International Workshop

Materials for Today's Energy Challenges

Padova, 3-4 June 2019

BOOK OF ABSTRACTS

Levi Cases
Società Chimica Italiana Divisione di Chimica Inorganica
Società Chimica Italiana Divisione di Elettrochimica
PARTICULAR MATERIALS
surfaces
INSTM
fkv PASSIONEIDEESOLUZIONI
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Schaefer Italy Nanoscale Measurements Nanotechnology - Vacuum Technology
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Scope

Nowadays, one of the main challenges that humankind has to face is how to generate enough energy for maintaining our standard of life without damaging the environment in a permanent way. Therefore, a radical change of the current energy infrastructure is required. In this context, Materials Science is expected to play a key role providing fundamental knowledge and applied materials in a variety of fields ranging from heterogeneous catalysis, photovoltaics and electrochemistry to photonics and microelectronics.

“Materials for Today’s Energy Challenges” aims to bring together international scientists from all domains of Materials Science for energy related applications to provide a forum for sharing views and discussing about the most advanced research directions in the Materials Science-energy nexus. An overview of the most recent advances in heterogeneous catalysis and electrocatalysis for energy production and storage will be provided.

Main topics
- Hydrogen and solar fuels production
- Electrocatalysts for oxygen reduction and evolution reactions
- New technologies for CO_2 valorization
- New materials for water splitting
- Electrochemical devices for energy storage
- Photovoltaics

Organization

Chairs
Dr Laura Calvillo (University of Padova, Italy)
Prof Stefano Agnoli (University of Padova, Italy)

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Gaetano Granozzi (University of Padova, Italy)
Siglinda Perathoner (University of Messina, Italy)

Scientific Program

Monday 3 June 2019

9:00 – 10:45	**REGISTRATION**
10:45 – 11:00	**OPENING**
	Chair of the Session: Gaetano Granozzi
11:00 – 11:50	**PL1- Peter Strasser**, Technical University of Berlin *Free electrons to molecular bonds and back – The electrocatalytic dark side of solar fuels and solar chemicals*
11:50 – 12:20	**KN1- Nicolas Alonso-Vante,** Université de Poitiers *Unraveling factors that affect the electrochemical hydrogen reaction*
12:20 – 12:40	**O1- Norberto Manfredi,** University of Milano-Bicocca *Organic sensitizers for dye-sensitized water splitting*
12:40 – 14:00	**Lunch break**
	Chair of Session: Jan Philipp Hofmann
14:00 – 14:30	**KN2- Andrea Lamberti,** Politecnico di Torino *Advanced nanomaterials for energy harvesting and storage: the cases of dye-sensitized solar cells and supercapacitors*
14:30 – 14:50	**O2- Alessandro Minguzzi,** University of Milano *Recent advances in (photo)electrocatalysis by scanning electrochemical microscopy and X-ray adsorption spectroscopy*
14:50 – 15:10	**O3- Nicola Schiaroli,** University of Bologna *Synthesis gas production by steam/dry reforming of the clean biogas*
15:10 – 15:30	**O4- Christoph Griesser,** University of Innsbruck *Synthesis and characterization of Mo_2C films as a promising catalyst for the electroreduction of small molecules*
15:30 – 16:00	**Coffee break**
	Chair of Session: María Escudero Escribano
16:00 – 16:30	**KN3- Alexis Grimaud,** Collège de France *Controlling the redox reactions on the surface of solids by tuning the electrolyte structure*
16:30 – 16:50	**O5- Anu Baby,** University of Milano-Bicocca *Tuning the hydrogen evolution reaction at the Pt(111) surface with 2D material and non-precious metal*
16:50 – 17:10	**O6- Maria Victoria Martinez-Huerta,** Instituto de Catalisis y Petroleoquimica – CSIC *Identifying active sites for Ti-Co bifunctional catalysts for oxygen reduction and water oxidation catalysis*
17:10 – 17:30	**O7- Giulia Tuci,** ICCOM-CNR *Tailoring N-decorated carbon nanotubes as highly efficient electrocatalysts for the selective CO_2 reduction to CO*
17:30 – 17:35	**CERIC-ERIC**
17:35 – 18:10	**Flash poster presentations**
18:15 – 19:45	**Poster session + Spritz**
20:30	**SOCIAL DINNER**

Tuesday 4 June 2019

	Chair of Session: Nicolas Alonso-Vante
9:00 – 9:50	**PL2- Beatriz Roldan Cuenya**, Fritz Haber Institute *Operando insight into electrocatalytic and thermal conversion of* CO_2 *to valuable chemicals and fuels*
9:50 – 10:20	**KN4- Maria Escudero Escribano**, University of Copenhagen *Tailored interfaces for enhanced oxygen electrocatalysis*
10:20 – 10:40	**O8- Marco Bersani,** Particular Materials *Bridging the gap in nanomaterials upscaling*
10:40 – 11:10	**Coffee break**
	Chair of Session: Alexis Grimaud
11:10 – 11:40	**KN5- James Ball,** University of Oxford *Advances and challenges in perovskite photovoltaics*
11:40 – 12:00	**O9- Matteo Amati,** Elettra *Operando characterization of SOFC components at the submicron scale by scanning photoemission imaging and spectromicroscopy*
12:00 – 12:20	**O10- Xavier Companyó,** University of Padova *Transition-metal-free* CO_2 *fixation into new carbon-carbon bonds*
12:20 – 12:40	**O11- Fabio Dionigi,** Technical University of Berlin *Tracking structural transformations by operando X-ray scattering for the oxygen/water catalysis*
12:40 – 14:00	**Lunch break**
	Chair of Session: Stefano Agnoli
14:00 – 14:50	**PL3- Fabrizio Cavani,** University of Bologna *Heterogeneous catalysis: the frontline for advancement in tomorrow's industrial chemistry and energy sectors*
14:50 – 15:20	**KN6- Jan Philipp Hofmann,** Eindhoven University of Technology *Functional characterization of photoelectrodes by X-ray photoemission spectroscopies*
15:20 – 15:40	**O12- Claudio Ampelli,** University of Messina *Sustainable production of chemicals and fuels from* CO_2*: towards the realization of an artificial leaf using non-critical raw materials*
15:40 – 16:10	**Coffee break**
	Chair of Session: Andrea Sartorel
16:10 – 16:40	**KN7- Antonella Glisenti**, University of Padova *Next generation solid oxide cells: building advanced functionality through doping and nanocomposition*
16:40 – 17:00	**O13- Serena Berardi,** University of Ferrara *On the role of semiconductor/catalyst junction in first row transition metal-based photoanodes*
17:00 – 17:20	**O14- Etienne Boutin,** Université Paris Diderot *Beyond CO. Efficient multi-electrons, multi-protons* CO_2 *electrochemical reduction into fuel with Co molecular catalyst*
17:20 – 17:40	**O15- Carmelo lo Vecchio,** CNR - ITAE *Excursus and new achievement of M-N-C cathode catalysts in acidic media for direct methanol fuel cells applications*
17:40 – 18:00	**POSTER AWARDS AND WORKSHOP CLOSING**

Plenary lectures

PL-1

Free electrons to molecular bonds and back – The electrocatalytic dark side of solar fuels and solar chemicals

Peter Strasser

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Electrochemistry and electrocatalysis play prominent roles on the dark side of solar fuels and chemicals. They lie at the heart of the interfacial conversion of free electrons into molecular bonds – and back into free electrons. For these electrochemical transformations to occur with the smallest possible energy losses and the utmost atom efficiency, optimized nanostructured multi-component catalyst materials are critical, yet for many desirable multi-electron solar fuel reactions unknown. The successful discovery and development of novel nanostructured electrocatalyst materials requires insight into the relation between their atomic-scale structure and their catalytic performance. Unraveling such relations is thus a scientific priority.

In this talk, I will highlight some advances of our recent work on the electrochemical reduction of CO_2 into value-added fuels and chemicals on conventional and unconventional non-metallic catalysts. I will also touch on novel nanostructured water splitting electrocatalysts for acid and alkaline environments. Focus will be placed throughout on a thorough understanding of structure-activity relations of the new catalytic materials and their liquid-solid interfaces.

PL-2

Tuning CO_2 electroreduction selectivity by rational catalyst and electrolyte design

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The efficient electrochemical conversion of CO_2 (CO_2RR) to valuable fuels and feedstocks is a highly sought process towards the minimization of the carbon footprint. However, higher selectivity towards C_{2+} products must be achieved before a broad industrial use can be envisioned. Better efficiency can be attained by tuning the morphology (size, shape, dispersion), oxidation state, composition of the catalyst, NP/support interactions, and by a rational selection of the electrolyte. In addition, understanding the changes that a catalyst may experience on its surface during a reaction is crucial in order to stablish structure/composition-reactivity correlations. Here, mechanistic insight into CO_2RR will be provided by using as target materials plasma-activated metal surfaces (Cu, Ag, Sn-Ag) and size- and shape-controlled mono and bimetallic NPs including Cu, Cu_2O, Zn, Cu-M (M=Zn, Co, Ag) NPs with spherical and cubic shapes. Pulsed electrolysis will be used to gain further insight into the role of Cu_2O species in C_{2+} product selectivity.

A synergistic combination of spectro-electrochemical methods, *in situ* microscopy (EC-AFM), *operando* X-ray absorption spectroscopy (XAS) and *quasi in situ* X-ray photoelectron spectroscopy (XPS) were used to gain insight into the morphological, structural, and chemical transformations underwent by the NPs during CO_2RR. I will illustrate that the as-prepared state of the mono and bimetallic NPs is drastically different from the structure and surface composition of the working catalyst.

PL-3

Heterogeneous catalysis: the frontline for advancement in tomorrow’s industrial chemistry and energy sectors

Fabrizio Cavani

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Roadmaps for advancement of science and technology in chemistry and energy sectors highlight the key role played by catalytic materials. The practical implementation of Circular Economy, Bio-economy and Low-Carbon Economy principles is based on the development of innovative heterogeneous catalysts, able to “close the cycle” in the exploitation of raw materials, in the recovery and reuse of by-products and wastes, in the minimization of CO_2 end-of-life emissions.

In this lecture, a few emblematic examples will be illustrated, as detailed below:

- Multifunctional catalysts for the valorization of by-products and wastes in the field of (bio)-fuel additives.
- Highly specific catalysts for the exploitation of shale-gas components, and the production of added-value chemicals
- Spinel-type ferrites for the chemical-loop reforming of bio-alcohols, aimed at H_2 generation with intrinsic separation of CO and CO_2.

Keynote lectures

KN-1

Unravelling factors that affect the electrochemical hydrogen reaction

Nicolas Alonso-Vante

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Hydrogen is considered an ideal source of energy for sustainable development whose combustion with oxygen only provides water as a by-product without carbon dioxide. In addition to the classic hydrogen production processes, electrochemistry, using electricity from renewable energy sources, and photoelectrochemistry constitute an ideal approach for water electrolysis to produce H_2.[1]

The process of water electrolysis involves two half-reactions, namely, the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). For practical applications, however, efficient (photo)-electrocatalysts are needed because of the existence of overpotentials (i.e., the difference between the practical potential and the thermodynamic potential). Recent literature reveals that crystalline phase conversion,[2] morphology design [3] and/or doping modulation [4] are strategies [5] that can improve the electrocatalytic properties of nanostructures for the hydrogen evolution reaction in acid and alkaline media. During this reaction the adsorbed $(*)\text{-H}_{ad}$ and $(*)\text{-OH}_{ad}$ species interact with additional intermediates (e.g., proton-coupled electron transfer) to generate the product. In addition, the effect coming from the supporting material (local interaction) is, in most cases, underestimated, even under the knowledge that, under certain conditions, the supporting material is active on its own.

Herein, in order to track the effect from the supporting material, selected catalytic nanostructures (based on precious and non-precious centres) supported on surface chemical modified carbon materials (e.g., amorphous carbon, carbon nanotubes and graphite) were generated to anchor chemically and/or photochemically selected catalytic centres. With the support of various physical-chemical characterization techniques, the resulting electrochemical evaluation suggests that, in an acid or alkaline environment, the hydrogen evolution reaction is favoured when such electrocatalytic nanostructures interact with the supporting material, observing, e.g., that the HER kinetics proceeds via Volmer-Heyrovsky as the rate determining step of the reaction. Therefore, the combination of high specific surface area, a variety of active sites, and cost-effective nanomaterials is a key research concept.

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KN-2

Advanced nanomaterials for energy harvesting and storage: the cases of dye-sensitized solar cells and supercapacitors

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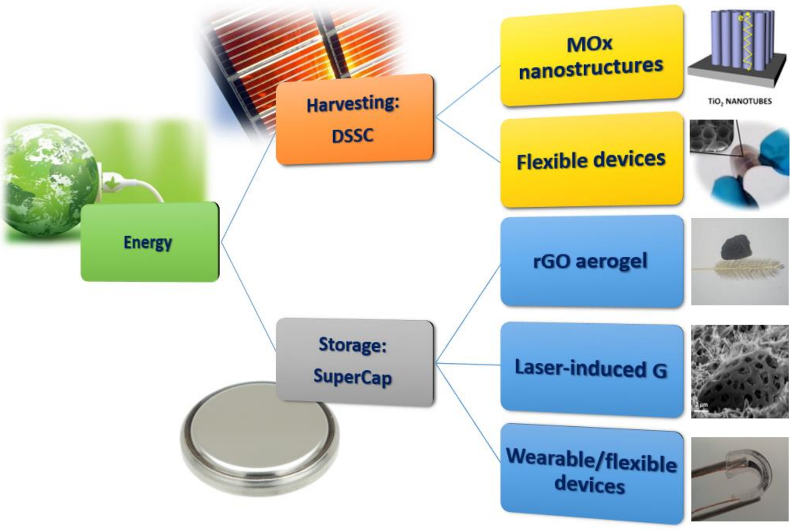
Great effort has been expended and assets spent to improve technologies for the conversion of renewable energy resources; day-by-day we face increasing energy consumption. Considering the request to reduce the dependence on conventional resources and develop a new energy landscape, renewable energy sources must be complemented by efficient energy storage systems characterized by robust technologies and at low associated costs.

In this context, nanostructured materials represent a huge class of interesting candidates to overcome the actual limitations of several energy technology fields. Indeed, the nanostructuration has been proved to be the key to overcome some of the restrictions of traditional bulk materials allowing the exploitation of dimension scaling-down effect on their physico-chemical properties. They have now been widely used in the design of energy saving and harvesting devices, such as mechanical nanogenerators, lithium-ion batteries, supercapacitors, fuel cells, photovoltaics, and even for hydrogen production by water photolysis. In this broad context I will present the most important results obtained by Materials and Processes for Micro and Nanotechnologies Group at Politecnico di Torino (MP4MNT@PoliTO, https://areeweb.polito.it/ricerca/micronanotech/main-page) about nanomaterials for energy harvesting and storage applications focusing the attention on some metal-oxide (such as TiO_2 and ZnO) and graphene-based materials (like rGO aerogel and laser-induced graphene) and in particular their application in dye-sensitized solar cells [1-2] and supercapacitors [3-4].



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KN-3

Controlling the Redox Reactions on the Surface of Solids by Tuning the Electrolyte Structure

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Mastering the complex ion and electron transfers on the surface of solids is at the heart of the development of efficient oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) heterogeneous electrocatalysts. This is especially true for the OER which, when compared to the HER, shows sluggish kinetics associated with large overpotential, i.e. large energy loss. Recent developments in the field have allowed to pin point one critical intermediate, namely the formation of electrophilic oxygen species,[1-3] which is controlling both the activity but also the stability of transition metal oxides used as OER catalysts. While this finding has been critical to understand the activity/stability relationship observed for the OER catalysts, it sets up a limit for the development of active and stable catalysts.

This realization thus forces us to explore new grounds in order to break this activity/stability correlation. Hence, rather than to combat this trend, we decided to embrace the reactivity of high valence transition metal oxides towards water in order to develop a new class of catalysts. For that, we explored a family of iridate and ruthenate compounds with a layered structure previously described as promising Li-ion battery electrodes. Upon oxidation, these materials were found to be capable of chemically oxidizing water, and the charge transfer associated with this oxidation balanced by the intercalation of hydrated cation from the electrolyte, leading to a so-called EC mechanism. These catalysts, for which the electrolyte penetrate in the bulk of the solid catalyst, are at the frontier between heterogeneous and homogeneous catalysts, and can be described as intercalation-stabilized chemical catalysts. Mastering the hydration enthalpy of the cation in solution, we could trigger or in contrary suppress this new mechanism which thus allowed us to compared the kinetics associated with this mechanism with the kinetics associated with a classical “surface heterogeneous” mechanism. Doing so, we could find that this new mechanism shows a 5-fold increase in kinetics while allowing for stabilizing the surface and the performances of the catalysts. In this talk, we will discuss the promises offered by mastering this new OER reaction, as well as describing the new challenge facing us to control the electrolyte solvation structure on the surface of these new catalysts.[4,5]

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KN-4

Tailored interfaces for enhanced oxygen electrocatalysis

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The slow kinetics of the oxygen reduction and evolution reactions (ORR and OER, respectively) impede the widespread uptake of renewable energy conversion technologies such as fuel cells and water electrolysers. This talk will present some recent strategies aiming to understand and tailor the activity and stability for ORR and OER electrocatalysts.

Model studies using the rotating disc electrode (RDE) technique are suitable to investigate the ORR activity trends [1], understand the structure-activity-selectivity relationships [2] and rationally design efficient nanoparticulate catalysts [3]. We recently used Cu/Pt(111) near-surface alloys to study the ORR in alkaline electrolyte [4]. Our results show that the ORR shares the same reaction intermediates in both acidic and alkaline electrolytes. On the other hand, we systematically studied the ORR activity and stability trends by controlling strain effects on Pt-lanthanide alloys [1]. The active phase consists of a compressed Pt overlayer formed by leaching of the lanthanide metal [5]. *In situ* grazing incidence X-ray diffraction studies on Gd/Pt(111) show that the overlayer is very stable at fuel-cell relevant potentials [6].

Despite the progress in the development of Pt-based electrocatalysts presenting high enhancement in ORR activity over pure Pt in RDE measurements, translating the activity enhancement to real devices remains a challenge [7]. Recently, we have presented a gas diffusion electrode (GDE) setup [8] which can be used for benchmarking of Pt-based electrocatalysts at fuel-cell relevant current densities (around 1 A cm^{-2}) [9]. Our results illustrate the importance of characterising the ORR electrocatalysts under realistic conditions.

Finally, exploring the OER activity and degradation mechanisms is essential to develop more efficient catalysts. Sub-monolayer amounts of IrO_x on top of RuO_x thin films minimise Ru dissolution [10]. This strategy may enable tuning the stability of active OER catalysts in acidic media.

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KN-5

Advances and Challenges in Perovskite Photovoltaics

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Perovskite-halides are an emerging class of materials that are well suited to low-cost, high-performance semiconductor devices such as solar cells, light-emitting devices, and transistors. In recent years the power conversion efficiencies of laboratory-scale solar cells based on perovskites have been improving at an unprecedented rate and are now approaching the performance of crystalline silicon. This progress has been enabled by a unique combination of properties that perovskites exhibit: versatile processibility using low-cost techniques under mild conditions; bandgap tunability across the visible-NIR spectrum through elemental and molecular substitution; moderate exciton binding energies that enhance the absorption coefficient whilst maintaining direct free-carrier photoexcitation; and a high tolerance to defects leading to low non-radiative losses and long charge-carrier diffusion lengths.

Here we will give an overview of perovskite materials systems, their fundamental properties, and their device characteristics. We will show how these characteristics will enable the development of the much-sought prospect of low-cost multijunction photovoltaics: a cell architecture that can overcome the thermodynamic limit that restricts the most successful existing commercial technologies. In particular, we will present recent progress on the development of thermally-stable low-bandgap perovskites deposited by vacuum evaporation; a challenging but fundamental component of all-perovskite tandem cells. Finally, we will provide a perspective on unresolved challenges that must be overcome to enable perovskites to become a viable photovoltaic material beyond the laboratory.

KN-6

Functional Characterization of Photoelectrodes by X-ray Photoemission Spectroscopies

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The storage of intermittent solar energy in chemical bonds, i.e. Solar Fuels, is the most promising way to a future greener energy infrastructure. Chemical specificity in the investigation of the multiscale transient phenomena during semiconductor-driven photoelectrochemical (PEC) redox reactions is the key to a comprehensive understanding and modelling of the processes occurring in Solar Fuel generators. Interfacial energetics and dynamics crucially determine the performance of semiconductor photoelectrodes for (solar) chemical energy conversion. We use a suite of lab- and synchrotron-based X-ray photoemission spectroscopies to investigate interfacial energetics and dynamics in inorganic photoabsorbers. Examples comprise the elucidation of the role of polymorphic marcasite in pyrite (both FeS_2) [1] in enhancing the photoresponse of pyrite based photoelectrodes as well as the evolution and tailoring of surface photovoltage in InP single crystal based model photocathodes for H_2 evolution. [2] Employing XPS based surface photovoltage measurements, we determine the impact of photoreduced surface states in $CuBi_2O_4$ photocathodes on their photoresponse. Using the Eindhoven lab-based near-ambient pressure PES facility, the role of varying surface adsorbates could be studied, which is an important step forward towards bridging interface characterization in (ultra-high) vacuum-based and electrochemical conditions. In this lecture, I will highlight the X-ray photoemission methods used and showcase application examples on sulphide, phosphide and oxide photoabsorbers.

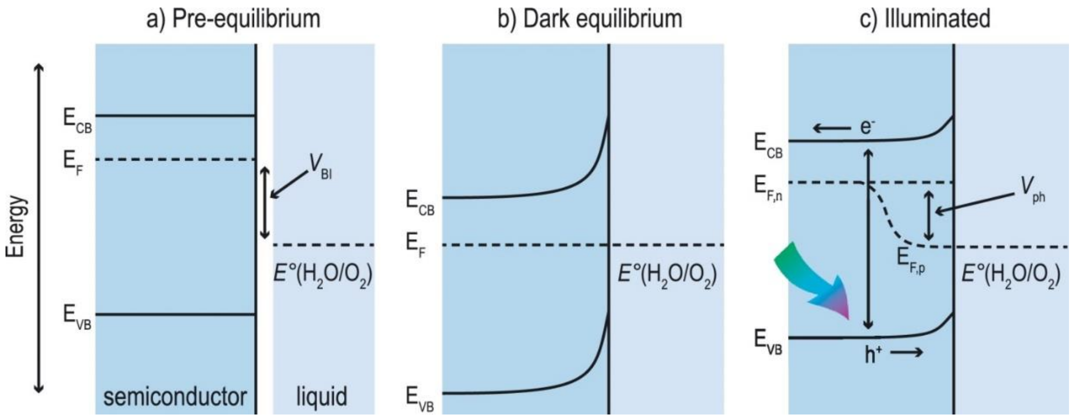

Figure 1. Formation of semiconductor – electrolyte junction (a) before equilibration and (b) after equilibration. (c) Emergence of surface photovoltage as response to above bandgap excitation. [3]

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KN-7

Next generation solid oxide cells: building advanced functionality through doping and nanocomposition

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Solid Oxide Fuel Cells (SOFCs)are versatile devices for conversion of chemical into electrical energy; thanks to the operating temperature, SOFCs do not need noble metals and can reach high efficiency also with C-containing fuels. Their diffusion to market will benefit from increasing stability and durability. To this purpose we decided to skip Yttria Stabilized Zirconia-based technology and focus on development of devices capable of operating at intermediate (600°C) instead of high (800-1000°C) temperature: Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFCs). Further enhancement is represented by Reversible Solid Oxide Cells. R-SOCs can work as fuel cell, converting chemical energy of fuels into electric energy or as electrolysers, using, as an example, exceeding energy from renewable sources (wind, solar) to convert wastes into fuel.[1] These devices open new perspectives for energy storage particularly when power and kinetic are relevant. Our research is focused on the C-based fuels and wastes: the developed R-SOCs are expected to be active in fuel cell configuration using biogas as fuel (with a dry-reforming approach, as an example) and in electrolyser configuration converting CO_2+H_2O into syngas (co-electrolysis). The optimization of these advanced devices require the development of electrodes stable under oxidizing and reducing environment (even at rather high temperature) and to be electrocatalytically active both in oxidation and reduction. Another challenge is the development of symmetric cells (Reversible Symmetric Solid Oxide Cells – RS-SOCs); in symmetric cells both the electrodes have the same composition (Symmetric Cells are intrinsically Reversible) thus minimizing problems related to the compatibility, stability and durability but also the production cost.[2] Also in this case the required functionalities have been developed starting from cheap and sustainable perovskites and brownmillerites. Both R-SOCs and RS-SOCs are mainly intended as medium to high scale devices for sustainable conversion and storage of energy from renewable sources. Single Chamber Solid Oxide Fuel Cells (SC-SOFCs), in contrast, are small devices for rapid production of energy. In SC-SOFCs there is no separation between the anodic and cathodic compartments and thus the device can be very simple and miniaturized. To reach this objective, a high selectivity is required to manage correctly the relative amount of catalytic vs electrocatalytic activity to minimize external thermal input.

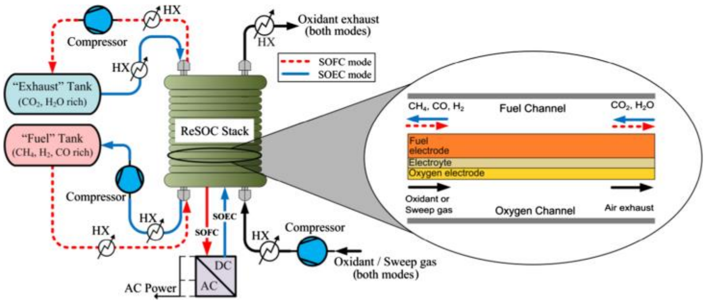

Figure 1 Scheme of a Reversible Solid Oxide Cell [1]

To build this complex functionality we started from very robust and stable oxides: perovskites and brownmillerites that are characterized by a very low economic and environmental impact. Perovskites are oxides of the type ABO3 with A a 12-coordinated cation (Rare earth or alkali metals) and B a 6-coordinated transition metal.[3] Brownmillerites derives by perovskites through the accurate creation of oxygen vacancies. In these compounds catalytic, electrocatalytic and conductivity properties can be tuned by means of several approaches: doping, exosolution, nanocomposition, nano-infiltration.[4-5] By means of these techniques the required functionality can be obtained and the devices developed.

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Oral presentations

OP-1

Organic sensitizers for dye-sensitized water splitting

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The need for an oil free energy policy is one of the most important goals of the next decades. Moreover, the need of hydrocarbons for more significant applications claims a reduction of consumption of these precious resources in energy production to keep their price acceptable. In this scenario, the organic design is strategic in order to get improved technological performances in dye-sensitized solar technologies (dye-sensitized solar cells, DSSCs, and dye-sensitized photoelectrochemical cells, DS-PECs). DS-PEC is an emerging technology, where the organic design is strategic in order to get improved performances. In the last years we have pioneered a multi-branched multi-anchoring D(-π-A)$_2$ geometry, now widely used in the field of dye-sensitized solar cells. [1, 2]

In this work we present the first systematic study on specifically engineered di-branched dyes for water splitting in DS-PEC (Fig. 1, left). Namely, we tested D-(π-A)$_2$ dyes where D is a substituted phenothiazine, phenoxazine or carbazole donor core, A is the acceptor-anchoring cyano-acrylic group, and π is a thiophene spacer (Fig. 1, right), previously used in photocatalytic hydrogen production. [3-6] The dyes were studied both in presence of a sacrificial electron donor (hydroquinone, H_2Q) and of a common Ru-based water oxidation catalyst (Ru(bda)pic$_2$). The phenothiazine-based dye [7] gave the best results thanks to its optical properties, IPCE and enhanced photocurrent in photoelectrochemical experiments.

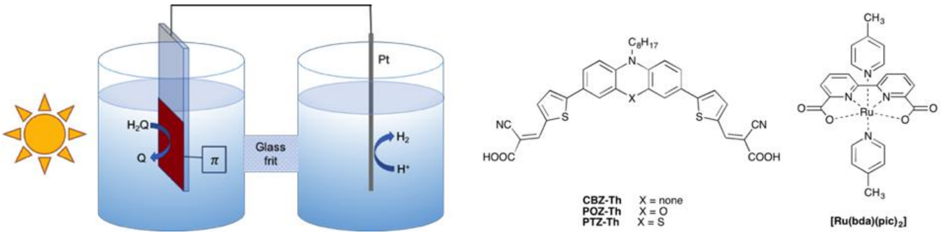

Figure 1: (left) Scheme of a DS-PEC (π = organic dye); (right) sensitizers and catalyst investigated in this work.

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OP-2

Recent advances in (photo)electrocatalysis by scanning electrochemical microscopy and X-ray absorption spectroscopy

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Among the different strategies for the search of new materials for energy conversion and storage, rapid screening and rational design are likely the most adopted ones. In this work, the two strategies are compared for the oxygen evolution reaction (OER) in water electrolysis and in photoelectrochemical water splitting.

Scanning electrochemical microscopy is capable of both the rapid screening of materials [1,2] and the investigation of reaction fundamentals [3].

Indeed, a deep understanding of reaction mechanisms is required for the rational design of catalysts by better defining structure/activity relations, and operando X-ray absorption spectroscopy (XAS) represents one of the most powerful available techniques to study the fine structure and the behavior of electrode and photoelectrode materials [4].

During the last years, we have been developing new methods and experimental approaches to better fit the capabilities of XAS in (photo)electrochemistry. Fixed Energy X-Ray Absorption Voltammetry (FEXRAV) represents a novel tool for fast and easy preliminary characterization of electrodes and photoelectrodes which consists in recording the absorption coefficient at a fixed energy while varying at will the electrode potential. Any shift from the initial oxidation state determines a variation of the X-ray absorption coefficient. As a result, FEXRAV gives important information by itself but can also serve as a preliminary screening of the potential window or for choosing the best experimental conditions for a better targeted XAS analysis. This led to new insights in the mechanisms of the OER [5,6].

We extended operando XAS approaches to the study of photoelectrodes adopting a novel differential spectra acquisition approach [7], that allows the direct comparison of spectra acquired in the dark and under UV-Vis illumination. More recently, we have carried out studies by time-resolved XAS out with the aim of studying the time-dependence of interfacial phenomena [8].

In this presentation, the potentialities of SECM and operando XAS in electrochemistry will be described and discussed, also for what concerns future perspectives.

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OP-3

Synthesis gas production by Steam/Dry Reforming of the clean biogas

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Biogas is the main candidate to replace the natural gas (NG) to produce fuels, chemicals and energy. After its purification, the clean biogas (CB) is a mixture of CH_4 and CO_2 in variable composition (CO_2: 35-50 % v/v). Currently, the CB is used to produce energy through cogeneration plants or to produce biomethane (after a CO_2-removal step) to be introduced in the NG network for domestic usage. The valorisation of the CB through the Steam Reforming process appears to be an attractive option to produce a wide range of products, but the CO_2 stream is hardly converted in the conditions in which the industrial process is carried out. An interesting option is represented by the combined Steam/Dry Reforming (S/DR) reaction, in which the addition of a limited amount of steam to the Dry Reforming (DR) process allows to overcome the main limits of the reaction such as carbon formation on the catalyst surface and its fast deactivation. With this premise, the present work aims at developing a process able to valorise the CB to produce synthesis gas suitable for many downstream applications such as Fischer-Tropsch and Methanol synthesis or H_2 production through an additional Water Gas Shift step. A deep study of different Ni-based catalysts was carried out tuning the catalyst properties and evaluating the effect of small amount of Rh on the catalytic performances. The Ni(Rh)/Mg/Al catalysts were prepared from hydrotalcite-type precursors by co-precipitation and, after calcination at 900°C, employed in combined S/DR of CB, feeding an equimolar mixture of CH_4 and CO_2 at 5 bar together with a variable amount of steam (S). The catalyst before and after reaction were deeply characterized by XRD, Raman, TG, H_2-TPR, CO_2-TPD, TEM and SEM techniques. With the aim to study the influence of the Rh content on the Ni-Rh catalyst performances four catalysts with a constant percentage of Ni (10 wt.%) but different amount of Rh (0.00, 0.03, 0.50, 1.40 wt.%) were synthetized. The activity tests (Fig.1) showed that the Ni-based catalyst performances are strictly related to the Rh content. Increasing the amount of noble metal, the CB conversion increased until a plateau was reached when the Ni-Rh(0.5) and Ni-Rh(1.4) showed the same catalytic activities. The H_2-TPR experiments showed that the presence of Rh catalysed the reduction of the NiO particles leading to well dispersed and more active Ni and Ni-Rh metal particles as confirmed by TEM images and EDX maps of the reduced samples before and after reaction.

