition, decrease in hydrogen adsorption/desorption peaks was observed. The latter suggests formation of SnO_2 in the shell. (Figure 1 A). The oxidation of methanol and ethanol in sulfuric acid on PtSn (Cu) / C showed onset potentials close to 0.05V(vs Ag/AgCl(sat), which are lower than those obtained on Pt (Cu) / C and PtRu /C (commercial catalyst). The catalysts of PtSn (Cu) / C obtained from Cu nuclei deposited at -0.10V and 15 minutes of spontaneous Sn deposition was more efficient for the oxidation of ethanol than those of Pt (Cu) / C and commercial PtRu / C. (Figure 1B).

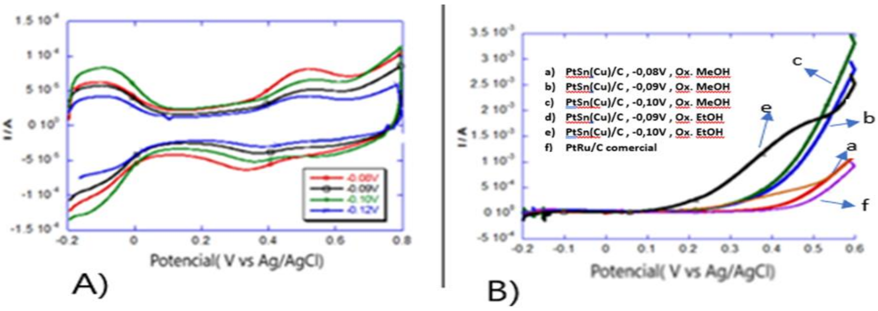

Figure 1. A) Voltammograms (at 20 mVs^{-1} potential scan rate) in a deaerated 0.5M H_2SO_4 of PtSn (Cu) / C synthesized from Cu nuclei deposited at different potentials. B) Voltammograms (at 20 mVs^{-1} potential scan rate) of PtSn (Cu) / C in a deaerated 1.0M MeOH + 0.5M H_2SO_4.

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P-ECE08

SÍNTESIS Y CARACTERIZACIÓN DE ELECTROLITOS POLIMÉRICOS PVA-VAVEOVA-KOH PARA SU APLICACIÓN EN BATERÍAS DE ZN

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Keywords: *Electrolito Polimérico tipo gel; Conductvidad Iónica; Baterías de Zinc; Voltametría Cíclica.*

En las últimas décadas es cada vez mayor el interés de los grupos de investigación por estudiar los electrolitos Poliméricos tipo gel (GPEs), ya que permite eliminar inconvenientes propios de los electrolitos líquidos como las fugas no deseadas, producción de gases, problemas de corrosion y peligro de explosión. Además, presenta ventajas como flexibilidad, buena estabilidad mecánica y térmica, buen contacto electrodo electrolito y facilidad de fabricación[1][2]. Estas propiedades hacen que este tipo de electrolito, sea considerado como excelentes sustitutos de los electrolitos líquidos y ser usados como separadores en baterías, superconductores o celdas de combustibles [3][4].

Los GPEs sintetizados estaban compuestos por PVA, el terpolímero VAVEOVA y diferentes cantidades de KOH, para su aplicación como electrolito en baterías de Zn/aire. Los GPEs una vez sintetizados, se han caracterizaron por diferentes técnicas espectroscópicas y electroquímicas. Como se pueden observar en los resultados de Voltametría Cíclica (Figura 1).

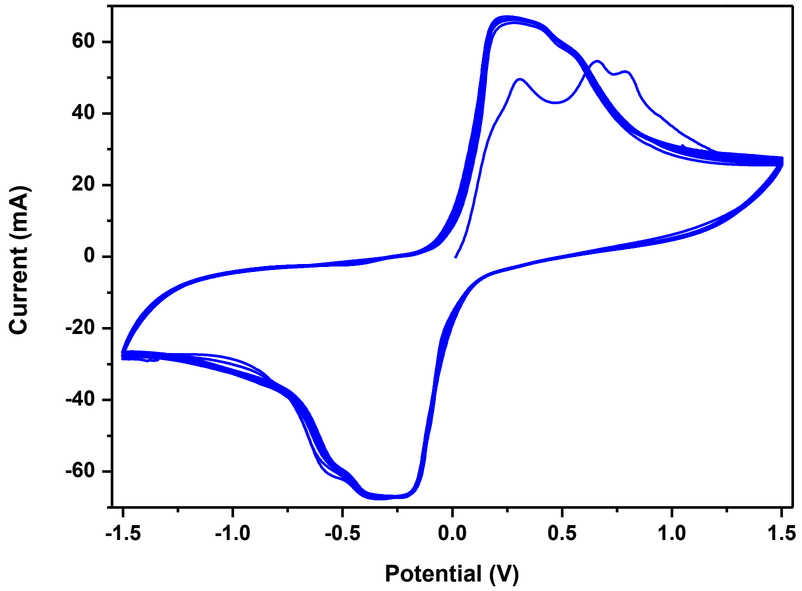

Figura 1. Voltametría Cíclica de GEPs

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P-MOE01

RELATIONSHIPS BETWEEN CHEMICAL PROPERTIES AND HOMO/LUMO ENERGIES USING ELECTROCHEMICAL MEASUREMENTS

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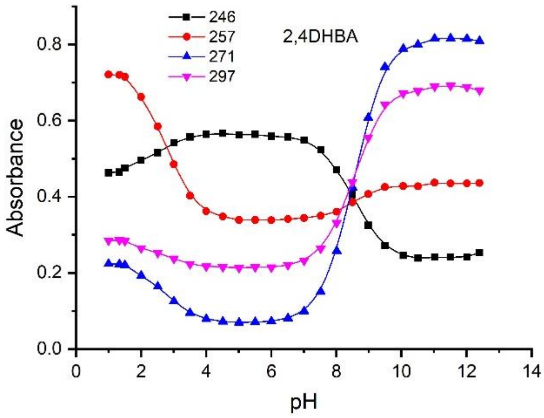
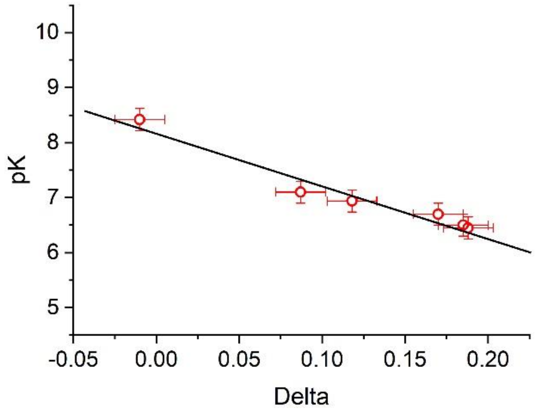
Keywords: *HOMO energies; dissociation constants; structure-reactivity relationship*

The energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) has been used in the understanding of organic reactions. For different species in solution, LUMO energies were related to the reduction potentials and HOMO energies were related to the oxidation potentials. HOMO energies were also related to the oxidation potentials of different compounds, mainly in the solid state. The exploration of the relation between the HOMO and/or LUMO energies and chemical properties as dissociation constants is of undoubtedly interest.

