



Collection of Abstracts



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Preface

After the editions of 2014 in Burgos, of 2016 in Gargnano and of 2018 in Madrid, the **4th edition of the E3 Mediterranean Symposium: Electrochemistry for Environment and Energy (E3MS)** returns in Italy at Orvieto as a joint event with 2022 edition of the Giornate dell'Elettrochimica Italiana (Orvieto, 11-15 September 2022). The two intertwined meetings share the interest for the themes of the electrochemical devices for energy conversion, production and storage (lithium-, sodium- batteries, fuel cells etc.), the use of electrochemical sensors and development of special electrochemical methods/electrodes for environmental analysis as well as all the aspects relevant to industrial electrochemistry: sustainable production processes, utilization of electrochemical methods for disposal, recycling, remediation, considering also the circularity of productive electrochemical processes and electrochemical decarbonisation. These main focusses of **4th E3MS** reveal the centrality of Electrochemistry as a science of the future for the realization of a sustainable, smart and green development.

Looking forward to meeting you in Orvieto,

The E3MS Organizing Committee



Organizing Committee



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Topics

1. Batteries, fuel cells, supercapacitors for energy conversion, production and storage
2. Electrochemical methods, sensors and special electrodes for environmental analysis
3. Electrochemical engineering: industrial processes, metallurgy, processes of disposal/recycling and remediation. Aspects of sustainability, environmental implications, decarbonisation

Timetable

Thursday 15th September 2022 - Sala dei 400 (1st Floor)

Chair	Time (CET)	Speaker / Topic
Petrucci	2.00 pm	Mascia (Keynote) / T3
	2.30 pm	Sires / T3
	2.45 pm	Vitulano / T3
	3.00 pm	Oriol / T3
	3.15 pm	Mais / T3
	3.30 pm	Isidro / T3
	3.45 pm	Clematis / T3
	4.00 pm	Garza-Campos / T3
4.15 pm		Coffee break (Sala EXPO-Ground floor)
Solla	4.45 pm	Scialdone / T3
	5.00 pm	Petrucci / T3
Sires	5.15 pm	Carvela / T3
	5.30 pm	Proietto / T3
	5.45 pm	Lado / T3
	6.00-6.15 pm	Chevallier / T3

Friday 16th September 2022 - Sala dei 400 (1st Floor)

Chair	Time (CET)	Speaker / Topic
Scialdone	08.50 am	Solla (Plenary) / T3
	09.30 am	Baglio / T1
	09.45 am	Minelli / T1
	10.00 am	Vacca / T1
	10.15 am	Li / T1
	10.30 am	Gatto / T1
	10.45 am	Tonti / T1
11.00 am		Coffee break (Sala EXPO-Ground floor)
Dini	11.30 am	Cifre-Herrando / T2
	11.45 am	Valero-Ruiz / T2
12.00-1.15 pm		Poster Session
1.15-2.15 pm		Lunch break (Sala EXPO-Ground Floor)
3.00-5.30 pm		Museum Visit

Bio-electrochemical systems for the removal of pollutants from soil and water: a model-based study

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Bio-electrochemical systems (BES) may be a sustainable alternative to conventional bio-based technologies for water treatment and soil remediation, as the processes occurs with simultaneous production of hydrogen (in bio-assisted electrolysis of water) or electricity (in microbial fuel cells). BES exploit the activity of electroactive biofilms onto the electrode surface, that use chemicals in the solution as substrates, so promoting their removal. Moreover, the activity of the biofilm may depolarise the electrode, so that the cell potential of bio-assisted electrolysis of water may be considerably lower than the potential of conventional electrolysis.

As the current densities of BES may be lower by orders of magnitude than industrial electrolysis, 3D electrodes with high surface per unit of volume are largely used, with carbon-based materials to promote biofilm adhesion and growth. These electrodes may show significant lack in efficiency due to mass transfer limitations, concentration gradients and resistivity of material and biofilm. Design of BES thus requires quantitative tools to predict the effect of operative parameters and geometry on the performance of the system.

A mathematical model of BES is here presented that combines transport equations and kinetics of the involved processes with the Poisson's equation to obtain a comprehensive representation of the system under transient conditions.

The model was applied to the different systems investigated in the experimental activities of the GREENER Project:

- a single-chamber BES with brush anodes operating under fed batch and flow conditions, with a single cell or multiple cells in series
- a two-chambers cell for bio-assisted electrolysis that combines the bioanode with a cathode where the reductive dechlorination of lindane occurs.
- a system with three terracotta-based soil microbial fuel cells (SMFC) piled together, where the effect of dewatering induced by evaporation of water at the cathode was considered
- a soil microbial fuel cell with planar electrodes in different configurations, where the activity of both anodic and cathodic biofilms was modelled.

The model was built and solved with parameters obtained from experimental data.

The 3D and 2D space-time profiles of the main variables of the processes, such as electric potential, concentrations and current densities were obtained and used to predict the performances of the system considered under different scenarios.

Acknowledgments:

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Thursday 15th Sept, h.2.00-2.30 pm- Sala dei 400 (1st Floor)

Electrochemical Degradation of the Antibiotic Piperacillin by Solar Photoelectro-Fenton at Near-Neutral pH in Continuous Mode

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Antibiotics are considered as highly effective pharmaceutical compounds for the treatment of bacterial illnesses. Nevertheless, these chemicals have been identified in wastewater treatment plants (WWTPs), eventually accumulating in natural water streams. Due to the negative effects that have been associated to the occurrence of pharmaceutical residues in the environment, their fate upon discharge into water bodies becomes poses important concerns. Under this scenario, the electrochemical advanced oxidation processes (EAOPs) have been proven as a promising alternative to conventional ineffective methods for the elimination of antibiotics [1]. The powerful electro-Fenton (EF) process is particularly relevant among the EAOPs. EF is based on the in-situ electrogeneration of H₂O₂, which reacts with a metal catalyst through the so-called Fenton's reaction to yield hydroxyl radicals ([•]OH). Furthermore, in the photoelectro-Fenton (PEF) process, the use of a UVA light source tends to be beneficial because of the improvement of the regeneration of the reduced form of the catalyst, as demonstrated from photoreduction reactions [1,2]. Aiming to apply a more cost-effective process, the use of a natural UVA light source in the solar photoelectro-Fenton (SPEF) process has emerged as an interesting alternative for pharmaceutical removal [2]. Nonetheless, it is worth mentioning that these Fenton-based EAOPs are typically carried out at acidic pH ~3, whereas the pH of most of the industrial and urban wastewater effluents is close to neutral. To overcome this drawback, the performance of stable iron complexes can be assessed in novel homogeneous EF, PEF and SPEF treatments. Recently, we explored the use of the ethylenediamine-*N,N'*-disuccinic (EDDS) acid as chelating agent to form the Fe(III)-EDDS complex, employing a small batch reactor to eliminate organic pollutants at circumneutral pH [3,4]. In this work, several EAOPs including the SPEF process at mild pH, with Fe(III)-EDDS complex as catalyst for the degradation of the antibiotic piperacillin (PIP), were evaluated employing a new tubular reactor in continuous operation mode. The influence of current density (*j*) on the H₂O₂ electrogeneration was performed at pH 3 to assess the H₂O₂ production, reaching 8.5, 12.0, 19.5, and 21.3 mM H₂O₂ at 10, 20, 30 and 40 mA cm⁻², respectively. Furthermore, the H₂O₂ generation at natural pH, as well as the influence of the hydraulic retention time, *j*, pH, Fe(III)-EDDS and PIP initial concentration during the elimination of the antibiotic by SPEF process in different aqueous matrices, were systematically assessed.

Acknowledgments

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Study of the electrochemical behavior of iomeprol in aqueous systems to provide a new approach for reducing the concentrations of iodinated X-ray contrast media in wastewater

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Due to their resistance to biological wastewater treatment iodinated X-ray contrast media (ICM), a class of diagnostics for radiographic contrast, have been detected in municipal wastewater effluents at relatively high concentrations (up to 100 $\mu\text{g L}^{-1}$), with hospitals serving as their main source [1], and have been frequently encountered in drinking water as well [2]. To provide a new approach for reducing the concentrations of ICM in wastewater, the electrochemical reduction of iodinated contrast media, exemplified by iomeprol (IMP), was examined in this study. In particular, to study the electrochemical behavior of iomeprol in aqueous systems, a wide range of available electrode materials was evaluated during preliminary cyclic voltammetry studies (CVs), to identify the materials which exhibited the best performances. Platinum, gold, silver, copper, glassy carbon (GC), nickel and INOX 304 were tested. The first five showed sensitivity to the analyte, while Ni and INOX did not, even if suitably treated to remove the external passivating layer. CVs were performed with IMP 10 mM in potassium phosphate buffer pH ~ 7 , using saturated calomel electrode (SCE) as reference electrode and platinum as counter electrode. The CVs were conducted starting from 0 V, moving towards more positive potentials and then negative ones, recording three cycles for each CV. Especially in the case of Pt, Au and GC, it was possible to observe that in the first cycle only reduction peaks were present, while oxidation ones appeared from the second one. This is easily explainable by considering that dehalogenation occurs in the reduction process, as often reported by literature [3,4]. According to it, dehalogenation can occur via two different mechanisms: the stepwise bond breaking or the concerted electron transfer. Therefore, inorganic iodine was produced in reduction and then detected through oxidation, justifying the appearance of new oxidative peaks. The presence of more than one reductive peak in the case of Ag, Cu and GC could be explained by considering a progressive breaking of the three C-I bond. CV of Pt showed no net reduction peaks, but only a shift in the hydrogen reduction. Au seemed to have a single reduction peak, but its broadness suggested a bond breaking similar to that of Ag, Cu and GC. In terms of peak position, that of Au, Ag and Cu had the less negative potentials, while GC needed potential around -2.0 V to be able to reduce iomeprol. This is an indication of a certain electrocatalytic capacity of the formers with respect to the latter. These data provide more insights into the mechanisms of ICM degradation in reductive processes.

