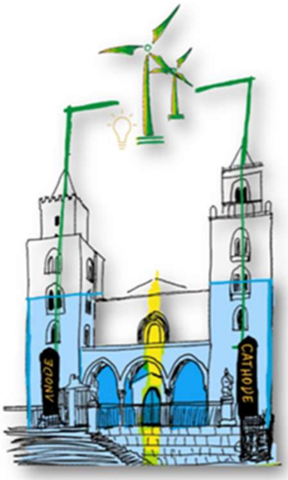

GIORNATE dell' ELETTROCHIMICA ITALIANA

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Hotel Cefalù Sea Palace

Cefalù, Italy

BOOK OF ABSTRACTS

Società Chimica Italiana
DIVISIONE DI ELETTROCHIMICA

Award presentations

Premio di Laurea “Metrohm Italiana”

Synthesis and performance of polymer membranes produced by ionotropic gelation for direct methanol fuel cells

Valentina Maria Volanti[i]

[i] Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy
e-mail presenting author: valentina.volanti@polito.it

A fuel cell is an electrochemical device capable of converting chemical energy, contained in a fuel, directly into electrical energy. In particular, Direct Methanol Fuel Cells (DMFCs), are among the most appealing green technologies in energy supplying for portable electronic devices due to the several advantages related to the usage of methanol aqueous solution, such as high volumetric energy density of methanol (i.e. 4820 Wh L^{-1}) [1], low operating temperature, easy fuel storage and transportation and quick refuelling [2]. One of the key elements for the operation of a PEMFC or DMFC is the polymer electrolyte, i.e., the ion exchange membrane. For the past four decades, Nafion®, manufactured by DuPont, has been used as the polymer electrolyte in DMFCs. However, Nafion® membranes also have some cons, such as high cost and low environmental sustainability of the production process, and most importantly, high methanol permeability, which can lead to a decrease in recorded OCV and catalyst poisoning at the cathode. As possible substitute of Nafion®-based membranes for DMFCs, composite chitosan/phosphotungstic acid membranes (CS/PTA) have been successfully tested as proton exchange membranes reaching high performances at 70 °C [3].

Current strategies to reduce methanol crossover enhancing DMFC efficiency are based on the modification of the polymer electrolyte membrane as barrier to the fuel diffusion. The introduction of filler nanoparticles can make difficult methanol diffusion because of membranes channel blocking inducing steric hindrance for methanol crossover and/or because of an increase in channels tortuosity [4].

In this work we synthesized composite CS/PTA proton exchange membranes with the addition of TiO_2 and Al_2O_3 particles to decrease methanol permeability but keeping high proton conductivity and durability, thus further increasing DMFC performance. The influence of fillers was assessed through X-Ray Diffraction, Scanning Electron Microscopy, liquid uptake, Ion Exchange Capacity and methanol permeability measurements. The addition of TiO_2 particles into proton exchange membranes led to an increase in crystallinity and to a decrease in liquid uptake and methanol permeability with respect to pristine CS/PTA membranes whilst the effect of the introduction of Al_2O_3 particles on the characteristics of membranes is almost the opposite. Membranes were successfully tested as proton conductors in a single module DMFC of 1 cm^2 as active area, operating at 50 °C fed with 2 M methanol aqueous solution at the anode and oxygen at the cathode. Highest performance was reached by using a membrane with TiO_2 (5 wt.%) particles, i.e. a power density of 40 mW cm^{-2}, almost doubling performance reached by using pristine CS/PTA membrane (i.e. 24 mW cm^{-2}). As general trend, all the power density values measured using membranes with the addition of filler, regardless on its nature, were higher than power density obtained by using a pristine CS/PTA membrane.

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Premio di Laurea "Photo Analytical S.r.l."

Non-enzymatic glucose detection: a scanning electrochemical microscopy investigation

N. Martino[1]

[1] *Laboratory of Applied Electrochemistry, Dipartimento di Chimica, Università degli Studi di Milano,*
via Golgi 19, Milano 20133, Italy
nazario.martino30@gmail.com

The continuous monitoring of glucose level in the blood is required to prevent and follow-up several pathologies and is particularly important in wellness and sport. The non-enzymatic detection of glucose becomes a key topic to overcome the low stability of enzimes [1]. This work investigates the glucose electro-oxidation reaction (GOR) mechanism using Pt electrocatalysts by the determination of the glucose amount adsorbed on Pt by means of Surface Interrogation Scanning Electrochemical Microscopy (SI-SECM).