The possible relationships between the HOMO energies and chemical properties (acid dissociation constants) is explored for the dihydroxybenzaldehydes (DHBs) and dihydroxy benzoic acids (DHBAs).

The pK values are obtained by UV-visible spectroscopy, except for 2,6DHBA for which the pK was determined by electrochemical measurements. The left figure shows an example.





The electrochemical behaviour of the different compounds was investigated by linear-sweep cyclic voltammograms, finding the occurrence of reversible or quasi-reversible processes, for half of the derivatives, and irreversible oxidations for the rest.

The differences of the peak potentials of the oxidation peaks of the dissociated and undissociated species (Delta) were obtained in the same conditions of pH, buffer solution and ionic strength. These differences, which are related to the difference in HOMO energies of both forms, showed good correlations with the values of pK, being the correlation for the aldehydes (showed in the right figure) more trustworthy than that observed for the acids.

It was concluded that the oxidation peak potentials in solution can be related to the HOMO energies. A relation between structure and chemical reactivity is proved for these derivatives.

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P-MOE02

CHARACTERIZATION *OF POLYMERS BRUSHES BUILT ON GOLD ELECTRODES.*

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Keywords: *Gold; SAM; monomer; polymer; grafting from*

The need to protect metal surfaces in an industrial way against corrosion, incrustations of biological material, etc., has led to the beginning of research that pursue the modification of surfaces with polymers, converting the growth of polymers into substrates of different nature and form, in a subject of great interest. Many important applications such as anti-corrosive coatings, masks for engravings, lithographs, anti-incrustations, treatments against ice and on photocatalytic surfaces are now being developed within this field [1].

In this work, we describe the construction of a film of polymer brushes on a gold surface by using the "*grafting from*" approach. This consists of the polymerization of the monomer of interest from a surface that is modified with an appropriate initiator or chain transfer agent [2]. Before starting with the construction of the polymer, a self-assembled monolayer (SAM) of 9-mercapto-1-nonanol (MNOH) molecules is built on a gold surface. As a second step, the modification of the -OH terminal groups with α-bromoisobutyryl bromide (BIBB) in the presence of triethylamine is necessary, to get the initiator-modified surface [1]. Finally, the polymerization process is carried out by using different monomers to obtain polymers with different characteristics.

The formed polymers are characterized by using the electrochemical techniques cyclic voltammetry and electrochemical impedance spectroscopy. Other techniques such as infrared-reflection-absorption and X-ray photoelectron spectroscopies and contact angle measurements are also used to get more insight into the nature of the formed polymer layers.

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Ministerio de Economía y Competitividad (MINECO) (Proyectos CTQ2014-60227-R and CTQ-2015-71955-REDT Red de Excelencia Sensores y Biosensores Electroquímicos), Junta de Andalucía (P10-FQM-6408) y Universidad de Córdoba.

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P-MOE03

SYNTHESIS AND CHARACTERIZATION OF GOLD NANOPLATES COVERED WITH POLYETHYLEN GLYCOL SELF ASSEMBLED MONOLAYERS

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Keywords: *gold nanomaterials; EG-SAMs; grafting from; Biomedicine*

The nanomaterials physical and chemical properties allow us to modulate their biological interactions in a way that they become suitable for use as therapy, imaging and diagnostic systems which make them an interesting option for biomedical applications. In this sense, gold nanoparticles of different size and shape have proven to be useful tools [1]. The understanding of how nanomaterials will behave in a biological system relies on the knowledge of the *nano-bio* interface, which is not totally known and is needed to be researched. Nanomaterials coated with self-assembled monolayers (SAMs) of polymers containing oligo- or poly-ethylene glycol (EGn) chain groups are known by their ability to diminish non-specific interactions with biological media [2].

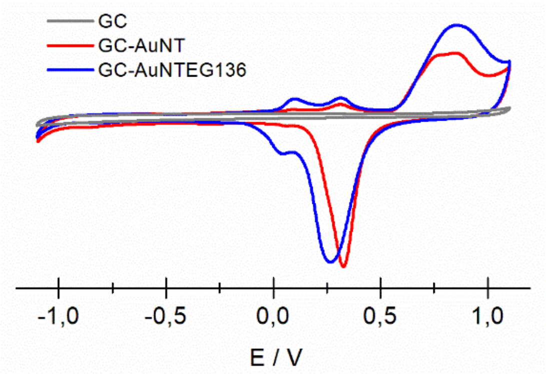

Figure 1. Cyclic voltammograms of the glassy carbon (GC) electrode surface (grey) modified with AuNT (red) and AuNT-EG136 (blue) nanoparticles by employing drop casting technique.

In this work, we present the synthesis and characterization of gold nanoplates (AuNT) that are subsequently coated with OEG polymers (AuNT-EG136) employing the "*grafting to*" approach. We are focused on the stability and general behavior of this nanomaterials in aqueous solutions. As the preparation of AnNT relies on the use of cetyltrimethylammonium chloride (CTAC), a surfactant needed for the separation of the different shapes obtained in the synthesis procedure, we are also interested in the elucidation of the mechanism of adsorption of these molecules and the ability of EGn molecules to displace them from the metal surfaces. The electrochemical characterization is carried out employing cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) and the characterization is complemented by UV-visible-NIR and IR spectroscopies, zeta potential and dynamic light scattering (DLS) measurements.

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Ministerio de Economía y Competitividad (MINECO) (Proyectos CTQ2014-60227-R and CTQ-2015-71955-REDT Red de Excelencia Sensores y Biosensores Electroquímicos) y Universidad de Córdoba; M.C. agradece al Ministerio de Cultura y Deporte Ayuda FPU17/03873.