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Thursday 15th Sept, h. 2.45-3.00 pm, Sala dei 400 (1st Floor)

Computational Fluid Dynamics Simulations Applied to Nitrate Electroreduction for Groundwater Treatment

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The pollution of natural water reservoirs, used worldwide as a source of freshwater for many activities including direct consumption, by nitrate anion has become a relevant issue. The uncontrolled exposure to this pollutant can cause serious health problems such as methemoglobinemia, especially to babies and children. Nitrate accumulation on those reservoirs arises from different routes like discharge of sewage from urban agglomerations or industry, leaching of nitrogen-based fertilizers and the spread of large volumes of manure from swine livestock. Aiming to remove nitrate from polluted water, eventually producing clean freshwater, several technologies have been developed over the last decades. Electrochemical reduction of nitrate is one of the most promising among them because it is a transformation technique, which can be even used for the generation of value-added products [1]. On the other hand, computational fluid dynamics (CFD) is a powerful tool for the design of chemical and electrochemical reactors, as it can be used to simulate and predict their behavior once the model has been validated [2]. The rotating cylinder electrode (RCE) reactor has been of great interest, especially for the improvement of electrochemical processes that are based on the cathodic reaction controlled by mass transport; metal recovery is a good example of this [3]. The mass transport in an RCE reactor is enhanced by increasing the rotation of the cylindrical electrode, which can attain turbulent flow at low Reynolds number ($Re > 100$). In this work, a model of an RCE reactor has been developed to simulate the kinetics for nitrate removal (620 mg L^{-1}) from 400 mL of synthetic solutions (nitrate transport number < 0.01) in the absence of migration transport, in a mixed control regime. Hydrodynamics and nitrate mass transport phenomena involved in the RCE system at different rotational speeds were considered by solving the Reynolds-Averaged Navier-Stokes and diffusion-convection equations by CFD after establishing the appropriate boundary conditions using COMSOL Multiphysics software. To solve the tertiary current and potential distributions, the nitrate reduction reaction was characterized by linear sweep voltammetry employing a rotating disk electrode made of the same material as the RCE. Tafel slope, exchange current density and the number of electrons involved in the reaction ($n = 8$) were determined. The model was validated through bulk electrolysis controlling the cathodic potential at different rotational speed of the RCE.

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Thursday 15th Sept, h. 3.00-3.15 pm, Sala dei 400 (1st Floor)

Electrochemical treatment of synthetic water containing PE and PET microplastics

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Nowadays the quality of water resources is seriously threatened by the discharge of various harmful pollutants that compromise its use for civil, industrial, and agricultural applications. A category of pollutants that is seriously endangering the health of water in rivers and seas is represented by plastics and their derivatives: the presence of microplastics (MPs) in the environment is becoming a problem for soils and seas as well as for the food chain of animals and humans. Relevant study exhibited that it was hard to remove MPs from water environment owing to their inert characteristics and small size [1]. Preliminary studies have demonstrated that most of MPs in wastewater treatment plants (WWTPs) can be eliminated by primary or secondary treatment, especially large MPs particles [2]; however, some MPs with small size remained to be released with the final effluent, entering the municipal waters and rivers directly. Due their high polymer properties, MPs keep stable under traditional physical processes, such as coagulation, sedimentation, screening, and flotation [3]. In view of this, the removal efficiency of MPs from effluents needs to be further increased. Advanced oxidation processes (AOPs) and biological degradation are two proposals that are currently being applied for MPs decomposition. Among the AOPs, electrochemical oxidation, based on direct oxidation of organic pollutants on the anode surface through charge transfer or indirect oxidation of pollutants by $\bullet\text{OH}$ or reagents such as active chlorine species in aqueous solution, is a very efficient method [4].

In the present work we reported the results related to the galvanostatic oxidation of polyethylene (PE) and polyethylene-terephthalate (PET) in a synthetic solution, in presence of active chlorine. A two-electrode cell was adopted, in which dimensionally stable anode (DSA) and Pt-grid were used as anode and cathode, respectively. Different cell configurations have been tested, both in batch and in continuous mode. During the electrochemical tests, samples were withdrawn for UV-Vis analysis, in order to evaluate the trend of both active chlorine (in the form of OCl^-) and reaction products along with total organic carbon (TOC) analysis. At the end of the electrochemical process, the synthetic solutions were filtered to recover the residual microplastics that have been then thermal treated at 70 °C for 48 h; the MPs have been subsequently analyzed to evaluate variations in weight, shape, and surface structure by Fourier-transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) analysis.

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Design and validation of electrokinetic techniques for the treatment of silty soils polluted with lindane production residues

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Years ago, environmental legislation on production processes was not very restrictive, partly because the consequences of future waste disposal were not known. One such production process in many parts of Europe was the production of Lindane, a pesticide widely used between the 1970s and 1990s, whose production efficiency was only 10-20%, generating a large amount of waste that was deposited in landfills close to the factories. As a result, there are numerous sites contaminated with compounds that are both harmful to the health of living beings and persistent in the environment.

Therefore, nowadays there is a great interest in the search of remediation techniques for contaminated soils. In this aspect, electrokinetic remediation techniques are presented as a good alternative [1] since they induce a series of processes that allow achieving high organic removal efficiencies in soils with low permeabilities. Among these processes, the induction of an electroosmotic flow that allows the movement of water through soils with low permeability and the generation of acid and basic fronts that move through the soil reacting with the compounds they find on their way that reducing their hazardousness

In this work, the applicability of electrokinetic remediation techniques for the treatment of silty soils from a real site contaminated with lindane production residues (HCHs) has been evaluated. For this purpose, two sequences of tests were carried out. In the first one, a typical electric field of 1V/cm was applied, the effect of electrode arrangement, operation time, addition of surfactants as well as the effect of electric field reversal were studied. The first observation was that the distribution of contaminants in the initial soil is very heterogeneous, which makes it difficult to establish a starting point in terms of concentration. Even so, it is possible to establish that removal occurs in all tests, with a rate of 19.2% to 72.59%. This is attributed to the processes that take place when the electric field is induced, whereby a decrease in concentration is observed in the vicinity of the electrode wells, being more pronounced in the cathodic zone. This is due to the dehalogenation process that occurs as a consequence of the generation of OH⁻ by the reduction of water, transforming molecules with 6-7 chlorine atoms (Hexa -heptachlorocyclohexanes) into 3-4 (Trichlorobenzenes and tetrachlorobenzenes). Subsequently, in order to determine the optimal operating conditions before being implemented in the field, a second sequence of experiments has been proposed. In this set, the effect of the electric field (2-4V/cm), the distance between electrodes and the addition of surfactant together with the polarity reversal time have been studied.

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Thursday 15 Sept, h. 3.30-3.45 pm, Sala dei 400 (1st Floor)

Solid Polymer Electrolyte-based systems towards real water treatment applications

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In the next future, Electrochemical Advanced Oxidation Processes (EAOPs) will act as a key role in the removal of pollutants from water. Despite the past and current efforts made by the scientific community, some gaps still require to be filled to reach the full EAOPs exploitation. The main issues, which hinder their market, are related to: i) process scale-up from lab to industrial scale, ii) removal of pollutant from real water matrix. This second aspect is not only related to the nature of the pollutant, which can be recalcitrant and hard to remove, but also by the aqueous matrix composition, and then by the electric solution conductivity. A too low value of such parameter would require a too high voltage and energy consumption to run the oxidation process. Recently, the employment of a solid polymer electrolyte (SPE) has been considered as a promising alternative to the addition of a supporting electrolyte [1,2].

To the best of the Authors knowledge, except the recent works by Rodrigo's group based on CabECO cell [3,4], the application of SPE in real water treatment is quite limited [5,6]. In this presentation, the Authors want to investigate the removal of two target pollutants from two different water matrices using SPE sandwiched between a BDD anode and a stainless-steel cathode. The attention has been focused on the removal of Mecoprop herbicide from groundwater, and the treatment of washing wastewater containing Reactive Black 5 dye. The performance of the electrochemical processes has been evaluated as a function of current density, mass transport condition, and water composition (inorganic ions, presence of other pollutants), with particular attention to the chemical oxygen demand removal and the energy consumption. Moreover, a first degradation analysis of the solid polymer electrolyte under operating conditions has been provided performing a series of removal cycles. This is a crucial point for the scale-up of the process and for the development of reliable electrochemical SPE-based systems.