Preliminary tests confirmed that electrogenerated Ru^{2+} can reduce the Pt oxide formed on the substrate [2]. Therefore, a microelectrode, placed at a short distance (5-10 µm) from the Pt electrode, can be used for in-situ generating Ru^{2+} and thus "titrate" the amount of electrogenerated Pt-oxide. We found that the presence of glucose in the electrolyte solution determined a smaller quantity of titrated Pt oxide, indicating a cemical reaction between glucose and PtOxide (or the interference of glucose in Pt-oxide formation) and thus the significant role of Pt and its oxidation states in the mechanism of glucose oxidation (Figure 1).

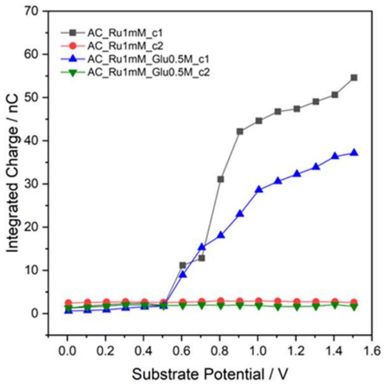

Figure 1. Integrated charge for interrogation of Pt electrodes under different finale substrate potential. Phosphate buffer, pH 7.3 with 1mM $Ru(NH_3)_6Cl_3$ with (blue and green curves) and without (black and red curves) 0.5M glucose.

Therefore, this work confirms the importance of glucose chemisorption on Pt catalysts and validates the most proposed models for non-enzymatic GOR electrocatalysis. The effectiveness of the SECM analytical method was confirmed, also thanks to recent improvements made to UME preparation [3]. Future researches will focus on identifying suitable redox couples for SI-SECM to quantify other reaction intermediates in the GOR.

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Premio di Laurea "Thasar"

Poly(biphenyl piperdinium): Synthesis, characterization and water electrolyzer cell tests of polymer-based anion exchange membrane[1]

A. R. Ferrari,[i] T. Caielli,[i] S. Bonizzoni,[i] E. Sediva,[i] A. Caprì,[j] M. Santoro,[j] I. Gatto,[j] V. Baglio[j] and P. Mustarelli[i]

[i] *Department of Material Science, University of Milano-Bicocca, Via Cozzi 55, 20125-Milano, Italy*

[j] *Institute for Advanced Energy Technology "Nicola Giordano", CNR-Consiglio Nazionale delle Ricerche, Via Salita Santa Lucia sopra Contesse 5, 98126-Messina, Italy*

e-mail presenting author: a.ferrari93@campus.unimib.it

Water electrolyzer cells based on polymer Anion Exchange Membranes (AEMs) allow the use of platinum group metal-free catalyst such as nickel and iron, non-critical raw materials. This reduce the costs of the device and lower the price of green hydrogen. Their scalability and industrial adoption is limited by the poor stability in alkaline environment of the membrane. Tow major degradation mechanisms take place: nucleophilic substitution and Hofmann elimination [1]. New promising class of AEMs are the poli(aryl piperidinium) (PAP), that incorporate an aromatic free-heteroatom backbone with the piperidinium cationic grup [2]. Exceptional stability of N,N-dimethylpiperidinium in alkaline environment is due to the conformation of the six-membered ring that disfavour the Hoffman elimination [3]. The simplest and less expensive polymer of this family is the poli(biphenyl piperidinium), wich has been long considered unsuitable for applications in water electrolyzer due to his poor mechanical properties, excessive water uptale and swelling ratio [4].

Through optimization of the polymerization parameters (stoichiometry of monomers, temperature and time) we obtained a mechanically resistant and thin membrane (≈ 15 μm) with tensile strength of 33.3 ± 0.7 MPa in dry form. Significant reduction of water uptake and swelling ratio corroborate an optimized polycondensation reaction. The membrane reaches an ambitious ionic conductivity of 185 mS cm^{-1} (80 °C, 100 % RH) and is chemically stable for 360 h in 1 M KOH at 80 °C. Finally, we performed electrolyzer cells test achieving superior performance than the PAP-commercial membrane (Figure 1) (PiperION^{TM}).