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P-FEC01

RGB SPECTROELECTROCHEMISTRY AND ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY OF A POLY(AZURE A) FILM

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Keywords: *poly(Azure A); digital video; RGB video electrochemistry; Electrochemical impedance*

Azine-based polymers have been investigated as redox and conducting polymers in the last decades [1]. RGB video electrochemistry proved a powerful tool to investigated the color changes on different electrodes surfaces [2]. In the present work, the electrochemical impedance spectroscopy and the RGB video electrochemistry have been coupled to provide a new vision about the electrochemistry of poly(Azure A) films deposited on transparent indium-tin oxide (ITO) electrodes (Figure 1). The multiparametric analysis of sinusoidal responses of the red, green and blue channels extracted from the digital videos at 30 frames per second showed interesting information about the RGB intensity amplitude relation among the three channels at different oxidation states of the film [3].

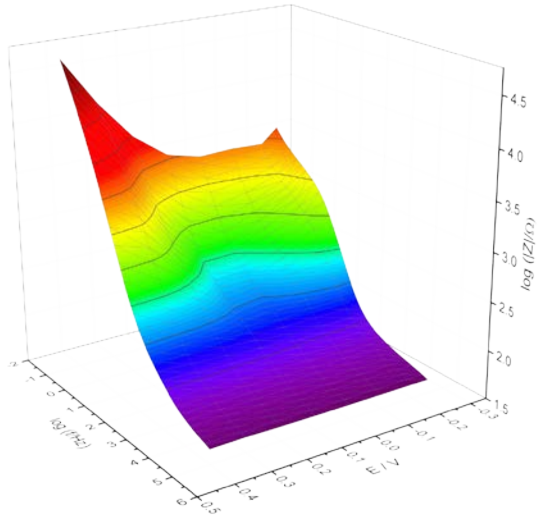

Figure 1: Evolution of impedance module of PAA in 0.1 M K_2HPO_4 and KH_2PO_4 (pH 7) between 0.4 V and –0.2 V

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Acknowledgments
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P-ECP01

VALORIZATION OF BLACK LIQUOR BY HYDROGEN PRODUCTION FROM ELECTROCHEMICAL OXIDATION OF SUGAR ACIDS

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Keywords: *biomass valorization; electrolysis; hydrogen production; sugar acids oxidation; black liquor*

Hydrogen will play a significant role in the future of the sustainable energy system since it can be used in many applications such as portable electricity generator in fuel cells or as an intermediate in industrial processes. Electrochemical water splitting is a promising clean technology for H_2 production, but a limiting factor is the high energy requirements (+1.23 V) and the sluggish kinetics of the anodic half-reaction, the oxygen evolution reaction (OER). Interestingly, the OER can be potentially replaced by a more thermodynamically favorable reaction. Biomass oxidation [1] is placed at the forefront as the alternative option and can be considered a renewable and sustainable energy source, which may also be available from low-value industrial byproducts.

For instance, black liquor, a side stream from the paper and pulp industry, is mainly composed by organic compounds, such as lignin and sugar acids. The future use of lignin in value added products may be possible, but the sugar acids fraction does not have any evident application. Therefore, the valorization of black liquor by efficiently employing the sugar acids could make the whole pulping process more economical and sustainable.

This work evaluates the oxidation of sugar acids from black liquor as an alternative anodic reaction for hydrogen production by electrolysis. A bimetallic PdNi electrocatalyst was developed in order to enable the oxidation at lower energy requirement than water splitting. A complete approach to understand the oxidation of sugar acids is considered including the study of the oxidation of selected models species such as secondary alcohols, gluconic acid and a complex mixture of organic compounds coming from a glucose degradation reaction that mimic a real sample. The effect of the inorganic fraction of black liquor containing several sulfur-based species is also evaluated.

This study provides a good understanding of the possibilities to use sugar acids for the sustainable generation of hydrogen by electrolysis as a way to valorize black liquor from a pulp mill.

Acknowledgements:
Authors gratefully acknowledge financial support from the Swedish Energy Agency (Project 44666-1).

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P-AEC01

DEVELOPMENT OF A RAPID AND SIMPLE SENSOR FOR DETERMINATION OF CATALASE ACTIVITY IN REAL SAMPLES.

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Keywords: *Catalase activity; electrochemical sensor; screen-printed electrode; real samples.*

Catalase is an enzyme present mammalian tissues with antioxidant activity because can catalyse the reaction that degrades hydrogen peroxide into water and oxygen. Therefore, catalase activity is one of the redox parameters related to oxidative stress, and antioxidant activity. In this way, its determination is widely use in clinical assays, since a raised catalase activity level in serum or blood may means the presence of several diseases [1].

An integrated, low-cost, small, portable and rapid electrochemical sensor has been developed for the detection of catalase activity using screen-printed electrodes that could be used as a diagnostic tool. With this device and a very simple methodology, the detection of catalase activity has been carried out employed smaller times than in the conventional methods that usually requires high-cost instrumentation, need specialized personnel to carry out the assays and control the equipment and are time-consuming [2]. Therefore, electrochemical sensor is shown as an interesting alternative to those conventional methods, due to their excellent features, such as robustness, simplicity, fast-response time and capability of miniaturization and “in-situ” detection.

Herein, a simple and fast method for the electrochemical detection of catalase activity using disposable screen-printed electrodes is presented. A portable reader is programmed with the electrochemical method and adequate calibration plot. The electrochemical behaviour of this sensor was carefully evaluated assessing aspects such as sensitivity, limits of detection and reproducibility. The reader has been employed in for the determination of catalase activity in real serum samples providing similar results than conventional methods.

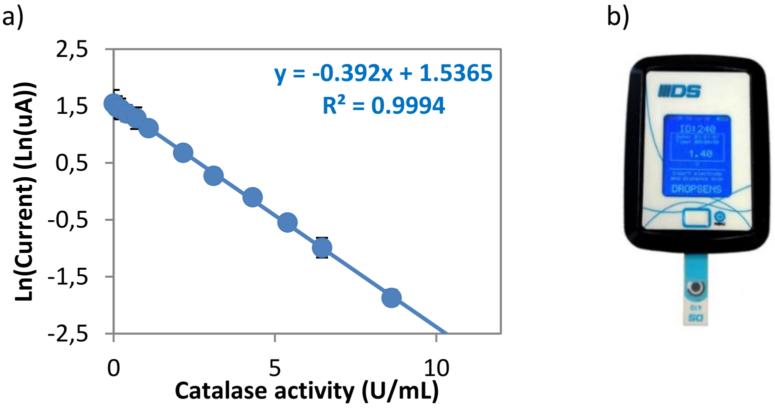

Figure 1. (a) Calibration plot of catalase activity at different catalase concentration in presence of 1 mM H_2O_2. (b) Developed electrochemical device.