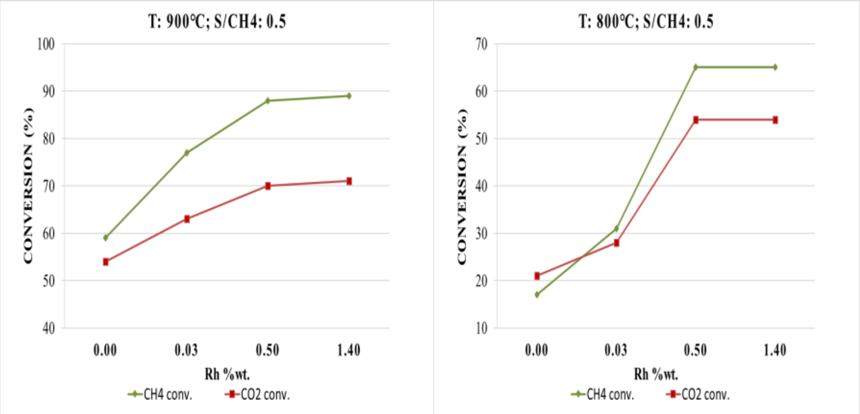

Fig. 1: CH_4 and CO_2 conversions of the catalysts with increasing amount of Rh in two different reaction conditions.

The H_2/CO molar ratio of the outlet stream was between 1.2-2.7 as a function of the working temperature and the amount of steam fed. By a further medium temperature shift (MTS) upgrading-step, it was possible to further increase the H_2-content of the outlet stream using a Cu/Zn/Al/Zr catalyst [1] and working in a temperature range of 250-350°C. This type of configuration leads to advantages in the energy balance of the process, decreasing also the capital and operational costs of the plant. The CO content in the outlet stream was < 1.2 % making the produced syngas suitable to produce chemicals or, after a CO_2-removal step, for the feeding of SOFC to produce energy.

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OP-4

Synthesis and characterization of Mo_2C films as a promising catalyst for the electroreduction of small molecules

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Transition metal carbides (TMCs) have been brought into focus as cost-efficient and abundant alternatives to noble-metal catalysts [1]. Molybdenum carbides are considered promising (electro-)catalysts due to their favorable electronic properties that are also described as platinum-like and can be applied for the electrochemical hydrogen evolution reaction (HER) and the carbon dioxide reduction reaction (CO_2RR) [2].

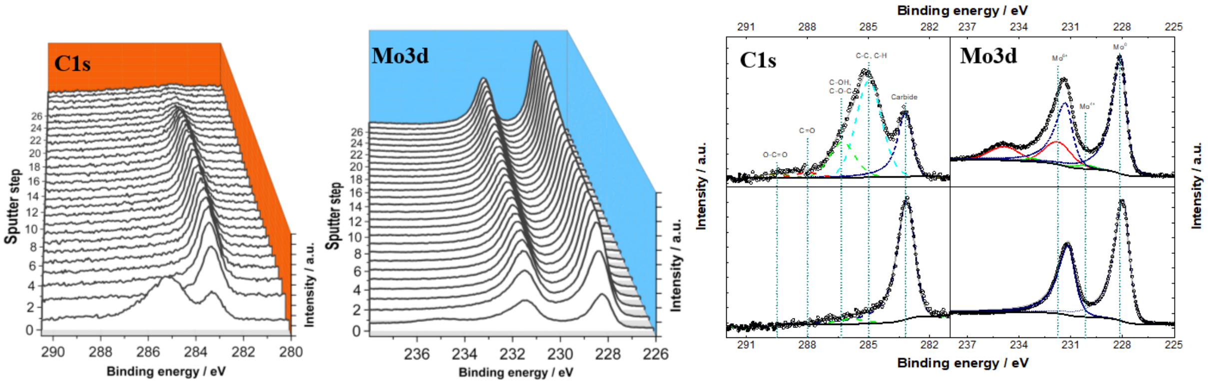

Figure 1: (left) Depth profile of the C1s core level spectrum of Mo_2C (left), depth profile of the Mo3d core level spectrum of Mo_2C (middle) and high-resolution spectra of the C 1s and Mo 3d core level spectra (right upper panel) before sputtering and (right lower panel) after 60 s of sputtering (sputter step 4) [3].

This work presents two synthesis routes for the formation of homogeneous and continuous Mo_2C film electrodes. Direct carburization and physical vapor deposition (PVD) by magnetron sputtering have been used to yield thin and highly crystalline Mo_2C films. Comprehensive sputter depth profiles have been obtained with X-ray photoelectron spectroscopy (XPS), combined with interface analysis of focused ion beam (FIB) cut lamellae of the films through transmission electron microscopy (TEM) and energy dispersive X ray spectroscopy (EDX). The oxidation behavior of the PVD film has been investigated with XPS. The elemental distribution of both, carburized and PVD films, has been found to be homogeneous across the carbide layer, with native Mo oxide covering the surfaces. The presence of native surface oxides is considered central for their application as HER or CO_2RR (electro)catalysts. Electrochemistry coupled with DEMS and XPS shows that during and prior to the HER, the surface composition of Mo_2C is substantially altered, which will certainly affect the nature of the active site. This is a property of Mo_2C electrodes that is very likely central to its (electro)catalytic performance in general.

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OP-5

Tuning the hydrogen evolution reaction at the Pt(111) surface with 2D material and non-precious metal

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The hydrogen evolution reaction (HER) is the process where protons from the electrolyte combine with the electrons from the metal electrode catalyst to produce atomic hydrogen adsorbed on the metal surface. The reaction ends when these hydrogen atoms then form molecular hydrogen and thereby desorbs from the surface of the catalyst. The bonding between the catalyst and the proton should be optimal such as to favour the formation of adsorbed H atom and at the same time not so strong as to hinder the H_2 molecular desorption to occur. The main applications of HER are in the cathodic half cells of water splitting and fuel cells. The efficiency of such a cathodic material depends on how strongly or weakly the H atoms are adsorbed on the metal catalyst. We present an experimental and theoretical study of the state of the art HER metallic electrocatalyst platinum (Pt) by tuning its reactivity with graphene (Gr) and iron (Fe). Using density functional theory (DFT) the reactivity of hydrogen (H) in the two systems namely Gr/Pt(111) and Gr/Fe/Pt(111) is investigated. The presence of Gr is observed to increase the selectivity/permeability to protons [1] and at the same time weaken the H adsorption compared to bare Pt [2]. This should favour H diffusion at the interface and hence H_2 molecular desorption. The H adsorption weakens further in the presence of Fe and even more with Gr and Fe. In addition to platinum the performance of gold (Au) in the presence of Fe and Gr has also been studied and compared in this work.

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OP-6

Identifying active sites for Ti-Co bifunctional catalysts for oxygen reduction and water oxidation catalysis

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The electrochemical oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) have gained widespread attention owing to its significance in electrochemical energy storage and conversion including unitized regenerative fuel cells or metal–air batteries [1]. In the last years, the use of alkaline membranes in electrolyzers and fuel cells has promoted the study in new non-noble metals as catalysts.

In this work, a modification of synthesis method [2] has been investigated to obtain composites of Ti-Co and N-doped graphene using urea as nitrogen source. We investigate the effects of varying the annealing temperature and holding time in the synthesis method on the structure and activity of this material system. The as-synthetized composites were labelled as TiCo/NrGO-700 (1h), TiCo/NrGO-800 (1h), TiCo/NrGO-800 (3h), Ti/NrGO and Co/NrGO. Catalysts were physico-chemically characterized by different solid state techniques such as XRD, TEM, XPS and including the use of X-ray absorption spectroscopy to study the local structure and chemical state of these catalysts. The electrocatalytic activity towards ORR and OER has been measured by a three-electrode system, using a glassy carbon rotating disk electrode under alkaline conditions.

This work evidences a significant influence of temperature and holding time of the TiCo/NrGO composites synthesis on the structure and electrocatalytic activity (Figure 1). Catalyst treated at 800ºC for one hour displays the best activity toward ORR and OER in alkaline medium. The oxidation state of cobalt appears to be a determining factor in the electroactivity of composites.

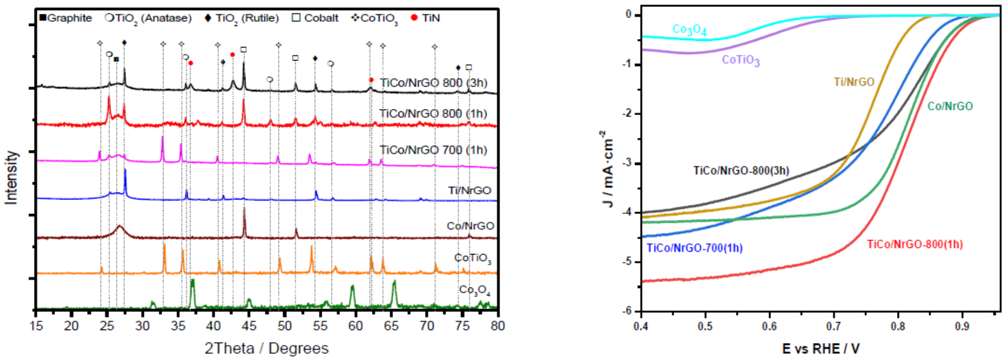

Figure 1. XRD patterns of composites and commercial $CoTiO_3$ and Co_3O_4 samples (left) and ORR polarization curves in O_2-saturated, 0.1M NaOH, 10 mVs^{-1}, 1600 rpm (right)

Acknowledgements

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OP-7

Tailoring N-decorated Carbon Nanotubes as Highly Efficient Electrocatalysts for the Selective CO2 Reduction to CO

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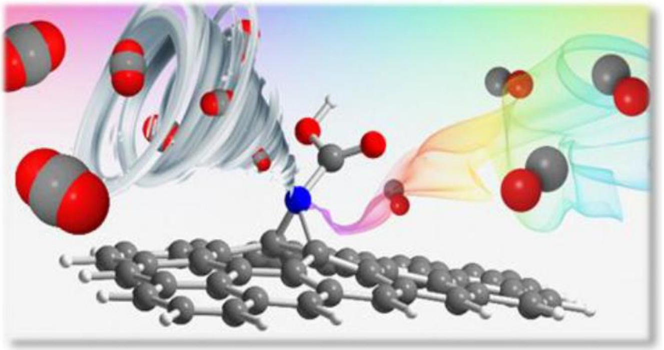
The electrocatalytic reduction of CO_2 into chemicals and/or energy vectors of added value is a highly challenging approach to cope with the growing global energy demand while limiting the impact of atmospheric CO_2 levels on climate changes and related global warming issues.[1] To date, large efforts in this area have been focused on the development of metal-containing catalysts and in particular precious and noble metals (*i.e*. Pd, Au, Ag, and Cu) [2] that however suffer of poor sustainability both from an economical and an environmental viewpoint. Relatively few examples of metal-free catalysts for CO_2 electroreduction have been developed up to now, most of them raising from the class of light-heterodoped carbon nanomaterials.[3] In particular, a series of N-doped carbon-based systems have been investigated but the nature of active sites responsible for CO_2 electroreduction still remains highly controversial.[4]

Recent findings from some of us have demonstrated how a fine tuning of the surface properties of carbon nanomaterials can be conveniently achieved by chemical functionalization of their outer surface with tailored N-containing heterocycles.[5] The chemical approach allows a precise control of N-dopants in terms of N-configuration and electronic charge distribution, offering a unique tool to the comprehension of the role played by specific N-functionalities in the activation of small molecules. In this contribution we report the chemical decoration of MWCNTs with NH-aziridine groups ($MW@N_{Az}$) and their application as highly efficient and selective metal-free electrocatalysts for CO_2 reduction to CO. With a Faradaic efficiency (FE) close to 90 % at -1.2 V (vs. Ag/AgCl/KClsat.) and productivity as high as 48 $NL_{CO}h^{-1}g_{N}^{-1}$, $MW@N_{Az}$ ranks among the metal-free systems with the highest performance reported so far. At the same time, a privileged view-point on the structure-reactivity relationship of light-heterodoped CNMs in the process is provided.[6]



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OP-8

Bridging the gap in nanomaterials upscaling

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The upscaling in nanomaterials production represents the main bottleneck for the successful transfer of lab-scale results to industrial products and processes. To this day, scalable synthetic techniques force the acceptance of compromises in terms of quality or processability that eventually limit or slow down the penetration of nano-based solutions in industry. Here we present a green and flexible process that has enabled the upscaled production of over 50 different compounds including oxides, metals, sulfides, MOFs, based on a continuous flow technology with supercritical water. Its application has allowed for unprecedented experimental approaches in fundamental studies in energy storage and catalysis, examples of which will be provided.

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OP-9

Operando characterization of SOFC components at the submicron scale by scanning photoemission imaging and spectromicroscopy

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Fuel cells are electrochemical devices providing efficient and environmentally-friendly production of electricity directly converting the electrons exchanged in a redox reaction (such as a combustion) into electric current. One of the still unresolved issues that impedes their widespread applications is related to the limited durability of crucial components and mass transport events that deteriorate the performance. The authors have developed methodologies based on synchrotron soft X-ray photoemission imaging and spectromicroscopy, allowing detailed chemical and morphological analysis of the cell components, and providing information about the processes at the interconnections, electrodes and electrode/electrolyte interface occurring under operation conditions.

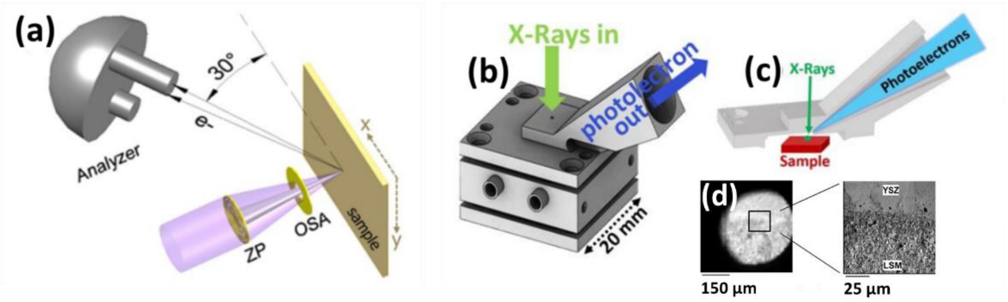

Figure: (**a**) SPEM Layout (**b,c**) Effusive cell layout (**d**) photoemission map, through the effusive cell, of the electrode electrolyte interface

The Scanning PhotoEmission Microscope (SPEM), hosted at the ESCAmicroscopy beamline at the Elettra synchrotron light source, uses a direct approach to characterize chemically surfaces and interfaces at the submicron scale, i.e. the use of a small focused X-ray photon probe to illuminate the sample (Figure). The focusing of the X-ray beam is performed by using a Zone Plate (ZP) which is a Fresnel type lens. The SPEM can operate in two modes: imaging and spectroscopy. In the first mode the sample surface is mapped by synchronized–scanning the sample with respect to the focused photon beam and collecting photoelectrons with a selected energy. The second mode is X-ray Photoelectron Spectroscopy (XPS) from a submicron spot. The X-ray beam can be downsized to a diameter of 120 nm, which allows imaging resolution better than 100 nm. The overall energy resolution is better than 200 meV [1].

Only recent electron energy analysers with differentially pumped lens systems allow to perform *operando* XPS up to few mBar (near ambient pressure). Nevertheless due to technical complexity and low efficiency it was not possible to export such solution to photoemission spectromicroscopy so far. Results of innovative solutions developed for photoemission microscopes, based on effusive cells (see figure) where high- and low-pressure regions are separated by small apertures of few hundreds micrometers for photons and photoelectrons [2], will be presented and discussed.

Recent achievements in the chemical and electronic *operando* characterization of fuel cell components will be presented, as for example the characterization of a Self-Driven Single Chamber SOFC [3], characterization performed also under *operando* near-ambient pressure condition [4], providing an overview of the capabilities of this powerful technique.

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OP-10

Transition-metal-free CO_2 fixation into new carbon-carbon bonds

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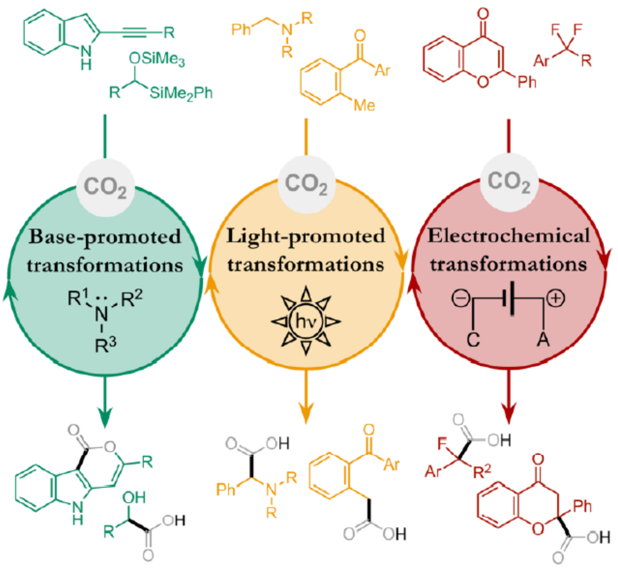
Utilizing renewable resources is an essential requisite for a sustainable society. In this light, the utilization of CO_2 as a sustainable C1 source has recently attracted significant attention within the scientific community. CO_2 is abundant, inexpensive, non-flammable and readily available carbon feedstock, embodying the ultimate renewable carbon source on our planet. At the same time, the activation of CO_2 towards chemical transformation has proven a challenging task, due to its thermodynamic stability and kinetic inertness. Although its utilization in synthetic chemistry has been exploited at industrial level since the second half of the 19th century,[1] these classical methods are restricted to the use of highly reactive substrates or harsh reaction conditions. Remarkably, the progress of transition-metal catalysis has entailed the development of catalytic transformations capable of activating CO_2 in a more benign and mild manner. [2] Nevertheless, the use of precious and/or toxic metal-based catalysts does not fulfil the overarching goals of green chemistry. Since the turn of the century, the use of simple organic molecules as catalysts, known as organocatalysis, has emerged as a complementary and more sustainable discipline of catalysis. [3] In this context, significant efforts have also been devoted to the development of organocatalytic CO_2 transformations. [4] The existing methodologies can be broadly classified according to the nature of the chemical transformation. On the one hand, there are nonreductive transformations, where new C-O and C-N bonds are formed without change in the formal oxidation state of the CO_2 carbon centre. On the other hand, there are the reductive transformations, where the formal oxidation state of the carbon centre is reduced, mainly involving the generation of C-H bonds, resulting in significance energy storage.



Scheme 1. Main approaches towards the transition-metal-free construction of carbon-carbon bonds with CO_2.

Because the carbon-carbon (C-C) bond constitutes the backbone of almost every single organic compound, the reactions towards C-C bond formation are amongst the most useful and fundamental transformations in organic chemistry. Hence, the use of CO_2 for the construction of this essential motif in a green and sustainable manner represents a formidable goal for the chemical community. [5] This talk will discuss the recent progress towards the construction of C-C bonds using CO_2 as sustainable C1 feedstock, focusing on the base- and light-promoted transformations under transition-metal-free conditions. Special attention will be directed on the methodologies that work efficiently under mild catalytic conditions as well as the corresponding catalytic activation pathways of the CO_2 molecule.

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OP-11

Tracking structural transformations by operando X-ray scattering for the oxygen/water catalysis

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The storage of energy from renewable sources, i.e. wind and solar radiation, into fuels and their subsequent conversion to electricity allow matching the intermitting nature of renewable energy sources to the energy demand of human activities. Water splitting into hydrogen and oxygen and the related back reaction represent a clean way to achieve such energy transformation, which is interesting due to the high gravimetric energy density of hydrogen. The oxygen evolution reaction (OER) and the oxygen reduction reaction (ORR), involved respectively in the forward and backward reaction, are associated with higher conversion efficiency losses in comparison with their half-reaction counterparts. Therefore, catalysts with superior activity for these reactions are of high interest. Understanding the reaction mechanism and identifying the catalytically active sites is important in order to improve the performance of the state-of-the-art catalysts. However, the atomic structure under reaction condition can be different than in the as synthesized phase. In this contribution, we will present *operando* wide angle X-ray scattering (WAXS) results providing insights into important structural changes leading to formation of catalytic active phases or associated to degradation mechanisms.

For the OER, NiFe layered double hydroxides (LDHs) are recognized among the most active catalysts in alkaline electrolytes [1]. Their crystal structure is known and is composed of layers of edge sharing metal oxygen octahedra that are intercalated with water molecules and charge balancing anions. Despite their structure is well characterized, there are evidences that the OER active structure of LDH catalysts during OER is different than the one of the as prepared materials [1]. Using *operando* WAXS we identified the structure of the catalytically active catalyst state and observed that both the interlayer and in-plane distances contract under operating conditions [2]. These results are important to validate the structures used in theoretical models to predict the OER mechanism and ultimately to develop strategies to improve the OER activity of NiFe LDH catalysts.

The same *operando* WAXS methodology can also be applied to study degradation mechanisms. For ORR, octahedral PtNi alloy based nanoparticles shows very high activities in thin film rotating disk electrode measurements in acid [3]. However, the prevention of Ni loss and morphological stability under operation are still challenging. Using a combination of *operando* WAXS and *ex situ* X-ray fluorescence spectroscopy (XRF) we found that a structural transformation is involved in the degradation mechanism occurring while cycling the applied potential. This consists in the dealloying of the Ni rich phase with associated Ni loss [4]. The sensitivity of this process to operating conditions such as the upper potential limit of the cycling protocol was investigated.

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OP-12

Sustainable production of chemicals and fuels from CO2: towards the realization of an artificial leaf using non-critical raw materials

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The combination of the electrochemical reduction of CO_2 with carbon-neutral energy sources is an attractive and sustainable strategy to produce solar fuels and chemicals and to close the anthropogenic carbon cycle at once [1]. In this context, A-LEAF is a project of the European Commission for developing an efficient and economically viable photoelectrocatalytic (PEC) cell [2]. The base concept is that CO_2 and H_2O can be processed by a direct electrocatalytic route to produce O_2 and high value-added carbon products, through the implementation of an artificial-leaf-type device. The role of INSTM/University of Messina (UniME) within A-LEAF project is to design and realize a full PEC prototype, through the optimization of electrodes and testing under relevant industrial conditions (high current density) to validate performance. The electrodes must be constructed starting from earth-abundant materials (i.e. Cu, Fe, Ni and Co) and they must be easily scalable to facilitate the industrial implementation. In this contribution, the main aims and activities of A-LEAF project will be described with particular emphasis to INSTM/UniME tasks by showing some of our preliminary results obtained within the project. Moreover, some previous results about the preparation of the electrodes will be discussed. In general, the main issues that limit the performance of a PEC cell refer to: i) light harvesting and charge separation, ii) electron conductivity and mass diffusion, iii) yield and type of products formed. The correct choice of the electrodic materials and the design of 3D nanostructured electrodes are the key factors to improve the above aspects and enhance the photo-catalytic activity, limiting overpotential within the cell [3]. Specifically, we prepared two types of nanostructured electrodes: i) one based on highly ordered TiO_2 nanotube arrays (prepared by controlled anodic oxidation) used as the photo-anode and ii) the other one based on Cu (or Fe) nanoparticles (NPs) deposited on carbon nanotubes (CNT) used as the electro-cathode. The electrodes were assembled together with a Nafion® membrane (like PEM fuel cells) and located in a compact lab-scale device with two separate compartments for each half-reaction. Then, the electrodes were characterized and tested in the processes of i) water photo-electrolysis for the production of H_2 and ii) CO_2 reduction for the generation of fuels. Water splitting results showed the formation of about 128 micromoles of H_2 in one-hour light irradiation, without adding sacrificial donors and with a photo-conversion efficiency as high as 2.5%. This attractive result (if considering that non-doped TiO_2 was employed as the photo-anode) can be ascribed to the enhanced visible light absorption of TiO_2 nanotube arrays, due to their structural resonance effect, and to the reduced charge recombination due to their improved electron transfer [4]. Coupling a photo-anode with Si based materials and multijunction cells may strongly improve solar-to-fuel efficiency (>12%). On the other hand, CO_2 conversion allowed obtaining not only CO and formic acid (as it usually occurs in conventional cells) but also methanol, ethanol, acetic acid, isopropanol and acetone. The formation of these products may be due to the catalytic sites located at the interface between the small Cu (or Fe) NPs and CNT surface, favouring the electron transfer and C-C bond formation [5,6]. Moreover, the effects of the fluid dynamics inside the PEC device, the charge distribution on the nanostructured electrodes, the UV-visible light absorbance, the mass diffusion of protons, the electron transport, the kind of the electrolyte, the pH, the separation of the two half-reactions, the reaction phase (gas vs. liquid) have been evaluated. The preliminary results in terms of overall cell efficiency and yield are very promising, opening the route for the future implementation of PEC artificial-leaf-type cells into the world energy scenario.

Acknowledgments*: This work was funded by the European Union through the A-LEAF project (732840-A-LEAF), which is gratefully acknowledged.*

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OP-13

On the role of semiconductor/catalyst junction in first row transition metal oxide-based photoanodes

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The production of alternative fuels through the exploitation of solar energy is one of the most pursued strategies to relieve the global energy thirst. With this aim, a viable but challenging approach consists in the development of photoelectrochemical cells for water splitting.[1] These devices mimic the natural photosynthetic process by storing sunlight in the form of chemical energy of the products formed at the two (photo)electrodes (namely O_2 and H_2).

In this contribution, we will extend our previous work on all iron oxide-based photoanodes, able to efficiently perform the semireaction of water oxidation.[2] In particular, we will report on the preparation of thin layers (70 nm) of crystalline hematite, and their further functionalization with amorphous nickel-iron oxides *via* pulsed laser deposition.[3] In the resulting composite photoanodes, the sunlight absorption and charge carrier generation properties of hematite are effectively coupled with the catalytic activity of the mixed oxides.

The direct comparison with the all-iron and all-nickel catalytic counterparts, as well as the key role of the amorphous catalysts' morphology (porous *vs* compact) on the overall performances of the photoanodes will be also discussed, confirming the pivotal role of the formation of adaptive semiconductor/catalyst junctions[2,4] for the optimal operation of this kind of interfaces.

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OP-14

Beyond the CO. Efficient multi-electrons, multi-protons CO_2 electrochemical reduction into fuel with Co molecular catalyst

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Carbon dioxide (CO_2) atmospheric concentration is one of the major issues we are facing. It is due to the massive use of fossil energies over the last decades. This concentration will keep rising until robust technologies emerge to store renewable solar electricity into dense and stable forms. Catalyzing CO_2 reduction into valuable molecules is a challenge that would help answering these problems.

Over the last decades, our group has focused on transition metal complexes as tunable catalysts for the electrochemical and photochemical reduction of the CO_2. Thanks to mechanistic studies that provide a deep understanding of the elementary steps of the processes, new catalysts have been developed on rational basis so as to increase their activity, selectivity and to enable performing reactions in water[1,2]. Furthermore, upon implementing catalysts into films and enhancing CO_2 mass transport, high current density with excellent control selectivity have been achieved[3].

Following these studies, CO can also be used as a starting reactant toward more reduced molecules (Figure 1) and the first reports of a molecular catalyst being able to reduce CO_2 and CO into methane under photo-stimulated conditions using visible light at room pressure and temperature have been published by our group[4,5].

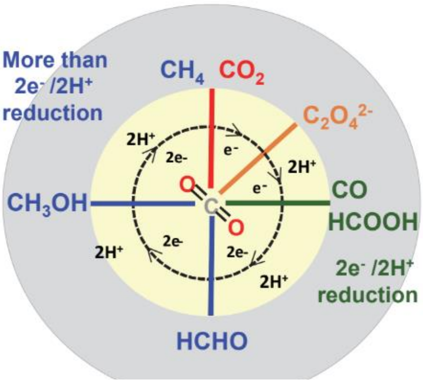

Figure 1. Running the CO_2 clock.

This presentation will cover our very recent studies where Co based molecular catalyst efficiently perform multi-electrons and multi-protons electrochemical reduction of CO_2 and then can catalyze CO conversion into more reduced products[6].

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OP-15

Excursus and new achievement of M-N-C cathode catalysts in acidic media for direct methanol fuel cells applications

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Direct methanol fuel cells (DMFCs) are emerging technologies for electrochemical conversion of the chemical energy of a fuel (methanol) directly into electrical energy, with a low environmental impact and high efficiency. Two main challenges have to be overlapped for this technology: 1) the slow kinetics of the reactions which requires the use of Pt group metal (PGM) catalysts, characterized by suitable activity, and 2) the methanol crossover from the anode to the cathode side through the membrane, resulting in a mixed potential at the cathode side where the simultaneous methanol oxidation (MOR) and oxygen reduction reactions (ORR) occur. A lot of research group are checking to solve this problem by studying non-PGM materials in order to obtain a similar performance of Pt-based electrocatalysts, never reached until now. On the other hand, the research in this field is addressed to the study of electrolyte membranes, more impermeable to the methanol. In such polymer a tortuosity is created in order to permit mainly the water crossover. Another option for improving the performance of the DMFC is to individuate methanol tolerant cathode catalysts, i.e. able to selectively react with O_2 and not with the permeated methanol. Thus, these electrocatalysts must behave as an excellent cathode material and a worst anode catalysts. In these regard, Fe-N-C based electrocatalysts have attracted a special interest due to the promising characteristic in terms of extraordinary methanol tolerance of such compounds and in terms of performance when deposited at the cathode of a DMFC.

Herein, an excursus of the recent advancements achieved in DMFCs by using M-N-C catalysts is presented. The analysis is restricted to M-N-C catalysts mounted at the cathode of a DMFC or investigated in rotating disk electrode (RDE) configuration for the ORR in the presence of methanol in order to study alcohol tolerance. The main synthetic routes, characteristics of the catalysts and the last achievement by our group are also presented.

Poster presentations

P-1

Water-Splitting Hybrid Carbon Nanotube-based Iridium Catalysts Having Sulfonate-functionalized NHC ligands

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The hybrid materials resulting from the covalent attachment of iridium N-heterocyclic carbenes (NHC) complexes bearing 3-methyl-imidazol-2-ylidene and 3-(propyl-3-sulfonate)-imidazol-2-ylidene ligands to carbon nanotubes (CNT) through ester functions (samples **CNT-1-Ir** and **CNT-2-Ir**, Figure 1), being the latter a new derivative of the CNT-NHC-Ir family,[1-3] efficiently catalyzed the water splitting reaction under chemical and electrochemical conditions. The local structure around iridium atoms in the heterogeneous catalysts has been determined by means of EXAFS applied before and after water splitting reactions (Figure 1). The first coordination shell, 6 light elements surrounding the metal, is similar in both fresh and post-catalytic catalysts, but a slight increase in the oxidation state of iridium atoms is observed after reaction. **CNT-2-Ir** sample has shown an improved catalytic performance compared to the unfunctionalized material **CNT-1-Ir** (Figure 2), with TOF_{50} numbers up to 1140 h^{-1} using Ammonium Cerium(IV) nitrate (CAN) as electron acceptor, at [CAN]/[Ir] ratios higher than 2000. The positive effect of the presence of a polar sulfonate group in water oxidation has been also observed in the related molecular catalyst $[Ir(cod)\{MeIm(CH_2)_3SO_3\}]$ (**3-Ir**), being more active than $[IrCl(cod)\{MeIm(CH_2)_3OH\}]$ (**1-Ir**), suggesting an stabilization effect of the sulfonate group in the iridium coordination shell toward the high valent iridium species participating in the water splitting mechanism. The hybrid catalysts were less active than related molecular catalysts although their productivity has been improved by allowing successive additions of CAN or at least three recycling experiments, as result of the heterogenization (Figure 2). On the other hand, the electrochemical water splitting by CNT-based hybrid materials resulted much more efficient. The positive influence of the water-soluble sulfonate wingtip in the hybrid catalysts has been identified too, allowing TOF values close to 22000 h^{-1} at 1.4 V (Figure 2).

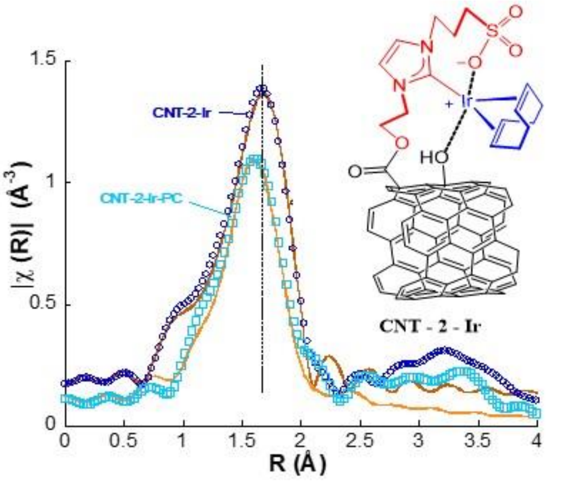

Figure 1. EXAFS measurement of Ir first coordination shell in **CNT-2-Ir** before and reaction.

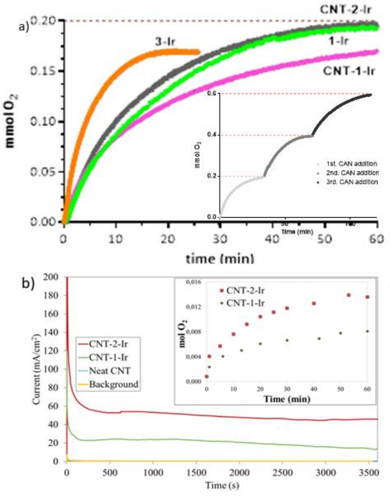

Figure 2. a) Chemical and b) electrochemical water splitting reaction by CNT-Ir hybrids.