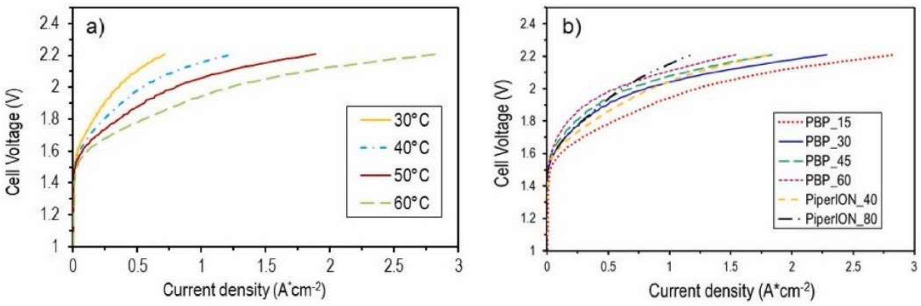

Figure 1: a) J-V curves of the poly(biphenyl piperidinium) with thickness of 15 μm. b) Comparison of J-V curves at 60 °C of the home-made PBP and PiperION^{TM}.

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Premio di Dottorato "Fondazione Oronzio e Niccolò De Nora"

Electrochemical Biosensors for Characterization of Cancer Metabolism

Simona De Zio[i], Marco Malferrari[i] and Stefania Rapino[i]

[i] *Department of Chemistry "Giacomo Ciamician", University of Bologna, Via F. Selmi 2, 40126 Bologna, Italy*
e-mail presenting author: simona.dezio2@unibo.it

The study of cancer metabolism has a great importance for cancer research, as metabolic heterogeneity plays a fundamental role in therapy resistance and disease poor outcome. The characterization of metabolic heterogeneity is fundamental to understand cancer development, metastasis, and therapy resistance. [1] Electrochemical biosensors, used as probes of the Scanning Electrochemical Microscopy technique, can be useful tools to characterize, with a high spatial resolution, the concentrations of key-player metabolites of tumor microenvironment (*e.g.* glucose and lactate). The PhD project was focused on the development and optimization of enzyme-based biosensors able to detect glucose and lactate concentrations both at single cell level and in *ex vivo* tissue samples.

Glucose micro-biosensors developed through pyrrole electropolymerization on Pt microelectrodes in presence of a redox mediator, demonstrated to be suitable to detect glucose also in hypoxic conditions and were employed to investigate the glucose consumption profile of single breast cancer cells in a hypoxic medium. [2]

Lactate and glucose micro-biosensors were used as SECM probes *i)* to characterize the metabolism of 3D cancer models obtained by 3D-bioprinting and *ii)* to obtain information on the lactate levels in ovarian cancer; in this latter study, the electrochemical measurements for the quantification of lactate levels were coupled with histological and immunohistochemical investigations. This unique approach allows to study the tumor metabolic heterogeneity of ovarian cancer.

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Premio di Dottorato "Fondazione Oronzio e Niccolò De Nora"

Smart and sustainable point-of-care electrochemical devices

Luca Fiore[i,z]

[i] *Department of Chemical Science and Technologies, University of Rome "Tor Vergata", Italy*
[z] *Sense4Med srl, via Bitonto 139, Rome, Italy*