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P-AEC02

STUDY OF VOLTAMMETRIC BEHAVIOUR OF FENANTYL USING DISPOSABLE ELECTRODES

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Keywords: *Fentanyl ; Drug analysis ; Voltammetry ; Screen printed electrodes.*

Drug addiction is one of the most significant problems affecting the lives of many individuals, whose consequences had escalated to become a worldwide public health threat. For this reason, its control and monitoring are of great interest in areas such as medicine, forensic science, and social sciences [1]. Therefore, the development of analytical methods that allow the rapid detection of target substances in biological fluids is a subject of great importance and relevance within analytical chemistry.

The analysis of opioid-like drugs has been done using analytical techniques such as gas and liquid chromatography, electrophoresis, spectrophotometry, mass spectrometry, and electrochemistry. Electrochemical techniques provide a sensitive, selective, low-cost, and portable alternative to current screening approaches. Also, these electrochemical sensing platforms offer opportunities to miniaturization and have allowed the creation of devices with a wide variety of designs and materials, of disposable nature and low cost, to perform in situ analysis.

Novel psychoactive substances (NPS) are synthetic analogs of controlled substances that produce similar pharmacological effects to their original counterparts. They comprise several classes of drugs including opioids. In general, NPS is designed by making modifications to the chemical structure of other medications. Among these, the compounds related to fentanyl and fentanyl analogs pose a severe threat because of their devastating consequences.

A voltammetric sweep of a Fentanyl solution, using carbon-screened electrodes, shows the existence of two well-developed oxidation peaks that respond quantitatively to the concentration of the drug. Therefore, they can be used for quantification in different media.

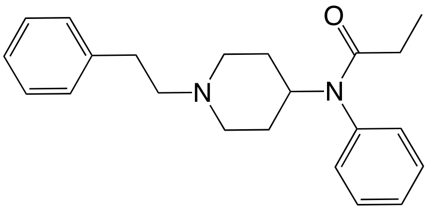

Figure 1. Fenantyl structure

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P-AEC03

EFFECTS OF NON-TARGET IONS IN TWO POLARIZABLE INTERFACE SYSTEMS: A GENERAL ANALYTICAL THEORY

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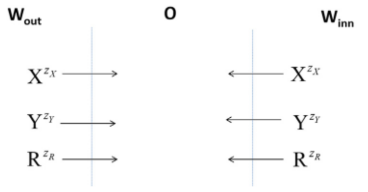
***Keywords**: two polarizable interfaces; ion-transfer voltammetry; analytical theory; compensating ions; lipophilicity*

A very general theoretical framework is developed for the voltammetry of two polarizable interface (2PI) systems in the presence of an arbitrary number of transferable ionic species in the two side phases. Analytical equations are derived for the current response in any voltammetric technique, regardless of the charge number, concentration and lipophilicity of the ions. Hence, with respect to previous theoretical treatments, a more general and realistic view is gained in order to address situations where a) the compensating ion is not present in a large excess and/or b) several ionic species (such as impurities) act as compensating ions. The theoretical results point out that the effects on the voltammetric response can be misinterpreted as a) due to Ohmic drop and/or to finite transfer kinetics and to b) the presence of multiple analytes.



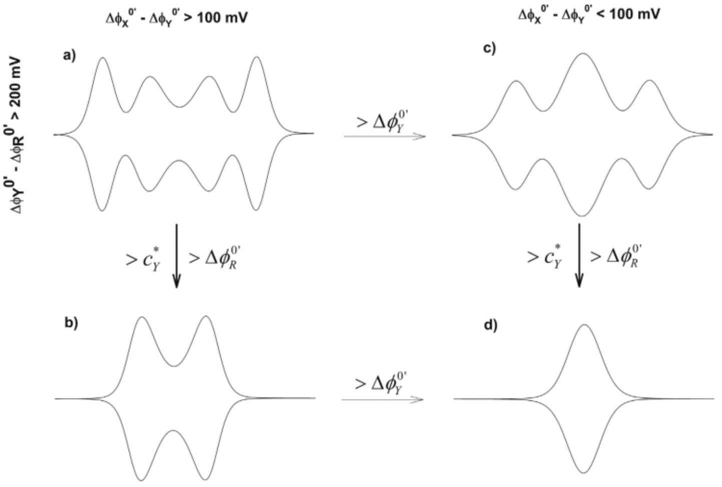


Figure 1. Possible situations in the cyclic square wave voltammetry of 2PI-systems with the analyte (X) having access to both interfaces and in the presence of two compensating ions (Y, R) as a function of their relative concentration and lipophilicity.

As shown in Figure 1, the concentrations and charge numbers of the target and compensating ions have remarkable effects on the positions, magnitude and shape of the voltammograms. Criteria will be given for understanding, predicting and quantifying the experimental results based on the number and position of the signals and on the corresponding values of the peak-to-peak separation in cyclic voltammetry (CV) and the half-peak width in cyclic square wave voltammetry (cSWV). The theoretical results have been validated experimentally in water | 1,2-dichloroethane | water cells.

Acknowledgements: Fundación Séneca de la Región de Murcia (Project 19887/GERM/15).

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P-AEC04

CONSTRUCT, TESTING AND APPLICATION OF A NEW ELECTRODE FOR THE DETERMINATION OF IODIDE IN PHARMACEUTICAL PREPARATIONS

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Keywords: *ISE-I^-; potentiometric; preparation, characterization and checking; determination of iodide in pharmaceutical preparations.*

Ion selective electrodes (ISEs) are an important analytical tool, increasingly used and constantly evolving, for the determination, quickly and easily, of the activity and, therefore, of the ionic concentration in different solutions [1].

One of the main problems of commercial ISEs is their high price relative to their useful life. Thus, for example, a selective iodide electrode can cost more than 1100-1300 euros and have an average life, depending on use and care, of between 1-3 years. Due to this high cost, more and more attempts are being made to manufacture low-cost electrodes that retain the analytical properties of commercial ISEs. In this work we will demonstrate that you can build an iodide electrode for less than 20-30 euros and that it works practically the same as a commercial one.

To fabricate the I^- electrodes we have followed the procedure of Dobčnick and colbs. [2], with some modifications. It is a "somewhat peculiar" Ag/AgI electrode; iodide is deposited on the silver by means of a chemical pre-treatment of a pure Ag wire with $HgCl_2$, instead of the usual electrochemical treatment [3].