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Circular Approach to the Removal of Pharmaceutical Residues from Wastewater Using Two Pyrolyzed MOFs

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In recent years, scientists specialized in water treatment have shown great interest and concern about the so-called emerging pollutants, which include a diversity of pharmaceuticals. These pollutants have been detected in bodies of water in concentrations that could quite certainly cause an adverse impact on ecosystems and, therefore, various strategies are being developed to remove and/or degrade them in an effective, efficiently, and eco-friendly manner. The objective of the present work is the removal of two drugs spiked into an actual water matrix, following a two-stage scheme: first, using an adsorption process with graphene powder (rGO) and, subsequently, treating the residual drug concentration by means of electrochemical advanced oxidation processes (EAOPs). The adsorption of the fluoxetine (FLX) and naproxen (NPX) was carried out in a stirred-tank reactor, with a volume of 2.5 L. The initial FLX and NPX concentrations were 51 and 45 mg L⁻¹, respectively, and their time-course was monitored by reversed-phase HPLC. More than 40% of each drug and almost all the natural organic matter present in the raw wastewater was removed by adsorption. The organic matter content was monitored through the quantification of total organic carbon (TOC). The electrochemical treatments needed in stage 2 were heterogeneous electro-Fenton (HEF), heterogeneous photoelectro-Fenton with UVA light or sunlight (HPEF and HSPEF, respectively). They were performed at small scale as well as in a 2.5 L pilot plant coupled to an FM01-LC filter-press cell, which was equipped with an air diffusion cathode for the electrogeneration of H₂O₂ and a dimensionally stable anode (DSA). The applied current density was varied between 5 and 50 mA cm⁻², and to promote the occurrence of Fenton's reaction, a catalyst prepared from pyrolysis of a synthesized MOF was added [1]. A low concentration of catalyst (~0.3 g L⁻¹) was employed, being all the experiments made at natural pH (~5.8). The total degradation of both drugs was ensured, reaching at least 50% removal of the organic matter content; most of the residual TOC corresponded to non-toxic carboxylic acids. Furthermore, aiming at a circular approach, the electrochemical regeneration of the adsorbent was carried out by means of the same EAOPs but using a magnetic catalyst instead, allowing its facile recovery [2]. The regeneration of the adsorbent allowed the application of several reuse cycles, achieving regeneration efficiencies higher than 90% thanks to the high oxidation activity of the hydroxyl radical formed via Fenton's reaction. According to the obtained results, it can be concluded that the use of HEF, HPEF and HSPEF for water treatment and electro-regeneration of graphene can become an interesting and environmentally friendly technology.

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Electrochemical treatment of wastewater containing NaCl. Methods to increase the removal of organic pollutants and minimize the formation of toxic by-products.

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In many cases, wastewater can contain both organic pollutants and NaCl. Electrochemical methods allow to treat very effectively organic pollutants in the presence of NaCl. However, the utilization on an applicative scale of this route is limited by the fact that usually the high removals of organics is coupled with the generation of significant amounts of chlorinated by-products. The role of several operative parameters on the performances of the process was systematically evaluated using phenol as a model organic pollutant. It was shown that the removal of phenol and TOC and the generation of many by-products including chlorophenols, chloroacetic acids, chlorate and perchlorate dramatically depend on the adopted operative conditions (i.e., nature of anode and cathode, current density and concentration of chlorides). The use of boron doped diamond anode gave the highest removal of TOC but also the highest final concentrations of chlorate and perchlorate and the lowest concentrations of chloroacetic acids. Conversely, the use of DSA anodes gave the lowest generation of chlorate and no perchlorate. The use of lower current densities and higher air pressures allowed as well to reduce the concentrations of these compounds. Moreover, lower amounts of chlorinated by-products were achieved using suitable cathodes [1].

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Electro-peroxone on BDD cathodes for the mineralization of quinoline

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Electro-peroxone has proved to be an effective process for the degradation and mineralization of persistent and emerging pollutants. The combination of ozone and electrolysis at carbon-based cathodes implies the occurrence of several simultaneous reactions that boost ozonation by the in-situ formation of powerful oxidants, without the need for reagents addition.

One of the most appealing carbon-based materials that have been recently developed is the Boron Doped Diamond electrode (BDD). Because of its characteristics of wide-potential window and the outstanding ability to electrogenerate hydroxyl radicals from water oxidation, the BDD electrode is widely used as the anode [1]. However, only a few studies adopt the BDD electrode as the cathode. Instead, BDD is a promising candidate for the electro-peroxone process due to its extraordinary chemical resistance and limited production of hydrogen peroxide.

In fact, a key issue in the electro-peroxone process is the service life of the electrode materials that, though exposed to low current density values, work under utterly aggressive and corrosive conditions. Moreover, an exceeding amount of hydrogen peroxide can compete with the ozone direct reduction and result in lower efficiencies.

In this work, the degradation of an emerging pollutant, namely quinoline, by electro-peroxone on BDD cathodes is proposed. Quinoline is a nitrogen-heterocyclic compound, commonly detected in coal gasification wastewater and widely used as a precursor in the synthesis of dyes and drugs. Being recalcitrant and toxic, highly oxidizing treatments are needed for its removal.

The degradation and mineralization of the molecule have been maximized by studying the effect of the main operative conditions mainly current density, pH, and ozone flow.

Much focus has been devoted to evaluating the durability of cathodes. To this aim, electrodes with different life services have been characterized and compared by scanning electron microscopy (SEM), cyclic (CV) and linear sweep (LSV) voltammetry, IR and Raman spectroscopy, electrochemical impedance spectroscopy (EIS), and corrosion tests.

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An integrated device view on electrochemical green hydrogen generation and CO₂ fixation

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Global warming is one of the greatest environmental concerns for citizens, that affects the quality of life of millions of people. This has promoted recent interest in the use of green energy, seeking to avoid or, alternatively, minimize the consumption of fossil fuels. Nowadays, due to this issue, the development of alternative and renewable energies, especially solar and wind energy, has been promoted to produce electrical energy. However, these energies present production and demand-side supply difficulties, especially in their large-scale storage, which has led many of the present research focuses on the development of energy storage systems. At this point, electrochemical technology has become a key solution to this problem. Hydrogen production by electrolysis and the fuel cells to regenerate electricity are at a very mature state. However, storage is not solved now and one of the main alternatives that are proposed to solve this problem is the use of flow batteries based on hydrogen-halogen compounds as renewable energy storage systems [1]. In this sense, the use of H₂-Cl₂ cells presents better reaction kinetics (chlorine redox kinetics), regarding H₂-O₂ fuel cells [2]. During the hydrogen production, chlor-alkali electrolyzers have shown to be very efficient from the viewpoint of economy [3].

This work will assess the feasibility of coupling renewable energy, more specifically solar photovoltaic energy, into each of the elements of a system consisting of an electrochemical cell and a carbon dioxide absorption column on a pilot-scale. For this purpose, a chlor-alkali PEM reversible fuel cell has been developed and integrated with a spray-drying absorber [4], it may contribute to reduce the carbon footprint, while helping to regulate the green energy production. Hydrogen (H₂) and chlorine (Cl₂) gases produced during the chlor-alkali electrolysis are used to regenerate electricity in a PEM fuel cell. This system has two significant advantages: the high oxidation capacity of chlorine as compared to oxygen and the formation of sodium hydroxide (NaOH) as a by-product. This by-product is used in an absorption column to retain carbon dioxide (CO₂) in the form of carbonates and bicarbonates, thus increasing the sustainability of the energy storage system. In this way, this final mixture of carbonates is fed into a solar concentrator, which is capable of transforming the final liquid effluent into a solid. Previous studies have evaluated the feasibility of integrating photovoltaic solar panels with reversible PEM chlor-alkali fuel cells and spray absorption column at the bench scale [5]. In this work is shown details of the technology as well as results of a case study at pilot scale.

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How far are we from the valorization of waste-CO₂ to formic acid via electrochemical routes for the applicative scale?

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To date, the decarbonization of the world economy and storage and production of energy from alternative C-based sources is considered a relevant topic. The electrochemical conversion of CO₂ has been widely investigated since the 1870s as a promising strategy to convert waste-CO₂ into value-added chemicals [1,2].

Recently, it was highlighted that, among the several emerging technologies for CO₂ conversion to value-added products on an applicative scale, electrochemical technologies are the closest to commercialization due to the numerous start-ups and established companies being invested in this area (e.g., Opus-12, Dioxide Material, and Carbon Recycling International) [3]. These technologies have attracted attention due to some unique advantages (including operating at low temperature, easy scale-up stages, use of excess electric energy from intermittent renewable sources, and small environmental impact). However, to be suitable at an industrial scale, the process should present simultaneously high current densities, faradaic efficiencies close to 100%, high concentrations and long-term stability [4].

The objective of this work is to show how far this technology is from being implemented on an industrial scale and to critically discuss the main strategies to improve the process for the synthesis of formic acid/formate. To conclude, a technical-economic overview will be discussed, highlighting the main factors that affect the scalability of the process on an industrial scale.

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Lithium Recovery by Injectable Electrochemical Ion Pumping Cell

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Demand of lithium is expected to increase drastically in coming years driven by the market penetration of electric vehicles powered by Li-ion batteries, which will require faster and more efficient Li extraction technologies than conventional ones (evaporation in brines). The Electrochemical Ion Pumping Cell (EIPC) technology based on the use of Faradaic materials is one of the most promising approaches. However, its relatively short lifespan prevents its commercial deployment. Herein, a new EIPC concept based on the use of semi-solid electrodes is proposed for the first time, which takes advantage of the rheological characteristics of semi-solid electrodes that enable simple and cheap regeneration of the Regenerative Electrochemical Ion Pumping Cell (REIPC) systems after reaching its end-of-life. A proof-of-concept for REIPC is accomplished by simple replacement of the semi-solid electrode demonstrating a remarkable electrochemical performance (e.g. 99.87 % cycle⁻¹, 99.98% h⁻¹, 3-4 mAh cm⁻²) along with a competitive ion separation (e.g. 16.2 mgLi·gNiHCF⁻¹, 4 gLi m⁻² and 15.6 Wh·mol⁻¹). The use of semi-solid electrode offers other unique features such as a significant cost reduction of 95% for every regeneration regarding conventional EIPC, proving that REIPC concept successfully addresses the issues associated to the sustainability and recyclability of the conventional EIPC's for lithium capturing [1].