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P-2

Spray-cast perovskites: towards large-scale production of perovskite solar cells

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Perovskite solar cells (PSCs) have become a hot research topic in photovoltaics community because of their low cost, easy assembling and high-power conversion efficiency (PCE), nowadays overcoming 24%. However, there are still many challenges for the commercialization of this type of devices, among which stability and scalability are the main ones. Attempts to transfer the large-area solution coating processes, available for polymeric solar cells, to PSC have already been made, although a higher exploitation of the active material is required. The hybrid organic-inorganic perovskite materials, the solar cell active materials, show, however, poor stability towards long and/or high light illumination, temperature and humidity, which lead to perovskite (PVK) degradation and consequently to the efficiency drop of PSCs. [1,2,3]

We have developed a new method to synthetize PVKs, starting from nanoparticles of lead (II) iodide produced by laser ablation synthesis in solution (LASiS). We spray cast firstly the NPs onto a substrate, secondly the other precursors to obtain the perovskite layer. The relevant feature of the thin films produced with this methodology (see figure 1) is the presence of a graphitic phase linked to the PVK nanocrystals, reason why we called these perovskites C-PVKs. [4] The graphitic phase is found to be responsible of a suppressed hysteresis, [5] which is usually observed for traditional solution processed films. It is expected that combining these C-PVK materials with a large-area deposition technique, like spray-coating, both stability and scalability of PSCs could be improved. Furthermore, with our approach we are able to deposit PVK thin films on non-flat substrate (figure 2). This is particularly important for perovskite-silicon tandem solar cells applications, where the silicon bottom cell is made with a textured structure to reduce the scattered light and to increase the PCE of the whole device. [6,7] Goal of the project is to synthetize C-PVK materials to study the stability of solar cells realized with these films.

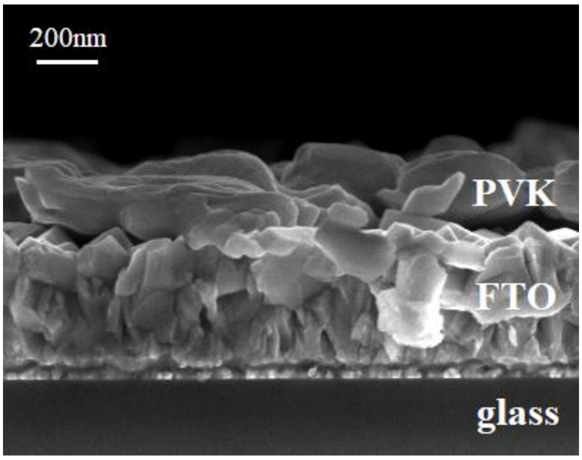

Fig.1 SEM image of PVK/FTO/glass

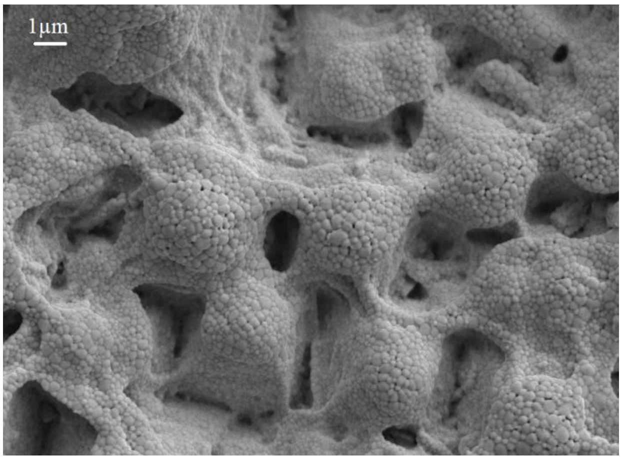

Fig.2 SEM image of PVK/NiO/textured Si

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P-3

The effect of different degradation protocols on the oxygen reduction and oxygen evolution bifunctional catalysts

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A unitized regenerative (or reversible) fuel cell (URFC) is a device that can work in both fuel cell and water electrolyzer mode. It presents several advantages compared to Li-batteries as there is no need for long charging time, it presents a long-term energy storage solution and has high energy density [1]. The best oxygen reduction reaction (ORR) catalyst is Pt and its alloys while the best oxygen evolution reaction catalysts are based on Ir (Ru) and their oxides. Unfortunately, both of them are only catalysing one of those reactions efficiently (Pt is bad for OER and Ir/Ru are bad for ORR). Therefore, a simple mixture of both materials is currently still a state-of-the-art bifunctional catalyst. However, there are some serious drawbacks to this technology besides the sluggish kinetics for ORR and OER, which are the lack of good support and poor stability. The latter is an important issue as the material needs to be stable in a wide range of potential and an aggressive (oxidative and acidic) environment [2].

Here, we present the stability of our homemade high-performance bifunctional catalyst made of $PtCu_3$-Ru-Ir nanoparticles supported on $TiON_x$/graphene during different degradation tests. Three protocols were chosen to highlight the effect of different potentials window. Two of them are frequently used to test bifunctional catalysts, i.e., cycling in the "ORR potential window" (0.4 to 1.0 V vs. RHE) and cycling in the "OER potential window" (1.2 to 1.6V vs. RHE). The last protocol is the full potential window (0.4 to 1.6V vs. RHE). We note that the latter one is usually not investigated. However it is important for the real application as the URFC device will undergo switches of potential during start-up/shut-down that are not represented by the two other tests.

These different tests reveal the importance of the separation between the fuel cell mode and the electrolyzer mode in a URFC device as the activity only decreases slightly after the ORR and OER degradation but strongly after the full window test.

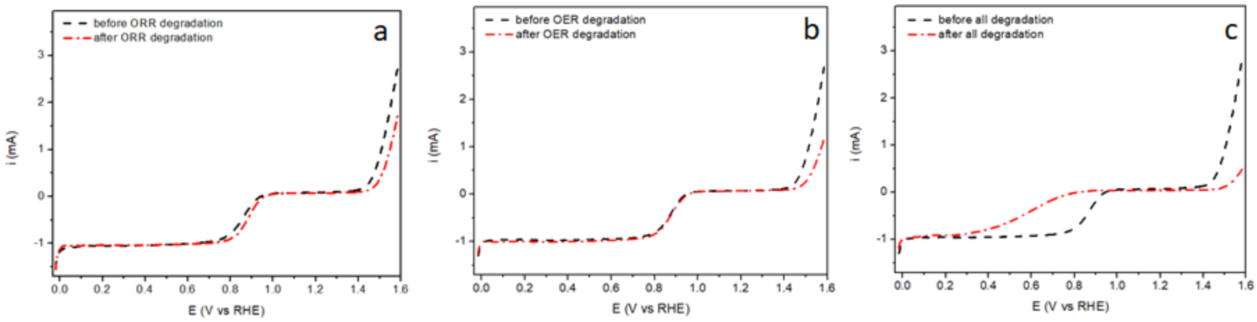

Figure 1. Comparison of ORR and OER activity before (black) and after (red) degradation protocols: (a) 10 000 cycles between 0.4 and 1.0 V vs RHE (ORR degradation) (b) 10 000 cycles between 1.2 and 1.6V vs RHE (OER degradation) (c) 10 000 cycles between 0.4 and 1.6 V vs RHE (ORR+OER degradation).

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P-4

The effect of film thickness on the photoelectrochemical properties of nanoporous anodic tin oxide layers

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Nanostructured SnO_2 materials are extensively investigated due to many advantages like stability in an aqueous environment, nontoxicity, and environmental friendliness. That is why they are commonly used as photoanodes for photoelectrochemical water splitting (PEC) [1–2]. Anodic oxidation of metallic Sn seems to be an extremely promising strategy for the fabrication of nanoporous SnO_x layers. However, in case of properties of anodic tin oxide films, a lot of issues are still not clear. One of these is the impact of the morphological parameters on the properties of the semiconductor. It should be mentioned that very recently we proposed a simple method allowing, for the first time, fabrication of nanoporous tin oxide layers with various pore diameters by simple changing the potential during anodization carried out in strongly alkaline electrolyte. We also found that anodic films with larger pore diameters (~50 nm) obtained at the potential of 4 V exhibit slightly greater photoelectrochemical response and narrower band gap values in comparison to anodic SnO_x layers with much smaller pores (10 – 15 nm) synthesized at 2 V [3].

Here we present, for the first time, the study on the effect of anodizing duration and, in consequence, the thickness of the anodic film, on the properties of SnO_x layers. The anodic tin oxide layers were obtained in typical 2-electrode cells at the potential 4V and the solutions of 1M NaOH used as an electrolyte.

The nanostructured photoanodes were investigated by FE–SEM and correlated with thicknesses such obtained layers. All studied samples were annealed in air at 200 °C for 2h. Finally, band gap energies were determined from UV–Vis reflectance measurements. Photoelectrochemical characterization of samples was carried out using a photoelectric spectrometer in a conventional 3-electrode configuration at the potential of 1 V in the range of 200 – 500 nm in borate buffer solution. Our study showed that the thickness of anodic film significantly affects the efficiency of the photoelectrochemical water splitting process – the photoelectrochemical response was higher with increasing thickness. Moreover, it is an important step on the way to use this approach for the fabrication of anodic tin oxide layers with complex internal morphologies offering enhanced photoelectrochemical response.

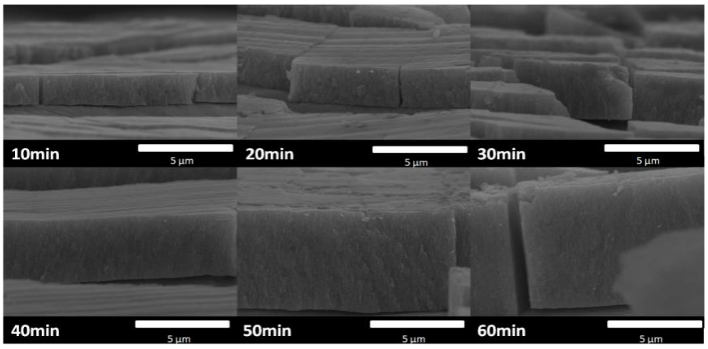

Fig. 1. FE-SEM images of anodic tin oxide layers obtained at the potential of 4V in 1M NaOH for various durations.

Acknowledgments
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P-5

Optimization of the synthesis of novel bioelectrodes modified with a cationic dextran derivative and lactic acid bacteria

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Due to steadily increasing demand for electricity and gradual depletion of fossil fuel, the search for alternative energy sources has been gaining more and more attention of researchers. Simultaneously, the environmental awareness of society is rising, and the postulates of the so-called "Green Chemistry" are taken into consideration [1]. Mentioned above phenomena contributed to the intensive development of research related to bioelectrochemistry, especially to bioelectrochemical systems (BESs), because they potentially could be one of the technological solutions of energetic problems [2, 3]. BES utilizes microorganisms, like specific groups of bacteria, yeast or algae, which can colonize an electrode or occur as planktonic forms in the electrolyte. Those organisms are able to convert chemical energy from organic matter (e.g., pure glucose or mixture of organic compounds from wastewater) to electric energy. The efficiency of those setups strongly depends on biological, thermodynamical and technical factors. One of the key ones is the bioelectrode – material type, morphology, conductivity, toxicity toward microorganisms, stability during long term study, etc. As far as we know, here we present for the first time a novel polycation/gold electrode with lactic acid bacteria (*Lactobacillus rhamnosus* GG) [4]. A pretreated copper foil was sputtered with a thin gold layer, which was then electrochemically thickened. Next, the surfaces of samples were covered by a cationic dextran derivative (using Layer-by-Layer method). The morphology of as-prepared electrodes was characterized, among others, by scanning electron microscopy (SEM), infrared spectroscopy (IR), and atomic force microscopy (AFM). The metabolic activity of lactic acid bacteria after culturing on the electrode surface was examined by MTT assay. What is more, both samples, with and without living component, were tested electrochemically (voltammetric measurements). The study reveals that a well-developed lace-like bacteria network was formed at substrates. Furthermore, bacteria probably exhibit electrochemical activity. Furthermore, the influence of different culturing parameters (e.g., glucose concentration, temperature) on the generated current efficiency of the system was tested.

Acknowledgments
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P-6

Critical Raw Material free Ba,Mn-based perovskites for sustainable development: building functionalities through doping.

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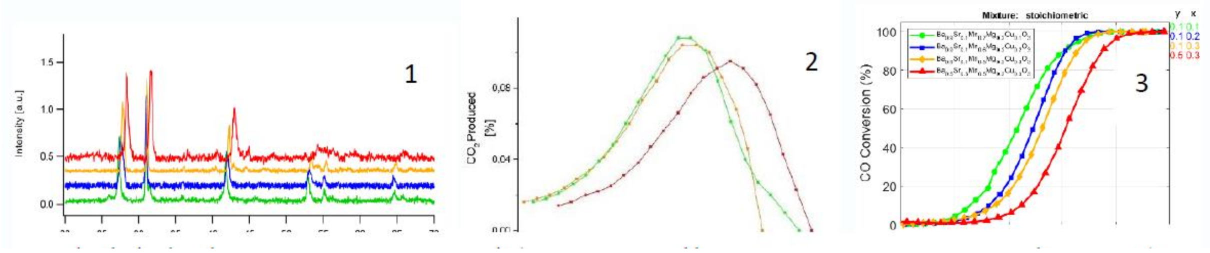
In this contribution several Sr and Cu doped Ba-Mn based perovskites of the type $Ba_{1-y}Sr_yMn_{1-0.2-x}Mg_{0.2}Cu_xO_3$ are prepared by wet chemistry procedure (citrate route) and characterized. The parent perovskite has been designed to be free of critical raw materials (noble metals and rare earths) [1]. Mg was added to enhance the formation of oxygen vacancies and thus oxygen mobility and catalytic performances. In order to study the effect of the doping in Ba and Mn sites the following catalysts were investigated: $Ba_{0.9}Sr_{0.1}Mn_{0.7}Mg_{0.2}Cu_{0.1}O_3$, $Ba_{0.9}Sr_{0.1}Mn_{0.6}Mg_{0.2}Cu_{0.2}O_3$, $Ba_{0.9}Sr_{0.1}Mn_{0.5}Mg_{0.2}Cu_{0.3}O_3$ and $Ba_{0.5}Sr_{0.5}Mn_{0.5}Mg_{0.2}Cu_{0.3}O_3$. With the aim of studying the effect of dopants on oxygen mobility, exchange capability and, finally, catalytic activity we considered automotive exhausts abatement as functional and challenging application. The most efficient catalysts to this purpose, are supported noble metals (Pt, Pd or Rh) whose high costs and supply risk impose the need for alternative. The investigation on perovskites and the understanding of the fundamental aspects of their activity and properties are very relevant and will impact on several aspects of sustainable development, from energy conversion and storage to abatement of pollutants (also in fixed plants). The doped perovskites have been prepared by wet chemistry procedure and characterized by means of X-Ray Diffraction (XRD), X-Ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Analysis (EDX), Temperature Programmed Reduction (TPR), and BET. Moreover, different reactions and reaction environments have been tested: in fact, we observed different reactivity when comparing CO oxidation, CO assisted NO reduction, tight and loose contact oxidation of soot by O_2 or the reactivity in a mixture simulating the automotive exhaust (at both stoichiometric and O_2-limiting conditions), including steam, CO_2 and hydrocarbons. XRD confirmed the insertion of dopants inside the unit cells (fig. 1). Comparison between model reaction results suggest that $Ba_{0.9}Sr_{0.1}Mn_{0.6}Mg_{0.2}Cu_{0.2}O_3$ and $Ba_{0.5}Sr_{0.5}Mn_{0.5}Mg_{0.2}Cu_{0.3}O_3$ have less capacity to stabilize superficial oxygen vacancies, causing a loss in activity towards NO reduction. Increasing amount of Cu in the structure undermines CO oxidation activity, but high Sr doping (50%) can recover some of that activity at temperatures above 350 °C. The comparison between tight and loose contact mode soot oxidation test (fig. 2) allowed to assess the effect of high dopant loading.In tight contact, 50 % doped Sr perovskite loses activity with respect to the other samples, but in loose contact no significant difference were noticed among them. This lead to the consideration that high dopant loading can increase the distortion of the structure at the point which oxygen mobility is hindered. The test in complex mixture (fig. 3) indicated $Ba_{0.9}Sr_{0.1}Mn_{0.7}Mg_{0.2}Cu_{0.1}O_3$ as the most promising material.



Results obtained on the $Ba_{1-y}Sr_yMn_{1-0.2-x}Mg_{0.2}Cu_xO_3$ serie (green y=0.1 x=0.1;blue y=0.1 x=0.2; orange y=0.1 x=0.3; red y=0.5 x=0.3)
Figure 1. XRD patterns Figure 2. Tight contact soot oxidation test; Figure 3 Stoichiometric mixture, CO conversion results

[1] COM/2017/0490 final on the 2017 list of Critical Raw Materials for the EU

P-7

Photo(electro)chemical water treatment for the degradation of emerging contaminants

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Contaminants of emerging concerns (CECs), including pharmaceuticals, cannot be effectively removed by typical water treatments, being thus discharged into the environment. Therefore, they may have adverse impact on aquatic organisms and on human health.

In this contribution, we will present a photoelectrochemical method for the wastewater treatment. Our approach capitalizes on the visible light absorption by two n-type semiconductors (namely WO_3 and $WO_3/BiVO_4$ n-n junctions) followed by the generation of charge carriers. While the photogenerated holes can be exploited to perform oxidation reactions at the semiconductor/electrolyte interface, the photogenerated electrons can travel through the circuit towards the cathode, where they can be used for the production of the green fuel H_2.

Atenolol and carbamazepine have been chosen as representative CECs for both photochemical (PC) and photoelectrochemical (PEC) degradation of pollutants by WO_3.[1] In a typical experiment, the photoanode was immersed in an aqueous solution containing the drug (10 mg/L) and irradiated. At the same time, a positive bias was applied, and the degradation reaction followed by HPLC. Under these PEC conditions, we managed to oxidize up to 80% of atenolol and 60% of the recalcitrant carbamazepine within 3 h of irradiation, with 4-5 times acceleration of the kinetics with the respect to the PC approach.

Moreover, HPLC-MS investigations allowed for the identification of the degradation intermediates, which disappeared after prolonged irradiation, confirming the complete mineralization of both drugs.

Regarding $WO_3/BiVO_4$ junctions, the selected target CECs were Ketoprofen (KTP) and Levofloxacine (LFX). In this case, PEC experiments showed high percentages of degradation of both these pollutants, with the complete mineralization of the sole LFX after prolonged illumination times (not observed in the case of KTP).[2]

The different behavior of the two semiconductors has been rationalized through EPR spectroscopy measurements, which evidenced the formation of OH radicals only in the case of WO_3. Indeed, in this semiconductor the photoproduced holes are powerful oxidants, able to oxidize water to $OH^{\cdot}$, the ultimate responsible for the complete mineralization even of the most recalcitrant pollutants.[1] On the other hand, the lower oxidant power of photogenerated holes in $BiVO_4$ leads to the formation of H_2O_2, which anyway contributes to drugs degradation, with similar experimental results (*i.e.* the complete mineralization to CO_2) only as far as stable aromatic species are not formed as the oxidation products.[2]

In summary, our photoelectrochemical devices allow for the conversion of a renewable, abundant and widely geographical distributed source of energy (sunlight) into a clean energy vector (H_2), with the simultaneous decontamination of wastewater from CECs, which are not easy to remove otherwise.

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New dyes for DSSC

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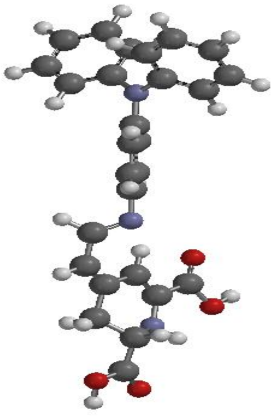
Our group has been working on the development of different dyes for DSSC including synthetically modified natural dyes, multinuclear self-assemblies and carbene Fe(II) complexes.

Natural dyes are modified by introducing donor electron groups on the betalamic core in order to increase excited state directionality and steric hindrance to block recombination[1].

Multinuclear dyes are based on $[Ru(TMAM)_2CN_2](TFSI)_4$ (Ru-TMAM) antenna and Z907 in order to extend the reach a panchromatic sensitization[2].

Finally we are working on the charge transfer dynamics Fe(II) complexes[3] having a great potential for efficient sensitization.



Example of a modified natural dye

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P-9

CO_2 electroreduction studies on Mo_2C films

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Transition metal and metal oxide carbides (TM(O)Cs) are known as promising non-noble metal electrocatalysts for hydrogen evolution reaction (HER) and/or CO_2 reduction reaction (CO_2RR), due to their low cost, high mechanical and chemical stability and their similar electronic properties to noble metals.[1] Theoretical calculations predict a deviation from the C and O binding energy scaling relations for metal carbides, which could result in lower overpotentials and higher selectivity for the CO_2RR to the products of interest.[2] In apparent analogy, the formation of methane on molybdenum carbide (Mo_2C) electrodes at lower overpotentials than copper (Cu) has been reported in recent literature.[3]

In this study, the catalytic activity of Mo_2C electrodes towards HER and CO_2RR was investigated. Mo_2C films were synthesized by direct carburization of polycrystalline molybdenum (Mo) substrates with hydrogen and methane (see Figure 1). The cyclic voltammetry coupled with differential electrochemical mass spectrometry (DEMS) was used to determine the electrocatalytic activity of carburized films and to detect reaction products. Furthermore, rotating ring disk electrode (RRDE) experiments were used to confirm the formation of previously observed products. The obtained results strongly suggest the formation of CO, while the reduction of CO to other products is still under investigation. For a better understanding of the electrocatalytic properties of Mo_2C, potential dependent changes of the surface during HER and CO_2RR were systematically investigated by using ex-situ emersion X-ray photoelectron spectroscopy (XPS). This method can provide detailed insights into the relation between electrocatalytic activity and surface chemistry of Mo_2C in general.

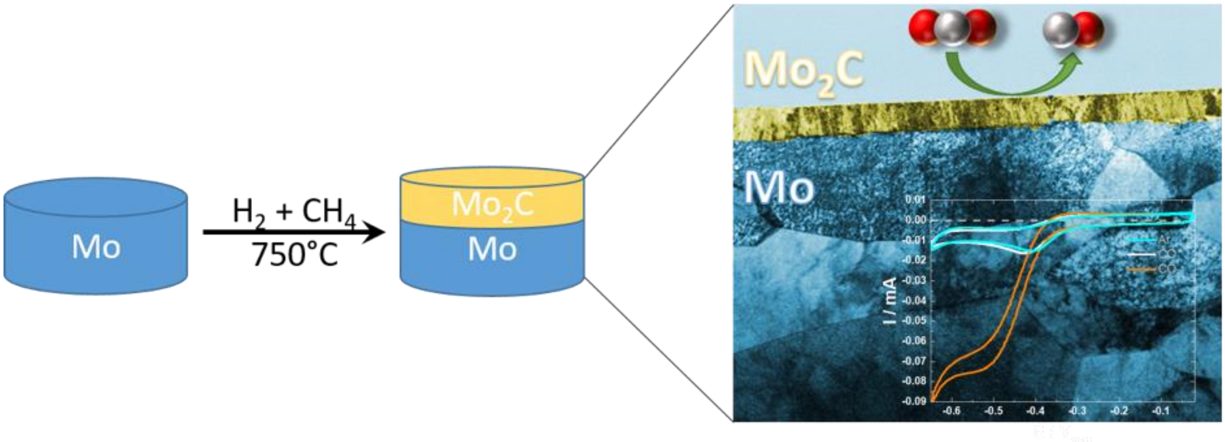

Figure 1: Scheme of the direct carburization of Mo and TEM-image of Mo_2C film on Mo substrate.[4]

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P-10

Shifting oxygen charge towards octahedral metal: a way to promote water oxidation on cobalt spinel oxides

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Cobalt spinel oxides are a class of promising transition metal (TM) oxides for catalyzing oxygen evolution reaction (OER). Their catalytic activity depends on the electronic structure. In a spinel oxide lattice, each oxygen anion is shared amongst its four nearest transition metal cations, of which one is located within the tetrahedral interstices and remaining three cations are in the octahedral interstices. This work uncovered the influence of oxygen anion charge distribution on the electronic structure of redox-active building block Co-O. The charge of oxygen anion tends to shift toward the octahedral-occupied Co instead of tetrahedral-occupied Co, which hence produces strong orbital interaction between octahedral Co and O. Thus, the OER activity can be promoted by pushing more Co into octahedral site or shifting the oxygen charge towards the redox-active metal center in CoO_6 octahedra.[1]

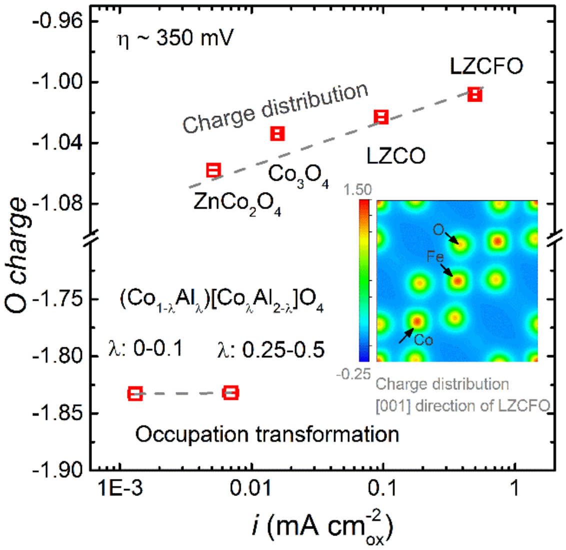

Figure. OER activity (specific current at an overpotential of ~350 mV) as a function of computed oxygen charges

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P-11

Gas-phase continuous-flow catalytic transfer hydrogenation of alkyl levulinates with (bio)ethanol: an improved process for GVL production

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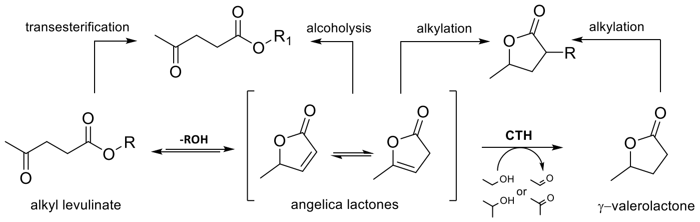
Levulinic acid (LA) and its esters (e.g. methyl and ethyl levulinates, ML and EL respectively) are polyfunctional molecules that can be obtained from lignocellulosic biomass. Because of LA particular structure and reactivity, the United States Department of energy has classified it as one of the top 12 building block chemicals [1]. Nowadays, the most common strategy for its valorisation is the chemical reduction in order to obtain valuable compounds such as fuel additives, solvents and other added-value chemicals. In this way, γ-valerolactone (GVL) is of particular interest. Indeed, GVL has been proposed both as an innovative "green" solvent (due to its low toxicity, stability and high boiling point) and as bio-based liquid fuel and additive with properties similar to ethanol but with a lower vapor pressure, which improved the combustion at similar octane numbers and a higher energy density. [2] The most common approach for the GVL production is the LA hydrogenation with molecular hydrogen (H_2). This is typically performed in batch systems, with high H_2 pressures and with noble metal catalysts, making it expensive and less applicable due to the extreme conditions [3]. The need for an alternative approach has led to the study of catalytic transfer hydrogenation (CTH) through the Meerwein-Ponndorf-Verley (MPV). This approach uses organic molecules (e.g. alcohols) that are capable of acting as a hydride transfer agent (H-donor), in order to reduce a molecule containing a carbonyl group. In this way, some interesting results, in terms of GVL yield, have been achieved by working in batch conditions and liquid phase (at high or autogenic pressure) using secondary alcohols (mainly isopropanol) as reducing agent with zirconia-based (ZrO_2) catalysts.[4] Hence, in this study we have synthesized a high SSA ZrO_2 (120 m^2/g) and we've tested it for first time in the gas-phase continuous-flow CTH of alkyl levulinates and alcohols in a wide range of reaction conditions. A complete characterisation of both the fresh and the exhaust catalysts has been performed by both ex-situ and in-situ techniques (NH_3 and CO_2-TPD, DRIFTS, TGA etc.). Interestingly, ethanol has been proved to be active for the target reaction allowing to obtain an average GVL yield of around 70% for more than 300 minutes of time-on-stream in the optimised conditions (250°C, atmospheric pressure) at complete conversion of the alkyl levulinate (both ML or EL). The reasons of this peculiar catalytic activity are related to the bifunctional properties of ZrO_2 surface sites.[5] Indeed, the presence of both Lewis acid and basic sites lead to a synergistic effect on the concurrent activation of both the alcohol (H-donor) and the carbonyl of the substrate. In addition, since ethanol can be easily obtained from biomass, tests using bio-ethanol as H-donor have been conducted. To determine reaction pathways and overall reaction network (Scheme 1), mechanistic studies were performed using the intermediates as reactants and varying the contact time. Moreover, long-term stability tests were carried out to evaluate the performance of ZrO_2 and deactivation of the catalysts was observed. This behaviour was ascribed to both the deposition of heavy carbonaceous compounds over the catalytic surface and to a progressive shift from Lewis to Brønsted acid sites. Finally, the in-situ regeneration of the catalyst was performed by calcination at 400°C in an air flow. In this way the catalytic activity of ZrO_2 was restored.



Scheme 1: Simplified reaction pathway for the CTH of alkyl levulinates with alcohols toward GVL and the main by-

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P-12

Electroreduction of carbon dioxide by porous Au-nanostructures prepared by Pulsed Laser Deposition

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Burning fossil fuels to meet the ever-growing energy demand of modern society comes with the inevitable price of releasing increasing amounts of carbon dioxide in the atmosphere. These anthropogenic CO_2 emissions contribute to greenhouse effect and to its well-known consequences on climate.

Therefore, in order to establish a virtuous CO_2 cycle, it is necessary to develop strategies focussed on the transformation of carbon dioxide into useful products.

To this aim, one of the most pursued approaches in the scientific community is the electrochemical reduction of CO_2, using suitable metallic cathodes.[1] Furthermore, one can envisage an electrochemical system in which the grid power is provided *via* the exploitation of renewable energy.

Among the metals used as cathodes, gold has been widely used since it almost selectively forms carbon monoxide as the main CO_2 reduction product.[2] Furthermore, several reports evidenced the importance of nanostructuring the Au-based cathodic interfaces in order to boost CO formation over the competitive proton reduction in aqueous media.[3]

In this contribution, we will report on the preparation of two different kind of porous Au-nanostructures, and their use as cathodes for CO_2 reduction in aqueous electrolytes.[4] These cathodic materials were synthetized by pulsed laser deposition, a versatile and easy-to-scale technique, already implemented in industrial processes.[5] The results obtained with the nanoporous catalysts evidenced the formation of syn-gas ($CO+H_2$), together with smaller amounts of formic acid, outperforming a planar gold foil used as reference.

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P-13

Characterization of nanostructured tin oxide synthesized on metallic Sn foams

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Recently, nanostructured tin oxide fabricated by simple anodic oxidation (anodization) is attracting a great interest due to its promising properties which generate a wide range of applications including solar cells [1], supercapacitors [2], gas sensors [3] or Li-ion and Na-ion batteries [4].

Nanostructured metal foams is a relatively new class of materials, which combines properties of metals and nanostructured materials. One advantage of such structures is their high surface area and ultra-low density [5]. Therefore, a strategy based on metallic foam anodization seems to be very promising, because such material may enhance the properties of SnO_x.

Here, we present some preliminary results on the fabrication of nanoporous tin oxide layers by simple anodization of Sn foams. Firstly, metallic foams were obtained by simple cathodic electrodeposition in acidulated $SnCl_2 \cdot 2H_2O$. Then, as obtained material was subjected to anodic oxidation in NaOH electrolyte. In this work, we investigated the effect of anodization time (600 s, 1200 s, 1800 s) on the morphology of anodic films. All other anodizing conditions were as reported in our previous work [6]. An example of as-obtained material is shown in Figure 1. As can be seen, nanoporous SnO_x layers were successfully obtained and no discontinuities and cracks are present within the anodic films.

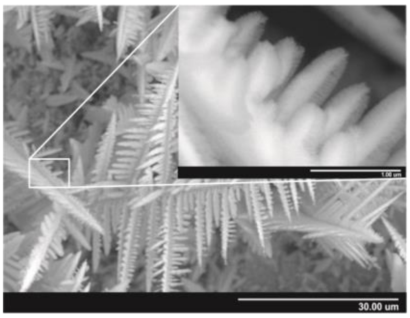

Figure 1. FESEM images of the anodic tin oxide foam obtained by electrodeposition and anodization in the alkaline electrolyte at the potential of 4 V for 1200 s.

The morphology and composition of all studied samples were confirmed by FE-SEM and XRD. The band gap of synthesized materials was estimated based on UV-Vis reflectance spectra. It was confirmed that samples anodized during 1200 s exhibit the red-shifted absorption edge in comparison to these oxidized for 600 s and 1800 s. Photoelectrochemical properties of as-received materials were also investigated.