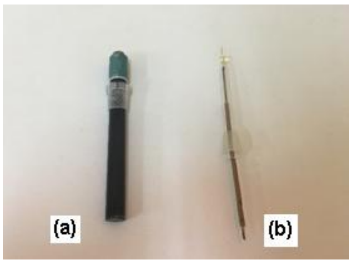

Figure 1. Electrodes for the determination of I^-

(a) ISE comercial Metrohm 6.0502.160

(b)Electrodo fabricado en este trabajo

Figure 2. Electrodic System

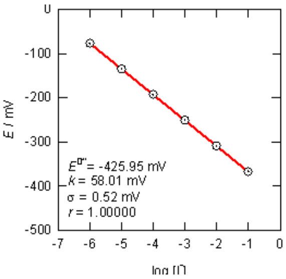

Figure 3. Electrodic System Nernstian behavior checking

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Acknowledgement
The authors dedicate this work to our Technicians Miguel Rojas Morales on the occasion of his retirement and to the new Technicians Sandra Petit Mejías for her help in the assembly of the electrodes.

[§]Final Degree Work in Pharmacy of R.C.G.C.

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P-AEC05

LOW-COST MICROCONTROLLED POTENTIOSTAT FOR EDUCATIONAL PURPOSES AND PORTABLE APPLICATIONS

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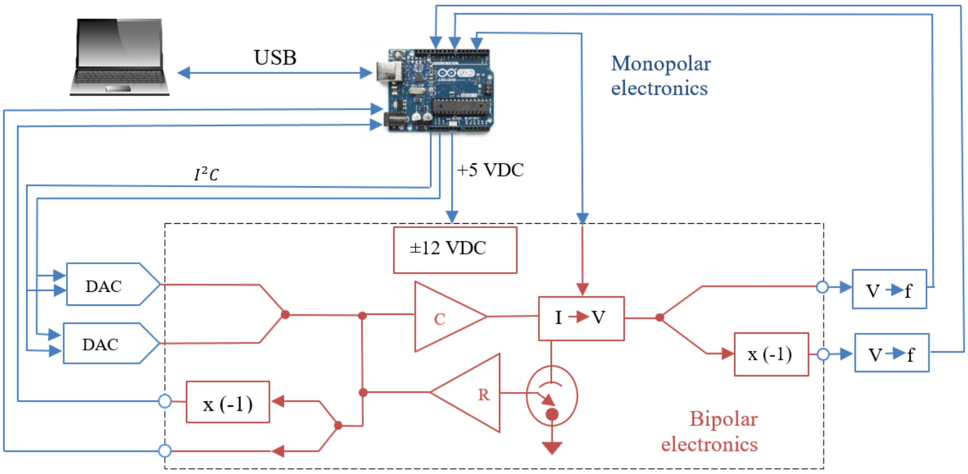
Keywords: Potenciostat; high resolution; low-cost; high performance

High-end potentiostats are very expensive instruments due to their high capabilities. Although the price makes this instrument difficult to achieve, its high performance makes it an instrument widely used in research by both professionals and students in practice. Low-cost potentiostats already exist [1]–[3], and they are mainly used for in-situ routine measurements or teaching demonstrations. This kind of instruments used to have low performance due to a scarce variety of available technics, low resolution, low speed or limited work potential range.

We have worked on making a low cost microcontrolled potentiostat with similar characteristics to a high-end potentiostat. We have designed an instrument capable of apply voltages up to ± 4 volts with a resolution of 1 mV. Also, it can read currents between 1 nA to 10 mA with only two ranges of sensitivity. Although the potenciostat is powered with only 5 volts, it can manage bipolar voltages and currents having low power consumption, so it can be powered only by the Arduino USB port.



It can perform electrochemical measurements with the most commonly used techniques such as chronopotentiometry, chronoamperometry, cyclic voltammetry, differential pulse voltammetry, stripping techniques, etc. Multiple parameters can be programed, and the recorded data can be sent through the USB connection to a central computer.

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P-AEC06

A POTENTIOMETRIC STUDY ABOUT THE INTERACTIONS OF IONIC SURFACTANTS WITH GRAPHENE NANOSHEETS

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Keywords: *Ion-selective electrodes; graphene nanosheets; ionic surfactants; interaction; dispersion.*

Graphene, GN, is a two-dimensional carbon material and was discovered by Novoselov et al. in 2004 [1]. The special 2D crystal structure of graphene gives it unique electronic, thermal conductivity and mechanical properties [2]. It has attracted wide attention in scientific community due to the applications of graphene nanosheets, GNs, in nanoelectronics and nanophotonics [3]. GNs show a low solubility in aqueous solution. The presence of attractive Van der Walls and π-π stacking interactions among the sheets provokes their assembly. The quality of the dispersion of these sheets in water can be improved by the addition of chemical species (dispersing agents), such as ionic surfactants [4]. The amphiphilic nature of the surfactants favours their adsorption on the nanosheets and decreases the agglomeration of the GNs.

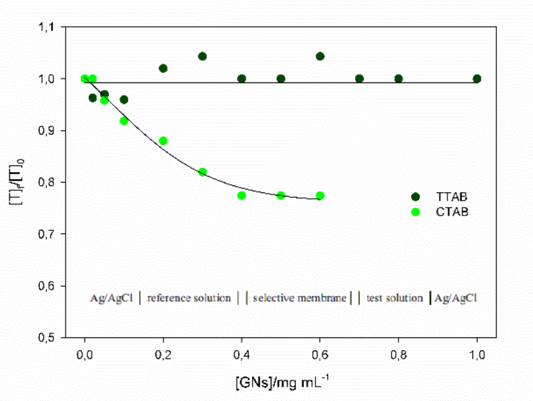

Figure 1. Plot of the relative free surfactant concentration versus the GNs concentration.

The dispersion of GNs in aqueous solution has been studied in the presence of several ionic surfactants. The surfactants used were the well-known OcTAB, CTAB, TTAB and CTS. The interactions among ionic surfactants and GNs were performed by measuring the electromotive forces of solutions containing both compound using ion-selective membrane electrodes. The potentiometric experiments showed a sigmoidal dependence of the free surfactant concentration on the GNs concentration for all the ionic surfactants used (Figure 1). This behaviour confirms the cooperative character of the surfactant/graphene nanosheets interactions. The forces corresponding to the binding of the surfactants with GNs are driven by hydrophobic interactions between the hydrocarbon tails and the sheets.

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P-AEC07

GALVANOSTAT ADAPTATION TO AN AUTOMATIC COULOMETER WITH PHOTOMETRIC END POINT DETECTION

M. Calero Castillo, E. Roldán González, M. M. Domínguez Pérez, G. López-Pérez, D. González-Arjona*

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Keywords: *instrumentation; microcontroller, coulometry; photometry*

The prototype of a programmable galvanostat [1] has been adapted to build up a coulometric titrator at constant current. A versatile colorimetric simple device has been developed and evaluated for the end point detection. The whole assemblage is controlled by an Arduino UNO microcontroller. A developed program specifically designed, interact directly with an Excel spreadsheet. The program read and validate the setup parameters within the spreadsheet, avoiding the microcontroller reprogramming [2]. Figure 1, shows the schematic block diagram of the software developed.