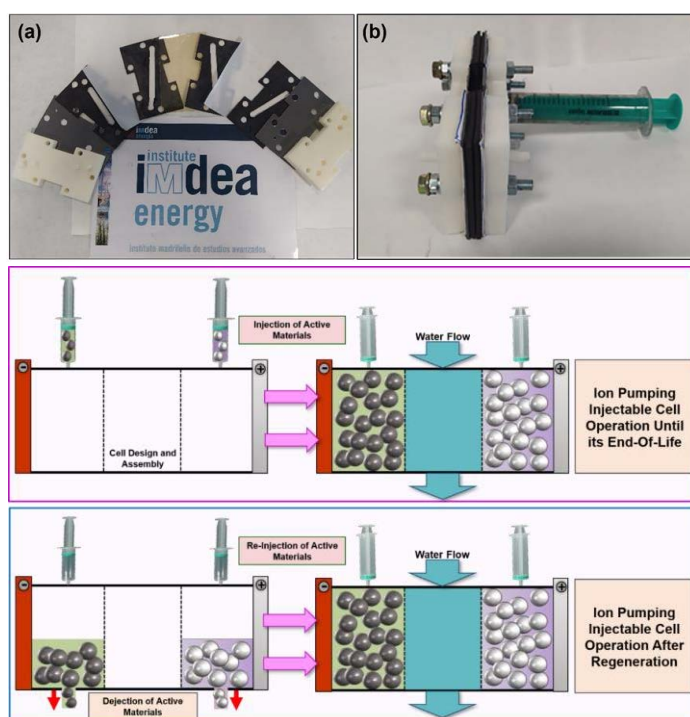


Figure 1: Pictures of (a) the different components of the REIPC, and (b) regeneration process by dejection / injection of semi-solid electrode from / into the assembled REIP cell along with a scheme of the process.

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One-step recovery of platinum from used PEMFC catalyst coated membranes by simultaneous electroleaching and electrodeposition in ionic liquids

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Platinum is one of the most efficient catalyst for proton exchange membrane fuel cells (PEMFC), and significant amounts of this expensive material are required to reach the aimed production of PEMFC functioning vehicles. Polluting recovery Pt recovery process such as pyrometallurgy and hydrometallurgy processes are used so far to reuse the precious metal. However, the presence of fluorine in the polymer present in PEMFC make the recovery process more dangerous because of HF emission. Safer and more sustainable recycle paths must be developed to ensure Pt recovery for future hydrogen mobility development. Here, we propose an efficient non-toxic recovery process for Pt. The one-step process proposed in a patent [1] was developed and optimized to enable the simultaneous Pt electroleaching and electrodeposition in ionic liquid mixture implying 1-Butyl-3-methylimidazolium chloride (BMIM Cl) and 1-Butyl-3-methylimidazolium trifluoromethanesulfonate (BMIM TFSI). The electroleaching of Pt directly from the catalyst coated membrane (CCM) was enabled through the use of metal mixed oxide mesh anodes to ensure the full contact of the Pt nanoparticles with both the anode and the electrolyte. The almost complete electroleaching was obtained by adapting several parameters such as chloride concentration, platinum ions concentration, temperature, and process duration. The process is also compatible for the other type of membrane electrode assembly: gas diffusion layer electrodes (GDE). Platinum electrodeposition occurs on recycled gas diffusion layer (GDL), which avoids the use of new material. A one-step recovery of Pt was developed, directly from CCM to recycle GDL in sustainable and safe ionic liquid mixture as electrolyte. It constitutes a promising and an innovative way to recycle Pt, an expensive and essential metal for the wide development of hydrogen mobility.

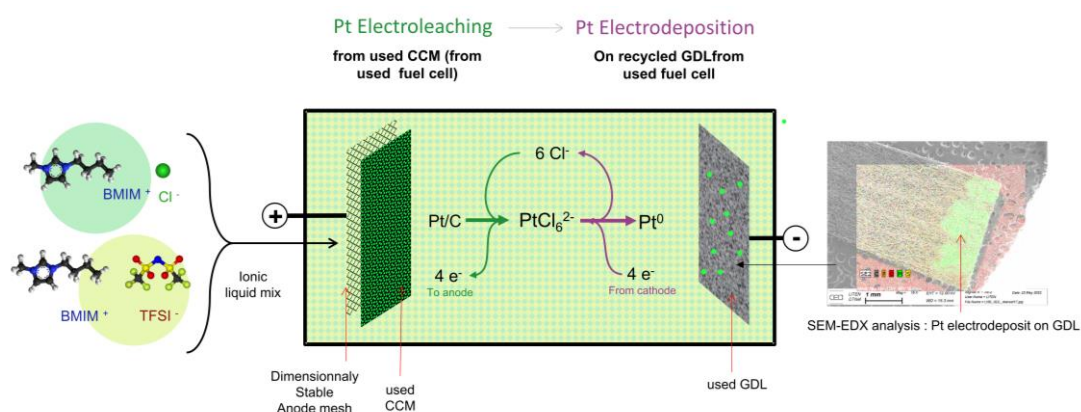


Figure 1: Simultaneous electrolixiviation and electrodeposition of platinum directly from used CCM on recycled GDL

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Electrochemical Reduction of CO₂ to Formate on Nanoparticulated Bi-Sn-Sb Electrodes

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Over the last century, human activities have dramatically increased the concentration of greenhouse gases in the Earth's atmosphere, mainly carbon dioxide (CO₂). This uncontrolled emission of greenhouse gases is leading to global warming. The effects of this climate change are becoming increasingly evident, and measures need to be taken to minimize its environmental and economic impact. In this sense, there is a clear scientific consensus on the importance of developing strategies to mitigate the consequences of atmospheric CO₂. Among other alternatives, electrochemical routes are receiving much attention as they not only allow the removal of CO₂ but also its valorization into useful chemicals. In this work, the process of electrochemical reduction of CO₂ to formic acid/formate with Bi-Sn-Sb nanoparticles is studied [1]. The different nanoparticles were synthesized, supported on carbon (Vulcan XC-72R), and subsequently used for the fabrication of electrodes. The nanomaterials and electrodes used were characterized by TEM, SEM, XPS and ICP-OES. Electrochemical experiments were performed in an H-type electrochemical cell using KHCO₃-KCl solutions saturated with Ar or CO₂. The results obtained showed that electrodes containing Bi-Sn-Sb nanoparticles exhibit good activity and selectivity for the electrocatalytic reduction of CO₂ to formate. In particular, Bi₉₅Sb₀₅/C and Bi₈₀Sn₁₀Sb₁₀/C electrodes showed a significant improvement in the stability of the system and kept efficiency values towards formate higher than 50% after 24 h under continuous operation conditions. The limited stability of the currently used electrocatalysts is one of the main obstacles for the industrial development of this process.

Acknowledgements

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Anion-exchange-membrane water electrolysis using a NiFe_2O_4 catalyst at the anode

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Hydrogen is a promising vector for the storage and transportation of energy generated from renewable sources. Hydrogen production via water electrolysis is considered the "greenest" way because it does not produce any direct carbon emissions when powered by renewable sources. Among the different technologies of electrolyzers, increasing interest is registered by that one based on anion-exchange membranes (AEMs). AEM electrolyzers combine the advantages of both the liquid alkaline and proton exchange membrane (PEM) technologies in terms of the higher purity of generated H_2 , better efficiency, dynamic behaviour, and the possibility of using inexpensive catalysts. The latter characteristic makes AEM electrolyser cheaper than PEM-based systems; however, the performance is still limited. Thus, it is mandatory to develop more active catalysts, in particular, for the oxygen evolution reaction (OER), which is the limiting process characterized by a large overpotential.

In this work, a NiFe_2O_4 spinel-type catalyst has been synthesised by a liquid-phase method, at atmospheric pressure, via the so-called *oxalate* route. The brown precipitate obtained was then filtered under vacuum and dried in an oven at 80°C overnight. Then it was calcined at 350°C , in air, for 2 h. The catalyst has been physicochemically characterised by using X-ray diffraction (XRD), to confirm the spinel structure, and X-ray photoelectron spectroscopy (XPS), to identify the species present on the surface. Electrochemical characterizations were carried out in a 5 cm^2 single cell at a temperature ranging between 30 and 60°C under atmospheric pressure. Electrochemical measurements were performed using a potentiostat-galvanostat device PGSTAT302N equipped with an FRA module (Autolab). An alkaline solution (1M KOH) was supplied by a peristaltic pump to the anode compartment of the single cell, with a flow rate of 5 ml/min . A current density of 3 A cm^{-2} has been recorded at 2.2 V and 60°C .