Acknowledgments
Magdalena Gurgul acknowledges the financial support from Ministry of Science and Higher Education, Poland (Grant No. 0196/DIA/2018/47)

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P-14

Fabrication of current collector using a composite of polylactic acid and carbon nano-material for metal-free micro-supercapacitors with graphene oxide separators and microwave exfoliated graphite oxide electrodes

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The method of fused deposition modelling is used for the preparation of current collector from the composite of polylactic acid (PLA) and carbon nano-material (CNM) [1]. The collectors are investigated by IR and Raman spectroscopy. Metal-free supercapacitor was built on the base of microwave exfoliated graphite oxide electrodes, graphene oxide membrane as the separator and the current collectors from the polymer-nano-carbon composite. The electrochemical investigations are performed for the supercapacitor (SC), including its cyclic stability in the 1M H_2SO_4 electrolyte. Preliminary experiments show that there are several areas of research that will increase the specific capacity of the SC. These areas include, for example, the optimisation of the thickness of the separator and the reduction in the thickness of the current collector.

It is also shown that, with other identical conditions, the SC with PANI electrodes, PLA-CNM current collectors and **graphene oxide separator exceeds in capacity one with Nafion separator.**

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P-15

Cathodic corrosion: An efficient method for the preparation of mixed metal oxide nanomaterials with enhanced (photo)electrocatalytic activity

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Cathodic corrosion is a versatile electrochemical synthesis method that has been demonstrated as a powerful tool in the preparation of metal,[1] alloy[2] and, more recently, metal oxide nanoparticles that display notable catalytic performance.[3,4] Here we present a facile combinatorial approach for the electrochemical synthesis of high surface area mixed-metal oxide nanostructures. First, we will report the synthesis of bulk binary alloys with well-controlled composition by combinatorial, suspended droplet alloy fabrication (SDA) (Fig. 1A).[5] The process is followed by the synthesis of metal oxide nanoparticles with well-defined and homogenous composition using the cathodic corrosion method (Fig.1B). Finally, we will present the structural characterization of the different earth-abundant, mixed metal oxides acquired and their (photo)electrocatalytic activity towards key reactions such as the oxygen evolution reaction and electrochemical reduction of carbon dioxide (CO_2RR).[6]

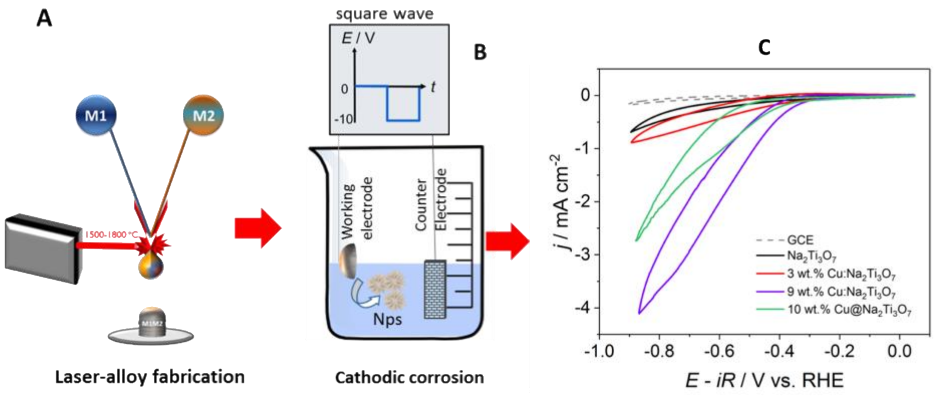

Figure 1. (A) Simplified experimental setup for the synthesis of metal alloys by SDA. M1 and M2 correspond to feeding motors of different metal wires. (B) Simplified cathodic corrosion experimental setup for the electrochemical etching of the alloys. (C) CO_2RR profiles of Cu-titanate nanomaterials, produced via cathodic corrosion, in 0.1 M K_2HPO_4/KH_2PO_4 (pH 8) buffer; v = 50 mV s^{-1}.

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P-16

X-ray microspectroscopy study of electrolyte-cathode interface in Solid Oxide Fuel Cells

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Solid-oxide fuel cells require materials that are mechanically and chemically resistant, such as doped cerium oxide or zirconium oxide[1], and perovskite mixed conductors. The high working temperatures, and the intimate contact between electrolyte and electrode can bring about cation diffusion and solid-state reactions between the cell components. To investigate the local and chemical structure of the species at the interfaces, we recently employed X-ray microspectroscopy on electrode-cathode bilayers[2,3].

We investigated the interface between several different electrolytes, either proton conducting or oxide-ion conducting, and perovskite electrodes, after annealing at high temperatures (1100 °C for 12-72 h) to simulate the fabrication processes and prolonged operation. The interfaces were studied with space-resolved X-ray absorption spectroscopy using the focused submicrometer-sized beam available at the ID21 beamline of ESRF. We used XRF to obtain concentration maps of all elements, and collected microXANES spectra at Ca, Mn, Fe, Co and Ce absorption edges.

We found that the rate of interdiffusion of the cations across the interface, and the formation of secondary phases, depends critically on the specific electrolyte/electrode pair. Moreover, microXANES spectra indicate that some cations show space-resolved changes in their oxidation and coordination state during diffusion.

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P-17

Iron-based macrocycles SAMs probed by EC-STM towards oxygen reduction reaction (ORR)

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FeN_x centres embedded in mesoporous carbon matrixes (Fe-N-MCs) are supposed to exert a catalytic effect towards oxygen reduction reaction (ORR) [1]. This retains a primary role for their further exploitation in fuel-cells and metal-air batteries with the aim to reduce the associated voltage losses due to the slow ORR rate. Fe-N-MCs are investigate to substitute platinum as the main catalyst material in PEMFC, since its availability is limited and implies high costs.

In Fe-N-MCs iron can be coordinated by 2 to 4 nitrogen atoms and notwithstanding many investigations are currently ongoing [2], there still exists a general lack of information about the main factors governing the ORR electrocatalysis promoted by FeN_x sites. Electrochemical scanning tunnelling microscopy (EC-STM) is a powerful technique, which allows to directly visualize the electrochemical behaviour of a system at the molecular scale. In this paper, the (111) facet of an Au single crystal was systematically functionalized with Fe(II)-phthalocyanine or Fe(III)-phthalocyanine chloride solutions. Self-assembly occurred at the solid/liquid interface, and ordered monolayers, especially for Fe(II)-phthalocyanine, were probed thanks to STM setup. Additionally, being connected to a bipotentiostat, the crystal can be polarised as working electrode of the “four-electrodes setup” [3].

In fig. 1.a, the Fe(II)Pc adlayer shows a topographic profile of $\Delta Z_{(Ar)} \approx 0.25$ Å in Ar purged electrolyte (0.1 M $HClO_4$), whereas it becomes $\Delta Z_{(O_2)} \approx 0.9$ Å in O_2 saturated electrolyte, as shown in fig. 1.b, where the higher protrusion appears shifted from the molecular centre, indicating a probable end-on O_2 adsorption geometry at the Fe centre. By polarizing the FeN_4/Au electrode at sufficiently large potentials suitable for ORR, the central protrusion disappears, indicating that adsorption no longer occurs, and ORR is proceeding at high rate.

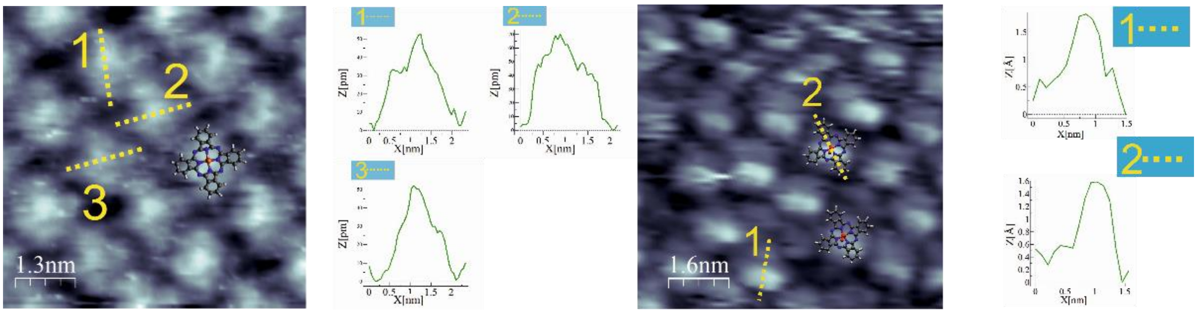

Figure 1. a) High-resolution EC-STM image of Fe(II)Pc adlayer on Au(111) in deaerated 0.1 M $HClO_4$. Parameters: I_t= 1.05 nA; U_b= -352 mV; E_{app}= 625 mV vs RHE. The insets show the corresponding topographic profiles. b) High-resolution EC-STM image of Fe(II)Pc adlayer on Au(111) in O_2 saturated 0.1 M $HClO_4$. Parameters: I_t= 5 nA; U_b= -385 mV; E_{app}= 625 mV vs RHE. The insets show the corresponding topographic profiles.

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P-18

Self-supported Iridium Network as a Highly Active Electrocatalyst for Oxygen Evolution in Acidic Electrolyte

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Hydrogen production from water-electrolysis is expected to play an important role in the replacement of fossil fuels [1]. Polymer-based proton exchange membrane (PEM) electrolyzers are very promising due to their high current densities, low ohmic losses and high load following capability. However, it is challenging to develop catalysts that resist the harsh corrosive acidic conditions, especially for the anodic oxygen evolution reaction (OER) [2]. As a result, only Iridium-based electrocatalysts have shown both sufficient stability and activity for commercial use. Currently, the lack of efficient and stable support material is limiting the utilization of the highly scarce and expensive iridium metal.

Herein, we present a novel catalyst concept consisting of a high surface area self-supporting nanoporous Ir-network. The synthesis was performed using alternating physical vapor deposition (PVD) of Ir and Co followed by a single dealloying step. The residual nanoporous Ir-network was characterized both structurally and electrochemically showing a unique morphology with excellent activity combined with enhanced stability.

To our knowledge, this is the first time that a PVD method have been employed for fabrication of active unsupported high surface area Ir-based OER catalysts.

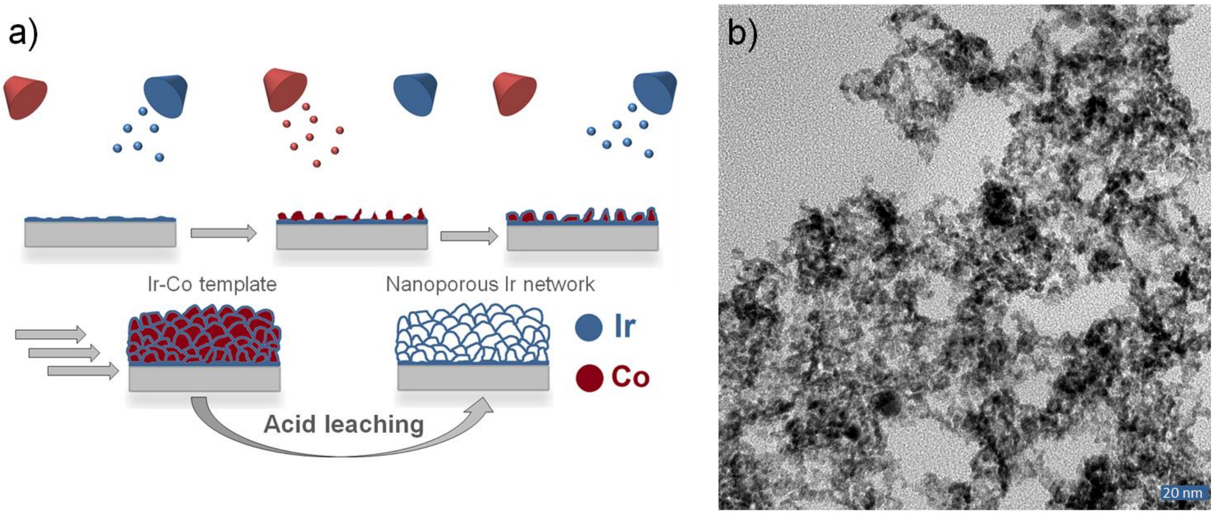

Figure 1 a) Schematic illustration of the PVD synthesis process b) Representative TEM micrograph of the nanoporous Ir network catalyst.

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P-19

Sulfonated graphene oxide as innovative self-assembling electrolyte for PEM fuel cells

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Sulfonated graphene oxide (SGO) membranes have been developed and evaluated as a viable alternative to Nafion® in polymer electrolyte membrane fuel cells (PEMFCs). Even though Nafion® is currently the most widely used electrolyte in PEMFC systems, some crippling drawbacks induce the need of finding feasible replacements. In particular, Nafion® suffers a severe conductivity drop upon dehydration, which limits the possibility of operation in conditions of high temperature and low relative humidity [1]. As shown in previous works, graphene oxide (GO) appears to be an excellent candidate for making both freestanding [2] and polymer-based hybrid membranes [3], thanks to its good mechanical properties and to the presence of oxygen-containing functionalities that are likely to improve water retention. However, we verified in a preliminary study [4] that, at high temperatures, GO suffers a partial loss of the chemical groups which foster protons transport and a lowering of the structural integrity of the carbon network. Hence, its properties may be enhanced by functionalization with some acid groups more tightly bound to its skeleton, e.g. sulfonic acid groups ($–SO_3H$) analogous to those of Nafion®.

In this work, we present an effective method for the sulfonation of graphene oxide, based on the reaction between sulfuric acid and a commercial aqueous dispersion of GO. Different samples have been prepared by varying the quantity of sulfuric acid employed in the sulfonation reaction, and an optimal acid-to-GO molar ratio has been identified, taking into account an empirical formula of GO. Such formula has been derived, as a first approximation, from the elemental analysis of the commercial solution and confirmed by the results of SEM and EDX analysis. The sulfonated membranes have been widely characterized by ATR-FTIR, XRD, SEM and EDX spectroscopies, thermogravimetric (TG-DTG) analysis, optical microscopy and static contact angle (OCA) measurements. These techniques confirmed the effective functionalization of GO and the stability of sulfonic acid groups even after water uptake (WU) experiments, which have been carried out at different temperatures and relative humidity. The ion exchange capacity (IEC) of the different samples has been evaluated as well, and a correlation among WU, IEC and degree of sulfonation (DS) can be established. Test results showed that sulfonated membranes have an improved WU behaviour with respect to both Nafion and unfunctionalized GO, especially at low temperature and humidity (**Fig. 1**); they also show an IEC value higher than 1 meq/g, which is even better than IEC determinations reported for Nafion® [5]. The increase of the amount of sulfuric acid seems to be beneficial for both properties. Then, one sulfonated membrane has been selected and subjected to a preliminary test in a lab-scale hydrogen-fed fuel cell. Promising results have been found from the point of view of mechanical resistance, even though a low open circuit voltage (OCV) has been measured (0.63 V) at 40 °C, which might be ascribed to hydrogen crossover issues. These issues should be addressed in future developments of such components. However, after testing, the active area showed absence of carbon residues left by the gas diffusion electrode (GDE), which are a typical problem in the case of Nafion®.

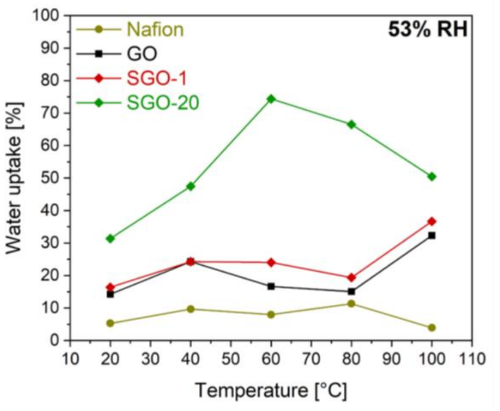

Fig. 1. WU as a function of temperature at 53 % relative humidity. Two different acid-to-GO molar ratios are reported.

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P-20

Synthesis of nanoalloys via Laser Ablation in Liquid and study of their activity towards the Oxygen Reduction Reaction in alkaline media

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Nowadays nanoparticles are pervasive in science and technology. Laser synthesis and processing of colloids (LSPC) demonstrated that it is possible to obtain nanoparticles of various types, such as metals, oxides, carbon allotropes, or alloy. LSPC includes three main approaches: laser ablation in liquid (LAL), where nanoparticles are obtained by laser ablation synthesis in solution (LASiS) of a bulk target; laser fragmentation in liquid (LFL), where smaller nanoparticles are obtained by the fragmentation of larger nano- or micropowders dispersed in the liquid; and laser melting in liquid (LML), where nanoparticles are obtained by a mixed process of melting and vaporization of pristine nano- and microparticles.[1] In particular, LAL proved to be a very efficient way to synthesize alloy nanoparticles, also with metastable or unconventional structures.[2-3] Besides, LASiS is amenable of automatization and remote control with PC or smartphones.[4]

Here we will describe two different types of alloy nanoparticles, AgCo NPs and AgFe NPs, obtained via LASiS. These materials are studied electrochemically for the Oxygen Reduction Reaction (ORR), which is the cornerstone of many important energy conversion devices, such as fuel cells and metal-air batteries. [5] In this contest, the investigation of catalysts based also on earth abundant elements, such as Fe and Co, or non-critical energy elements such as Ag, is pursued toward the replacement of Pt, which has long been the most efficient catalyst for ORR, but it is also an energy critical element.

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P-21

Hydrogen and acrylate generation by electrochemical reforming of bioalcohols

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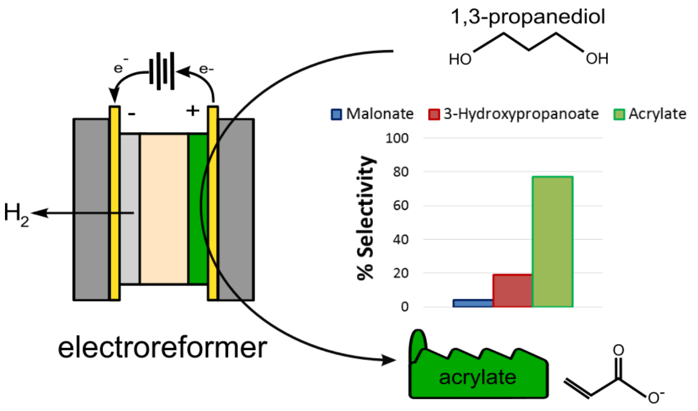
The production of hydrogen by the electrolysis of water is a well-established technology. However, it does not have a significant commercial impact due to its high-energy cost. A traditional Proton Exchange Membrane (PEM) electrolyzer needs more than 45 kWh kg(H_2)$^{-1}$ to achieve a significant rate of hydrogen production.[1] This is the main reason why water electrolysis accounts for only a small proportion of the world’s hydrogen production (c.a. 4%). Since the thermodynamic barrier of water electrolysis consumes 68% of the whole energy input of the device, our strategy for reducing the energy cost is the replacement of the unfavorable anodic oxygen evolution reaction with a more suitable reaction: the partial oxidation of an alcohol to a carboxylate. This process needs only 20 kWh for the evolution of one kilogram of hydrogen at the same working conditions of traditional PEM electrolyzers, with a net energy saving of about 44%. Such electrolytic processes that lead to the concomitant generation of hydrogen and industrially relevant chemicals, like acetate and lactate, are often indicated as “electrochemical reforming”, or “electroreforming”.[2] In order to obtain selective oxidation of alcohols to carboxylic compounds of interest to the fine chemical industry, several anodic catalysts have been investigated, ranging from nanostructured palladium catalysts to rhodium organometallic compounds.[2,3] Here we present an anode based on palladium nanoparticles deposited onto a carbon-ceria support Pd(10%)/C:CeO_2 (50%/50%) which is able to selectively oxidize the 1,3-propanediol biomass derived alcohol to potassium acrylate, a very important raw chemical. The production of acrylate is coupled with the generation of pure hydrogen (99.99%). We had and in depth study of the operative conditions of the electroreformer to optimize the selectivity of the alcohol oxidation reaction to potassium acrylate: at 400 mV and 80°C in a “single pass mode”, the selectivity is of the 80% for acrylate.[3]



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P-22

Long Range BTBT-Peptide 1D Supramolecular Assemblies

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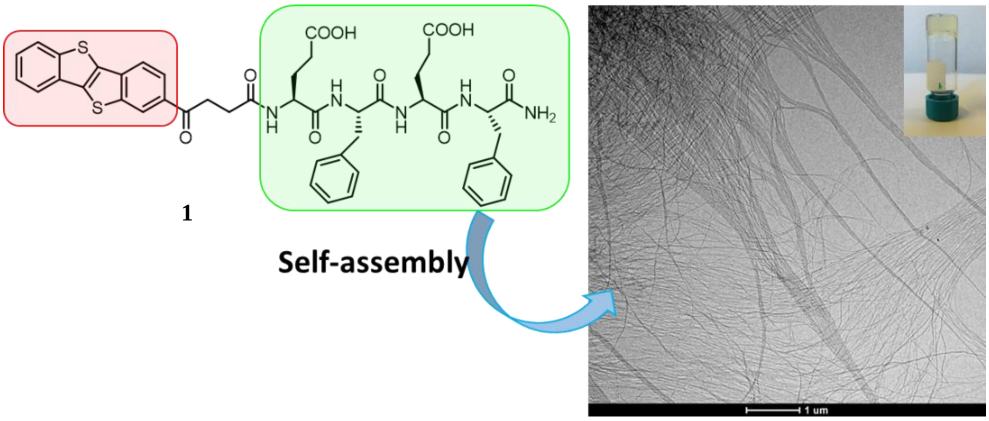
The controlled self-assembly of small π-conjugated molecules into well-defined nanostructures is a powerful tool for the fabrication of supramolecular optoelectronic materials. In particular, supramolecular gelation has demonstrated to be an efficient approach for the production of highly ordered long-range assemblies of small electronically active molecules [1]. Still, a major challenge in this field is the fabrication of biocompatible materials in aqueous media for bioelectronics. We have previously successfully used the conjugation of self-assembling peptides with small-π-conjugated molecules as efficient strategy for the fabrication of supramolecular hydrogels with a well-ordered packing of chromophores [2-3].

[1]benzothieno[3,2-b][1]-benzothiophene (BTBT) is a promising chromophore characterized by high hole mobility, easiness of synthesis and high chemical stability. The experimental mobility values of BTBT reported are generally within a range of 1-100 $cm^2V^{-1}s^{-1}$, with a record value of 170 $cm^2V^{-1}s^{-1}$ [4]. Reaching high mobilities in OFETs (and generally in all devices) is enticing as it allows faster operation of transistors and energy savings by reduced calculation times [5]. Substitution of BTBT with alkyl chains allows to fabricate solution processed semiconducting films from organic solvents and, very recently, self-assembled nanowires were obtained in aqueous media by conjugation of a peptide amphiphile [6]. Nowadays, the supramolecular gelation and the formation of long-range self-assembled 1D structures is still to be demonstrated.

In this study we report the synthesis of the peptide-BTBT conjugate **1** and, for the first time, the formation of supramolecular hydrogels with the BTBT core is shown. This molecule self-assembles into 1D-nanostructures in aqueous media as shown by transmission electron microscopy. Absorption and emission spectroscopies as well circular dichroism studies demonstrated that the formation of the 1D fibers is driven by both intermolecular hydrogen bonding between peptide chains and π-π stacking between chromophores and exceptionally the fibers obtained are several micrometres length.



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P-23

Peptide-chromophore conjugates for the dispersion of SWCNTs in water

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Since their first observation by Iijima [1], carbon nanotubes (CNTs) have been the focus of considerable research due to their exceptional electronic, thermal and mechanical properties for a broad range of fields including nanoelectronics, energy storage, energy transfer, photovoltaics and biomedical [2,3].

However, practical applications remain elusive due to their insolubility in water and organic solvents, their tendency to aggregate and make tight bundles, and the heterogeneity, both in diameter and chirality, with which nowadays carbon nanotubes are produced. To overcome these issues, a non-covalent functionalization strategy may be used, whose strengths are that it preserves the intrinsic properties of CNTs and does not need of special instrumentation [4].

In this study we report the use of a peptide topological template for the dispersion of SWCNTs in water. The molecule has two well-differentiated spatial domains. One of them functionalized with solubilizing groups (side chains of glutamic acids) and the other one functionalized with π-conjugated chromophores *via* azide-alkyne click chemistry that are meant to tweeze the CNTs.

Details on the preparation and characterization of such nano-tweezers will be given, together with preliminary evidence on their ability to disperse CNTs in water.

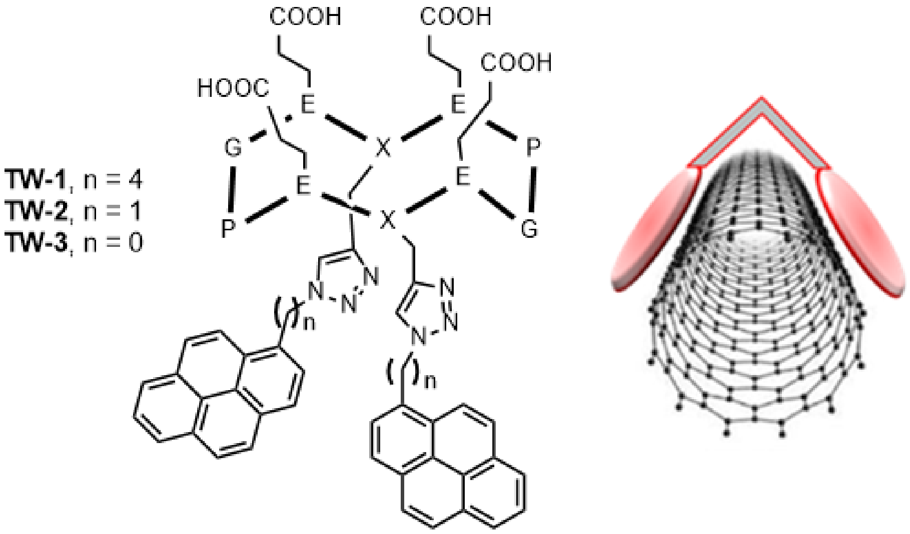

Figure 1. Structure of tweezers TW1-3 and cartoon showing the interaction of a molecular tweezer with a SWCNT.

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P-24

New avenues to transition metal phosphide incorporated heteroatom doped carbon nanostructures for efficient electrocatalysis

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Transition metal phosphides (TMPs) have emerged as an intriguing class of efficient electrocatalysts finding widespread application in hydrogen evolution reaction (HER), oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) etc. Unfortunately, however, currently adopted wet chemistry and solid-gas synthesis techniques rely on the use of surfactants/ toxic organic solvents or toxic gas which restricts facile fabrication of TMPs. Moreover, hybridizing TMPs with suitable carbon support (graphene, carbon nanotubes etc.) which favorably optimizes the electrochemical activity of TMPs is often achieved via post-synthesis modification further complicating the synthesis procedure.

In an attempt to overcome these limitations, we have recently developed a solid state, phosphine free method to fabricate Co_2P nanoparticles encapsulated N,P co-doped CNTs.[1,2] These catalysts were applied as a bi-functional electrocatalyst for HER and OER. In order to increase the surface area and loading of Co_2P nanoparticles, we next designed Co_2P encapsulated CNTs grafted N,P co-doped hollow spheres via MOF-templated strategy which exhibited superior catalytic activity compared to Co_2P@CNTs.

We then introduced sub-2nm IrP_2 nanoparticles encapsulated bilayer N, P co-doped graphene as a novel electrocatalyst which exhibits better HER activity than benchmark Pt/C in acid, neutral as well as the alkaline medium. Interestingly, careful tuning of the reaction parameters also enables the synthesis of phase pure Ir_2P nanoparticles supported N,P co-doped graphene..

In conclusion, the strategies developed here can be extended to fabricate a variety of TMPs with widely varied applications.

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P-25

Electrochemical behaviour of InSb thin films with different crystal structures in 0.5 M NaOH

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Indium antimonide is a semiconducting material with a wide range of potential applications due to its narrow band gap (0.17 eV at 300 K) [1], small effective electron mass (0.014 m_0) [2], and one of the highest electron mobility of ~78000 cm^2 V^{-1} s^{-1} [3]. Particularly advantageous is the use of InSb in the form of nanowires. There are many methods which allow to obtain InSb nanowires, for example: molecular beam epitaxy (MBE), chemical beam epitaxy (CBE), pulse laser deposition (PLD), and many others. Mentioned techniques are energy and time consuming, require elaborate equipment and operate on complex preparation procedures. One of the most affordable methods used for their synthesis is a template-assisted electrodeposition within the pores of anodic aluminum oxide (AAO) [4]. After electrodeposition of nanowires, the AAO template is typically dissolved in a NaOH solution. The possible and undesirable dissolution of InSb nanowires can weaken electrical transport properties of nanowires. Therefore it is important to investigate the corrosion behavior of InSb in alkaline solution.

In our research we used a simple model like InSb thin films which enabled greater control of the specific surface area of the tested samples, which is extremely important from the point of view of the reproducibility of the obtained results. InSb thin films were electrodeposited on a graphite foil. The electrochemical synthesis was carried out in a citrate bath containing 0.06 M In^{3+} and 0.045 M Sb^{3+} . The pulse electrodepositions were conducted in a conventional three-electrode cell with a platinum counter electrode and SCE as a reference electrode. The electrodeposition was performed at room temperature at E_{on} = -2.3 V and E_{off} = -0.5 V vs. SCE. The duration of pulse ‘on’ was in the range from 1 ms to 1000 ms, and the ratio $t_{on} : t_{off}$ was constant (1:5). All thin film synthesis lasted 15 min. The obtained InSb films were tested in a 0.5 M NaOH solution using electrochemical techniques such as open circuit potential measurements, cyclic voltammetry, and Tafel analysis. The morphology and composition of as-obtained thin layers before and after electrochemical tests were analyzed by SEM and EDS.

The results confirmed, that the pulse time during electrodeposition of InSb affects the composition and crystal structure of the synthesized material, what was performed simultaneously on a different type of substrate material in our other studies [5]. The elongation of the pulses time contribute to increase the percentage of antimony in thin films and smaller crystal sizes. Among the InSb films, those with the largest crystallite size (synthesized using t_{on} = 1 ms and 10 ms) are the most susceptible to corrosion in 0.5 M NaOH, what has been confirmed by the highest corrosion rate of 1.5 and 1.3 mm per year, respectively. The InSb thin films with a nanocrystalline/amorphous structure (t_{on} = 100 ms and 1 s) are more resistant to the corrosion than the crystalline and metallic films [6].

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P-26

Free-standing carbon electrode for the oxygen evolution reaction

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N -functionalized hydrothermal carbon materials (N-HTC) with spherical morphology were prepared by hydrothermal synthesis utilizing glucose and urotropine as starting materials. The molar ratio of glucose and urotropine has been varied and the powder materials were pelletized, resulting in mechanically stable disc electrodes. By increasing the amount of nitrogen, N-contents from 5 wt% up to maximal 8 wt% were obtained after pyrolysis at 1000 °C. The pellet can then be used as an anode for water splitting. In literature, there are still no direct evidence of metal-free carbon as electrocatalyst for oxygen evolution reaction. By comparing the N-functionalized sample and without functionalization, we found that the former has superior stability under water splitting condition (relative high potential). Up to one week of stable oxygen production was achieved. The result indicates that nitrogen facilitates oxygen evolution reaction. Besides, the nitrogen species also hinders carbon corrosion, proved by a simple Hoffmann cell measurement. Pellets with different synthesis condition as well as nitrogen content are compared in order to get the optimized synthesis condition.

For better understanding, methylene blue adsorption and mercury intrusion porosimetry are used to characterize the pore structure of the carbon materials. The relative work function and conductivity of the carbon pellet are determined by Kelvin-probe and Van-der-Pauw methods, respectively. A conventional three-electrode assembly is used to characterize the electrochemical performance, including activity, stability as well as mass transport property by cyclic voltammetry, chronopotentiometry and electrochemical impedance spectroscopy (EIS). A transmission line equivalent circuit model is used to fit the EIS complex spectra, where the diffusion resistance and reaction resistance can be determined. The two resistances are very important reaction key performance indicator for oxygen evolution reaction, as it can distinguish a diffusion process from a reaction. The gas products as well as electrolyte after electrochemical test can be analysed by mass spectrometry, ESI-MS, UV-VIS spectroscopy, etc. From the mass spectrometry results, the mole fraction of oxygen in the total product gas can be determined, determining the selectivity of the reaction.

P-27

Growth of graphene nanoribbons from molecular functionalized precursors on different single crystal metal surfaces: a comparative study

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In the field of organic semiconductors, nanostructures based on graphene are very attractive, due to the possibility of finely tuning their band gap in a wide range, with applications in nano- and opto-electronics [1]. Among them, graphene nanoribbons (GNRs) are the most promising [2]. The attention is focused on the bottom-up synthesis of GNRs from molecular precursors supported on metal surfaces (mainly gold, silver and copper): thus GNRs have atomically-precise widths and edges [3,4]. The main goal of this study is the comparison of the synthesis outcomes on different surfaces, to optimize the production of long-range ordered and highly unidirectional GNRs with well-defined transport properties.