The system has been checked with some reagent electrochemically generated. For iodomteric titrations (ascorbic acid, thiosulphate), a two platinum wires have been used as electrodes in a two compartment cell. Acid-base titrations have been carried out using NaBr as electrolyte in a single cell compartment. A Pt wire as cathode is used for the generation of hydroxide ion and a silver electrode as anode. Using this configuration in the anode the silver is oxidized avoiding the water oxidation.

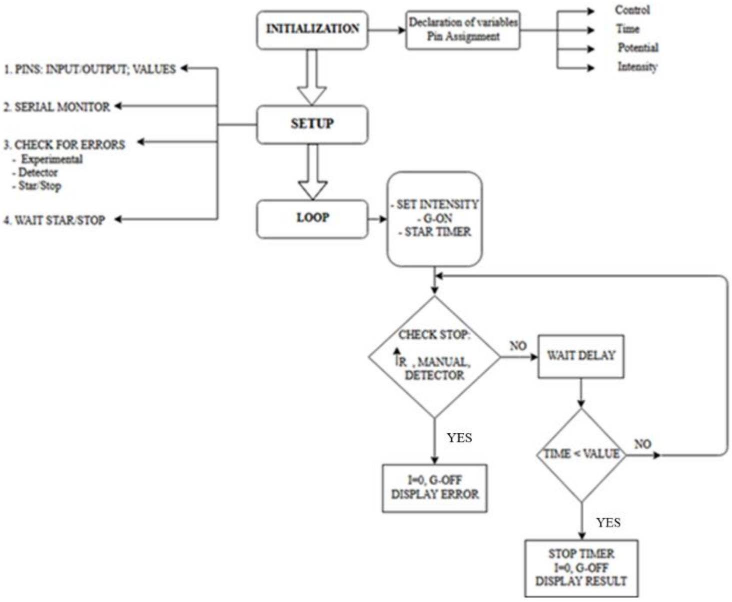

Figure 1. Block diagram of the coulometric program

The colorimetric end point detector is based on the combination of a LDR as detector and a RGB LED as light emitter. This combination allows the selection of the light colour having the best sensitivity. Selection of the hardware components and the procedure developed have allowed very satisfactory determinations of quantities of substances in the range of 1 to 10 µmol, with an error around 1%. Moreover, the versatility of the developed system can be reflected with possible improvements, as the monitoring the voltage during the electrolysis process. Thus, it will be possible check if only the reaction of interest is taken place.

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P-MEC01

ROLE OF THE ARCHITECTURE AND FIXATION OF ZnO-BASED SUNLIGHT PHOTOCATALYTS ON THEIR ECOTOXICOLOGICAL EFFECTS ON MICROALGAE

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Keywords: *sunlight photocatalysis; biomimetic; bioinspiration; photocorrosion; ecotoxicological effects on microalgae.*

The need for ecofriendly water pollution solutions is driving researchers to develop efficient sunlight photocatalysts with enhanced photocorrosion resistance and reduced ecotoxicological effects. In this study, bio-inspired ZnO@ZnS core@shell fractal and dendritical micro/nanoferns were synthesized according to a facile electrochemical method, followed by chemical sulfidation (**Figure 1**). The optimum biomimetic ZnO@ZnS core@shell micro/nanoferns exhibit an excellent sunlight photocatalytic performance for the mineralization of a mixture of three different persistent organic pollutants in a real algae culture medium. The efficient photocatalytic performance is demonstrated in terms of photo-remediation, photocorrosion resistance, and minimal ecotoxicological effects on *Spirulina (Arthrospira) platensis* (microalgae). In fact, this is an extremely effective process comparable to or better than the most competitive state-of-the-art ZnO photocatalysts, but with negligible photocorrosion or ecotoxicological effect on microalgae. Remarkably, the ZnO@ZnS core@shell structures exhibited outstanding photocatalytic activity compared to the pristine ZnO catalyst by a factor at least 6. In-depth analysis of the ecotoxicological effects on microalgae by determining the Zn(II) release, photocatalyst–microalgae interaction, and production of reactive oxygen species (ROS) shows drastic improvement of algae viability when supported ZnO@ZnS core@shell micro/nanoferns (compared to pristine ZnO or unsupported structures) are used. Altogether, the optimized ZnO@ZnS photocatalysts are excellent, ecofriendly photocatalysts for water remediation in complex media or when combined with biological microorganisms to complement or enhance their phytoremediation.

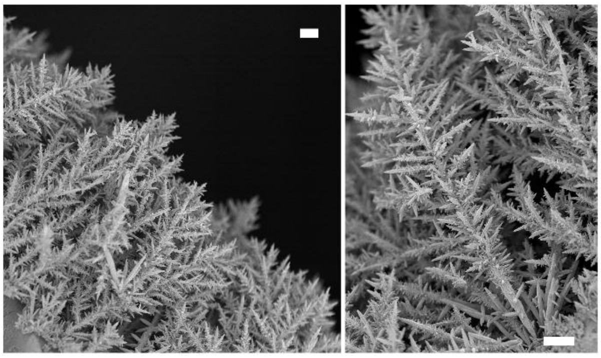

Figure 1. ZnO@ZnS micro/nanoferns. Scale bar: 5µm. Adapted from Ref. [1] with permission from Elsevier.

Acknowledgments: A. S. would like to acknowledge funding from the EMPAPOSTDOCS-II program. The EMPAPOSTDOCS-II programme has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement number 754364.

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P-MEC02

SIMULTANEOUS PHOTOLUMINISCENCE AND RAMAN SPECTROELECTROCHEMISTRY

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Keywords: *spectroelectrochemistry; photoluminescence; Raman.*

Raman Spectroelectrochemistry (Raman-SEC) and Photoluminescence SEC (PL-SEC) have been widely used to study complex electrochemical processes [1,2]. In all cases, the two techniques have been used independently in different experiments. In some cases, samples can evolve with time, being very difficult to extract complementary information about processes taking place in the sample because, actually, those analytical techniques are not interrogating exactly the same sample. Therefore, the development of analytical tools that provide information of different nature concomitantly with the electrochemical experiment is fundamental to understand systems that can evolve with time.

Our group developed a new combination of Raman SEC and UV/Vis absorption SEC in a parallel configuration in a single experiment [1]. In this work, we present a new analytical technique combining PL-SEC and Raman-SEC, allowing us to obtain complementary information about the same chemical system (Figure 1).