e-mail presenting author: luca.fiore@uniroma2.it

The growing need to have rapid and user-friendly analyses has recently led to the diffusion of miniaturized, portable, and easy-to-use analytical tools. Today, laboratory testing is still crucial, but over the years the need for performing analysis outside the laboratory has become important. In this contest, Point-of-care (PoC) systems have been extensively developed. These devices can perform fast analysis to evaluate the status of patient health in timely fashion. The ideal PoC test should be cost-effective and user-friendly giving a rapid response. Furthermore, PoC devices should be designed in order to show the following features: robustness, selectivity, and sensitivity. The PoC output signal depends on the transducer used. The most common are optical and electrochemical, such as pregnancy tests and glucose-meters, respectively. Furthermore, in the last years, research is focusing on the use of sustainable and cost-effective approaches. To this regard, paper is an obvious choice as a support material, thanks to its wide range of outstanding properties, such as low cost, eco-sustainability, versatility, affordability, and biocompatibility. Indeed, paper can be used to fabricate microfluidic system integrated into the PoC devices, conferring to these smart analytical tools several fascinating features, such as i) the sampling of the real matrices; ii) the management of the solution flow without external equipment; iii) its use as a reservoir to contain the reagents by loading the paper network with a few µL of the reagent solution; iv) its capability to pre-concentrate the sample by adding several aliquots of the sample through several steps and thus increasing the sensitivity of the measurement, and v) the absence of any additional system for the detection of the target analyte in the aerosol phase. Paper-based devices have multifarious properties that have been exploited in combination with different nanomaterials to realize devices customized to specific applications. In Chapter 1, some of the most relevant examples reported in the literature are described. In this scenario, during my PhD period, the research was focused on developing PoC devices for biomedical applications, combining the electrochemical-based analytical tool with a paper-based system, employing the properties of the paper substrate in different ways. In the first work (Chapter 2), I demonstrated the possibility of using a filter paper pad to sample sweat for pH monitoring during physical activity. Investigating new methods to employ the features of the cellulose network, in the second work (Chapter 3), the filter paper was used as a reservoir to contain all the reagents necessary for glucose detection in tear samples. In Chapter 4 we demonstrated the suitability of using office paper as a substrate to print the screen-printed electrodes, delivering eco-friendly, easy-to-use, and disposable devices for iron detection in serum. To further explore the paper features potentially applicable to PoC systems, in Chapter 5 the peculiarity of the paper was used not only as a support to print the screen-printed electrodes, but also to exploit the porosity of the paper network to load the analyte directly in the aerosolized phase. Overall, in these chapters, I demonstrated the suitability of the paper to easily sample the solution, to use it as a reservoir of all the reagents needed for the measurement, and as a support to print the screen-printed electrodes. In another successful example of exploiting paper in PoC devices (Chapter 6), I designed a microfluidic wearable immunosensor completely integrated with a paper-based system for cortisol detection.

Another part of my research work dealt with the development of PoC devices with the final goal to design sensing system to be industrially scalable. In this case, polyester was chosen as the support for producing the screen-printed electrodes, because the high robustness of this material meets the requirements of mass-production at the industrial level.

Premio di Dottorato “Engitec Technologies”

Study of materials and interphases for electrochemical energy storage from renewable sources

Giampaolo Lacarbonara

University of Bologna, Department of Chemistry “Giacomo Ciamician”
Via F. Selmi, 2, 40126, Bologna, Italy
giampaol.lacarbonar2@unibo.it

Higher demand for energy storage systems accompanies the concept of electrification. Ideally, new technologies must have an ever-higher energy density, lower costs, more extended durability, and the use of more sustainable materials. Nowadays, mostly lithium-ion batteries are used for different purposes. Batteries should be refined depending on their application in a future in which sustainable energy demand increases. On the one hand, it is fundamental to improve their safety, prevent failures and damages, increase energy density, and reduce production costs.On the other hand, new battery materials and architecture are required to satisfy the growing demand. A clear understanding of materials and processes during operation must be established to move these technologies closer to realization. This thesis explores different electrochemical storage systems and new methodologies to investigate complex and dynamic processes to make the future battery even more reliable.

In Li-ion systems, in-situ electrochemical dilatometry has been used to predict structural changes and the related processes of a model electrode. On the material side, a MnOx–graphitic carbon composite obtained by electrolysis of CO_2 via molten Li_2CO_3 is characterized and used to prepare a negative electrode for LiBs with an environmentally sustainable aqueous process.

One strategy to achieve a high energy density storage system is to employ lithium metal anodes. In this framework, controlling the lithium electrolyte interphase is fundamental to limit the uncontrolled dendritic deposition responsible for safety issues. Ammonium hexafluorophosphate is demonstrated to be a suitable additive for modifying the interphase. Galvanostatic deposition/stripping cycles, electrochemical impedance spectroscopy, in situ optical microscopy, and operando confocal Raman spectroscopy have been used to study lithium metal-electrolyte interphase in the presence of the additive.