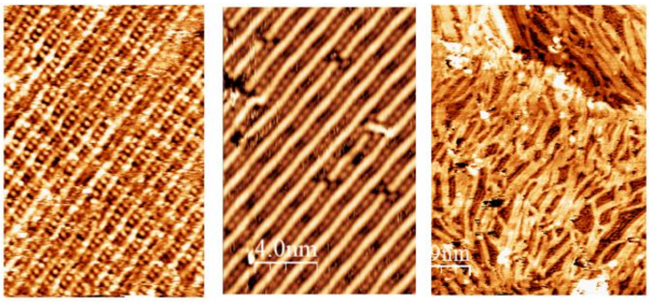
In this work different types of GNRs depending on the metallic surface used for deposition are synthesized. 4,4''-dibromo-p-terphenyl (DBTP) is chosen as molecular precursor [5], while Au(110), Au(100) and Ag(110) from single crystal are used as substrates. The synthesis is performed in ultra-high-vacuum conditions ($1\text{-}2 \times 10^{-10}$ mbar). The organic precursors are vapour-deposited on the surface *in situ*. Each sample undergoes several steps of annealing for a variable time, and after each step the interface is characterized through Scanning Tunneling Microscopy (STM) and Low Energy Electron Diffraction (LEED), in order to gain information on the overlayer topography and local density of states, and overlayer-substrate registry.

The synthesis pathway is performed first by the room temperature deposition of the brominated precursor. Then, the following steps are thermoactivated: an annealing at lower temperature promotes Ullmann coupling between the precursor units to form long polymeric wires (poly-p-phenylene, PPP), while another annealing at higher temperature activates cyclodehydrogenation reactions that lead PPP wires to laterally fuse and form GNRs [6].

On Au(110) short and narrow GNRs are obtained, with a quite good alignment along preferential directions. On Au(100) the GNRs are longer, the width distribution is equally narrow, and the long-range order is very high, with overall better results than on Au(110).

Ag(110) shows intermediate properties of the GNRs: the main difference is the clear formation of an organometallic intermediate between Ag adatoms and debrominated precursors before the formation of PPP wires (Fig. 1).

Finally, the synthesized GNRs are characterized *ex situ* by the acquisition of Raman spectra to prove their stability in air: in particular, the presence of the main vibrational modes of GNRs and the absence of fingerprints related to the degradation of GNRs in ambient conditions are verified.



Organometallic intermediate (390 K) → PPP formation (440 K) → GNRs formation (670 K)

Figure 1 – Scanning Tunneling Microscopy images of the synthesis of GNRs from DBTP on Ag(110)

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P-28

Low temperature CO_2 methanation on Ni doped catalysts on open-cell foams

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The hydrogenation of CO_2 to CH_4 is one of the most promising Power to Gas technologies. To achieve a high CH_4 productivity in this exothermic process, an active and stable catalyst as well as the heat management are mandatory [1]. Open-cell metallic foam structured catalysts address the weakness of pressure drop in multitubular fixed bed reactor and enhance heat transfer [2].

Here, high loaded Ni-catalysts containing Y, La or Ce as dopant (Ni/X/Al = 70/5/25 molar ratio, X = Y, La, Ce) are prepared by electrodeposition of hydrotalcite (HT) compounds on NiCrAl foams (cell size 450 µm). After calcination and reduction at 600 °C, the activity is evaluated in the CO_2 methanation at 1 bar and GHSV = 38,000 h^{-1} (WHSV of ~400-600 L kg_{cat}^{-1} h^{-1}) with concentrated feedstocks ($H_2/CO_2/N_2$ = 4/1/1 and 4/1/0), recording axial temperature profiles.

Ni/Al-HT precursors with controlled composition, structure and textural properties are electrodeposited on the foam surface (Fig. 1a). Dopants modify the reducibility and basicity of the catalysts calcined at 600°C and the stability of Ni^0 nanoparticles in reaction conditions (Fig. 1b), affecting the reaction mechanism. Consequently, the activity is greatly enhanced by dopants at low temperature (Fig. 1c).

The most active Ce-containing sample attains a high activity at T_{oven} = 300 °C (~78% Conv. CO_2, 98% Sel. CH_4), outperforming a coprecipitated pelletized catalyst (~58% Conv. CO_2, 95% Sel. CH_4), and it is stable for 66 h time-on-stream.

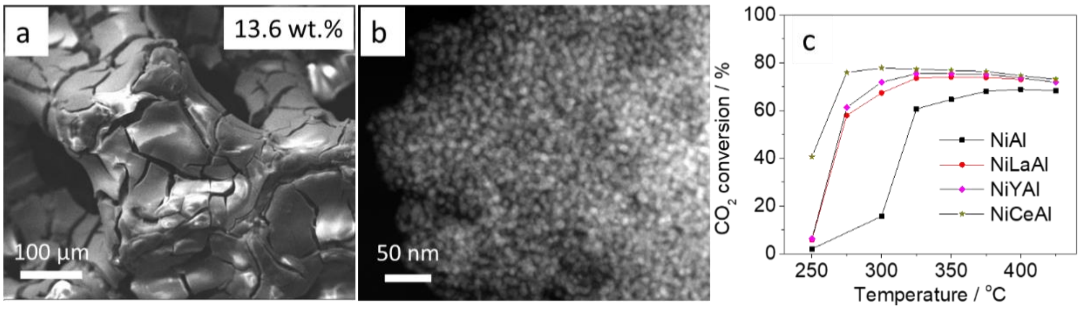

Figure 2: NiCeAl catalyst: a) SEM image of the electrodeposited sample and b) HAADF-TEM image after reaction. c) CO_2 conversion on the structured catalysts prepared.

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P-29

The effects of different iron precursors on catalytic performance of Fe-N-C catalyst for ORR in PEMFC

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Among M-N-C catalysts, Fe-N-C is the most interesting system in terms of activity and stability. However, the types of active sites in these catalysts are still not well understood. Fe-N_x centres are considered the real active site for ORR, even though other co-catalyst centres in the form of core-shell nanoparticles are supposed to be necessary for improving the tetraelctronic reduction of oxygen [1]. These catalysts are usually obtained by co-pyrolysis of a carbon and an iron-nitrogen precursor, where N-groups act as the coordinating environment for metal ions [2]. The performance of these catalysts is governed by the density of accessible atomically disperse active sites and since the amount of metal required is theoretically very small, a homogenous dispersion of iron centres is fundamental. So, the first parameter to tune is the equilibrium between micro- and mesopores. The second aspect is the structure of metal source, which may induce different catalytic activity [3].

In this work, we evaluate the influence of different N-based ligand to obtain Fe-chelating complexes. The issue is to understand whether there is a correlation between the structure of the complex precursor and the catalytic performance of the resulting catalysts after the pyrolysis. Two parameters have also taken into account: (i) the hydration state and (ii) the molar ratio of iron precursors and carbon source [4]. The activity of Fe-N-C catalysts was tested by cyclic voltammetry and RDE or RRDE technique. Figure 1 reports a comparison of different Fe-N-M catalysts prepared starting from complexes of phenanthroline, porphyrin and cyclam ligands. So far, the sample from Fe(phen)$_3$Cl$_2$ showed the best catalysts activity for ORR with a yield of H_2O_2 at 0.0 V vs. RHE below 1 %. Conversely, FeCyclam complex does not allow to obtain an active catalyst due to the low nitrogen content as evidenced by the elemental analysis [5]

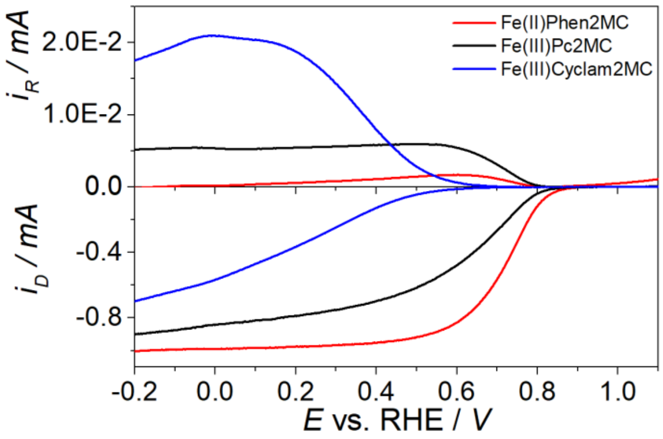

Figure 1: LSV with RRDE of different catalysts with different ligands (1,10 phenanthroline, cyclam and phthalocyanine) at *v* = 2 mV s^{-1} and ω = 1600 rpm in a O_2 purged 0.5 M H_2SO_4.

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P-30

Electrochemical investigation on Ruddlesden-Popper perovskite for IT-SOFC

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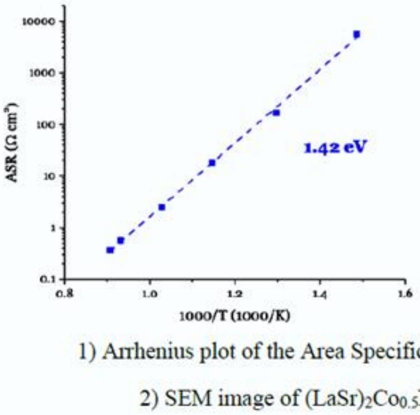
Solid oxide fuel cells (SOFCs) are characterized by solid oxide electrolytes and thus require high working temperature for assuring good performances. The high temperature allows to avoid the use of noble metals but is detrimental for cell duration and cost. In this research cobalt-nickel based perovskites have been studied as cathode for intermediate temperature SOFCs (IT-SOFCs 600-800 °C): in particular a Ruddlesden-Popper (RP) perovskite phase $(LaSr)_2Co_{0.5}Ni_{0.5}O_4$ was considered. RP perovskites of the K_2NiF_4-type structure are receiving considerable attention because of the flexible oxygen stoichiometry, fast oxygen ion diffusion, rapid surface exchange kinetics [1]. The electronic conductivity of the parent compound La_2NiO_4 is around 100 S/cm at 800°C and the ionic conductivity is usually better than that of corresponding ABO_3 perovskites. The substitution of La with Sr and of Ni with Co was observed to improve phase stability and to increase the oxygen exchange capability due to the presence of cobalt in different oxidation states.

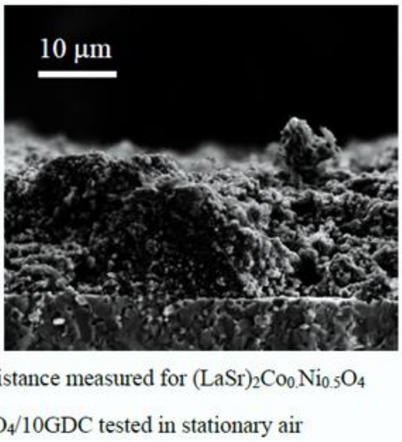
The cathode powder, $(LaSr)_2Co_{0.5}Ni_{0.5}O_4$, was prepared (through citrate method followed by a thermal treatment in air at 900°C) and accurately characterized by means X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature programmed reduction (TPR) and electrochemical impedance spectroscopy (EIS).

To study the performance as electrodes for IT-SOFCs, the electrochemical impedance spectroscopy (EIS) on $(LaSr)_2Co_{0.5}Ni_{0.5}O_4$-based symmetrical cells was carried out. The chemical compatibility between electrode and electrolyte was studied by mixing together the powders and firing at high temperature under the same condition used for the preparation of symmetrical cell (1200 °C under air, 1 h). The XRD carried out after the thermal treatment, did not show any secondary phases induced by the thermal treatment.

The electrolyte selected was 10% gadolinium doped ceria (10GDC) which has shown the best chemical and mechanical compatibility with the electrode. The symmetric cell $(LaSr)_2Co_{0.5}Ni_{0.5}O_4$/GDC/$(LaSr)_2Co_{0.5}Ni_{0.5}O_4$ tested under stationary air has achieved an area specific resistance (ASR) of 2.51 Ω cm2 at 700°C but dropped to 0.56 Ω cm2 at 800°C. The activation energy obtained for $(LaSr)_2Co_{0.5}Ni_{0.5}O_4$ was 1.42 eV, which is very close to the $(LaSr)_2CoO_4$ one reported in literature (1.40 eV). Interestingly, Skinner et al. [2] obtained, for undoped and Srdoped Ruddlesden-Popper nickelates the following values: 0.85 and 1.61 eV for diffusion and oxygen exchange processes, respectively, in La_2NiO_{4+d} while these values decrease to 0.57 and 1.29 eV respectively for $La_{1.9}Sr_{0.1}NiO_{4+d}$. The comparison with the data obtained in the present confirms that the addition of higher amounts of Sr helps reducing Eatt. The good electro-catalytic performance observed on $(LaSr)_2Co_{0.5}Ni_{0.5}O_4$, confirm the feasibility to be used as cathode on IT-SOFCs.

1





2

1) Arrhenius plot of the Area Specific Resistance measured for $(LaSr)_2Co_{0.}Ni_{0.5}O_4$

2) SEM image of $(LaSr)_2Co_{0.5}Ni_{0.5}O_4$/10GDC tested in stationary air

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P-31

Nitrogen Doped Graphene Electrocatalyst decorated with Transition Metals for the Oxygen Reduction Reaction

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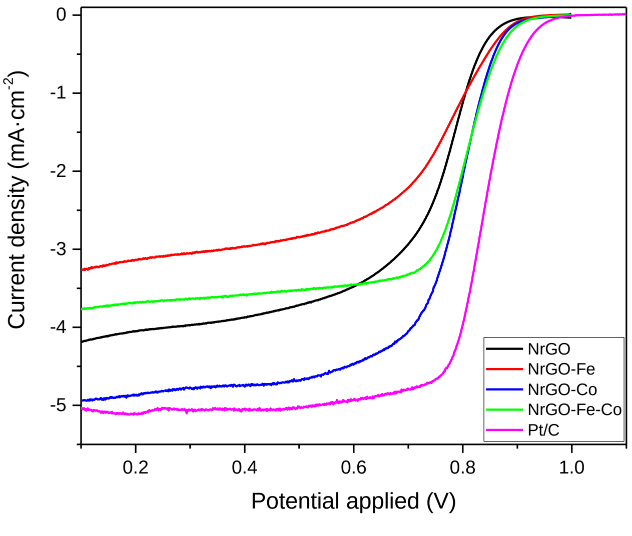
The development of non-noble metal electrocatalysts towards the oxygen reduction reaction (ORR) is a key step to launch fuel cells (FCs) into the market. Carbon-based materials, such as graphene, have been proposed as an alternative to platinum group metals (PGMs) at the cathode of FCs because they are inexpensive, widely available and active towards ORR.

The modification of reduced graphene oxide (rGO) structure by doping procedures with heteroatoms (N, P, S, B) and with earth-abundant metals creates structural defects which can enhance the ORR activity [1]. In particular, the creation of active sites formed by Me-N-C species (Me = Co/CoO, Fe, Ti, Mn, etc.), is highly related with an enhancement in the catalytic activity towards the ORR [2].

The aim of this work is the synthesis of nitrogen-doped rGO and its modification with Fe and/or Co nanoparticles. N-doped graphene has been obtained by thermal treatments of GO and urea at different temperatures. Non-noble metals supported on rGO have been prepared by reduction of metal salts with sodium borohydride, and finally treated at high temperature and acid leached.

The electrocatalysts have been characterized using X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy and elemental analysis. The catalytic activity for the ORR has been measured using a three-electrode cell in alkaline medium (0.1M NaOH) with a rotating disk electrode (RDE). Initial results show that all catalysts present good onset potential for ORR, being cobalt-based catalysts those with the highest activity.



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P-32

Dye-Sensitized Photoanodes for Water Oxidation based on Non-Covalent Molecular Assemblies

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The bio-inspired process known as "Artificial Photosynthesis" exploits the solar power to convert water and carbon dioxide, into synthetic fuels with high energy densities, the so-called "solar fuels", such as hydrogen, methane, and methanol, obtaining O_2 as waste-product. A promising technology in this field is represented by photoelectrochemical cells (PECs), exploiting photoelectrodes obtained by coupling semiconducting materials and electrocatalysts: in these devices, the fuel synthesis occurs at the photocathode upon reduction of protons or CO_2, while O_2 is evolved at the photoanode upon oxidation of water.

However, photoelectrochemical water oxidation still represents a major obstacle toward efficient solar fuel generation. In this regard, dye sensitized photoanodes embedding molecular water oxidation catalysts (WOC) are promising candidates to match solar emission spectrum at low energy radiation while combining fast catalysis [1]. In the present work [2], a di-cationic perylene bisimide (PBI, Fig.1a) dye has been used in combination with the deca-anionic tetra-ruthenium polyoxometalate [3] (Ru_4POM, Fig.1b) WOC: the former features a strong and broad absorption in the Vis range (400-600 nm), great oxidizing power and stability toward oxidation; the latter consists of a tetra-ruthenium(IV) core, favouring sequential holes accumulation, stabilized by oxidation resistant POM ligands. The combination of electrostatic interactions with the pi-stacking ability of the dye offers a simple non-covalent approach for the assembly of these two components onto semiconducting metal oxides. When nanostructured WO_3 is used, the resulting photoelectrodes show extended absorption up to 600 nm and light harvesting efficiency up to 40%, and show promising results in photoelectrochemical water oxidation, with quantitative faradaic yield towards O_2 and absorbed photon to current efficiency (APCE) up to 1.4%. Further studies, involving the development of new polycationic PBIs, aim at tailoring the structure and improving the stability of the molecular assembly onto the semiconducting substrate.

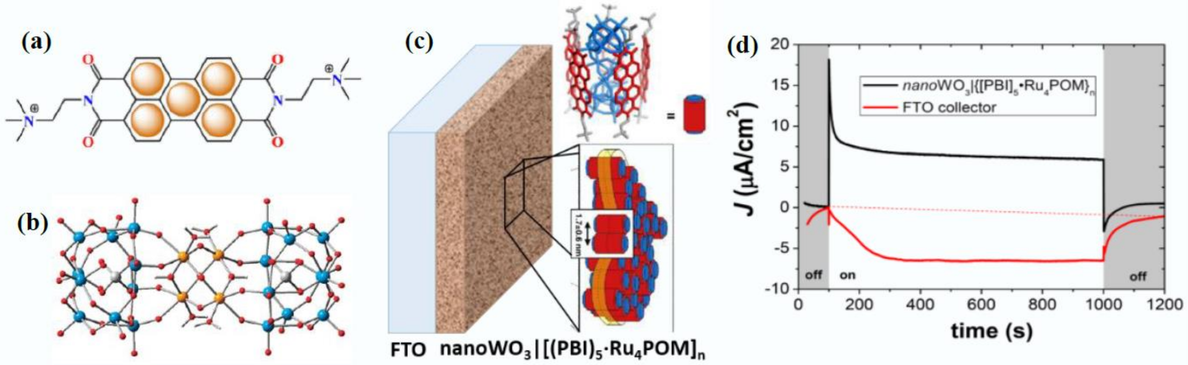

Fig.1: (a) (N,N'-bis(2-trimethylammonium)ethylene)) perylene 3,4,9,10-tetracarboxylic acid bisimide. (b) Structure of Ru_4POM, $\{Ru_4(\mu\text{-}OH)_2(\mu\text{-}O)_4(H_2O)_4[\gamma\text{-}SiW_{10}O_{36}]\}_2^{10-}$. Blue: W; orange: Ru; gray: Si; red: O. (c) Structure of nanoWO_3|$[(PBI)_5 \cdot Ru_4POM]_n$ photoanode built onto FTO support (magnification: structure of one layer of $[(PBI)_5 \cdot Ru_4POM]_n$ aggregate self-assembled onto nanoWO_3). (d) Quantification by generator-collector method of O_2 evolved at the photoanode during photochronoamperometry (0.75 V vs NHE, λ>455 nm, 0.1 M $NaClO_4$ pH 3).

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P-33

Towards novel selective electrocatalysis processes on Pd atomic ensembles

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During the past years, there has been an urgent necessity to develop sustainable processes of Green chemicals and fuels production [1]. Electrocatalysis stands as one of the most promising strategies as it enables control over electrochemical steps involved in the process through applied potential, thus making it possible to avoid hazardous chemical mixtures and reaction conditions which are typically used in traditional chemical processes [2]. Tailoring electrochemical interfaces and creating specific atomic ensembles on the surface of the catalyst can give rise to highly selective and efficient reactions. Atomic ensemble control has allowed tuning the activity and selectivity of electrochemical energy conversion reactions such as the oxygen reduction reaction [3,4]. Such structures hold promise for novel electrochemical reactions for the production of renewable chemicals. Additionally, atomic ensemble control involves lower loading of noble metal atoms, giving this approach an advantage from an economic standpoint.

This work aims to investigate the role of Pd atomic ensembles in novel electrocatalytic reactions for the production of green chemicals. Pd electrodeposition on Au (111) single crystalline electrodes allows the formation of Pd atomic ensembles that act as selective adsorption sites for the reactants [5]. Herein, Pd deposition was investigated by electrodeposition of $PdSO_4$, H_2PdCl_4 in acidic medium relative to a surface alloy of Pd_{1-x}/Au_x. The alloy was prepared by engineering mixtures of both metal ions for the preparation of an atomic ensemble with a specific geometric configuration. Pd/Au (111) electrodes were characterized by electroanalytical techniques, Figure 1, allowing identification of the best method to recover the Au (111) electrode surface. Moreover, the chemical composition of the active phase was investigated by Angle-Resolved X-ray Photoelectron Spectroscopy (AR-XPS). Studying the electrode structure-reactivity relationships can give insight in how changing the binding of reaction intermediates affects selectivity. Ultimately, the design of bimetallic catalysts with geometric atomic ensembles holds promise towards enabling efficient and selective production of green fuels and chemical as well as adding insight to the fundamental understanding of electrocatalytic processes in general.

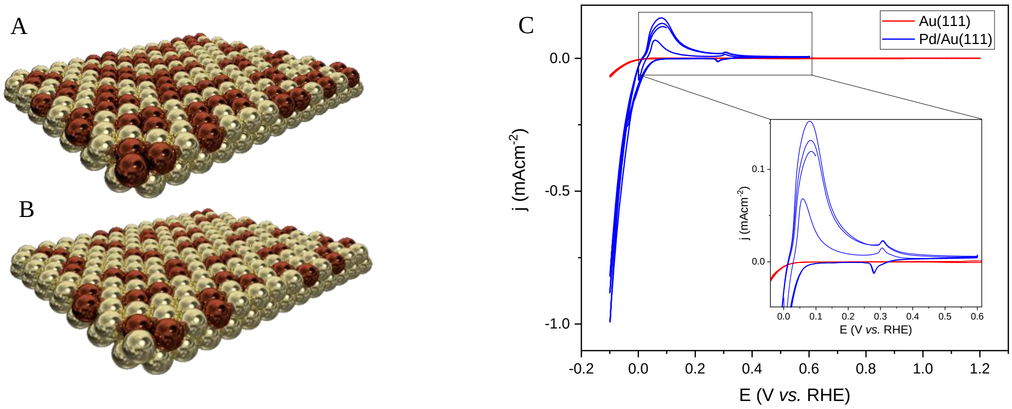

Figure 3. Illustration of Pd atomic ensembles with different configurations on an Au (111) electrode (A and B). Cyclic voltammetry of a Pd monolayer on Au (111) in 0.1M H_2SO_4, v=5mV/s (C).

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P-34

Modelling of the Gravimetric and Volumetric Capacity of Hydrogen Storage System based on Metal Hydrides

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Considering hydrogen as a future widespread vector for renewable energy, its storage is still a crucial step to be improved. The purpose of research is to achieve high gravimetric and volumetric capacities at low pressure and temperature. These two parameters represent, respectively, the amount of hydrogen stored over the weight and volume base of the system. In this regard, hydrogen storage using metal hydrides (MHs) is particularly favourable [1]. However, to meet the needs required by specific applications, it is important to define the hydrogen storage system, which is mainly related to the selection of the proper MH and to the design of the container [2]. The latter strongly influence the gravimetric and volumetric capacities of the storage system. The challenge is to develop a container in which the right compromise is achieved, especially for mobile applications, among H_2 storage gravimetric and volumetric density, integrity of the container at operative conditions and dynamic performances of the gas [2]. Thus, an important role to design a system is played by modelling and simulation of parameters.

In this work, we present a simple approach, based on a series of simulations, to evaluate the influence of MH property (i.e. the gravimetric and volumetric capacity of the hydrogen carrier) and tank geometry (i.e. tube diameter) on the gravimetric and volumetric capacity of a hydrogen storage system [3]. First of all, the boundaries of the system were defined, i.e. the container, the H_2-carrier and the thermal fluid necessary for the heat transfer, but not considering piping and valves used as auxiliaries. No thermo-fluid dynamic effects were evaluated. For the comparison, an amount of hydrogen stored in the system was taken equal to 1 kg.

The main aim of simulations is to show the potentiality of different solid-state hydrogen storage materials, so different MHs (i.e. Hydralloy, $NaAlH_4$, $LaNi_5$, $LiBH_4$, MgH_2) have been examined. For the tank, we considered the simple geometry of a tube with an external jacket for thermal fluid circulation. In order to consider the influence of properties of the material for the container, in the simulations, the use of either aluminium or steel was evaluated.

Finally, a more accurate simulation was also performed, considering experimental kinetic and thermodynamic data obtained from the study of hydrogenation and dehydrogenation in Hydralloy and $La_{0.9}Ce_{0.1}Ni_5$ powders.

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P-35

Synthesis and characterization of black zinc oxide anodic layers

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The vision of lack of energy in the near future provokes an intensive investigation of alternative energy sources which, in opposite to fossil fuels, will be ecological and renewable. One of the most promising sources which fulfill all demands seems to be Sun. For instance, solar energy can be used for photoelectrochemical water splitting to generate gaseous hydrogen. On the other hand, solar energy could be utilized in photocatalysis, which may help in solving another important issue, i.e., environmental pollution. Both aforementioned applications require the use of semiconducting materials.

Among many different semiconductors, zinc oxide (ZnO) seems to be a very attractive material due to its unique properties including good photocatalytic activity, abundance in nature, low cost, and environment-friendliness. What is more, zinc oxide can be obtained in different nanostructured forms, also by electrochemical methods [1,2].

Considering its simplicity, versatility, and low cost of synthesis, anodic oxidation (anodization) of metals seems to be an excellent method for the formation of nanostructured ZnO layers. Moreover, appropriate optimization of reaction conditions allows for obtaining different kinds of nanostructured oxide layers on the metal surface.

Here, we present some results on the formation of dark nanoporous zinc oxide layers by anodic oxidation of metallic zinc in 1 M sodium hydroxide. Anodizations were carried out in a two-electrode system at different potentials (2 V and 4 V) for different times at room temperature. Some samples were annealed at 200 °C and 400 °C for 2 h to investigate the effect of thermal treatment on the morphology, chemical composition, and crystallinity of as-obtained oxide layers [3].

The morphology of the synthesized ZnO films was analyzed by using a Field-Emission Scanning Electron Microscope (SEM). The crystallinity and phase composition of ZnO nanostructures were examined by XRD and XPS measurements. Defective nature of oxide was confirmed by photoluminescence measurements. Photoelectrochemical characterization of the synthetized materials was also performed.

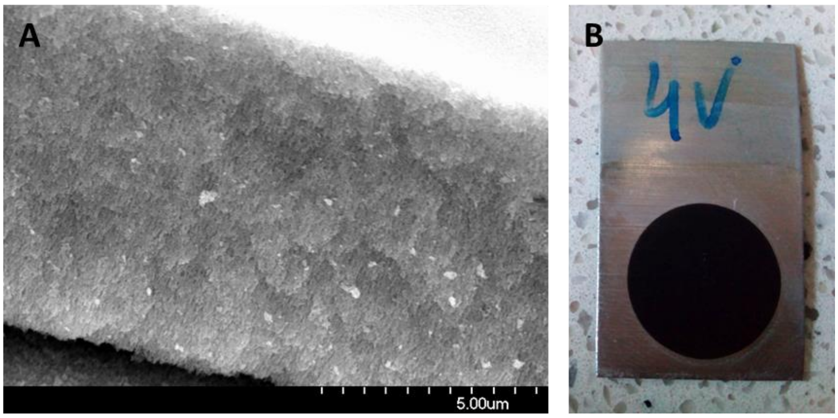

Figure 1. SEM (A) and optical (B) image of the anodic ZnO layer obtained in 1 M NaOH at 4 V for 30 min.

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P-36

Surface Engineering of Chemically Exfoliated MoS_2 in a "Click": How To Generate Versatile Multifunctional Transition Metal Dichalcogenides-Based Platforms

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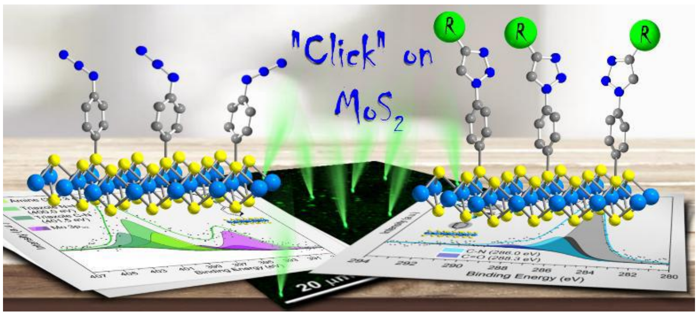
The development of functional layered two-dimensional (2D) transition metal dichalcogenides (TMDs, e.g., MoS_2, WSe_2 and $MoTe_2$) as inorganic substitutes of graphene have recently gained great attention due to their wide range of applications.[1] To date, several surface functionalization strategies of MoS_2 have been reported to improve the processability and the chemical reactivity of these 2D inorganic flakes.[2] However, much work has still to be done in order to bridge the gap between the wealthy exohedral functionalization chemistry of carbon-based 2D platforms and that of TMDs.



Following our experience on post-synthetic modification (PSM) of organic (carbon nanotubes, CNTs) and organic−inorganic networks (metal-organic frameworks, MOFs) under Cu_{I} mediated azide−alkyne cycloaddition protocol, [3] we have found a convenient and highly efficient methodology for the decoration of MoS_2 nanosheets with aryl-azido groups. Their subsequent post-synthetic modification via "click chemistry" in the presence of terminal acetylenes or defined binary acetylene mixtures have been used to generate homo- and hetero-decorated MoS_2 flakes. The successful functionalization and post-derivatization of MoS_2 samples have been systematically followed through the main physico-chemical (SEM microscopy, fluorescence lifetime imaging), spectroscopic (IR, Raman, XPS, UV−vis), and analytical techniques. [4]

Overall, this study will represent a milestone in the simple and highly versatile MoS_2 nanosheet engineering, offering a convenient approach to confer multimodality to this new and emerging class of 2D inorganic materials. This approach aims at widening the applicability range of these materials in several technological fields.

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Acknowledgements
Authors thank the TRAINER project (*Catalysts for Transition to Renewable Energy Future* - Ref. ANR-17-MPGA-0017) and Italian MIUR (PRIN 2015, Project SMARTNESS 2015K7FZLH) for financial support.

P-37

Graphene Nanoplatelets as an Alternative Microporous Layer Material for PEMFC: Performance and Durability Evaluation

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Traditional fossil fuel-based energy generators are no longer a viable long-term solution. Polymer electrolyte membrane (PEM) fuel cells are a valid and environment-friendly alternative. Their optimization has led to the introduction of microporous layers (MPLs) to improve the feeding of gases, the electrical performance and the water management in the cell.

In this work, the effects of different carbonaceous phases in MPLs for PEMFCs are reported. A conventional ink with carbon black (CB) powder and an innovative one featuring graphene nanoplatelets (GNP), in addition to a small portion of carbon nanotubes, have been produced and used to coat carbon cloth gas diffusion layers (GDLs), which were previously hydrophobized [1].

Morphological and electrical properties of these samples have been assessed and then compared to determine which characteristics contribute to a possible enhancement of the fuel cell performance. Through-plane water permeability and porosity of the samples have been correlated to the optimal working temperature: GNP-based MPLs provide the best performance in dry condition (T = 80 °C, RH = 60 %), while CB-based samples work better at lower temperature (T = 60 °C, RH = 60 %). An evaluation of the ohmic and mass transfer resistances has been performed: the comparison between the two electrical behaviours displays small differences, if the best performing conditions are considered (Fig.1).

In addition, an optimized ex-situ mechanical accelerated stress test (AST) has been applied to both samples to assess their durability and understand which factors could lengthen their lifetime. GNP-based samples show a high resistance, mainly due to the absence of large and visible cracks on its surface. On the contrary, CB-based MPLs are more prone to detachment of material, which lead to a quicker deterioration of the component and a larger potential loss upon AST.

Future developments are suggested, as the employment of both carbonaceous phases in a mixed composition MPL to gain benefits from both of them [2].

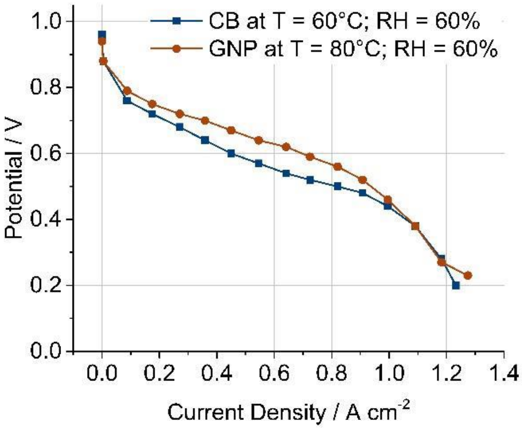

Figure 1. Polarization curves of: CB at T = 60°C and RH = 60%; GNP at T = 80°C and RH = 60%.