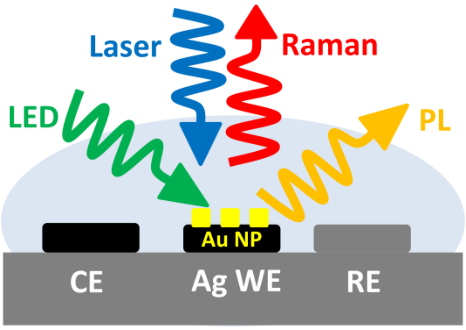

Figure 1. Schematic view of the proposed technique

Raman signal provides a lot of structural information but Raman bands are usually very weak. For this reason, a SERS substrate is mandatory to enhance the Raman response. To perform these experiments registering simultaneously both, photoluminescence and high enough Raman signals during an electrochemical experiment, gold nanoparticles were synthesized and used to modify the working electrode.

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P-MEC03

AC-ELECTROGRAVIMETRY OF PRUSSIAN BLUE FILMS IN CSCL AQUEOUS SOLUTION.

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The development of treatment processes for the fast and efficient recovery of radioelements like Cs^+, are currently being studied by many researchers. In this work, we have studied the charge transport rates in Prussian Blue (PB) films with different degree of order in the crystalline structure controlling the deposition time and current. These films were galvanostatically deposited on gold electrodes supported by a quartz crystal in acid aqueous cesium chloride solution. The role of the cesium cation on the reversible electrochemistry of Prussian Blue thin films was analysed through in situ combination of two different impedance techniques. Electrochemical impedance spectroscopy provides information on the electron transfer. Ac-electrogravimetry allows the study of the exchange of free water, cesium, and proton ions to be elucidated [1,2]. Impedance measurements were of great interest to obtain a more accurate knowledge of the charge transport processes that take place through an electroactive film.

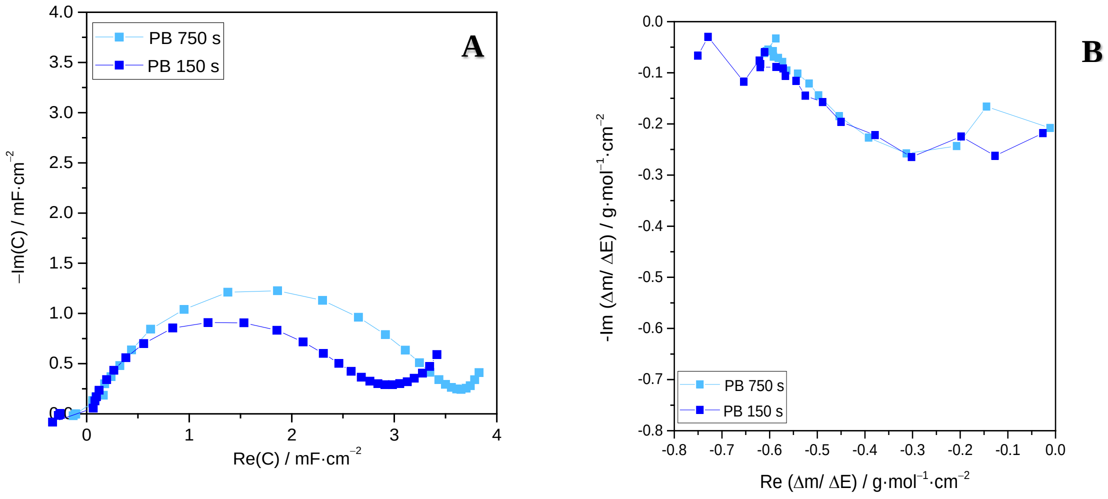

Fig 1. **(A)** Electrochemical impedance spectroscopy presented as capacitance plots of a two PB films with different degree of crystallinity at E = 0.25 V vs Ag|AgCl|KCl$_{(sat)}$ in CsCl 0.5 M and pH 2.98 solution. **(B)** Mass impedance spectroscopy transfer function of a two PB films with different degree of crystallinity at E = 0.25 V vs Ag|AgCl|KCl$_{(sat)}$ in CsCl 0.5 M and pH 2.98 solution**.**

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P-MEC04

SECM SURFACE ANALYSIS OF GRAPHITIZED CARBON FOAMS COATED BY REDUCED CARBON OXIDE AND PLATINUM.

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Keywords: SECM; carbon foam; RGO; platinum

Scanning Electrochemical Microscopy (SECM) is one of the scanning probe microscopies in which a microelectrode, as a working electrode, is placed at a controlled distance above the substrate to obtain an electrochemical signal which value is related with the distance to the substrate surface and its electrical properties. A singular aspect that makes SECM different from other electrochemical techniques is the possibility to study unbiased samples. In this case, the applied voltage does not control the potential of an unbiased substrate, and so, the perturbation of the studied substrate is negligible.

In this work a type of carbon foam is studied which production procedure has been developed using the AR24 mesofase pitch. This has been widely used as appropriate precursors for high performance carbon materials. Both charcoal and graphite foams are excellent for numerous thermal, mechanical and electrical applications. Carbon foams pore size, pore shape and pore size distribution could be varied. These materials, previously graphitized to enhance its electric conductivity, will be characterize to assess their potential use in electrocatalytic, energetic and catalytic applications. Additionally, the surface of those foams will be modify with reduced graphene oxide and Pt nanoparticles.

Graphene and related materials have recently emerged as outstanding materials due to a range of properties such as high mechanical strength, high electron mobility, thermal conductivity, etc. Due to their high surface area and conductivity, graphene materials have also been used for electrochemical applications such as supercapacitors, batteries, sensors, etc. Therefore, the characterization of the electroactivity of graphene materials is necessary and different electrochemical techniques such as cyclic voltammetry and electrochemical impedance spectroscopy have been widely used for this purpose. SECM has appeared as a technique that can be used to test electron transfer kinetics, electroactivity and conductivity of these materials [1].

Figure 1 shows the surface analysis by FESEM and SECM. The characteristic pores of this carbon foam materials could be clearly distinguished in the FESEM image. From the SECM results, an unusual high increase of the positive feedback signal in the inner of the pores (further away from the tip electrode than the foam surface) is detected. This behaviour may be due to the presence of strongly oriented faces on the surface of the pore reminiscent of a graphite structure.

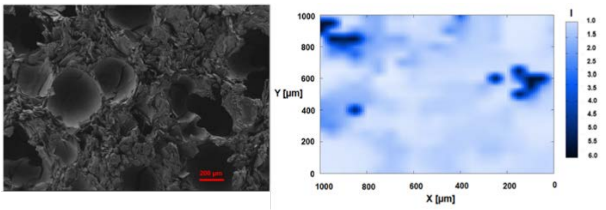

Figure 1. FESEM and SECM images of the surface of a graphitized carbon foam.