RFBs are proposed as an ideal choice for large stationary applications because of the low-cost and earth-abundant materials employed. An all-copper aqueous RFB (CuRFB) has been studied in all its aspects. The stabilization of cupric cations in the aqueous electrolyte is solved by complexation with chloride anions. Spectro-electrochemical tests in diluted solutions have been used to get information on the electrochemical behavior of electrolytes with different chlorocomplexes distributions. In concentrated solutions, electrolyte composition was optimized by varying copper-to-chloride ratios and the counter-ion of the chloride complexing agent. On the electrode side, carbon activation was optimized to improve the kinetics of the reaction. The effect of the modification was studied in terms of reactivity at the interface and RFC performance. One of the main obstacles to RFB commercialization is the crossover of the redox species through the membrane. A new method for permeability studies was designed using scanning electrochemical microscopy (SECM). The Cu(II) permeability of several commercial and modified membranes was tested, obtaining direct visualization of copper (II) concentration in space. To monitor the effect of the crossover, a novel system for monitoring the state of charge (SoC) during the RFB operation was designed and assessed.

Premio di Dottorato “in Memoria del Prof. Armando Gennaro”

M-N-C Electrocatalysts Supported on Engineered Carbon Materials for the Reduction of Oxygen

M. Mazzucato, C. Durante

Dept. of Chemical Science, University of Padova, Via Marzolo 1, 35131, Padova, Italia
e-mail presenting author: marco.mazzucato@unipd.it

Fuel cells represent a valid alternative to traditional energy sources that use fossil fuels since H_2 and O_2 are respectively used as fuel and oxidants in a reaction that mainly produces H_2O. In general, those devices include the electrochemical reduction of oxygen (ORR). This reaction is well known and studied since it has slow kinetics and therefore requires large quantities of catalysts. The reaction could proceed toward two different pathways, a 2 electrons reaction giving H_2O_2 and a 4 electrons reaction giving H_2O. Speaking of fuel cells, and therefore of the 4-electrons route, for the commercialization of these devices, the traditional catalysts based on Pt-supported carbon must be replaced with cheaper materials. Carbonaceous supports with a discrete porous structure, doped with N and Fe, have proven to be able to catalyze the reduction of O_2 with performances that can approach Pt-based materials. Although numerous studies have been conducted on the subject, there is still a strong debate on the nature of active sites (FeN_x) in these systems and, in particular, on how the experimental conditions of synthesis allow to control their formation. One of the fixed points of these studies, which normally still combine spectroscopic techniques with electrochemical techniques, is that the primary centers of O_2 reduction to H_2O are the FeN_4 sites, however, the conditions that lead to the formation of these sites and the quantification require a in-depth study. In this Ph.D. project different M-N-C-based materials have been studied to evaluate the influence of the porosity of the carbonaceous support on the formation of the Fe-N and C-N sites and consequently on the electrocatalytic activity, confirming the role of microporosity [1]. Also, the effect of the precursors of Fe and N was studied showing that $Fe(phen)_3Cl_2$ is a desirable choice [2]. Later bi-metallic systems were studied, by adding Sn to the mixture [3], and finally, the study of the C-N group was achieved by grafting organic molecules on the surface. One big part of the project was to show that gas diffusion electrode (GDE) setups are perfectly suitable for these materials and allow to completion of the information obtained with typical rotating electrode (RRDE) analysis [4]. All materials were studied by deeply combining physicochemical and electrochemical characterization techniques. Figure 1 summarizes the studied effects.