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P-38

Influence of copper modification on photoelectrochemical properties of anodic nanostructured WO_3

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The optical and photoelectrochemical properties of nanostructured semiconducting materials have been studied for many years. Among them, tungsten oxide deserves special attention due to its optical and catalytic properties. WO_3 is an n-type semiconductor with 2.5 – 3.2 eV indirect band gap. Tungsten oxide, especially in the nanostructured form can find promising applications as sensors, in photocatalytic degradation of organic dye or in photoelectrochemical cells. It is widely recognized that doping with transition metal ions can enhance photoelectrochemical properties of nanostructural semiconductor metal oxides [1 – 4].

WO_3 photoanodes were prepared by electrochemical anodization of the tungsten foil in 1 M $(NH_4)_2SO_4$ + 0.075 M NH_4F at 50 V. Furthermore, a modification of anodic oxide layers with Cu ions was performed. A wet impregnation and chemical deposition of copper particles were tested as the methods for tailoring WO_3 photoelectrochemical properties. In order to obtain a photoactive phase, as-prepared materials were annealed at 500 °C for 2 h. The preparation of samples is illustrated in Figure 1. A complex characterization of received samples was performed using SEM, EDS and XRD measurements. Photoelectrochemical tests were carried out in a Teflon cell with a quartz window in a three-electrode system, where nanoporous tungsten oxide was used as a working electrode, platinum foil as a counter electrode, and Ag/AgCl as a reference electrode. The measurements were carried out in a 0.1 M KNO_3 solution.

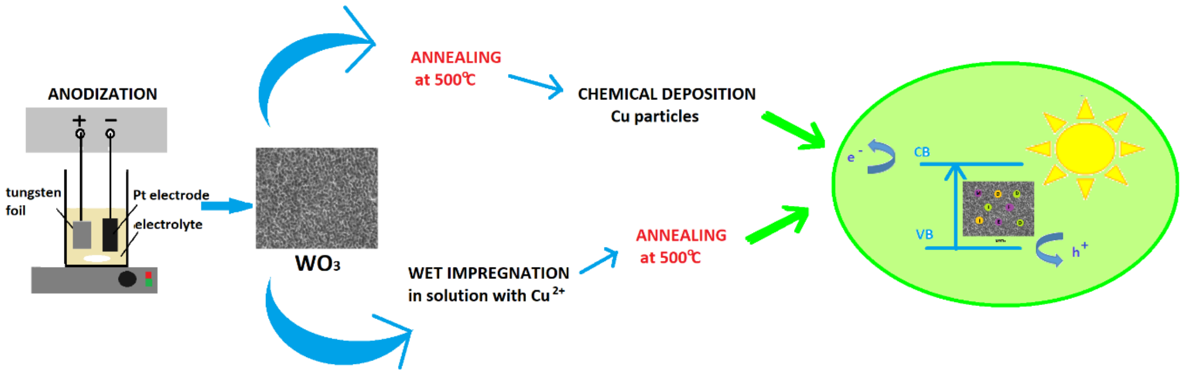

Fig. 1. The scheme showing the synthesis of Cu modified anodic WO_3 layers.

To sum up, the wet impregnation and chemical deposition of metal particles are easy and effective methods for modification of WO_3 with Cu. Photoelectrochemical properties of pristine WO_3, copper oxide/WO_3 and WO_3 with surface deposited Cu particles were compared.

Acknowledgements
This work was supported by National Science Centre, Poland (Project No. 2016/23/B/ST5/00790).

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P-39

Cu_2O-based nanostructures for photoelectrochemical water splitting

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Nowadays converting solar energy directly into chemical fuels is considered as one of the most promising strategies to tackle the increasing energy demand. The photoelectrochemical (PEC) water splitting is an attractive method to produce solar hydrogen directly from water in a cost-effective, sustainable, and environmentally friendly manner.[1,2]

In this work, we have developed p-Cu_2O-based nanostructured photocathodes for hydrogen generation from solar water splitting (HER). Although Cu_2O has favourable band energy positions for water splitting there are two main challenges limiting its application as an efficient and durable photocathode for water splitting: unfavourable ratio of the carrier diffusion length over the light absorption depth and the poor stability. In order to solve the first issue high quality Cu_2O nanowires have been grown on Cu-coated fluorine-doped tin oxide (FTO) substrates by a controlled anodization followed by an appropriate thermal treatment. X-ray diffraction, Raman and Reflectance analysis have confirmed the formation of crystalline Cu_2O nanowires with a band gap of 2.03 eV. With the aim to improve the stability of Cu_2O nanowires their surface has been covered through overlayers based on n-type metal oxides (TiO_2, ZnO and Ta_2O_5) by atomic layer deposition (ALD). X-ray photoelectron spectroscopy and the elemental maps obtained by energy dispersive spectroscopy have confirmed a homogeneous and conformal deposition. Finally, a n-Cu_2O layer has been also introduced between Cu_2O nanowires and the protective layer to optimize the p-n interface. All the prepared photocathodes have been tested in a photoelectrochemical cell (Figure 1) to evaluate the photocurrent, the efficiency for hydrogen generation and the stability over the time.

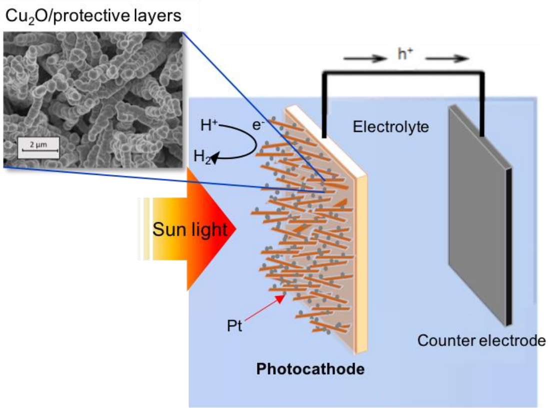

Figure 1. Scheme of the photoelectrochemical cell with Cu_2O based photocathode

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P-40

Graphene-based materials as catalyst support for low temperature fuel cells

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Graphene-based materials (GMs) show high conductivity, surface area and mechanical strength [1]. Thus, GMs are expected to play an important role as catalysts for proton exchange membrane fuel cells (PEMFCs). Improvement of Pt utilization and enhancement of oxygen diffusion trough GMs-based catalyst layer during the oxygen reduction reaction (ORR) have been reported [2]. GMs also improve the dispersion and distribution of metallic nanoparticles, and therefore, an intensification of the catalytic activity toward several reactions was usually observed [3].

In the current work, graphenic materials were obtained by chemical reduction of graphene oxide (GO) employing sodium citrate (rGO) and dimethylsulfoxide (S-rGO) as reducing and doping agents. Pt nanoparticles were supported on rGO (Pt/rGO), S-rGO (Pt/S-rGO) and carbon back (Pt/C) considering a nominal metallic loading of 20 wt % by the formic acid method. X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM) and Raman spectroscopy techniques were used to characterize the materials. Their catalytic performance toward the ORR was evaluated in a PEMFC test station. In all performed studies, 20 wt % Pt/C (ETEK) was employed as anode and pure hydrogen and oxygen were supplied to the anode and cathode, respectively.

Main results indicate an enhancement of the catalytic activity by GMs-based materials in comparison to the carbon black-based one. These results confirm a high correlation between the physicochemical properties of the synthesized materials and the catalytic performance developed in a PEMFC.

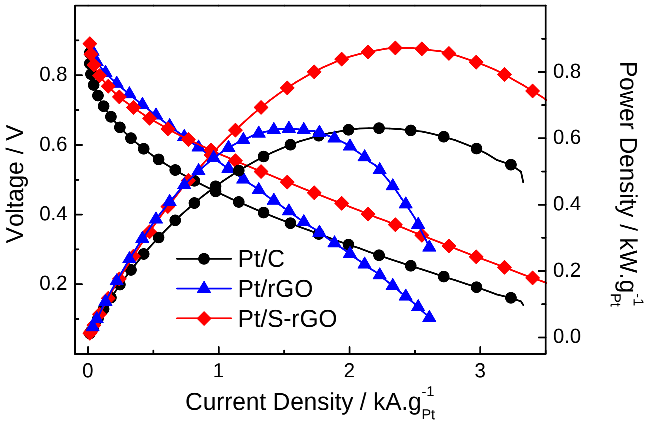

Figure 4. Polarization and power density curves of acidic PEMFC comprising Pt/C, Pt/rGO and Pt/S-rGO as cathode catalyst layer. Commercial Pt/C (ETEK) was used for the anode catalysts layer. Operation conditions: H_2/O_2 anode/cathode gas flow, 30 °C cell temperature and zero back pressure.

Acknowledgment

The Spanish Ministry of Science, Innovation and Universities (MICINN) has supported this work under project ENE2017-83976 -C2-2-R (co-funded by FEDER). G.G. acknowledges the Viera y Clavijo program (ACIISI & ULL) for financial support and L.M.R. thanks the ACIISI for the pre-doctoral grant.

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P-41

Ration Design of Pt-based Nanocrystals with Enhanced Oxygen Reduction Reaction Electrocatalytic Activity Toward Proton Exchange Membrane Fuel Cells

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The growing demand for hydrogen-based clean energy has prompted the development of high-performance proton exchange membrane fuel cells (PEMFCs), that convert hydrogen fuel to electricity. The sluggish kinetics on the cathode, where the Oxygen Reduction Reaction (ORR) occurs, requires improvements of the ORR catalyst cost and durability to become a useful technology. Platinum and Pt-alloys are the most used and available catalysts materials. One of their disadvantages is the high material cost, leading several research groups to develop more efficient materials that will lower the amount of platinum loading on the catalyst.

In this work, we have investigated Pt-Ni and Pt-Cu nanocrystals from colloidal synthesis. Several batches of the Pt-based catalyst supported on Vulcan carbon 72XC were produced to study the thermodynamic- and kinetic-based synthesis parameters that influence the shape, size and composition of the nanoparticles. Furthermore, we have analyzed the dependence of the ORR performance on the morphology of the octahedral nanocrystals.

We have observed a transition from octahedral to cuboctahedral morphology of 5 nm Pt-Ni nanocrystals and an inversion in the core-shell composition distribution that is usually reported for this catalyst[1] while reducing the partial pressure of oxygen during the synthesis (*Fig. 1*). The Pt-Ni octahedral and the Pt-Ni cuboctahedral nanoparticles lead to high activity toward ORR (>5 times of commercial Pt/C catalyst). In order to increase the exposed surface of the catalyst material and enhance the ORR activity, our research group previously reported the mechanism to obtain hollow Pt-Ni-Au nanocrystal[2]. In this current work, Ni-rich Pt-Ni octahedral nanoparticles sample were converted successfully in Pt-rich Pt-Ni nanoparticles by two-phase chemical etching process, the etched particles showed concave and hexapod Pt-skin nanoparticle.

In addition, we demonstrate that the ratio of surfactant can tune the size of core-shell Pt-Cu nano-octahedra from 8 to 18 nm with homogeneous size and shapes on carbon support. The Pt rich shell exhibits an increasing compressive strain with increasing of the surface in the {111} facets. In addition, the stability of the material was studied after durability tests. After 4000 cycles in acidic medium under argon saturation or under oxygen, the octahedral morphology of the samples was conserved, showing promises for an application in fuel cells.

This work involved the characterization of the materials by rotation disk electrode (RDE) and by high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM on an aberration-corrected FEI TITAN Themis operated at 200 kV), X-ray diffraction (XRD), Transmission Electron Microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS) and X-ray Fluorescence (XRF).

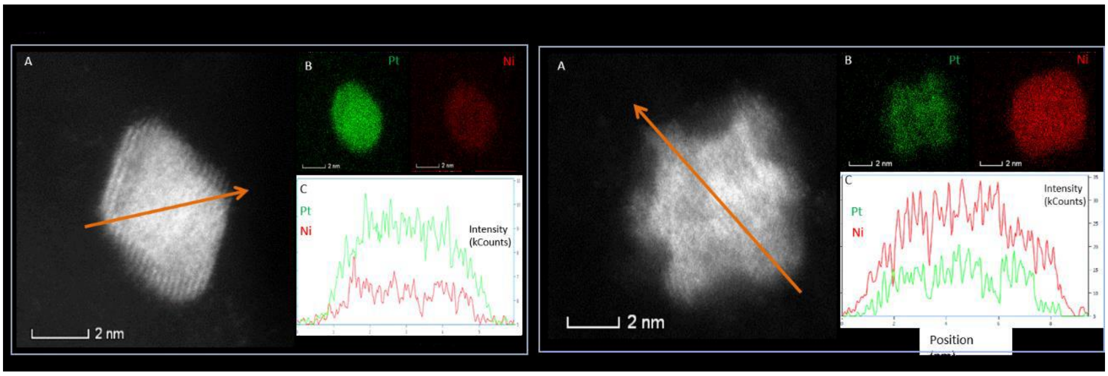

Figure 1. Pt-Ni nanoparticles supported on Vulcan carbon. (1) Octahedral nanoparticle Pt-Shell and Ni-core. (2) Cuboctahedral nanoparticle Pt-core and Ni-shell, A) High-angle annular dark-field (HAADF), High resolution STEM image. B) STEM-EDX atomic mapping and C) line profile in the direction of the orange arrow from A).

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P-42

A multiscale computational approach to investigate small gold nanoclusters optical features in solution

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Nowadays, the study of thiolate-protected gold nanoclusters is of the most promising and exciting research field in nanoscience. The intrinsic quantum confinement effects given by the small dimension of the metallic core, gives them unique properties in terms of optical, magnetic and catalytic features. [1]

Among all gold-based nanoclusters, $[Au_{25}(SR)_{18}]^q$ (R = organic ligand) received the most extensive attention [2,3]. Our work has the purposes of elucidate how the optical features of the $[Au_{25}(SR)_{18}]^0$ changes with respect to the charged form and to understand how different ligands can affect the equilibrium distances (and thus the optical features) of various nanoclusters systems in solution.

Time Dependent Density Functional Theory (TDDFT) simulations were performed on two X-Ray Diffraction (XRD) resolved structures of $[Au_{25}(SR)_{18}]^0$ finding that different orientations of the organic ligands (coming from different nanoclusters structures) gives different equilibrium geometries and a sensible modification of the inner metallic kernel structure and polarizability [4].

Metadynamics simulations were also performed on $[Au_{25}(SCH_2CH_3)_{18}]^0$, $[Au_{25}(SC_{16}H_{33})_{18}]^0$ and $[Au_{25}(SCH_2CH_2Ph)_{18}]^{-1}$ double clusters systems. The results show a tendency in forming cluster aggregates in the long chain substituted nanoclusters system. Surprisingly, the Coulomb repulsion among nanoclusters in $[Au_{25}(SCH_2CH_2Ph)_{18}]^{-1}$ system is well screened by the solvent and we recover a near cluster configuration minimum in the free energy profile. Finally, the free energy profile of the short-chained nanoclusters pair is almost flat, indicating that no aggregations naturally occur here.

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P-43

Synthesis and characterization of anodic TiO_2 modified with iron ions

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Titanium dioxide (TiO_2) as a biocompatible, non-toxic and well chemically stable semiconducting material [1] is used in medicine, photocatalysis or can be a promising semiconductor for light-assisted degradation of pollutants [2,3]. However, TiO_2 has a relatively high band gap (3.2 eV) which causes that only UV light can be absorbed ($\lambda < 400$ nm) by it [4]. There are many solutions and strategies to reduce its band gap and to increase the range of absorbed radiation [5]. One of the method, which in fact is not so popular, is impregnation with a solution containing iron ions.

Anodic titanium oxide was fabricated by a three-step anodization in an ethylene glycol based electrolyte containing 0.38% wt. NH_4F and 1.79% wt. H_2O at a constant potential of 40 V. The samples of nanoporous titanium dioxide layers were modified by the impregnation method with solutions containing various concentrations (5 – 100 mM) of iron ions followed by their annealing at three different temperatures (400 °C – 600 °C). The morphology and chemical composition of synthesized materials were investigated by using a field emission scanning electron microscope (FE-SEM/EDS), and their structures was determined by X-ray diffraction (XRD). The photoelectrochemical properties were also characterized.

The results showed that the structure of anodic TiO_2 samples impregnated with iron ions was changed depending on the concentration of transition metal ion and annealing temperature used (Fig.1). What is more, the modified titanium dioxide samples exhibited different photoelectrochemical properties from those observed for unmodified TiO_2 samples. Anodic TiO_2 samples showed a maximum absorption at 350 nm and depending on the modification conditions the maximum values of photocurrent density shifted towards higher wavelength values. In general, the calculated band gap values decreases with increasing the concentration of iron ions. In conclusion, the obtained materials can be promising nanomaterials with improved photocatalytic performance.

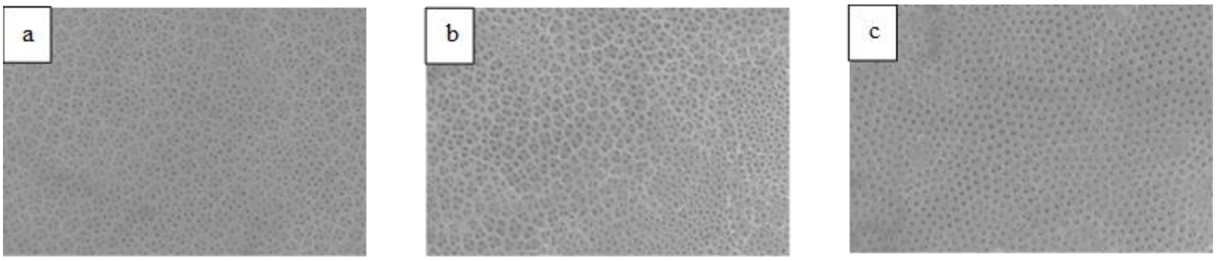

Fig.1 FE-SEM top-view images of modified TiO_2 samples by impregnation with solutions containing 50 mM Fe ions and then annealed at: a) 400 °C, b) 500 °C, c) 600 °C for 2h.

Acknowledgements
This work was supported by National Science Centre, Poland (Project No. 2016/23/B/ST5/00790).

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P-44

Electrolyte effects on Cu single-crystalline electrodes.

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Anthropogenic CO_2 is the greenhouse gas which mostly contributes to the global warming increase. There is an urgent need to develop novel technologies that capture and convert CO_2 into valuable feedstock molecules, aiming to compensate the imbalanced natural carbon cycle [1]. A friendly alternative to mitigate CO_2 is the combination of renewable electricity with heterogeneous catalysts. However, only Cu or catalysts based on Cu are capable to reduce CO_2 beyond CO and produce sufficient amount of interesting compounds: hydrocarbons and alcohols among other products [2]. The electroreduction of CO_2 (CO_2RR) evolves a very complex reaction mechanism and, consequently, reducing CO_2 selectively into one specific product is challenging. The surface state and specific nature of the active site as well as the electrolyte composition (pH, anion and/or cation nature) influences the selectivity of the CO_2RR [3]. Thus, fundamental work on well-ordered electrified interfaces is pivotal to understand which factors control selectivity [4]. Because of that, detailed understanding of the Cu(hkl)|electrolyte interface is needed. In particular, model studies, both under reaction conditions and without CO_2 (or CO, which is well-accepted as the key intermediate of the CO_2RR) in the electrolyte, are key in order to design more selective catalysts.

In the present communication, we investigate Cu(111) and Cu(100) single crystal electrodes in contact with different electrolytes and in a wide range of pH (from pH 1.5 to 12.5). Phosphate buffer solutions were mainly analyzed and later compared with other electrolytes. At each pH, solutions were saturated with CO aiming to compare how the interfacial properties of Cu(hkl) would be affected or modified under reaction conditions. Here, we discuss different aspects such as pH effects on the interfacial properties, specific anion adsorption and tentative surface restructuration or surface state changes with the applied potential and under reductive conditions. Figure 1 shows an example of the voltammetric response of Cu(111)|0.1M phosphate buffer at pH 9, which displays a sharp feature around -0.7 V vs. SHE related to phosphate adsorption/desorption (Figure 1A), and markedly influenced by the cathodic potential limit (Figure 1B)[5].

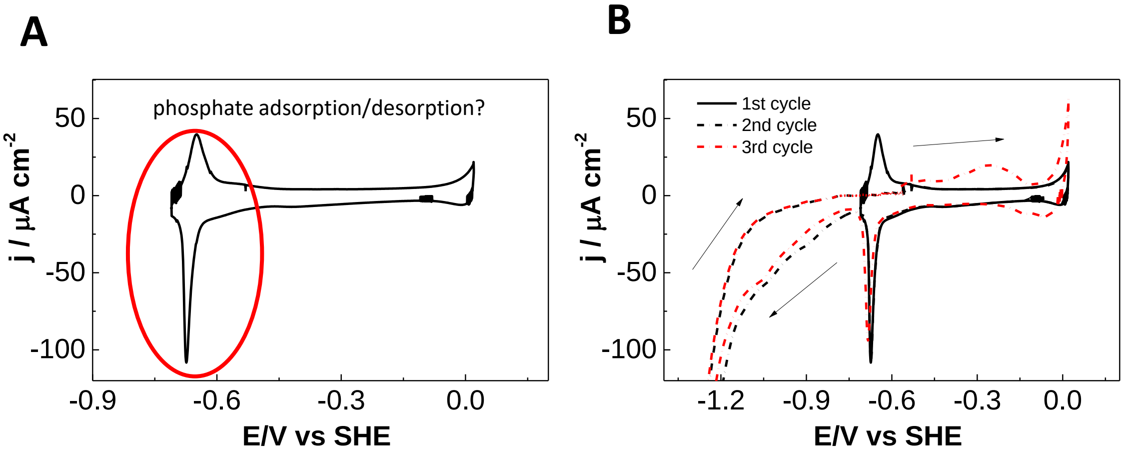

Figure 1: A) Blank cyclic voltammogram of Cu(111)|0.1M phosphate buffer (at pH 9) and B) corresponds to the same interface, but different cycles are recorded with different cathodic potentials limits: black solid line)-0.710V vs SHE, red and black dashed line) -1.36V vs SHE. Scan rate: 50mV/s

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P-45

Pd_3Y alloyed NPs prepared by Laser Ablation and their electrochemical activity versus Oxygen Reduction Reaction

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The main challenge for the final commercialization of polymer electrolyte membrane fuel cells (PEMFC) is the cathode oxygen reduction reaction (ORR), which is slow also at the state of the art Pt based catalysts. Recently, the preparation of Pt and Pd bimetallic systems in alloy form has attracted considerable attention because the amount of active metal could be reduced while the catalytic activity and stability may be improved, due to the so called "*geometric effect*" and "*ligand effect*", which involve the stain or the compression of the top-most metal catalyst layer so that the electronic interaction with the oxygen or its reduction intermediates orbitals can be modulated [1].

In this paper Pd_3Y nanoparticles were for the first time successfully prepared by laser ablation synthesis in organic solvent starting from a Pd_3Y target and tested as active electrocatalyst for ORR in both acid and alkaline electrolytes [2,3]. The formation of alloyed NPs was confirmed by TEM, XRD and XPS analyses *fig. 1a*, and *b*. XPS analysis revealed that when ethanol was used, the superficial Pd_3Y alloy reaches its maximum (46 %). The ORR investigation showed that the catalyst containing the highest amount of Pd_3Y alloy exhibits higher catalytic activity expressed in term of half wave potential, mass and specific activity when compared to a standard Pd/C. The effect of ClO_4^- and Cl^- anions was also investigated revealing the surprising poisoning effect of ClO_4^- for the Pd_3Y alloys.

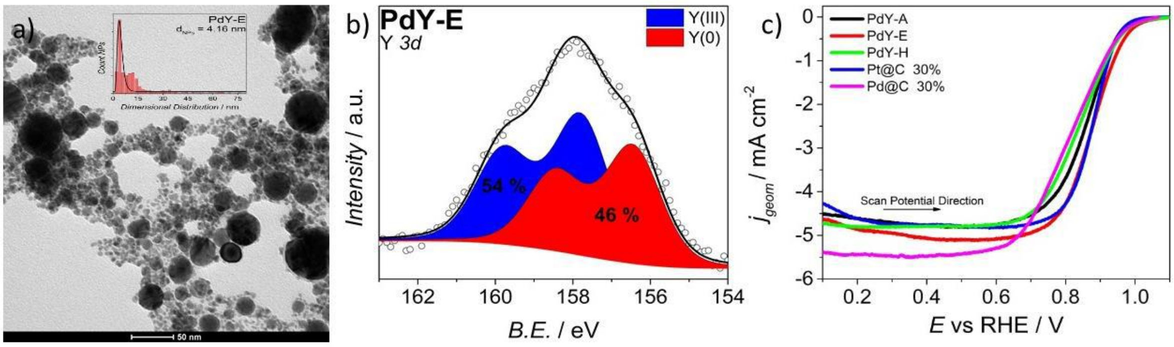

Figure 1: a) TEM image and size distribution for PdY-E, b) XPS spectra and deconvolution into single chemical components of Y *3d* XPS region for PdY-E and c) RDE linear sweep voltammetry curves of PdY-X and Pd@C and Pt@C in O_2-saturated 0.1 M KOH solution at 20 mV s^{-1} and rotation rate 1600 rpm.

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P-46

Maximizing Silver Catalyst Use in CO_2 Electrochemical Reduction: A Metal-organic Framework-mediated Approach

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CO_2 electrochemical reduction is widely regarded as one of the most promising methods to address CO_2 emission issue. Critical to the industrialization of this process is the development of cost-effective, stable, and efficient electrocatalysts. Plenty of research effort during the last few decades has focused on identifying the most suitable catalysts. However, as it is the case in classical heterogeneous catalysis, optimization of the final catalyst concerning active phase utilization is still a significant challenge. For example, if a pure metallic Ag electrode with a 0.5 mm thickness would be used in a commercial electrolyzer to achieve an 80% Faradaic efficiency operating at a current density of 100 mA/cm^2, the amount of Ag needed to process 1 ton of CO_2 per hour would be about 8 ton. In this spirit, the development of alternative electrode preparation methods that deliver full utilization of the active catalytic phase is of great importance.

Herein, we present a metal-organic framework mediated approach to achieve a highly cost-effective catalyst. A Ag coordination polymer is grown with a layer-by-layer method onto a carbon cloth electrode, and afterwards it is electrochemically reduced to metallic Ag (Figure 1). The resultant Ag catalyst exhibits outstanding activity and stability during a 120-min performance test (Figure 2). Compared with commercial Ag foil electrode, the carbon fiber supported Ag structure shows a mass activity of ~3 orders of magnitude higher.

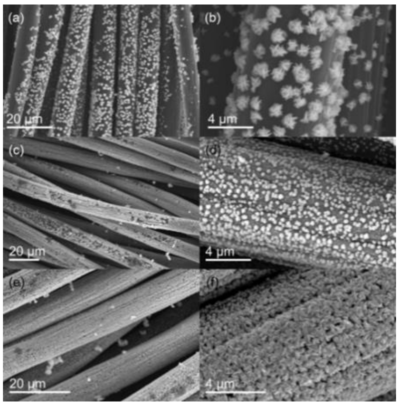

Figure 1. SEM images of carbon fiber supported Ag catalysts.

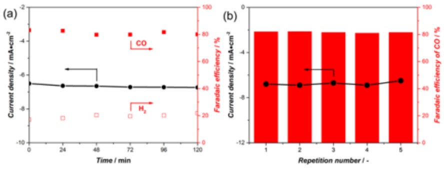

Figure 2. (a) CO_2 electrochemical reduction performance of Ag catalyst at -1.13 V vs. RHE and (b) Repeated CO_2 electrochemical reduction test with Ag catalyst.

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P-47

Hydrogen evolution on tungsten-based catalysts

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Hydrogen is one of the most important fuels for primary energy source in a new consumption model. However, some requirements as efficiency and high purity production proves challenging. Pt is currently the best catalytic material for the hydrogen evolution reaction (HER), but its cost and scarcity affects negatively to the implementation in the H_2 production market. The improvement of the catalytic performance toward HER has been related to the composition, geometry and electronic structure of the catalyst surface [1]. Thus, the study and design of new low-cost catalytic materials with high catalytic activity and durability are expected to have positive effects on the water-electrolyser industry. Potential alternatives for platinum-based electrocatalysts are transition metals such as tungsten [2].

In the present work, tungsten-based materials have been synthesized through a modification of the urea-glass route proposed by *Giordano et al.* [3], which is known to produce diverse crystalline phases. With this purpose, two samples were synthesized and compared with commercial W_2C. Scanning Electron microscopy (SEM), Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD) and X-Ray Photoelectron Spectroscopy (XPS) were employed to characterize the materials, while Differential Electrochemical Mass Spectroscopy (DEMS) was used to evaluate the catalytic performance toward the HER in sulphuric acid medium.

Main results indicate the formation tungsten-based materials with nanometric sizes and diverse crystalline phases (Figure 1A): sample A (W^0) and sample B ($W^0 + W_2C$). On the other hand, the commercial material reveals higher particle size and W_2C as main crystalline phase. Interestingly, DEMS allows precise determination of onset potentials for the HER and records accurate currents that are only associated to H_2. Thus, by-side reactions such as electrochemical reduction of surface oxide species are avoided [4]. The last is clearly observed in Figure 1B, in which linear sweep voltammograms (LSVs) and linear sweep mass voltammograms (LSMVs) are depicted at top and bottom panels, respectively. Thus, catalytic activity toward the HER increases in the following way: commercial W_2C < sample A << sample B. It can be concluded that the presence of both W^0 and W_2C phases improves the catalytic response.

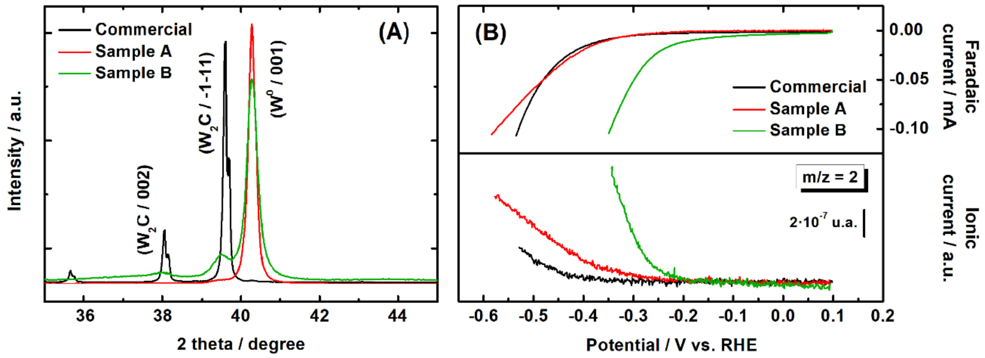

Figure 5. (A) XRD patterns for commercial and synthesized materials. **(B)** LSVs (top panel) and MSLSVs (bottom panel) for all employed catalysts in 0.1 M H_2SO_4 recorded at 1 mV s^{-1}.

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Acknowledgment
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P-48

S-N Dual Doped-Graphene as Co Support for the Oxygen Reduction Reaction in Direct Ethanol Fuel Cell

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Polymer electrolyte membrane fuel cells (PEMFCs) are promising 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, a real PEMFC has several drawbacks which decrease its working performance and increase its 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 present the best catalytic activity but their elevated cost, low abundance and poor durability appear as important barriers for the development of these devices. 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.

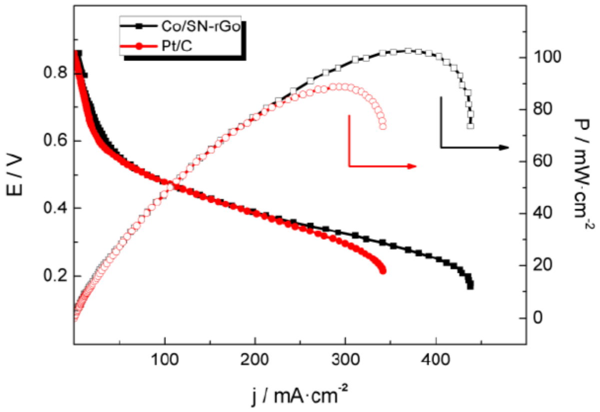

Figure 1. Voltage vs current density and power vs current density curves for single DEFC recorded at 90°C. Cathode catalyst: Co/SN-rGO (black) and commercial Pt/C (red). Anode: commercial PtRu/C. Anode fed with 2.0 M CH_3CH_2OH + 2 M KOH at 1.0 mL min^{-1}. Cathode fed with O_2 at 0.2 mL min^{-1}.

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P-49

Graphene-based materials as catalysts for CO_2 electroreduction

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The reduction of CO_2 following the electrochemical route is a novel and very interesting alternative way for CO_2 utilization, mainly for the reuse of concentrated CO_2 streams, in order to obtain valuable products (alcohols and hydrocarbons) with energy applications or for chemical synthesis. There are many studies of CO_2 electroreduction on different metal catalysts, their nature determining the final products and efficiencies. However, some technological issues must be solved to scale-up the process, such as the high overpotential requirement (≈ 1.5 V), the low CO_2 solubility or the H_2 formation by water reduction. Accordingly, it is necessary to develop new catalysts to improve the performance of the process.