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New Insights on HER under alkaline conditions

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Hydrogen has rapidly acquired the role of energy vector, thanks to its elemental abundance on earth and to the environmental and energetic issues at the basis of its production and usage as molecular H₂. Water as hydrogen source certainly adds appeal to the process because of its general availability as base material, the possibility of tuning the product quality, and the well-assessed reaction paths according to the adopted methodologies and conditions. Here, we focus on the alkaline electrolytic hydrogen production, which is considered more environmental friendly and economical respect to acid one[1], when a greater efficiency is achieved. In turn, the electrolyte governs the choice of the electrode materials and the relevant reactions[2], hence the energy consumption, the costs and the H₂ quality. Here, we discuss the use of a class of electrode materials which exhibit specific electroactivity[3] for HER/HOR with extended lifetime and reasonable costs. We specifically focus on Pd oxides supported on ZrO₂, a ceramic oxide, compatible with human tissues[4], whose role here is to enhance the electroactivity of classic Platinum Group Metals (PGM), thus significantly reducing the catalyst load ($\cong 0.3 \mu\text{g}/\text{cm}^2$ for 50 nm thickness, with a mass activity corresponding to $\cong 4 \text{ A}/\text{mg}$ at -50 mV vs RHE). To carefully control the electrocatalyst composition and morphology, the electrodes are prepared by ion-beam sputtering deposition on FTO supports, thus obtaining ordered depositions of ceramic and

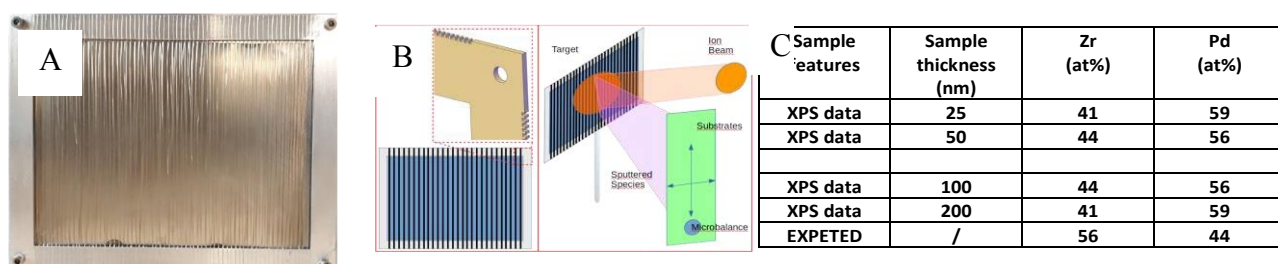


Figure 1. **A:** the target; **B:** schematic drawing of the composite target: Zr foil (blue) fixed on the target holder through an aluminium frame (grey) that, in turn, hosts the Pd wire (black); **B left up:** detail of the frame with hooking grooves for the Pd wire (pitch 1 mm); **C** Relative amount of Zr and Pd for different thicknesses and as expected from literature data[5] electrocatalyst (Figure 1).

The outcomes point to the synergistic effects between the precious metal catalyst and the ceramic support, not only in terms of chemical stability of the layer, but also of enhancement of the reaction rates. The electroactivity and stability of this novel electrocatalyst structure has been investigated by Cyclic Voltammetry and Electrochemical Impedance Spectroscopy for selected thicknesses (25–200 nm) of the active layer, deposited by ion beam sputtering. The results point to an effective enhancing of the electroactivity, as evidenced by the drastic reduction of the charge transfer resistance, thus allowing the parallel reduction of catalyst load even at increasing current densities. It is evident that the 50 nm deposit has the best electrocatalytic activity and the higher stability compared to 25, 100 and 200 nm that is related both to the thickness and to the equilibrium of Pd(0) and Pd(II). It can be speculated that the surface ratio between Pd(0) and Pd(II) of the catalytic material is influenced by the interactions with the underlying states and this interaction is strictly correlated with the thickness of the electrocatalytic materials as evidenced by the XPS measurements.

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Continuous-flow microbial fuel cells with electrodeposited MnO_x as catalyst for the oxygen reduction reaction

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The microbial fuel cells (MFCs) are a biotechnology that utilizes bacteria to create clean and renewable electrical energy by oxidizing organic substances in wastewater and represents a promising alternative for generating power. The performance of MFCs may be limited by several factors, such as the biofilm activity, the cell design and the cathodic material at which the reduction of oxygen occurs. The ORR rate represents a major factor to be considered in the design of low-cost and high-efficiency MFCs: currently, the common cathode materials are graphite, carbon cloth, and carbon paper often coupled with highly catalytic precious metals such as Pt and Pd [1]. The use of metal precious-free catalysts as cathode represents a way to reduce the costs: for this reason, several low-cost alternative materials have attracted the researcher attention. Among them, manganese oxide seems to be a promising candidate due to its lower cost and higher catalytic performance for oxygen electroreduction. Manganese oxides are abundant in nature and have previously been studied as a highly chemically stable, eco-friendly and cost-effective alternative to Pt in fuel cells [2].

In this paper, Mn oxide electrodeposited onto carbon cloth was prepared, coupled with a proton exchange membrane, and used as air-cathode in continuous-flow microbial fuel cells. The deposition was performed by cyclic voltammetry with different number of cycles to obtain different amount of Mn oxide catalyst. After the electrodeposition, an ink of activated carbon and carbon black was paint brushed and assembled to a Nafion® 115 proton exchange membrane by hot pressing at 105°C. The performance of the MFCs equipped with the prepared cathodes was assessed: the influence of the catalyst load on the electricity generation was investigated and compared with the performance of MFCs with Pt-based and carbon electrodes with no catalyst. EIS analyses were used to evaluate the contribute of anode and cathode and to quantify kinetics and structural parameters of the cathodes, and the effect of air humidity on the ORR.

Acknowledgments: This work is part of the project GREENER that has received funding from the European Union's Horizon 2020 research and innovation program under the grant agreement No 826312.

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Oxygen electrodes for Solid Oxide Cells based on Cu-rich perovskite-type oxides

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Solid Oxide Cells are electrochemical devices capable of operating in the fuel cell and electrolyzer modes. This flexibility is regarded as one of the main advantages in terms of their application in the distributed renewable energy-based systems [1]. In order to ensure the high effectiveness of the electrochemical reactions at the electrodes to take place in both directions, a set of requirements concerning thermomechanical properties, chemical compatibility with the solid electrolyte, as well as high mixed ionic-electronic conductivity and electrocatalytic activity must be maintained. The oxygen electrode (cathode) materials, which have been studied and developed so far, are commonly the Co-based perovskite-type oxides. Such compounds possess excellent electrocatalytic activity, and consequently, good performance of the constructed cells can be achieved. Nevertheless, due to the environmental issues, toxicity and high costs, there is a need to replace Co by other 3d metal, and in this regard, copper appears as highly-attractive [2].

In this work, Co-free $\text{La}_{1.5}\text{Ba}_{1.5}\text{Cu}_3\text{O}_{7\pm\delta}$ triple perovskite, as well as Cu-rich $\text{GdBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{2-y}\text{Cu}_y\text{O}_{5+\delta}$ series of double perovskites are evaluated as oxygen electrode materials for the Solid Oxide Cells. The conducted studies comprise evaluation of the phase composition and crystal structure, thermal expansion, oxygen content, total electrical conductivity and catalytic activity, as measured using the X-ray diffraction, dilatometry, iodometric titration, thermogravimetry, and 4-probe electrical conductivity methods, respectively. Screen-printing technique was used for the preparation of the oxygen electrode layers. The electrode polarization resistance R_p was evaluated in symmetrical cells. Button-type full cells were constructed using thin $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ electrolyte sinters. $\text{La}_{1.5}\text{Ba}_{1.5}\text{Cu}_3\text{O}_{7\pm\delta}$ oxide with $P/4mmm$ tetragonal symmetry was found to be stable up to 975 °C in air. It is structurally and chemically compatible with $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ electrolyte up to 900 °C, and shows moderate thermal expansion, with the coefficient of $13.2 \cdot 10^{-6} \text{ K}^{-1}$ and $18.8 \cdot 10^{-6} \text{ K}^{-1}$ for temperatures below and above ca. 400 °C. The total oxygen content in the material stays above 6.75, i.e. the average oxidation state of Cu is above +2. Measurements of the total conductivity confirmed high enough for the application (above 10 S cm^{-1}). The recorded R_p values were found to be exceptionally low, $0.019 \text{ } \Omega \text{ cm}^2$ and $0.041 \text{ } \Omega \text{ cm}^2$ at 750 °C and 700 °C, respectively. The measured power density output exceeded 160 mW cm^{-2} at 600 °C and 250 mW cm^{-2} at 650 °C for the button-type cell. The $\text{La}_{1.5}\text{Ba}_{1.5}\text{Cu}_3\text{O}_{7\pm\delta}$ electrode demonstrates also good performance in the electrolyzer mode. For the $\text{GdSr}_{0.5}\text{Ba}_{0.5}\text{Co}_{2-x}\text{Cu}_x\text{O}_{5+\delta}$ series with Co:Cu content close to 1, a favorable set of the characteristics was observed. It was found that copper allows to decrease the thermal expansion, while the oxides show suitable stability at high temperatures, as well as very high mixed electrical conductivity. Importantly, it seems that reactivity with ceria-based electrolytes could be mitigated in this case. At temperatures on the order of 800 °C, the R_p was found to be below $0.05 \text{ } \Omega \text{ cm}^2$. Also, very high power output exceeding 1500 mW cm^{-2} at 900 °C could be obtained, with good performance in the electrolyzer mode recorded as well.