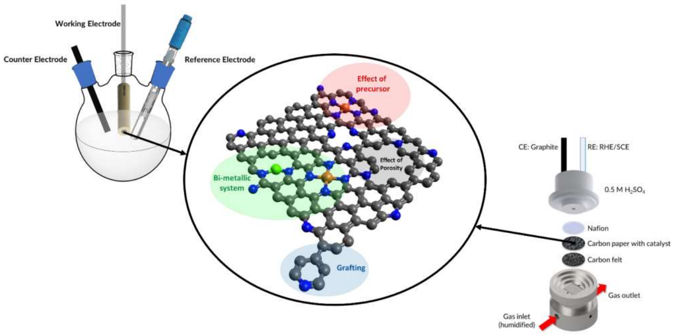

Figure 1: Covered topics in this PhD thesis project

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Premio “Luisa Peraldo Bicelli”

Oxygen reduction reaction on iron-phthalocyanine derived electrocatalysts: effects of temperature on surface chemistry and performance

Carlo Santoro,[i]

[i] *Electrocatalysis and Bioelectrocatalysis Laboratory (EBLab), Department of Material Science,*
University of Milan Bicocca, U5, Via Cozzi 55, 20125 Milan, Italy
e-mail presenting author: carlo.santoro@unimib.it

Fuel cells (FCs) are electrochemical devices capable of converting hydrogen into electricity. Within an FC, the oxygen reduction reaction (ORR) is the limiting reaction exhibiting sluggish kinetics, therefore high loading of precious metals is required. The switch to an alkaline environment helps in replacing platinum group metals (PGMs) with more affordable PGM-free materials. Atomically dispersed transition metals (TMs) coordinated in pyridinic nitrogen on a carbon backbone have shown to be promising electrocatalysts with important ORR electrocatalytic activity. In general, Fe-N$_x$-C (x = 2, 3, 4) is the most active electrocatalyst. The synthetic method to fabricate these materials is based on pyrolytic processes with controlled temperature and atmosphere. During pyrolysis, the morphology and the surface chemistry change prominently and these features in turn govern the ORR electrocatalytic activity. However, the processes occurring during pyrolysis are quite unknown and therefore deserve high attention as they led to the determination of the surface chemistry and morphology. Recently a couple of manuscripts investigating in-situ the morphological features that have been presented [1-2].

In this study, the effects of pyrolysis temperature (200-1000°C) and atmosphere (Ar or Ar/H$_2$) on the surface chemistry and morphology of the electrocatalyst were studied. Iron (II) Phthalocyanine (FePc) was bmixed with Ketjen Black and subjected to pyrolysis at different temperatures and atmospheres and hence the derived catalysts were scrutinized for ORR electrocatalysis. The surface chemistry and morphology were then correlated with the catalytic activity in alkaline and acidic media studied using the rotating ring disk technique (RRDE) through a structure-to-property relationship.

In the presented study, we show that the pyrolysis conditions affect importantly the nature and the proportion of the active sites considering both Fe-based and N-based that are crucial for the ORR pathway and kinetics in both extremes media. Temperature above 500-600°C led to the formation of nanoparticles of Iron oxides. X-ray photoelectron spectroscopy (XPS) showed the presence of numerous nitrogen-based functionalities including the Fe-N$_x$ moieties evaluated from the N1s spectra deconvolution. Their concentration varies with the different pyrolysis conditions.

Through RRDE, the electrocatalytic activities towards ORR in acid and alkaline environments were elucidated. In acidic media (0.5 M H_2SO_4), Fe-N$_x$-C synthesized at 600 ºC under both Ar and Ar/H$_2$ showed higher electrocatalytic activity, with half-wave potentials ($E_{1/2}$) of 0.70-0.72 V (vs RHE) producing low peroxide. A similar trend was detected in alkaline media (0.1 M KOH) but higher performance compared to the acid media was recorded. A prompt reduction in the performance was highlighted at higher pyrolysis temperatures (>700°C) where peroxide yield increased. The relationships between surface chemistry and morphology and electrochemical performance were clarified. This work presents a novel insight into the evolution of Fe-Nx-C electrocatalysts during pyrolysis with optimum performance.

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Oral presentations

Keynote Lecture

Graphene and related materials, from production to applications

Andrea C. Ferrari

Cambridge Graphene Centre, University of Cambridge, Cambridge, CB3 OFA, UK.
e-mail address: acf26@cam.ac.uk

Disruptive technologies are usually characterised by universal, versatile applications, which change many aspects of our life simultaneously, penetrating every corner of our existence. In order to become disruptive, a new technology needs to offer not incremental, but dramatic, orders of magnitude improvements. Moreover, the more universal the technology, the better chances it has for broad base success. Significant progress has been made in taking graphene and related materials from a state of raw potential to a point where they can revolutionize multiple industries. When it comes to electrochemical applications, Raman spectroscopy is an ideal non-destructive technique to study degradation in graphite anodes, as it is sensitive to doping, strain, defects, and interlayer coupling. I will discuss how in-situ Raman spectroscopy can unravel the signatures of Li-ion induced doping, intercalation staging and degradation upon cycling.