In the present work we propose the synthesis of different graphene based materials (MGs) as support for metallic nanoparticles of platinum and copper for CO_2 electroreduction. The physicochemical characterization of the catalysts was performed applying scanning electron microscopy (SEM), X-ray dispersive energy spectroscopy (EDX), Raman spectroscopy and X-ray diffraction (XRD). Cyclic voltammetry was used for studying the activity of these materials towards the carbon dioxide reduction reaction and the evolution of hydrogen that occurs in the same potential region. Both the synthesis method and the nature of the metal and the support have influence on the catalytic response. Best results were obtained with copper electrocatalysts.

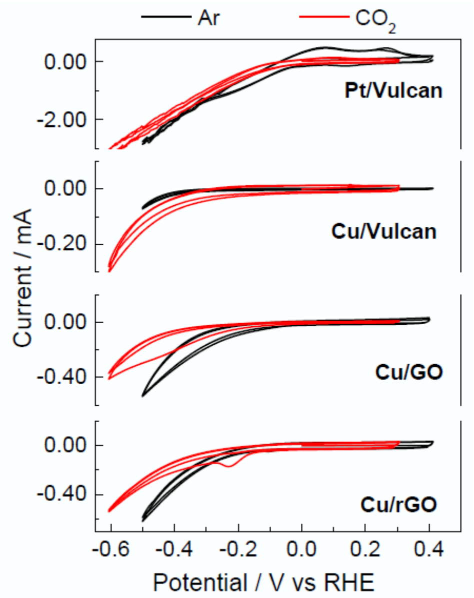

Figure 1. Cyclic voltammetries for Pt and Cu electrocatalysts in 0.1 M $NaHCO_3$ at 5 mV/s. Deareated solution (black curve) and saturated with CO_2 (red curve).

Acknowledgments
The Spanish Ministry of Science, Innovation and Universities (MICINN) has supported this work under project ENE2017-83976 -C2-2-R (co-funded by FEDER). G.G. acknowledges the Viera y Clavijo program (ACIISI & ULL) for financial support and L.M.R. for the pre-doctoral contract (ACIISI).

P-50

The mechanism of enhanced photochemical property on concentric nanotubes investigated by intensity modulated photocurrent spectroscopy (IMPS) and Chopped light measurements (CLM)

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In this contribution we describe the preparation and Photoelectrochemical (PEC) properties of Co_3O_4/TiO_2 concentric nanotubes (NTs).The NTs were prepared by a standard anodization process in NH_4F/HF solution, while the Co_3O_4 overlayer was deposited by Atomic Layer Deposition (ALD). The morphology, composition and optical properties of the TiO_2 and Co_3O_4/TiO_2 NTs samples were characterized by SEM and HR-EDX, X-ray Photoelectrons Spectroscopy (XPS) and UV-Vis spectroscopy. The photoelectrochemical properties were studied by Linear Voltammetry sweeps, Chopped Light measurements (CLM) and Intensity Modulated Photocurrent Spectroscopy (IMPS). The best performing samples were the as-grown Co_3O_4/TiO_2 NTs containing a passivating Al_2O_3 layer deposited on the Co_3O_4 /TiO_2 NTs nanostructure. Annealing treatments up to 400°C lead to a dramatic decrease in the PEC properties in terms of photocurrent for Co_3O_4 /TiO_2 NTs. This behaviour was attributed to the increased amount of CoO, which forms upon increasing the annealing temperature above 200 ° C. This study interestigly shows through the use of IMPS measurements that the strong increase in photocurrent obtained after ALD of Co_3O_4 on the TiO_2 NTs, clearly due to the wider absorption window extending into the visible region after Co_3O_4 deposition, does not correspond to an improved charge transfer efficiency and to a lower charge recombination with respect to pure TiO_2 NTs. This behavior was attributed to the existence of surface defects on the cobalt oxide layer that act as recombination sites for photogenerated e-h pairs. The decreased spike and overshoot transient characteristic of chopped light measurements (CLM) after an ultrathin amorphous Al_2O_3 passivating layer (~0.7nm) was introduced by ALD indicates that these recombination centers are probably present in lower amounts.

These results show the applicability of the developed ALD process for deposition of effective catalyst layers in

PEC water-splitting devices and also the powerfulness of IMPS for mechanism discovery in PEC water-splitting devices design.

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P-51

$La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ based anodes for Solid Oxide Fuel Cell

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In recent years, the enhanced interest into environmentally friendly production of energy promoted researches aimed at decreasing pollutant emission and at increasing efficiency and renewability in energy conversion and storage. The objective is to avoid or minimize the use of fossil fuels. Fuel cells have attracted attention because are highly efficient devices, that directly transform chemical energy of fuels into electrical energy, with low or no pollutants emission. In this contribution the development and optimisation of an innovative anode for Solid Oxide Fuel Cell is presented. A Ni-YSZ cermet is the state of art for anodes because of its low cost and high stability in reducing atmosphere. Unfortunately, it presents several disadvantages connected with the capacity of Ni to form NiO (leading to the cell degradation), to sinterize (with decrease of specific surface area) and to suffer of sulphur and C-poisoning (when using hydrocarbons as fuel). [1] $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ (*LSCM*) perovskite has been selected as a possible new anodic material. *LSCM* was first proposed by Tao et al. as an alternative material to traditional Ni-YSZ. [2] $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ has been synthesised using *Marcilly method*, starting from the correspondent metal oxides. [3] Then, it is characterised using different techniques. In particular, XRD is used, beside to understand the crystallographic structure, to evaluate the presence of all constituents inside the perovskite cell. TPR curves give information about the processes of reduction in the material of interest at different temperatures. It can be noted a single peak at 404°C related to the reduction of Mn^{4+} to Mn^{3+} that allows to quantify the atomic ratio between Mn(IV)/Mn(III). This is a particularly important information because with the redox couple is possible to tune the catalytic activity and electronic conductivity. In fact, the use if Mixed Ionic Electronic conductors can greatly enhance the efficiency removing the problem of the Triple Phase Boundary. The powder surface area is determined using BET (Brunauer – Emmett – Teller Surface Area) technique. While data concerning structure and granulometry are determined using SEM, see *Figure 1.* X-Ray Photoelectron Spectroscopy and Energy Dispersion X-Ray analysis have been used to study the composition of the electrode and to evaluate eventual segregation processes. The elevated porosity and surface area make of *LSCM* powder a good candidate as a possible electrode material. The next step is the evaluation of the compatibility with different electrolytes as LSGM and YSZ. To test electrochemical performance of *LSCM*, a symmetric cell is prepared based on electrolyte supported geometry. Different inks are created to optimise the adhesion of the electrode on the electrolyte pellets surface. A composite ink made of *LSCM* powder and electrolyte material is found to be the better choice in terms of adhesion. The ink is deposited on electrode surface using the tape casting technique. The cell is electrochemically tested utilising EIS. Both hydrogen and methane have been used as fuel. The material stability and performance in different was investigated. Moreover, composite anodes made by impregnation and infiltration of nickel on *LSCM* have been prepared. The slow amount of Ni chosen (5wt%) permits to avoid disadvantages connected with its utilisation. In the same time, the catalytic activity and electronic conductivity of the anodic material are significantly enhanced, supporting thus the idea that the *LSCM* based anodes can be an interesting opportunity. [4]

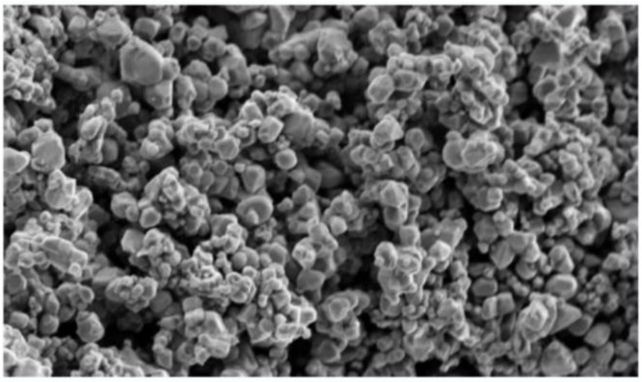

Figure 1

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P-52

Ruddlesden-Popper perovskite-based electrodes for Symmetric and Reversible Solid Oxide Electrolyser

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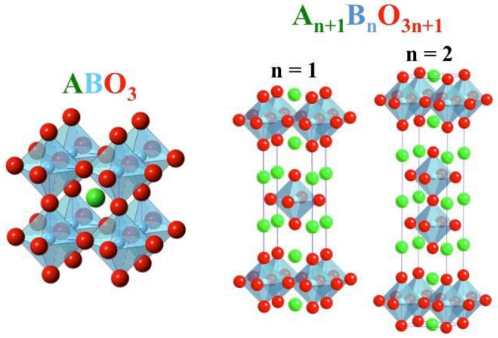
The high temperature solid oxide fuel cell (SOFC) promises a high conversion efficiency of chemical energy into electricity with consequently lower greenhouse gas emissions. Operated in the inverse process, the high temperature solid oxide electrolysis cell (SOEC) is an efficient way to produce hydrogen, possibly using renewable energy sources for water electrolysis. The contribution of thermal energy allows decreasing the need of electrical energy. Particularly interesting is the possibility to operate reversibly both as fuel cell and as electrolyser. This could offer a precious chance for efficient energy conversion and storage. Among the materials used as electrodes, perovskites as $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ (LSCM) and $La_{0.75}Sr_{0.25}Fe_{0.5}Mn_{0.5}O_{3-\delta}$ (LSFM) are gaining more and more popularity, not only because of their good conductivity at temperature about 750°C, but mainly because of their stability in both oxidizing and reducing environment as well as their good electrocatalytic activity both in oxidation and reduction. These perovskites, thus, can, in principle, be used in reversible and symmetrical cells. In Symmetrical Cells the same material is used both as anode and as cathode so decreasing the production cost and the risk of failures due to the poor compatibility between electrodes and electrolyte. In this contribution an innovative approach is attempted: higher ionic mobility and conductivity, in fact, is built through structure modification instead of chemical formulation.



Ruddlesden-Popper perovskites ($A_{n-1}A'_2B_nX_{3n+1}$, where A and A’ represent alkali, alkaline earth, or rare earth metal while B refers to transition metal, see figure) are interesting at this purpose because of the flexible oxygen stoichiometry, fast oxygen ion diffusion and rapid surface exchange kinetics related to the presence of the rock salt layer [1]. In this work, the target materials are two Ruddlesden-Popper perovskites: $LaSr_2MnCrO_{7+\delta}$ and $La_{1.2}Sr_{0.8}Mn_{0.4}Fe_{0.6}O_{4+\delta}$, (RP-LSCM and RP-LSFM). These materials should present the advantages of both perovskites (for composition) and RP-perovskites (for structure related mobility). RP-LSCM and RP-LSFM are developed and tested in the high temperature range for SOEC and SOFC applications. The two materials are prepared by means of an auto combustion-based citrate procedure, the so-called Marcilly method. This procedure allows obtaining the target materials with an optimal phase structure. The obtained materials are characterized using XPS, XRD, SEM-EDX and TPR. The materials are also tested in a Solid oxide fuel cell environment, using EIS and polarization curves. The results are to be compared with similar ones present in the literature [2] and the effect of structure and composition are evaluated.

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P-53

Towards efficient sustainable full-copper dye-sensitized solar cells

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To have enough clean and low cost energy for the future is one of the world's most important challenges. The sun could be the answer to our energy needs, since more energy from sunlight strikes the earth in one hour than all the energy consumed on the planet in one year. Following the discovery of Grätzel-type dye-sensitized solar cells (DSSCs) as a cheap and convenient way for harnessing the energy of the sun and converting it into electricity [1], there has been a lot of effort to improve the photo-conversion efficiency (PCE), trying to optimize every components of the device. In particular, an impressive amount of work has been devoted to optimize the sensitizer and the redox mediators [2].

Until recently, the most efficient dye-sensitized solar cells were based on polypyridyl ruthenium complexes as dye and the iodide/triiodide couple as electrolyte. However, the relatively high cost and environmental issues of Ru complexes encouraged the search for efficient noble-metal-free dyes. Besides, it was found that Cu-based mediators can outperform both iodine-based and Co-based electrolytes. These observations were the springboard for the first full-copper DSSCs in which a copper(I) dye is coupled with a copper(I)/(II) electron shuttle, of great interest for the development of novel sustainable, low cost and environmentally friendly DSSCs [3].

In the present work two new heteroleptic copper(I) sensitizers bearing a π-delocalized 2-(R-phenyl)-1H-phenanthro[9,10-d]imidazole (R = NPh_2 or OHexyl) ancillary ligand were prepared and well characterized. Both of them, like the related complex bearing 2,9-dimesityl-1,10-phenanthroline as ancillary ligand, can be coupled with the common I^-/I_3^- redox couple to prepare DSSCs with a good efficiency. They can also be combined with homoleptic copper redox couples to afford full-copper DSSCs with fair to good performance, depending on the nature of the electron shuttle.

Our results show that, in copper(I) dyes, the use of π-delocalized ancillary ligands is not sufficient to improve drastically light harvesting, electron transfer enhancement from electrolyte to dye and directionality for electron injection in the TiO_2 conduction band. In the investigated dyes, TDDFT calculations assign the main absorption band as a MLL'CT involving not only the bipyridine but also the phenanthroline ligand which upon TiO_2 sensitization should point in the opposite way of the TiO_2 surface. Such phenanthroline involvement in the excited state originating visible light absorption becomes therefore detrimental, implying a reduction in the charge transfer directionality. Further investigation on the tuning of this class of compounds should point to up-shift the phenanthroline-based LUMOs by electron donating ligands to avoid interfere on the low-lying MLCT transitions [4].

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P-54

CeO_2-ZnO mixed system for H_2 production in water photo-splitting under visible light

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Metal oxide semiconductor nanoparticles have become of paramount importance in many technological fields, such as sensors, varistors and LED. In addition, they have been also widely studied in the branch of photocatalysis, where ZnO and TiO_2 have achieved a considerable success, especially concerning the degradation of pollutants. However, both ZnO and TiO_2, being characterized by a band gap of 3.2 eV and 3.4 eV, respectively, can be photo-activated only if irradiated with UV light; this greatly limits their spread on the large scale application since the UV amount reaching the earth surface is just the 5% of the total radiation impinging the planet. During the last 50 years, a lot of strategies have been attempted with the aim to overcome this limitation, exploring different approaches to extend their photocatalytic response from UV to visible light.

For this ambitious project we used a mixed system based on CeO_2-ZnO that, with just 1% of Ce added during the wet synthesis route allowing the co-precipitation of CeO_2.

The structural and optical characterization have confirmed that Ce doesn’t enter in ZnO lattice forming extrinsic defects, but rather it forms CeO_2 nanoparticles stabilized on zinc oxide surface.

A pre-screening of the material photoactivity has been done with electron paramagnetic resonance (EPR) spectroscopy upon in situ irradiation: the results, confirmed by computational calculations, have revealed the working mechanism behind the photoactivity upon visible irradiation of the mixed material. Indeed, the formation of a heterojunction among the two oxides let an electron transfer from ZnO conduction band to the empty 4f level of Ce atoms, improving charge carriers separation; moreover, the optical gap of CeO_2 equal to 2.9 eV, increases the absorption of photons having energy in the visible range [1, 2].

It has been demonstrated that the mixed material CeO_2-ZnO is very active in the degradation of different emerging pollutants under visible irradiation[3-5], due also to the right oxidative potential exhibited. The reductive potential is, on the contrary too low in order to drive a water photo-splitting reaction. For this reason, as it will be presented in this study, Cu_2O has been impregnated on the surface of the mixed system as co-catalyst, with the role of increasing the reductive potential and the absorption in the visible range. The experimental evolution of the Cu species has been followed characterizing the material by means of EPR and UV-Vis diffused reflectance spectroscopy (DRS).

It will be shown how the impregnation improves H_2 evolution produced during water photo-splitting, performed irradiating the material with $\lambda \geq 420$ nm.

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P-55

Embedded molybdenum grids for back contacts: new architectures for large area CIGS-based bifacial solar cells

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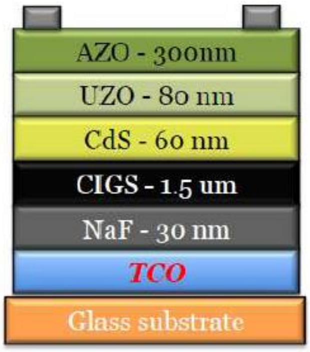
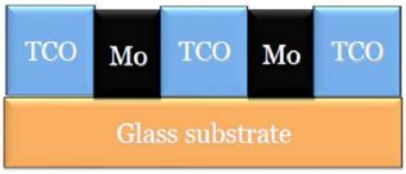
In this work we present the development of viable technological processes for the fabrication of efficient bifacial solar cells on larger areas of about 1÷4 cm2. A bifacial solar cell (BFSC) is a device able to absorb light both from its front and back sides. It can be achieved by replacing the standard metallic back electrode by a transparent conductive oxide (TCO) contact, which allows direct or diffused sunlight to reach the absorber also from the back of the cell. The BFSC considered are based on Cu(In1-xGax)Se2 (CIGS), grow by Low Temperature Pulsed Electron Deposition (LTPED), which is very reliable technique based on a far-from-equilibrium ablation of a solid target developed to obtain high quality thin films. Previous work consisted in replacing the standard molybdenum back contact with a suitable transparent conductive oxide (TCO), and then tuning the physical proprieties of both TCO and absorber in order to maximize the transport of the photo-generated carriers across their interface [1][2]. Thanks to the low temperature needed (compared to the growth methods), high-quality CIGS has been obtained without post-deposition selenization on alternative and novel substrates, including TCOs. BFSC fabricated on small areas (0.05 cm2) exhibited a front conversion efficiency ~15%, thus demonstrating that LTPED allows the deposition of CIGS on different TCOs avoiding the formation of a detrimental oxide interface barrier (such as Ga2O3).



We tested several architectures to improve the BFSC efficiency. Simple grids of Mo were deposited on TCO layers or vice versa. However, while the realization was very simple, the quality of the devices were not sufficient. The interfaces presented many stresses principally caused by metal fingers inside the absorber or the back-contact layer. The heating of the substrate during the absorber deposition and the different rate of sodium diffusion in Mo or TCO layer were fundamental. To avoid problems, flat surfaces and the absence of stress points on the interface between back contact and absorber layer are mandatory. For this challenge a new embedded Mo grid architecture was tested and gave good results. We used a photolithographic process in order to embed inside the TCO layer the molybdenum grid grown by DCsputtering with the same thickness of the TCO. Some adhesion/shunt problems are still present due to presence of metal fingers or different thickness between Mo/TCO. Recently, studies are under way to embed inside a Mo layer a TCO grid. This new process is apparently simpler than the previous one and allow to improve the total cell efficiency from 6% to 10%. Theoretically, it could also avoid the formation of the metallic fingers that gave major problems in the previous works.



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P-56

$Ca_2Fe_{1.95}Mg_{0.05}O_5$: Electrode Material For Reversible And Symmetrical Solid Oxide Cell

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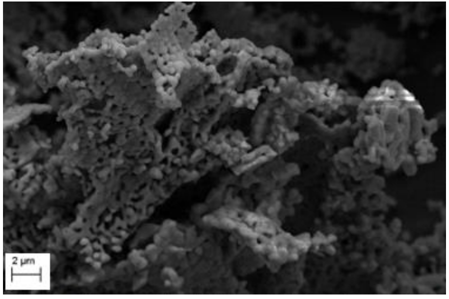
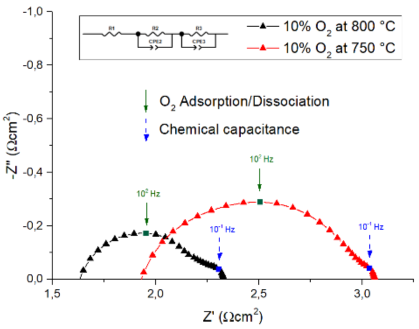
All of us knows fossil fuels related problems and the importance of finding new green and cheap alternative technologies for energy production. Solid Oxide Fuel Cells (SOFCs) can be a valid support in pursuing sustainable development. A way to reduce costs and to increase the reliability and life span of a SOFC is the creation of a Reversible Solid Oxide Cell (Re-SOC). Recent studies have shown interesting properties on brownmillerite compounds, which make them suitable as electrode material for Re-SOCs. A brownmillerite is an oxygen defective double-perovskite, with a structure $A_2B_2O_5$. Their oxygen vacancies are able to enhance the material ionic conductivity.[1] In this contribution, we focus on $Ca_2Fe_{1.95}Mg_{0.05}O_5$ (CFMO). Mgnesium doping was carried out to emphasize Fe^{3+}/Fe^{4+} redox couple and thus electronic conductivity.[2]



The powders were prepared by means of an autocombustion based citrate procedure (Marcilly method).[3] XRD shown the marked crystallinity of the powders; the comparison between the patterns of different batches, confirmed the good reproducibility of the synthesis. The TPR analysis has shown a hydrogen consumption higher than the theoretical value (calculated considering only Fe^{3+} cations presence), supporting the idea that different oxidation states for iron cations are present.[4]

The XPS semi-quantitative analysis has confirmed the absence of calcium or iron segregation on the powders' surface. The correct stoichiometry was confirmed also by EDX analysis. SEM images have shown the globular morphology of particles and a good porosity, also confirmed by BET analysis. The determined surface area is in good correspondence with typical perovskite and brownmillerite values in literature.

The material was electrochemically characterized as a cathode by EIS, obtaining promising ASR values (0.19 Ωcm^2 at 800°C). In order to verify stability and behaviour under different atmosphere conditions, EIS investigation of CFMO cathode was carried out at different oxygen partial pressures. At lower oxygen partial pressure a second semicircle at high temperatures (800 – 750 °C) appear. This signal is not dependent on temperature, but on oxygen concentration. Those characteristics and the stimulating frequencies (10^{-1} Hz) make possible the assignment of this signal to chemical capacitance process. The electrochemical characterization has been carried out before and after CFMO activation. The activation was performed by building nanocomposites of the type FeOx/CFMO by exosolution[5] and by wet impregnation (10 and 15 wt. %). The $Ca_2Fe_{1.95}Mg_{0.05}O_5$ has given a good response as cathode material. However, there are wide margins of improvement, because many parameters can be changed and optimized to find new solutions for symmetrical-reversible solid oxide cells.



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P-57

Crosslinked membranes of PBI-c-PVBC applied as anion exchange polymer electrolyte for fuel cells

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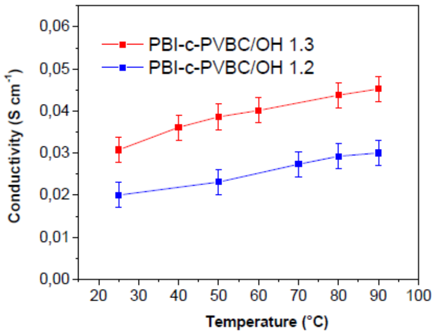
Development of alternative technologies is needed to face the actual energy challenges in order to reach a sustainable model. Fuel cells are attracting great interest because of their potential, they can be used coupled with renewable energies and electrolyzers to first store chemically the energy with the electrolyzer in form of hydrogen and then use it in a fuel cell to produce electricity when required. This hydrogen model could replace many combustion machines that are actually burning fossil fuels and work very well in tandem with batteries or other technologies. Other fuels are also available, like short chain alcohols [1], with the advantage of easier use and thus good functionality in the transition of changing the energy model. New and better materials are needed to improve fuel cells and electrolyzers performance, one of the key materials is the polymer electrolyte membrane used in low temperature fuel cells and zero gap water electrolyzers, especially for anion exchange use in alkaline media[2]. Crosslinked membranes of polybenzimidazole (PBI) with PVBC quaternized with DABCO show very good thermal, mechanical and chemical stability in the tests we have performed. They also have good conductivity values, higher than 20 mS cm-1 at 25 ºC, thanks to the quaternary ammonium groups in the structure and the presence of PBI. Different molar ratios of PBI:PVBC have been studied, from 1:1 to 1:3. The membranes of PBI-c-PVBC 1:3 have shown the best conductivity values, reaching 44 mS cm-1 at 80 ºC. The membranes were also characterized by IR and XPS, finding interesting insights about the crosslinking reaction with the last one. Other properties of the membranes like the gel fraction, KOH and water uptake and swelling behaviour were determined. Finally, the membranes were tested in a single cell fuelled with Ethanol 2M/KOH 2M as fuel and pure oxygen in the cathode at 60 and 90 ºC. The results show that the PBI-c-PVBC 1:2 and 1:3 membranes obtain the best performances, improving the commercial PBI membrane, showing them as promising candidates for application in the alkaline polymer electrolyte membrane fuel cell technology.



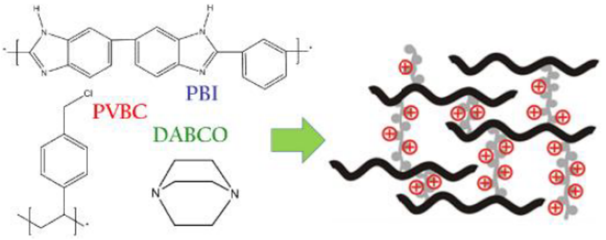


Figure 1. (Left) Ionic conductivity results of 1:2 and 1:3 PBI-c-PVBC membranes and (top) schematic resume of the synthesis.

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Acknowledgments

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P-58

Restructuring MOF to nanoscale bismuth electrocatalysts for highly active and selective CO_2 reduction to formate

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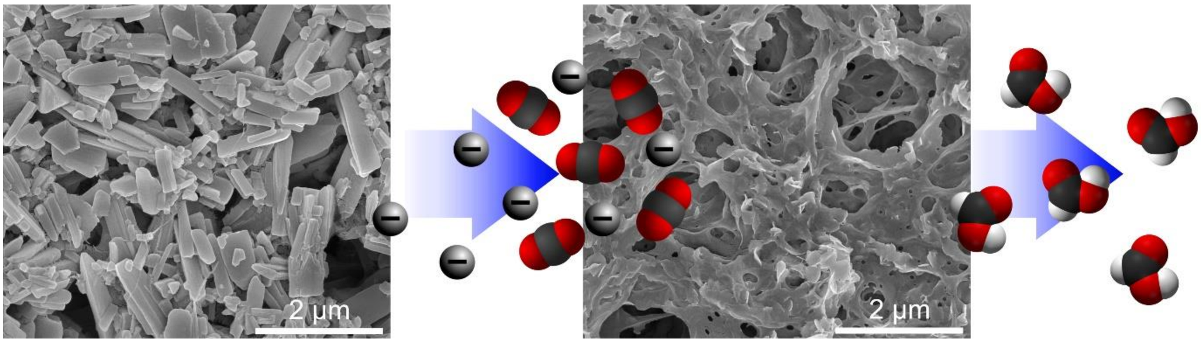
Metal-organic frameworks (MOFs) are porous crystalline materials with an organic-inorganic hybrid structure, combining metal centres and organic polytopic molecules used as linkers. Among several direct applications of MOFs, [1,2] these materials are studied as templates and precursors for the synthesis of carbonaceous matrices preserving high porosity and potentially including heteroatomic dopants or homogeneously distributed metal sites. [3] In this work we used Bi(1,3,5-tris(4-carboxyphenyl)benzoate) (Bi(btb)) [4] to obtain electrochemically *in situ* a carbon-based scaffold embedding Bi nanoparticles directly on the top of an electrode. This electrode, containing a low Bi load of ~30 μg cm^{-2}, exhibited good activity, selectivity and stability over the electrocatalytic reduction of CO_2 in aqueous electrolyte. Formate, anionic form of the industrially relevant compound formic acid, [5,6] was obtained as primary product. Most importantly, the mass activity of the obtained catalyst is competitive with the systems described in literature, based on electrodeposited Bi films derived from *e.g.* Bi salts [7] or Bi oxyhalides, [8] and outperformed previously reported Bi catalyst in the CO_2-to-formate batch reaction at overpotentials larger than 650 mV.



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P-59

Modular stand-alone photocatalytic reactor for waste water treatment: the HP Solar project

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Fig. 1 Modular stand-alone reactor

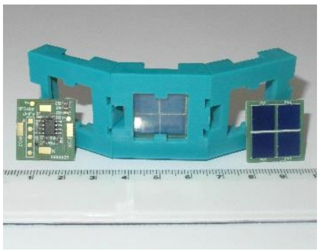

Fig. 2 Complete reactor element

Nowadays, the goal of waste-water industry is to observe water quality standards, providing safe water for civil use. Sure enough, adequate treatments must be adopted, based on materials and technologies able to guarantee efficient removal of emerging contaminants, like drugs and chemical pollutants, from different waste water sources. In last few decades, advanced oxidation processes (AOP) have been developed as emerging decontamination technologies, resulting in the total mineralization of most organic contaminants. Among these processes the photocatalysis is in particular the most promising one [1]. Photocatalytic degradation of organic pollutants can be performed by using a photoelectrochemical (PEC) cell, thanks to which solar radiation can be converted also into useful forms of energy or fuels, such as hydrogen, as added value to the process of decontamination.

We present a modular and completely stand-alone reactor (Fig. 1) for the photodegradation of organic compounds with the simultaneous production of hydrogen. The reactor is based on modules encapsulated in PVC frames which makes each element completely independent and waterproof. The frames can be connected together to form a cylindrical structure embedded between two tubes made of PMMA. The gap between the two tubes is used to pump water in the reactor, while the internal tube acts as a sink for the treated water. Each element (Fig. 2) is composed by a metallic cathode, the electronic components and a photoanode, which is in a tandem cell configuration with four Si solar cells connected in series, and. The photoanode consists of 1μm-thick film of colloidal tungsten trioxide (WO_3) deposited on a transparent and conductive FTO (Fluorine-doped Tin Oxide) layer over a glass substrate. WO_3 was chosen instead of the more commonly used titanium dioxide (TiO_2) thanks to its lower activation energy (~2.67eV) that allows to exploit also part of the visible solar spectrum. Moreover, this active material shows resilience to photo-corrosion, good charge-transport abilities and moderate hole diffusion length. WO_3 is photo-activated by light with wavelength below 470 nm (15% of AM 1.5 solar spectrum) generating OH• radicals for pollutants oxidation in water [2]. The spectrum portion that is not absorbed by the photoanode reaches the behind photovoltaic (PV) Si solar cells. As a result, the PV cells allow the increase of the photoanode potential with respect to the cathodic electrode for solar hydrogen generation and a higher photoanode conversion efficiency. Unfortunately, polarization effects occur and the catalytic efficiency drops down to a minimum after a few minutes. This limiting effect can be overcome by periodically applying a small reverse potential using the electronic components. In particular, a microcontroller, directly powered by the solar cells, provides the required voltages (+2.0↔+2.5 V, -0↔-0.3 V) and timings to reduce the polarization effects.

The reactor was developed within the HP Solar project, part of the POR-FESR 2014-2020 program funded by Emilia-Romagna Region and the European Union through the European Regional Development Fund. The results show an effective reduction of COD (Chemical Oxygen Demand) in wastewater samples provided by the local water treatment and management authority HERA S.p.A. Moreover, tests performed on emerging micro pollutants, like atenolol and carbamazepine, barely eliminated by current wastewater treatment (WWT) plants, display a photo-degradation of 60-70 % in 7 hours, suggesting the tertiary use of the reactor in WWT plants.

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P-60

Towards Stable and Conductive Titanium Oxynitride High-Surface-Area Support for Iridium Nanoparticles as Oxygen Evolution Reaction Electrocatalyst

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The rational design of electrochemical oxygen evolution reaction (OER) electrocatalyst is essential for the development of efficient and at the same time sustainable electrochemical energy conversion applications like electrolysis, electrosynthesis, batteries, etc. One of the remaining limitations of the low-temperature electrolyzers is the huge amounts of highly scarce and expensive iridium used as the OER electrocatalyst. Here we present functionality of high-surface-area support that efficiently reduces the noble-metal loading, effectively disperses the iridium nanoparticles and exhibits good electrical conductivity and stability. The new composites made of iridium nanoparticles finely dispersed on different $TiON_x$ supports, which were produced by a novel synthesis, were extensively characterized and shown to exhibit some electronic interaction with the support and finally as a promising OER electrocatalyst for the use in acidic media.

P-61

Industrial synthesis of perovskites for pollutants’ abatement activity

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Perovskites have stood out as versatile and innovative materials in the field of catalyst for exhaust control, thanks to their unique chemical properties. In particular they allow the possibility of incorporating different cations in the structure, resulting in a large range of compositions and therefore catalytic activities. A novel approach toward the abatement of pollutants, of which TWC can just be an application, aims to reduce the employment of noble metals and this is made possible by the design of metal cation doped perovskites with high catalytic activity [1]. The aliovalent doping in the perovskite A and B sites induces the formation of structural defects, different oxidation states and cation metal redox couples. [1]

A very relevant problem is in the synthesis of the catalysts both in terms of reproducibility and upscale. In this contribution a comparison between different synthetic industrial approaches in terms of properties and reactivity is carried out. Catalysts obtained by different routes, Flame Spray Pyrolysis (FSP) and co-precipitation (COP) have been compared. Doped manganates and ferrites have been considered because of their high fresh activity in TWC, low cost and absence of noble metals. FSP-obtained perovskites were produced with a prototype reactor owned by Lurederra, COP sample by Johnson Matthey.