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Assessment of FAA3-50 based MEAs for Anion Exchange Membrane Fuel Cell Application

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The transition towards climate neutrality by 2050 gives energy a central role, as energy is today responsible for more than 75% of the EU's greenhouse gas emissions. To reach climate neutrality, it is necessary to decarbonize at least six times faster than anything realized globally so far. It must drastically increase the share of renewable energy sources and clean energy carriers, and improve energy efficiency [1]. In line with the Paris Agreement, the European Commission, as part of the European Green Deal, proposed in September 2020 to raise the 2030 greenhouse gas emission reduction target, including emissions and removals, to at least 55% compared to 1990; increase at least 32% share for renewable energy, and improve the energy efficiency at least 32.5%. In this context, the electrochemical devices such as Fuel Cells (FC) and in particular polymer electrolyte fuel cell (PEFC) play an important role due to highly efficient electric power generation and low environment impact [2]. In recent years, FCs that use alkaline exchange polymeric membrane as an electrolyte (AEMFC) have recently gained significant interest [3-4]. In fact, the AEMFC is an attractive alternative to PEFCs, due to the faster reaction kinetics that permits to use non-platinum-group metal catalysts and thanks to the high pH of the electrolyte to allow less expensive metal hardware. In any case, the use of alkaline exchange polymeric membrane as an electrolyte require a development and optimization of the electrode structures and MEA. In this work, MEAs, based on FAA3-50 commercial membrane, were developed and electrochemically characterized in single cell configuration. It was evaluated the hydroxylic exchange procedure of membrane and ionomer, in order to better understand the polymer stability in alkaline conditions. It was developed and studied the electrodic structure in terms of ionomer content, presence of microporous layer (MPL) in the GDL, and MEA configurations (Catalyst Coated Substrate -CCS or Catalyst Coated Membrane -CCM). The developed MEAs were electrochemical characterized in a 25 cm² single cell in different operative conditions. Moreover, different electrochemical activation procedures were investigated, to understand how they affect the fuel cell performance.

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Electrodes and Membranes for Energy Storage and Conversion from Bacterial Cellulose

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Bacterial cellulose (BC) is a versatile and environmentally friendly material which has recently found a broad range of applications [1]. Traditionally used in the food industry, it is also known as *Nata de Coco*, but it is particularly attracting for the properties derived from its nanostructure. It is constituted by a 3D network of covalently connected nanofibers of pure cellulose. This infers strong mechanical properties and a high water sorption capability, giving place to a hydrogel-like aspect. It can thus be easily loaded with precursors and give place to functionalized 3D or porous structures of interest for electrodes and membranes with relevant properties in energy-related applications. We will show this by presenting four different examples of processing methods and respective applications:

- 1) A simple route to prepare porous carbons by simply soaking BC in alcohols before carbonization (Figure 1). This prevents the pore collapse upon drying, obtaining carbons with an ideal porosity for Li-O₂ batteries. We obtained large discharge capacity, rate capability and cycle life [2].
- 2) In-situ Ni-P grown on BC by electroless deposition. Small Ni-P particles are generated coating the cellulose fibers. The obtained self-standing, binder-free Ni-P/BC exhibits excellent H₂ evolution in neutral solution, with a small overpotential and good stability.
- 3) A Carbon/MnO₂ composite for Zinc-ion batteries with high rate capability and cycle life.
- 4) A BC/PVdF membrane obtained by solution infiltration applied to vanadium redox flow batteries.

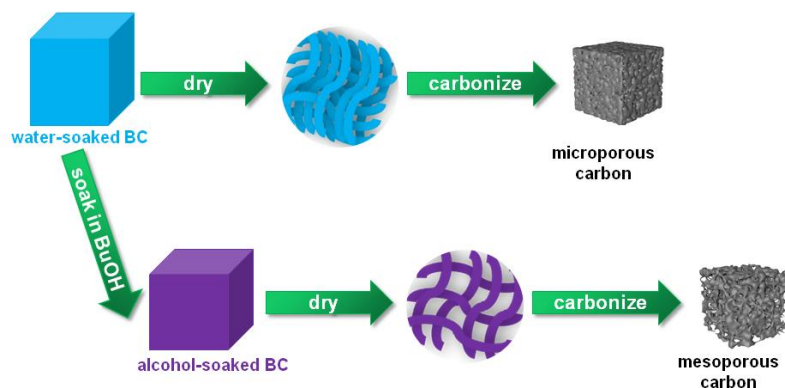


Figure 1: Scheme to produce mesoporous carbon from bacterial cellulose by alcohol treatment.

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Degradation of endocrine disruptors by PEC technique using optimised WO₃ nanostructures

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In the last years, an increase in the presence of new organic contaminants has been reported in wastewater and aquatic environments. Endocrine disruptors (ED) are a kind of environmental pollutants which can interfere with the endocrine system at certain doses causing an alteration in the hormonal processes. This work aims to investigate the degradation pathway of two different ED by photoelectrocatalysis (PEC) technique using tungsten oxide nanostructures.

The endocrine disruptors selected for the degradation were (a) 4-tert-butyl phenol and (b) dimethyl phthalate. As a result of their wide and large quantities used in industry, both chemicals have been recognised as significant environmental pollutants.

PEC using nanostructured electrodes has emerged as one of the advanced oxidation processes with great potential to degrade organic compounds present in contaminated water. WO₃ nanostructures are raising attention as an electrode for PEC due to their favourable properties such as suitable bandgap (≈ 2.6 eV which corresponds approximately to a wavelength of ~ 480 nm), high electron mobility, stability in acidic solution and very good surface stability.

In the present study, optimised WO₃ nanostructures have been synthesized by anodization method in an acidic electrolyte (1.5 M CH₄O₃S and 0.1 M Citric Acid). After the synthesis, PEC degradation of the two contaminants was carried out for 24 h applying a potential of 1 V_{Ag/AgCl} and simulated sunlight conditions (using AM 1.5 illumination). The process was followed by Ultra-High-Performance Liquid Chromatography and Mass Spectrometry (UHPLC-MS-Q-TOF), which allowed obtaining the concentration of the contaminant during the time and the identification of possible degradation intermediates.

Acknowledgments

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3D NANOSTRUCTURED SENSORS FOR ORGANIC AND INORGANIC PEROXIDES DETECTION IN AEROSOL

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Environmental pollution, particularly that involving emerging contaminants, is becoming a global problem. Hydrogen peroxide (H₂O₂) and organic hydroperoxides (OHP) are considered secondary photochemical products as radical initiators. They are known for their powerful reactivity being involved in important oxidation reactions of organic pollutants in the troposphere [1]. A variety of sophisticated instrumental techniques for H₂O₂ and OHP measurements in the aerosol or gas phase have been employed in the last years for environmental monitoring of organic peroxides as harmful tropospheric air pollutants, however, these methods are expensive, complex handling and a bulky instrumentation for continuous recording is required [2]. Electrochemical sensors are a prominent option because of their low cost, high sensitivity and simple manipulation. Among them, biosensors exhibit high catalytic activity and selectivity of enzymes. However, enzyme-based sensors involve low enzyme stability and easy denaturation by environmental changes and thermal and chemical instability. Moreover, the preparation and purification of the enzymes is time-consuming and expensive. Consequently, this communication focuses on the development of non-enzymatic electrodes for monitoring H₂O₂ and different OHP in aerosol.

The modification, characterization and performance of different carbon-based screen-printed electrodes were performed in a seminal work of our group [3] to develop a sensor that allows to analyze H₂O₂ and OHP in real environmental samples. The obtained electrochemical sensor -taking advantages of forming nanocomposites starting from conducting polymer subsequently doped with platinum nanoparticles- provided high sensitivity, selectivity and rapid response to H₂O₂ and OHP detection in aqueous phase.

With the aim of developing a sensor that further allows us increase the sensitivity (to be able to measure H₂O₂ and OHP in aerosol) and make it more economically sustainable for future real applications, a combination of platinum and nickel electrocatalysts was explored. This combination, which is widely studied in the literature for its synergistic effect, reduces the concentration of platinum used for the construction of the composite up less than half. For this work, the synthesis of the nanocomposite was carried out in one pot containing both a precursor monomer and metal salts, which decreases both the synthesis and handling time. This simultaneous co-electrodeposition of bimetallic Pt and Ni nanoparticles and formation of a conductive polymer turned out to form three-dimensional (3D) templates with homogeneous distribution of the bimetallic structure inside the polymeric matrix. Structures of this type have a large surface-to-volume ratio, making them excellent candidates for gas sensors prompting high sensitivity and fast response. H₂O₂ and various OHPs were added to a commercial diffuser at low concentrations (micromolar range); then, the steam was directed towards the surface of the electrode, which provided a fast and sensitive amperometric signal allowing continuous real-time monitoring of the hydroperoxides studied.