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P-MEC05

SPECTROELECTROGRAVIMETRY STUDY OF POLY(3,4-ETHYLENDIOXYTHIOPHENE)

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Keywords: *PEDOT; Supercapacitors; Video Digital RGB; Ac-Electrogravimetry*

Poly (3,4-ethylenedioxythiophene) has been widely studied up to now due to its good electrical conductivity, low density and its use in sensors and electrical supercapacitors. Polymerization of 3,4-ethylenedioxythiophene (EDOT) was carried out in a solution 0.1 M $LiClO_4$ and 0.05 M EDOT in aqueous medium by chronoamperometry using as a reference electrode Ag | AgCl | KCl (sat), as a counter-electrode, a platinum mesh and an indium tin oxide (ITO) transparent electrode as working electrode. The characterization of the polymer was carried out by coupling the video analysis to conventional electrochemical techniques (chronoamperometry and cyclic voltammetry), obtaining significant results such as the supercapacitor behaviour and the oxidation savings and the reduction of the species. In addition, it has been possible to verify that the analysis allows RGB to separate the faradic and non-faradic contributions, as well as the effect of the ohmic drop along the electrode. Time derivate color intensity d (I_R,I_G,I_B) /dt showed a good correlation with the current peaks and shoulders of the cyclic voltammogram identifying intermediate forms of PEDOT. The standard desviation of colour (stdR, stdB, stdR) can be related to the color homogeneity of the surface [1].

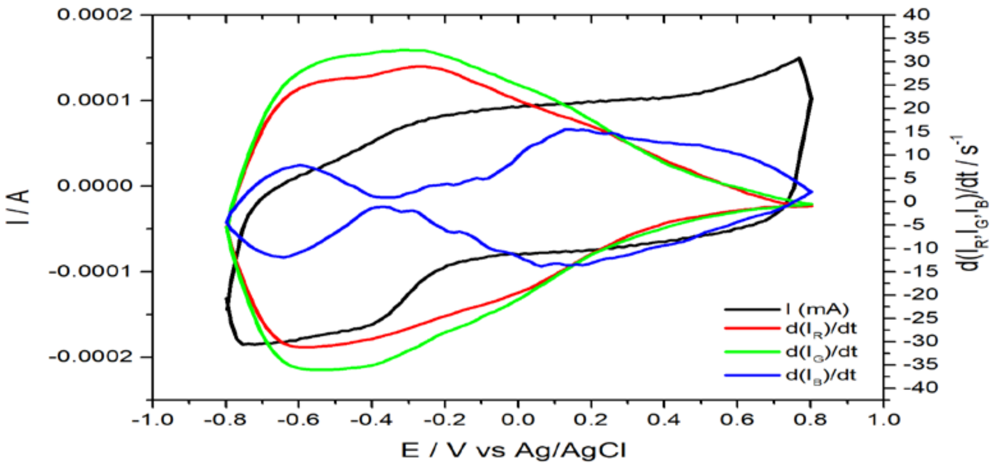

Figure 1. $d(I_R)/dt$, $d(I_G)/dt$ and $d(I_B)/dt$ during the cyclic voltammogram of PEDOT in 0.1M $LiClO_4$ at 0.1 V/s

Finally, PEDOT films were investigated by using Ac-Electrogravimetry, impedance and electrogravimetry spectroscopies in $LiClO_4$ solutions. Information about the movement of anions, cations, and solvent during the switching of PEDOT between oxidation states obtained [2].

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Acknowledgments
This work was supported by MINECO-FEDER CTQ2015-71794-R

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P-MEC06

MATERIALES COMPUESTOS CON LÍQUIDOS IÓNICOS PARA LA GENERACIÓN ELECTROQUÍMICA DE HIDRÓGENO

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Keywords: *reacción de evolución de hidrógeno; líquidos iónicos; carburos metálicos; DEMS; Tafel*

Actualmente, el hidrógeno es considerado como un vector energético para la transición hacia un futuro basado en el uso de energías renovables. En este contexto, los electrolizadores permiten obtener H_2 de alta pureza, pero emplean catalizadores basados en metales nobles que aumentan enormemente su coste. Los carburos de metales de transición aparecen como alternativa mostrando una buena actividad catalítica hacia la generación electroquímica de hidrógeno [1]. En la búsqueda de materiales más económicos se ha propuesto, además, el empleo de líquidos iónicos que mejoran la resistencia mecánica y la conductividad eléctrica de los materiales compuestos resultantes [2].

En este trabajo se han sintetizado diferentes materiales compuestos basados en carburos de metales de transición comerciales y hexafluorofosfato de octilpiridinio (IL) como líquido iónico. Estos materiales se han caracterizado mediante difracción de rayos X (XRD) y microscopía electrónica de barrido (SEM). Además, tanto la actividad catalítica como la cinética hacia la reacción de evolución de hidrógeno (HER) se ha estudiado mediante espectrometría de masas diferencial electroquímica (DEMS). En la Figura 1 se aprecia que la adición de un 5% de líquido iónico a los carburos de molibdeno y tungsteno resulta en un aumento de la actividad catalítica de estos materiales compuestos hacia la HER en 50 mV y 30 mV, respectivamente.

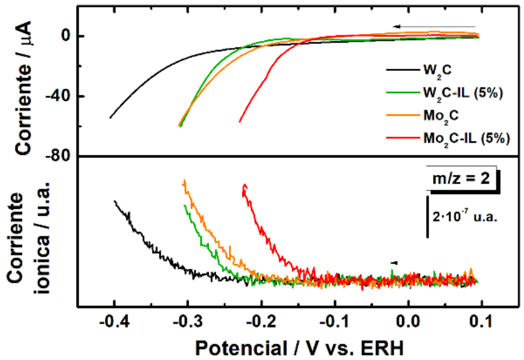

Figura 1. Medida de DEMS realizada para los carburos comerciales (Mo_2C y W_2C) y los materiales compuestos (Mo_2C+IL al 5% y W_2C+IL al 5%) en medio NaOH 0,1 M. Velocidad de barrido = 1 mVs^{-1}.

Por último, se presenta un estudio cinético de la HER sobre estos materiales, donde se han empleado las corrientes iónicas (m/z = 2) para calcular las pendientes de Tafel. Este nuevo método para hallar la etapa determinante de la velocidad mediante DEMS permite discriminar contribuciones a las corrientes de reducción distintas a la corriente de hidrógeno (e.g. corrientes de reducción de óxidos superficiales), pudiendo obtener pendientes de Tafel más exactas [3].

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