A first set of samples, consisting in 4 batches of $La_{0.6}Ca_{0.2}Fe_{0.8}Cu_{0.2}O_3$ (LCFC A, B, C and D respectively) collected at successive stages of the FSP, showed significant changes in morphology, composition and structural features. SEM images underline the formation of highly dispersed particles on a porous structure and, with the process advancement, of globular particles (diameter of about 100 nm), most likely combustion remains. LCFC A diffraction pattern, unlike B to D, suggests incomplete formation of perovskite phase, in favour of a mixture of oxides (La_2O_3, Fe_2O_3), as confirmed by XP spectra. EDX/XPS compositional analysis point out the surface segregation of La and Cu on the surface, whereas Fe segregates only in LCFC D. Significant differences are evident focusing on $La_{0.7}Fe_{0.8}Cu_{0.2}O_3$ obtained by FSP (LFC FSP) and coprecipitation (LCFC COP), these differences concern surface composition, presence of simple oxides and dopant insertion into the perovskitic cell. [2] (see Figures 1 and 2).

The comparison between FSP and COP was also carried out with a different perovskite, $La_{0.9}K_{0.1}Mn_{0.9}Co_{0.1}O_3$, to evaluate the generality of considerations, the two samples were obtained by FSP (LKMC FSP) and coprecipitation (LKMC COP): once again coprecipitation seems less effective in generating a pure perovskite phase (Figure 3). Interestingly the preparation procedure also affects the presence of active oxygen species, the reducibility and the reactivity in pollutant abatement reactions.

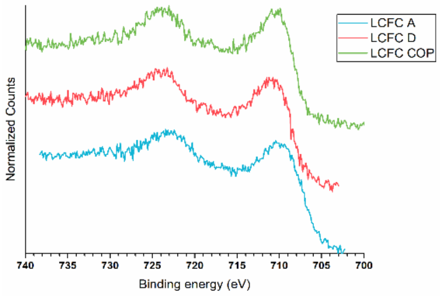

Figure 7. XP Fe2p spectrum of LCFC A, D and LCFC COP.

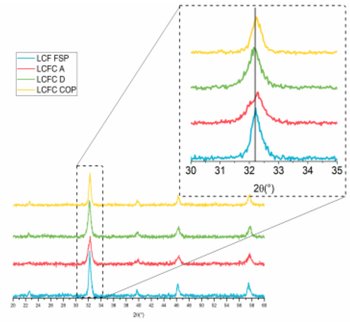

Figure 2. XRD pattern for LCF FSP, LCFC A, D and LCFC COP.

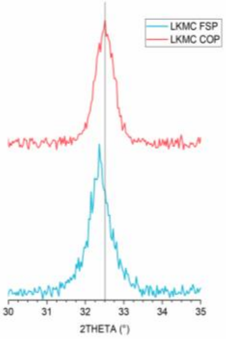

Figure 7. XRD pattern inset for LKMC FSP, COP.

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$La_{1-x}Sr_xMnO_{3-\delta}$, $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ and $Ba_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$: the Huey, Dewey and Louie of Solid Oxide Fuel Cell cathode materials

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Perovskite materials are widely studied as cathode materials for intermediate-temperature solid oxide fuel cells (IT-SOFC) for their relevant properties regarding electrocatalytic activity or stability. Nevertheless, a material that combines both it is not yet available. Among them, $La_{1-x}Sr_xMnO_3$ (LSM), $La_{1-x}Sr_xCo_{1-y}Fe_yO_3$ (LSCF), $Ba_{1-x}Sr_xCo_{1-y}Fe_yO_3$ (BSCF) were deeply investigated but their properties are not completely exploited or optimized [1]. Here results about these materials are presented to show new possible routes to employ them. All the reported electrode materials are investigated using different approaches, such as infiltration and composite electrodes. The study starts from LSM – based electrodes, which show a change in kinetic mechanism under particular operating conditions. These results open new horizons about the employment of this material, up today considered not suitable for IT-SOFC temperature range. A first application, with promising results, is proposed here with a LSM infiltration in LSCF and BSCF scaffold [2]. Fig. 1a shows the decreasing in degradation rate in LSM-infiltrated BSCF electrode compared with reference one. The presence of infiltrated-phase enhance stability and electrochemical activity of electrodes. Further promising results are obtained also by mixing BSCF and LSCF powders. Three different BSCF:LSCF ratio are considered to produce three different cathodes [3]. All the new compositions show an improvement of activity for oxygen reduction reaction, with very competitive values of polarization resistance (Fig. 1b). Moreover, one of these new electrodes has also a lowering of degradation rate compared with reference materials.

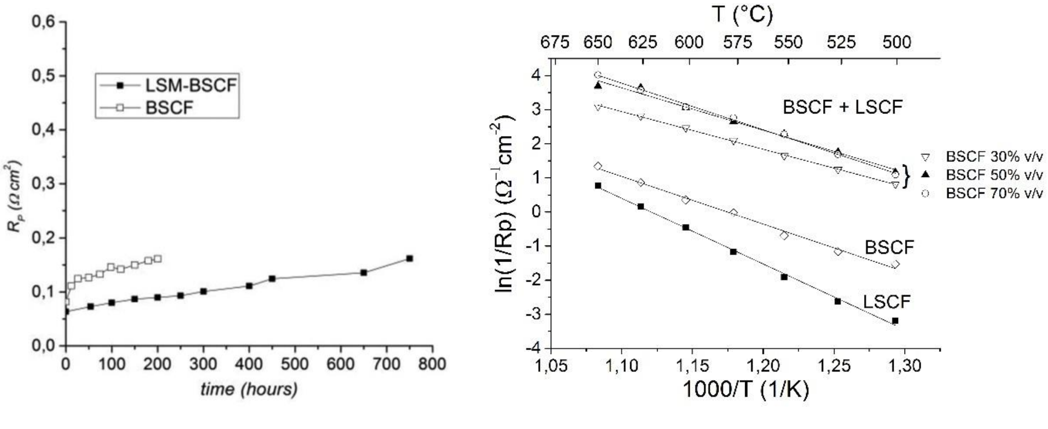

Figure 8 (a) Trend of cathode polarization resistance (R_P) over time for reference and LSM- infiltrated BSCF electrodes under a current load of 200 mA cm^{-2} at 700 °C (b) Arrhenius plot for different BSCF-LSCF electrodes compare to LSCF and BSCF reference materials

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Next-generation batteries: flow Lithium-Oxygen batteries as a promising technology to develop high energy storage systems

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The development of next-generation batteries is crucial to boost the shift from a fossil fuel society to a low carbon society. An emerging technology is represented by flow lithium batteries (FLBs): this technology combines in a unique solution the advantages of the high specific energy of lithium batteries and the modularity of redox flow batteries that allow to decouple energy and power.

Different kinds of FLBs have been proposed, including batteries featuring semi-solid anolytes and/or catholytes with Li-ion intercalation powders, such as LiFePO4 or $Li_4Ti_5O_{12}$, dispersed in organic electrolyte, and Li/S and Li/O_2 flow batteries.

However, these technologies are still not mature enough and advancements in materials and cell designs are fundamental to create a new battery generation.

BETTERY, an Italian Innovative Startup, has developed a new battery concept called NESSOX: NEw Semi-Solid flow lithium OXygen battery. This technology combines the high energy density of Li/O_2 batteries with the flexible and scalable architecture of redox flow batteries. NESSOX, featuring a lithium metal anode and a semi-solid, flowable catholyte, displays the highest practical specific energy and energy density ever reported, up to 500 mWh cm^{-2}, and current densities that are rather competitive with those featured by commercial Li-ion batteries (up to 4 mA cm^{-2}). In addition, thanks to its flowable catholyte, NESSOX features an extremely fast recharge technology obtained by "catholyte refueling". BETTERY aims to bring its new battery concept into the battery market, introducing a radically new battery concept.

Here we present and discuss the main technology features of NESSOX and the challenges faced by BETTERY to bring it into market.

Keywords: flow lithium batteries, Li/O_2 flow batteries, high-energy density

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Effect of Experimental Parameters on the Electrocatalytic Performance of a $NiCoO_x$ Catalyst for the OER

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Hydrogen production by water electrolysis is a key technology for an emission-free hydrogen economy. However, slow kinetics of the oxygen evolution reaction (OER) limits the water splitting process therefore efficient catalysts are needed. Rotating disc electrode (RDE) measurements are generally used to evaluate the performance of prospective materials. Powder samples are typically deposited as thin-film layers on an electrode substrate by the dispersion of the catalyst in different solvents and an additional binder.[1] Besides the intrinsic catalytic properties of the material, the electrochemical response can be affected by many factors such as impurities, catalyst loadings, binder, electrolyte concentration, mass transport, catalyst loadings, operating temperature, or type of gas saturated in the electrolyte. Conclusions regarding the catalytic properties of a novel material are insufficient without taking these parameters into account as seen in recent developments in electrocatalysis research. [2-4]

In this study, we focused on some of the above-mentioned factors on the catalytic performance of a commercially available $NiCoO_x$ catalyst for OER using a standardized measurement protocol to ensure reproducibility. Our findings show that parameters such as catalyst loadings (Figure 1), and oxygen removal play a significant role in the measured activity and stability of the $NiCoO_x$ catalyst towards OER.

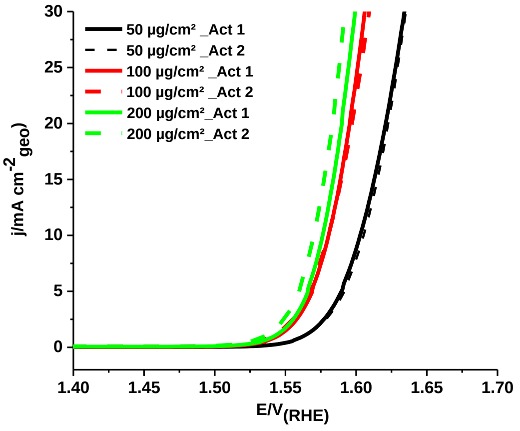

Fig 1: Effect of catalyst loadings on performance of NiCoOx towards OER; Activity measured before (Act1) and after (Act2) a 2h stability test

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P-65

Gas Evolution at Tuneable Porous Electrode Structures: Theory and Experiments

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Porous electrodes for PEM electrolyser and fuel cell technologies are optimized primarily to provide a high specific surface area for the desired electrochemical reactions. However, the increase in surface area comes at the cost of increased voltage losses due to the transport of reactant and product species through the porous medium. In gas evolving porous electrodes, the formation and transport of gas bubbles plays an important role: on the one hand, gas in the pores replaces the electrolyte phase, thus hindering ion transport and reducing the effective ionic conductivity in the porous electrode; on the other hand, gas bubbles cover and deactivate a portion of the catalyst surface area.

Gas formation and removal must be accounted for in the design of electrolyser electrodes. The presented work strives to unravel the fundamental relationships between structure, properties and performance of porous gas-evolving electrodes. The work combines an experimental approach using tuneable electrode structures [1,2] with a multiscale modelling approach [3]. The experimental approach utilizes defined micro-structured nickel surfaces prepared by photolithographic techniques as a systematic approach to correlate surface morphologies to their electrochemical performance in the oxygen evolution reaction in alkaline media [2]. Hexagonal arrays of micro-structured Ni cylinders were prepared with features of proportional dimensions to the oxygen bubbles generated during the OER process. Recessed and pillared features were investigated relative to planar Ni electrodes for their influence on OER performance and bubble release.

The modelling approach combines a macro-scale performance model of the electrode with a micro-scale model of gas evolution. At the macro-scale, a classic porous electrode model describes the transport of ions, electrons and oxygen using concepts of statistical physics of random composite media and accounting for the gas phase volume and distribution. The micro-scale model describes the formation and growth of gas bubbles based on chemical energy considerations. The model rationalizes the influence of structural parameters on the operation of porous electrodes and yields guidelines for electrode design [3]. The model was used to explore the behaviour of single nucleation sites as well as the interaction of multiple nucleation sites. It was found that existing bubbles on one nucleation site can suppress the formation of new bubbles on neighbouring nucleation sites because for the produced oxygen it is energetically more favourable to transfer into the existing bubble than to form a new bubble.

The combination of experiment and modelling work was used to analyse the complex dynamic current response in potential hold experiments. Correlations between bubble frequencies and feature sizes on the structured electrodes were explored. With the combination of controlled experiments and modelling fundamental insights on complex bubble dynamics are gained and conclusions for the manufacturing of high-performance gas evolving electrodes can be drawn.

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Electrolyte effects on the cyclic voltammogram of Pt(111) single-crystals

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Fundamental insights into the mechanisms governing electrocatalytic energy conversion is of fundamental interest for future energy schemes aimed at combatting fossil dependence and anthropogenic CO_2 emissions [1]. Electrocatalytic reactions take place at the electrodes surface-electrolyte interface (see figure 1a). In this interface, geometric and electronic effects determine the selectivity and efficiency of the electrocatalytic reaction [2,3]. The structure and properties of the electrochemical interface are affected not only by the potential applied to the electrocatalyst but also the pH of the solute [4].

Given recent advances on the generalized computational hydrogen electrode (GCHE), it is now possible to predict, using *ab-initio* density functional theory (DFT) [5], the most probable surface structure forming a 2D phase diagram. Herein, we present the basic methodology for such diagrams and correlate this with cyclic voltammetry measurements [6]. Cyclic voltammograms (CVs) of Pt(111) under different electrolyte conditions (see figure 1b) have been investigated using a rotating disk electrode (RDE) setup and correlated with DFT calculations. Our work addresses the impact cations, anions and pH have on the surface of Pt(111) electrodes.

The cathode catalyst at high-temperature polymer electrolyte membrane and phosphoric acid fuel cells (PEMFCs and PAFCs, respectively) suffers from poisoning from the adsorption of phosphoric acid anions. Thus, developing concepts that allow us to block the specific adsorption of anions from the electrolyte is essential for the rational design of active and durable catalysts for PEMFCs and PAFCs [7]. We studied the effect anions from H_3PO_4 electrolyte have on Pt(111) for the oxygen reduction reaction (ORR). Using Pt(111) and Cu/Pt(111) near surface-alloys (NSAs), it has been ascertained that the lower ORR activity of Pt(111)-like surfaces from H_3PO_4-poisoning (see figure 1c) could be described to a satisfactory level using the proposed DFT model [8]. Thus, this combination of experimental model studies and theoretical calculations opens up for a new and powerful tool for interpreting CVs of well-ordered metallic M(*hkl*) interfaces for a wide range of electrocatalytic reactions.

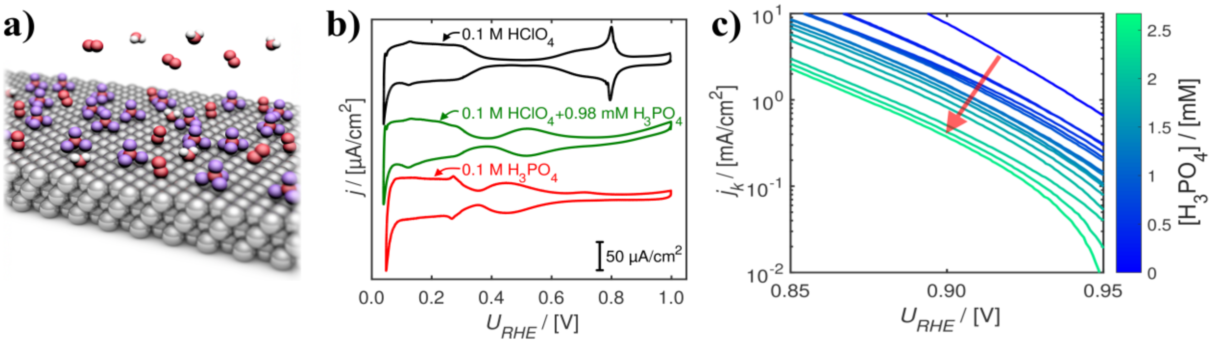

Figure 1: a) Illustration of M(111) interface with anions from a phosphoric acid electrolyte, OH, O_2 and H_2O (*Courtesy Prof. Kibsgaard*); **b)** CVs of Pt(1111) in Ar-saturated electrolyte at 400 rpm; **c)** Tafel plots of the ORR activity for a Cu/Pt(111) NSA taken at 1600 rpm in O_2-saturated electrolyte; All RDE data was obtained at room-temperature in 0.1 M $HClO_4$ with varying levels of H_3PO_4 poisoning.

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$BaCe_{0.65}Zr_{0.20}Y_{0.15}O_{3-\delta}$-$Ce_{0.85}Gd_{0.15}O_{2-\delta}$ MIEC dual-phase membrane for H_2 separation and purification

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The technology related to hydrogen separation and purification are a key element to the use of H_2 as an energy carrier and in other important technological applications. Dense ceramic membranes based on mixed ionic and electronic conducting (MIEC) materials are currently attracting growing interest for their potential application in H_2 separation membranes or in catalytic membrane reactors at T > 600 °C. [1, 2] Indeed, these systems can be used to produce ultrapure H_2 from natural gas (which is abundant and rather clean fraction of fossil feedstocks) or from syn-gas derived from biomass gasification. These devices selectively separate H_2 by incorporating it into their crystal structure as charge protonic defects and electrons/holes that are transported to the opposite side of the membrane under a H_2 partial pressure gradient, thus providing a non-galvanic separation, *i.e.* without external power. Moreover, if used as membrane reactors, they combine separation and reaction in a single unit, increasing the efficiency. In this context, ceramic-ceramic (cer-cer) composites have gained interest in the last 5 years thanks to their enhanced hydrogen permeability respect to single-phase materials. Among these, $BaCe_{0.65}Zr_{0.20}Y_{0.15}O_{3-\delta}$ (BCZ20Y15) and $Ce_{0.85}M_{0.15}O_{2-\delta}$ (M = Y and Gd) dual-phase membranes were recently explored by different groups. [3, 4] In particular, $BaCe_{0.65}Zr_{0.20}Y_{0.15}O_{3-\delta}$-$Ce_{0.85}Gd_{0.15}O_{2-\delta}$ (BCZ20Y15-GDC15) dual-phase material is currently one of the most studied cer-cer membrane reaching H_2 permeability values among the highest ever reported for bulk MIEC membranes (0.27 $mL \cdot min^{-1} \cdot cm^{-2}$ at 755°C). [3] Moreover, it shows also a good chemical stability under harsh reducing conditions and under CO_2- and H_2S- containing atmospheres. [5, 6]

This study provides a comprehensive overview of the recent results reached by our group in such MIEC material for H_2 separation. The long term stability of the BCZ20Y15-GDC15 composite system under reducing harsh environments containing H_2O, CO, CO_2, and sulphides is also shown.

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Surfactant-free Ir nanoparticles for the oxygen evolution reaction in acidic media.

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Water oxidation, or the oxygen evolution reaction (OER), is a key half reaction of many electrochemical processes for sustainable energy production such as water splitting and CO_2 reduction. The energy efficiency of an electrolyzer is to a large part determined by the performance of the OER electrocatalyst. To increase the efficiency, the use of active and stable electrocatalysts is needed, especially under acidic conditions, where polymer electrolyte membrane (PEM) electrolyzers are operated.

Nowadays, Ir-based catalysts are commonly used to minimize the overpotential of the OER [1 – 3]. However, the sustainable application of these scar materials is need. To reduce the content of precious metals and increase their active surface, a careful design of the catalyst is a must [4]. Ir-based nanoparticles have been widely studied to increase the activity per amount of Ir [5]. The use of surfactants is commonly used for the synthesis of small nanoparticles. However, the use of surfactant limits the scalable application of nanoparticles because the high energy and time consuming procedures to remove them [6].

Herein, we present a surfactant-free synthesis to produce Ir nanoparticles (ca. 2.5 nm) by simple thermal reduction of $IrCl_3$ in ethylene glycol. High reproducibility is achieved and confirmed by small angle X-ray diffraction (SAXS) and transmission electron microscopy (TEM). The electrochemical performances of the nanoparticles are evaluated for OER. Cyclic voltammetry is used to evaluate the electrocatalytic activity showing mass activities around 200 A g_{Ir}^{-1} at 1.55 V vs RHE. The electrochemically active surface area (ECSA) is calculated by hydrogen underpotential deposition on metallic Ir-based nanoparticles. Stability tests are performed by holding a current density of 10 mA cm^{-2} for 10 hours. The benefits of the surfactant-free synthesis are illustrated by comparison with nanoparticles obtained using polyvinylpyrrolidone (PVP) as surfactant.

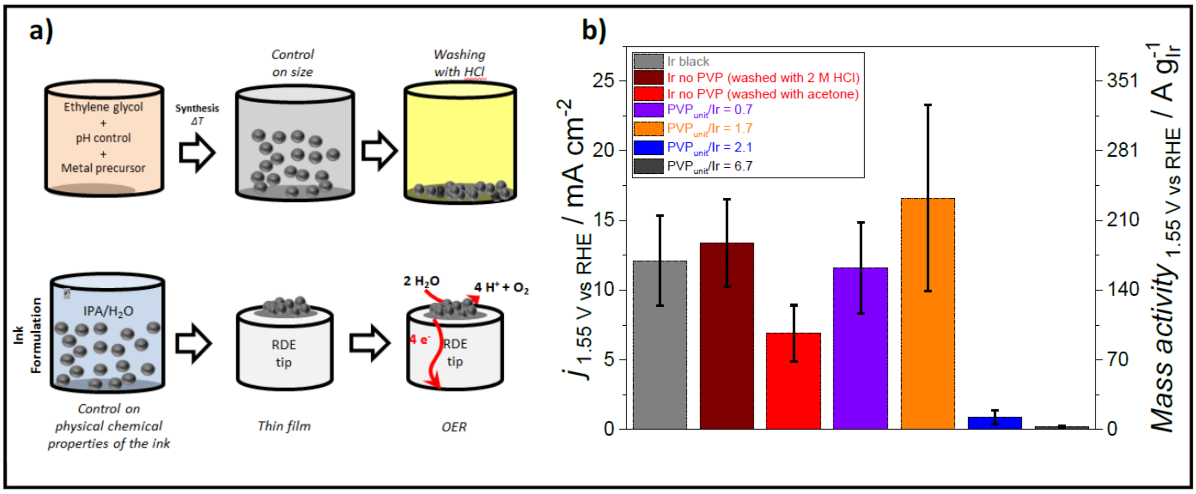

Fig. 1. a) General synthesis scheme of nanoparticles via microwave reaction. b) Comparison of the catalytic activity of Ir nanoparticles at 1.55 V vs RHE.

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Degradation of PtNi Bimetallic Alloy Under Operational Conditions of Proton Exchange Membrane Fuel Cells Studied via *in situ* GISAXS.

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In the last years, several Platinum-based bimetallic alloys have been studied as possible substituents of pure Platinum catalysts in Proton Exchange Membrane Fuel Cells (PEMFCs) to strongly reduce production cost. In particular, PtNi alloy was found to be a promising alternative to pure Pt due to its very good mass activity[1] and its competitive catalytic activity[2]. Despite these advantages, the acid-based environment in which catalyst has to operate, causes the dissolution of the less noble metal and the consequent degradation of the catalyst layer. In this picture, in situ Grazing Incidence Small Angle X-ray Scattering combined with electrochemistry is used to investigate the real-time kinetics of the surface degradation of PtNi alloy during electrochemical cycles. The study has been performed at different conditions, which simulate the real fuel cell operation and with different compositions of the alloy. Obtained results, complemented with in situ Electro-Chemical AFM, have been used to better describe the degradation of the aforementioned catalyst and to reveal in depth the structural and compositional changes during fuel cell operation.

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Electrocatalysis for Organic Synthesis: Dimethyl Carbonate Formation with Cu Electrodes

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The electrification of the chemical industry requires the development of alternative chemical synthesis routes. Dimethyl carbonate (DMC), which is an industrially relevant chemical, used for such products as plastics and batteries, can be formed by electrocatalytic synthesis. Mild reaction conditions are required relative to industrial means, as well as less hazardous conditions. We report on the electrocatalysis synthesis reaction of DMC with Cu electrodes, and provide an understanding of the mechanism of formation[1]. Methanol and CO are combined to form DMC under oxidative potentials. Both reagents may be sustainably sourced or generated from CO_2 reduction to allow for a sustainable Green Chemistry process of DMC production. A combination of techniques allowed us to investigate the reaction. Headspace-gas chromatography-mass spectrometry and *in situ* infrared spectroelectrochemistry was utilised to probe the reaction efficiency, rate and intermediates. We found that Cu electrodes produce DMC through a dissolved Cu-carbonyl intermediate. The oxidative dissolution of Cu and formation of the Cu-carbonyl has a high efficiency at > 90% while the solution phase process of forming DMC is low at ~ 6%. The results present the complexity of organic synthesis reactions and emphasise the importance of using multiple techniques of analysis. Development of the process is necessary to optimise the system and further work may lead to a viable method of electrocatalytic DMC production. The analysis may as provide insight into the mechanism of other electrosynthesis reactions.

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Metal Oxides-Bacterial Cellulose Based Air-Breathing Cathode in Microbial Fuel Cell

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Microbial fuel cell (MFC) has been nominated as an alternative to nonrenewable sources of energy capable of transforming organic matters directly into electrical power via microbial anaerobic respiration on the anode and oxygen reduction reaction (ORR) on the cathode. This technology is low cost because of utilizing waste matters as fuel. But low electricity generation is still a challenge in this system. Two main pathways are followed for bringing MFC to commercialization: i) increasing electricity generation; ii) using cheaper components like electrode materials and catalysts. Electrodes are the main parts of MFCs and they are of extreme importance for MFC’s operations and the majority of MFC’s cost is attributed to electrode materials [1].

Cellulose is one of the most abundant material worldwide and is an excellent choice to be exploited in electrode fabrication. Recently there are many efforts in using cellulose and its derivatives for making cheaper electrodes in energy storage devices. Bacterial cellulose (BC) produced by some species of bacteria like *acetobacter xylinum* is a three dimensional network of nano cellulose fibers. The latter can be easily modified by conductive materials like carbons and conductive polymers (e,g polyaniline) [2,3]. From this point of view, it has the potential to be used as a cheap substrate for high performance electrodes. Additionally, cathode catalyst which accelerates ORR has a considerable effect on the performance and final price of MFC. Platinum is known as a catalyst with high catalytic activity in ORR. It was the first choice for MFC technology. Despite high performance in ORR, Pt in microbial fuel cell is not a good choice because of two considerable reasons: i) durability issues and deactivation due to pollutants in MFCs; ii) high cost that makes MFCs uneconomical [4]. Therefore, an alternative low cost catalyst can help MFC become more practical technology. Metal oxides (MO_x) might be a suitable alternative and they are more resistant to contamination.

In this work, BC was coated by multi-walled carbon nano tubes and manganese dioxide (MnO_2). It was placed as an air-breathing cathode in a cubic MFC. Respect to our knowledge, it is the first time that BC is used as air-cathode. In this investigation the low cost BC-CNT-MnO_2 was compared with commercial electrodes. Here, the electrochemical test about the new and commercial electrodes are presented. The final goal is to reach a cheap, high performance and green air-cathode for MFC technology.

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$MoS_{2(1-x)}Se_{2x}$/Graphene hybrids for electrochemical hydrogen evolution reaction

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A useful way to tailor the optoelectronic properties of transition metal dichalcogenides is the composition alloying, i.e. exploiting ternary compounds by varying the molar fraction of the metal (i.e. $Mo_{(1-x)}W_xS_2$) or of the chalcogenide (i.e. $MoS_{2(1-x)}Se_{2x}$).[1-3] Precise control over the nanostructures composition, shape, band gap and optical properties can be reached, giving rise to materials that can be used also in hydrogen production with excellent results.

Here we present a study made on the hydro- and solvothermal growth of $MoS_{2(1-x)}Se_{2x}$ nanosheets on graphene (GO) based supports. The goal was to obtain an easy-to-tune Se:S ratio; therefore several precursors has been tested to induce the heterogeneous nucleation of $MoS_{2(1-x)}Se_{2x}$ nanostructures on the GO sheet, resulting in different coverages and morphologies of the active materials. However, having in mind the goal of improving the electrochemical activity of hydrogen evolution reaction, a suitable stoichiometric control of $MoS_{2(1-x)}Se_{2x}$ and optimization of morphology is required.

We grew our $MoS_{2(1-x)}Se_{2x}$ on GO system with different molar ratio and with the possibility of switching easily between two different hierarchical nanostructured morphology. Therefore, in this work, we highlight marked changes in electrochemical performances with different morphology and composition of $MoS_{2(1-x)}Se_{2x}$ alloys on GO.

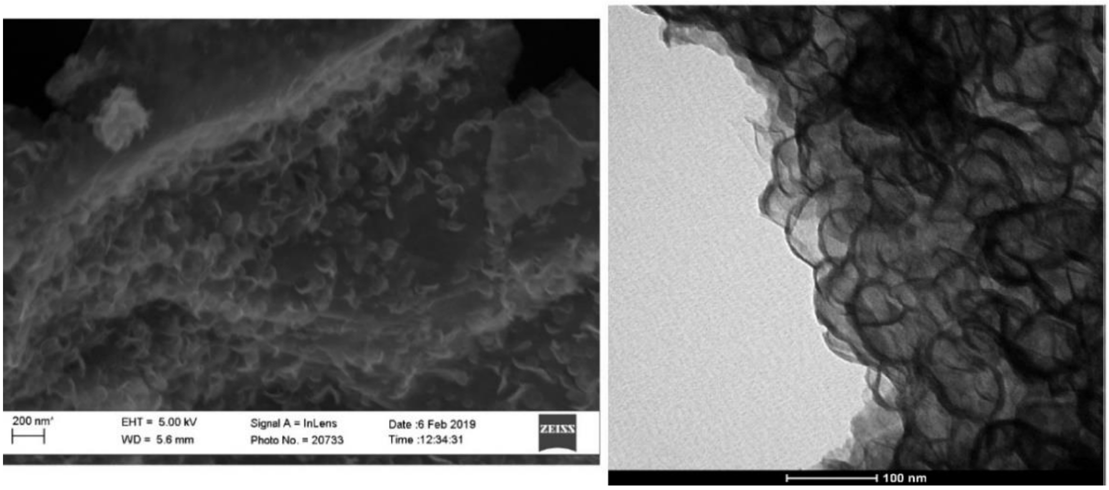

Figure 1: Electronic microscopy images of GO-$MoS_{0.9}$Se1.1 systems obtained by hydrothermal synthesis: Left, SEM of nano-flowers hybrid; Right, TEM image of inorganic fullerene-like material. Stoichiometry is evaluated by XPS.

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Electrochemical conversion of higher alcohols to added value chemicals and energy

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Fuel cells covert chemical energy into electrical energy with high efficiency, resulting in lower or zero emission of pollutants. They can produce energy for as long as the fuel and oxidant supply to the electrodes is maintained. Hydrogen is the best option as fuel, but high pressures are needed to achieve high (volume-related) energy densities[1]. For this reason, liquid alcohols with high volume energy density have been proposed as fuels. In addition to their high-volume energy density, higher alcohols can be obtained from many biological or industrial process. But breaking the C–C bonds is very difficult, and often leads to poisoning of the catalyst. An alternative is the in-principle easier oxidation of an alcohol to the corresponding aldehyde or carboxylic acid. This allows transforming higher alcohols to products with a higher value added at no energy cost or, in particularly favourable cases, coupled to the generation of energy, thereby obtaining a double benefit.

We have attempted to oxidise glycerol, an important by-product of biodiesel production, without breaking its C–C bonds. Our target is to generate using a fuel cell Dihydroxyacetone, Tartronic acid or Mesoxalic acid, all of them with a considerably higher market price than glycerol, with high selectivity and the highest possible energy efficiency.

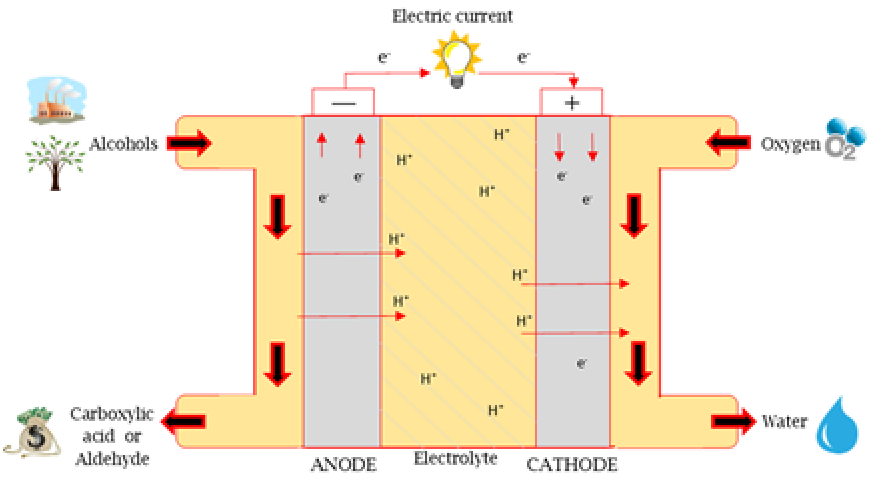

Fig. 1 Example of the fuel cell.

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