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POSTER ABSTRACTS

**Presentations on
Friday 16th Sept, h. 12.00-1.15 pm
Sala EXPO (ground floor)**

Synthesis of WO_3 and WS_2/WO_3 nanostructures for photoelectrocatalysis in hydrogen production

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The energy crisis is a global problem. Currently, the world's primary energy consumption comes mainly from the use of fossil fuels, whose reserves decrease over time and their combustion is causing great environmental pollution. Consequently, the idea of hydrogen (H_2) as a fuel appears as a need to replace fossil fuels by clean and suitable sources,

Photoelectrochemical (PEC) water splitting has been considered one of the most promising hydrogen production technologies using solar energy. Tungsten oxide (WO_3) has attracted much interest as a photoanode for PEC applications due to its excellent properties: good conductivity and charge-transfer properties, high stability in acidic solutions, resistance to photocorrosion and ability to absorb visible light. Furthermore, heterojunctions of tungsten with other metals, such as transition metal dichalcogenides (TMDs) are being studied in order to improve the performance of WO_3 as a photoanode,

In this work, the synthesis and deposition of WS_2 on WO_3 nanostructures have been studied in order to build a WS_2/WO_3 heterojunction with higher photoelectrocatalytic properties to use it as a photoanode for PEC water splitting.

On one hand, WO_3 nanostructures were synthesized by electrochemical anodization in an acidic electrolyte (methanesulfonic acid and citric acid) under hydrodynamic conditions (375 rpm). After that, an annealing treatment at 600°C was carried out in order to obtain crystalline WO_3 . On the other hand, WS_2 nanosheets were prepared from WS_2 powder by sonification. Finally, the WS_2 nanosheets were deposited into the WO_3 nanostructures by electrophoretic deposition. The deposition time was varied to study the best deposition conditions.

In order to characterise the samples, Field Emission Scanning Electron Microscopy (FE-SEM) has been used to study the morphology of the samples and electrochemical impedance spectroscopy (EIS) was performed to study their photoelectrochemical properties.

Finally, the different synthesized samples were applied as a photoanode for energy production in PEC water splitting tests and the photocurrent density response among the samples was compared.

Acknowledgments

Authors would like to express their gratitude to AEI (PID2019-105844RB-I00/AEI/10.13039/501100011033) for the financial support. M. Cifre-Herrando thank Ministerio de Universidades for the concession of the pre-doctoral grant (FPU19/02466). G. Roselló-Márquez also thanks the UPV for the concession of a post-doctoral grant (PAID-10-21). Finally, project co-funded by FEDER operational programme 2014-2020 of Comunitat Valenciana (IDIFEDER/18/044) is acknowledged.

Electro-oxidation of the Iodinated Contrast Medium Iopamidol on different electrode materials

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Iopamidol is one of the most widely used iodinated contrast media for radiological tests, whose presence has been detected both in water from hospitals and in effluents from wastewater treatment plants. Because of this and the lack of regulation Iopamidol is considered an emerging pollutant [1]. Despite its potential risk, there are very few studies on its degradation, and almost no research on its electro-oxidation. In addition, most of these studies do not achieve complete degradation and/or generate intermediate reaction compounds with high toxicity values, even higher than the toxicity of Iopamidol [2]. Therefore, it is necessary to address new studies for its elimination.

Advanced oxidation processes are considered among of the most effective methods for tertiary wastewater treatment. Particularly, the anodic oxidation has received great attention because of its simplicity, since it can oxidize and/or mineralize refractory pollutants by applying a potential/current on a suitable anode material. In this field, most studies have been carried out with expensive commercially-available anodes, like Ti/Pt and Si/BDD, to now, the most efficient electrode for the generation of highly-reactive hydroxyl radicals ($\bullet\text{OH}$). On the other hand, Pt-doped SnO_2 -Sb anodes constitute an attractive cheaper alternative for the electrochemical treatment of wastewaters, and their electrocatalytic response has been discussed [3].

In this work, the abatement of Iopamidol on Ti/Pt, Si/BDD and Ti/ SnO_2 -Sb-Pt(13 met.%) electrodes has been studied. The Ti/ SnO_2 -Sb-Pt(13 met.%) anode was prepared onto titanium substrate by the thermal decomposition method [4]. The elimination of Iopamidol was carried out by galvanostatic electrolysis in an undivided filter-press cell, in 0.5 M Na_2SO_4 M, and its concentration and that of by-products was followed by different techniques (UV-vis, COD, TOC, HPLC and ionic chromatography). Moreover, cyclic voltammetry was used to study the catalytic activity of the anodes.

The results (Fig. 1) indicate that the Ti/ SnO_2 -Sb-Pt(13 met.%) anode oxidizes 82 % (in 3 h) and achieves a complete elimination (in 24 h) of Iopamidol solution (500 ppm, 0.2 L). Although less efficient than commercial anodes, this work demonstrates that these cheaper electrodes overall exhibit good activity towards the elimination of Iopamidol.

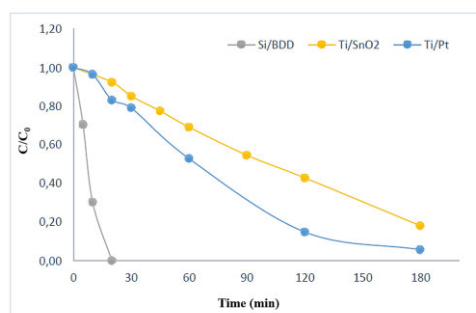


Figure 1: Normalized Iopamidol concentration during electrolytic treatments at $j = 50 \text{ mA/cm}^2$.

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ELECTRODEPOSITION IN ONE POT TO BUILD THREE-DIMENSIONAL PtNi/POLYMER NANOCOMPOSITE FOR PEROXIDES DETECTION IN AEROSOL/GAS PHASES

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In recent years, there has been a growing interest in designing advanced materials capable of being tuned for specific applications. In this regard, interest is on the rise of the synthesis, characterization and functionalization of materials with hollow architecture and mesoporous nanostructure. Conducting polymer composites containing metallic or metal oxide nanoparticles have drawn particular attention in the field of electrochemical sensing. One of the most interesting performances of these nanostructured materials has been focused on its significant sensing capacity suitable for gas detection applications [1].

Nanocomposite assembly by electrochemical methods provides a better control of the synthesis process compared to the chemical methods. The structure and properties of both electrodeposited components: nanoparticles and polymer, depend on the combination of solution composition, the electrolysis potential and charge passed synthesis.

This work investigates the formation mechanism of the electrochemically deposited of a 3D PtNi/ polymer nanocomposite by alternating layers of a polymer *azo* type (poly azure-A), whose properties have been previously studied by our research group [3], with platinum and nickel nanoparticles through a simple one-pot method. The number of voltammetric cycles used for the construction of the polymeric film as well as the potential applied for the reduction of metal salts led to different electrochemical properties of the nanocomposites supported by electrochemical impedance spectroscopy (EIS).

The 3D polymeric nanoarchitecture obtained showed an easily functionalizable morphology for (bio)sensing applications. In this regard, the modified electrodes were tested for H₂O₂ and organic hydroperoxides detection in aerosol phase in the micromolar range. To do that, the samples investigated were injected via a commercial diffusor containing a septum. In this way the electrochemical sensor was able to continuously monitor the amperometric response.

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Photoelectrochemical splitting of water with NiO-PANI composite cathodes

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In view of a sustainable way to produce energy, hydrogen plays a key role. Its production by water electrolysis, driven by renewable energy, and its subsequent use in a fuel cell, could represent a zero-emission process, globally eco-sustainable: the storage of H₂ could allow compensating the intrinsically alternate regime of renewable energy [1]. Among various approaches that can be used to obtain H₂, photoelectrochemical (PEC) water splitting technique can be considered. To this aim is addressed also the present work, by proposing electrode materials less expensive than noble metals, and operative costs, by lowering the required cell potential, thanks to the photo-potential generated at semiconductor electrode materials. Nickel oxide (NiO) is a potentially low-cost alternative to precious-metal as photocathode, and it can be obtained from selective corrosion of Ni/Al or Ni/Zn systems. More recently also Ni/Cu alloy has been used as precursor to fabricate porous Nickel by electrochemical dealloying: because Cu is chemically more stable than Ni, the selective dissolution of Cu is based on the passivation of Ni under suitable electrochemical conditions [2]. Moreover, the use of PANI as a conducting polymer for electrodes and supercapacitors is very attractive because of its good characteristics such as low cost, simple synthesis, high environmental stability, good electrical conductivity, good electronic and optical properties and reversible control of conductivity by charge-transfer doping and protonation [3].

In this work we investigate the corrosion of Ni/Cu films to obtain NiO porous electrodes; electrodeposition was performed in aqueous electrolytes, composed by 0.5M boric acid, with different concentrations of nickel (II) sulfate hexahydrate and copper (II) sulfate pentahydrate. The anodic dissolution was carried out in aqueous solution with 0.5 M of sodium sulfate and boric acid 0.5 M.

NiO-polyaniline hybrid composites were synthesized by a multi-step electrochemical procedure as follows: (1) electrochemical synthesis of NiO, (2) functionalization of NiO by electroreduction of 4-nitrobenzediazonium salt, (3) electrochemical reduction of the nitro group to amine, (4) electropolymerization of aniline onto the surface of the aminophenyl-modified NiO electrode.

In order to evaluate the performance of the samples, the trend of photocurrent with the potential was preliminarily investigated: depending on the sample, different polarization trends were obtained, and the plateau of photocurrent saturation was achieved at a different potential from the open circuit potential value. The as synthesized photocathode can be coupled with a photoanode in a PEC cell for light assisted water splitting.

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Selection of cathode materials for ozone-based electrochemical advanced oxidation processes

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To overcome the poor ability of ozonation to mineralize persistent molecules and complex effluents, novel technologies that imply the combination of ozonation with electrolysis have been recently proposed.

The occurrence of either direct reduction of ozone on selected cathodes, or its reaction with the in-situ electrogenerated species, enables the production of highly oxidizing radicals and results in a clear synergistic effect. The selection of a cathode that combines low cost, efficiency, and durability is the key to the process scale-up.

Currently, most of the research involves the use of a limited number of electrode materials mainly carbon-based to promote the formation of hydrogen peroxide thus obtaining the so-called electro-peroxone reaction. Instead, metal cathodes promote the formation of species capable of evolving, under acidic conditions, into hydroxyl radicals.

In this work, a variety of electrode materials, either carbon-based or metal-based, have been tested and compared to identify the most suitable candidate to use in the co-presence of ozone. The cathode examined were stainless steel (SS), platinum (Pt), copper (Cu), zinc (Zn), titanium (Ti), gold (Au), aluminum (Al), a silver-plated nickel (Ag/Ni) mesh, boron-doped diamond (BDD) and glassy carbon (GC).

In a first characterization, the ability of the material to directly reduce ozone has been assessed by means of cyclic voltammetry. The occurrence of hydrogen peroxide electro-generation by oxygen reduction has been monitored by electrolysis conducted in an undivided cell.

Then, the effectiveness of the most promising electrodes has been tested in the degradation of coumarin, as a model compound, in aqueous solutions. The organic degradation was monitored by UV-Visible spectroscopy and total organic content (TOC) analysis. The presence and nature of radicals have been verified in tests conducted with selective scavenging agents (tert-butanol and L-Histidine).

Finally, since the electrode materials used in these processes are exposed to extremely aggressive and corrosive conditions, their chemical-mechanical stability has been evaluated by cyclic voltammetry and accelerated aging tests.

Cu and Zn Electrowinning from Urban Waste Incineration Ashes Using an FM01-LC Filter-Press Cell

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Becoming less dependent on market fluctuations, acquiring greater environmental awareness, and making profit from massive waste has shifted the paradigm toward circular strategies that may have great positive impact on the economy and the planet alike. Unconventional sources of metals like urban waste ashes seem a good raw matter candidate, but they usually contain small amount of Cu that is accompanied by other metals such as Fe, Zn, Sb, Mo, Mn, or Ni. Since they are typically leached using acidic media, the application of additional processes is required for final recovery or separation. Recently, different technologies have been proposed to valorize acid solutions containing metals, including adsorption with activated carbon, ion exchange with resins and liquid-liquid extraction with organic solvents. Although they can be potentially useful for the recovery of metals and acid, they show two drawbacks: (i) An additional treatment is required to purify the acid or metal, and (ii) a regeneration stage of carbon, resin or organic phase used must be implemented, which increases the operation cost [1]. In this context, the electrochemical reduction emerges as an alternative technological for metal recovery in a strong acid medium. For example, regarding the recovery of Cu and Zn, good results have already been obtained using cells equipped with a rotating cylinder electrode [2,3]. In the present work, the recovery of Cu and Zn from urban waste ash leachate was studied using a 3 L pilot plant that included an FM01-LC filter-press cell equipped with a three-dimensional graphite felt cathode or a two-dimensional stainless-steel cathode. The parameters studied using a model solution were: (i) the applied current density; (ii) the presence of other metals such as Zn, Fe, Ca, and Mg; (iii) the solution pH; (iv) the initial metal concentration; and (v) the cathode material. Further, a solution that simulated the real conditions of the leachate, which contained different elements at pH ~1 was used. The treatment was carried out in three consecutive steps: (i) ferric ion removal, raising the pH to 4; (ii) Cu recovery with the 3D graphite felt cathode, at pH 2.5; and (iii) Zn reduction with the 2D cathode at the same pH. The complete recovery of Cu was obtained within a short time of electrolysis, starting from ~200 mg L⁻¹ of Cu²⁺, while recoveries close to 90% were obtained for Zn at longer time, starting from ~1600 mg L⁻¹ of Zn²⁺. The two-stage electrochemical treatment using a filter-press reactor could contribute to a cost-effective recovery of value-added metals such as Cu or Zn.

Acknowledgments

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Robocasted Steel as a Novel Cathode Material for Electrocatalytic Nitrate Removal: A Proof of Concept

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Robocasting is a specialized additive manufacturing extrusion-based 3D-printing technique in which a filament of paste (i.e., ink) is extruded from a small nozzle whose position is computer-controlled in accordance with a CAD model. A wide range of materials has been successfully printed, being the objects built up layer-by-layer to allow the creation of geometrically complex pieces that may be difficult or impossible to fabricate by casting or upon mechanization of a hard material. An ink for robocasting must be highly shear thinning to allow extrusion through fine nozzles, and also retain a degree of strength and stiffness to become self-standing after printing. There are several options to get these rheological conditions, being the use of inks based on a hydrogel as carrier one of them [1]. The type of atmosphere (inert, reducing, etc.) and temperatures involved during the thermal post-treatment depends on various factors. The steps involved during thermal post-treatment are basically: (i) the drying, aimed at evaporating the water contained in the extruded paste; (ii) the debinding, in which the organic binder is decomposed; and (iii) the sintering process, where the mechanical properties are enhanced by a solid diffusion process. In this work, the ink was a hydrogel constituted by a dispersed phase (metallic powder) and an aqueous based dispersant phase (with Pluronic F-127 as the binder), which presents the appropriate rheological properties to obtain a low density crack-free copper containing steel with a high final roughness and porosity, enhancing the surface area in comparison with a casted steel of analogous composition. The sintered steel has been studied as a proof of concept to become a potential electrocatalytic material, further being employed as a cathode for electrochemical nitrate reduction. Note that iron and copper belong to the most studied transition metals for this application due to their high conversion efficiency and remarkable selectivity towards ammonia, the main by-product. The ammonia generated during the nitrate removal poses no substantial problem since it could be easily eliminated from the treated water; otherwise, ammonia electrosynthesis can also be a secondary benefit from nitrate removal, matching perfectly with the idea of circular economy and waste valorization. Galvanostatic trials have been carried out in order to assess the electrocatalytic activity of the printed steel toward nitrate reduction, as compared to either a highly active casted mild steel [2] or a copper plate. This has allowed elucidating its activity through current efficiency calculation, as well as its aging evaluated from the surface changes after several electrolytic trials. In addition, the leaching of copper and iron to the treated solution, in the presence and absence of chloride ion in the model sulfate medium, has been analyzed. The metallic powder precursor composition and the printed steel characteristics have been determined by several techniques like confocal microscopy, XPS, XRD and fluorescence, revealing the main features.

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Strategies to Enhance the H₂O₂ Production for Water Treatment Using Mesoporous Carbons Obtained from Abundant Biosources

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The increase of sustainability in water treatment cannot only be reached by incorporating renewable energy sources to power the different devices, but more benign materials (i.e., with lower carbon footprint) are required. In the particular case of electrochemical technology for water decontamination, the electrode materials constitute the core, being crucial to enhance their efficiency to minimize the energy needs. The treatments based on the cathodic H₂O₂ electrogeneration have gained attention due to their high effectiveness upon conversion of this mild oxidant into the powerful hydroxyl radical (\bullet OH). It is well known that modifying the surface characteristics of carbons increases their efficiency for the two-electron oxygen reduction reaction (ORR). This may arise from their greater selectivity, as a result of the increase in the reduction potential to more positive values, and/or activity, usually having to reach a compromise between both parameters [1]. Our groups have undertaken a collaboration with the objective of synthesizing a series of carbonaceous materials from different abundant biosources following a varied range of procedures. Once obtained, the carbons were implemented in air-diffusion cathodes to evaluate their selectivity (RRDE characterization) and activity (voltammetric characterization, bulk electrolytic trials and capacity to yield the complete degradation of selected organic contaminants by Fenton-based processes) as compared to those of a commercial material. Chitosan and agarose, chosen as ecological biopolymers in this work, were manipulated to obtain a hydrogel, which was typically freeze-dried and pyrolyzed following different thermal steps up to 950 °C. In some cases, the effect of a novel steam post-treatment on the textural properties and performance was also investigated. It is shown that doping with N exerts a positive effect. When treating solutions of 150 mL of the drug acebutolol at pH 3.0 and at 30 mA cm⁻², with Fe²⁺ as a catalyst, 16 min were required to completely eliminate it by photoelectron-Fenton (PEF) using N-doped chitosan-derived carbon; the same system, with an undoped carbon, needed 20 min [2]. On the other hand, it is shown that the mesoporosity/microporosity ratio has a direct impact on the performance of the cathodes. Thus, agarose-derived carbon-based cathodes with improved textural properties and an optimized combination of micropore and mesopore volume, reached a faradaic efficiency of 95% in 30 min; in addition, acebutolol was eliminated from wastewater in 60 min, applying only 10 mA cm⁻² [3]. More recently, a hard template method has been employed to convert chitosan into mesoporous carbons with up to $V_{meso} = 2.408 \text{ m}^2 \text{ g}^{-1}$, evidencing that co-doping with N and S had an excellent positive impact on the cathode performance. This phenomenon led to significantly greater H₂O₂ production (i.e., highest among all chitosan-based cathodes tested) and faster degradation of the antibiotic moxifloxacin by electro-Fenton (EF) and PEF processes.

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