Keynote Lecture

Green hydrogen production by advanced electrolysis technologies

A. S. Aricò,[i]

[i] *Istituto di Tecnologie Avanzate per l'Energia "Nicola Giordano" - Consiglio Nazionale delle Ricerche - CNR-ITAE*
Via Salita S. Lucia sopra Contesse, 5 Messina, Italy
arico@itae.cnr.it

Europe is rapidly progressing towards a decarbonised energy system. An increasing use of renewable energy sources is expected to cause significant energy management issues. Water electrolysis supplied by renewable energy is the most important technology for producing "green" hydrogen for a variety of applications including transport, heat and electricity production, and industrial uses, e.g. ammonia, methanol, steel making processes etc. However, current alkaline electrolysers that make use of relatively cheap materials are characterised by poor dynamic behaviour and operate at low current densities [1]. On the other hand, conventional PEM electrolysers require a significant loading of platinum-group metals (PGMs) and make use of expensive titanium bipolar plates and diffusion media [2]. These aspects presently limit the possibilities for large-scale applications. A step-change in technology and operating conditions in terms of increase of current density and hydrogen pressure is needed. A novel approach in water electrolysis technology regards the use of a thin anion exchange membrane (AEM) and ionomer dispersion in the catalytic layer for hydroxide ion conduction [3]. This system combines the advantages of both proton exchange membrane and liquid electrolyte alkaline technologies allowing the scalable production of low-cost hydrogen from renewable sources. Another alternative is a PEM water electrolysis technology operating at high current density (4-5 A cm-2) to significantly reduce the capital costs. Recent innovations in terms of materials and systems for proton and anion exchange membrane water electrolysis, developed in the framework of various EU projects, are discussed. The focus regards the challenges addressed to make such technologies highly performing, durable and economically competitive.

Acknowledgement
The financial support from the Horizon Europe ADVANCEPEM project is acknowledged. This project is supported by the Clean Hydrogen Partnership and its member, including top-up funding by the UK Research and Innovation (UKRI), under grant agreement No 101101318.

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Keynote Lecture

Perspective of Redox Flow Batteries towards Long Duration Energy Storage

Luca Magagnin

Dip. Chimica, Materiali e Ing. Chimica G. Natta, Politecnico di Milano
e-mail presenting author: luca.magagnin@polimi.it

Long duration energy storage (LDES), as a system able to store energy for more than 10 hours, is a key point for solving the intermittency issues with renewable energy production. While shorter-duration energy storage (SDES) (usually 1-4 hours) can support some renewable energy generation intermittency, as more and more renewables are added to the grid, LDES is needed to store energy to be dispatched during long stretches when solar or wind are not producing [1]. Redox Flow Batteries RFBs have emerged as relevant candidates to address the sustainable energy generation, considering their unique capability to decouple power and energy. At the moment, among all RFBs systems, the most investigated and advanced technology is the vanadium based RFB, characterized by an energy efficiency equal to 80% and energy density ranging 15-45 Wh/l [2]. However, nowadays the main bulk of research is focused on finding an economically convenient and technically competitive flow battery chemistry, able to ensure long lifetime and high energy efficiency [3,4].

In this study, electrochemical LDES will be discussed in terms of sustainability, introducing vanadium free RFBs able to withstand a large number of charge/discharge cycles at low costs, making this battery systems suitable for energy storage in long duration applications.

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Keynote Lecture

Quantitative Selective Measurements of sub-Millisecond Dynamics of ROS/RNS Production During Phagocytosis with a Nanoelectrochemical Sensor

Christian Amatore,[1,2] Yu-Ting Qi,[3] Hong Jiang,[3] Wen-Tao Wu,[3] Fu-Li Zhang,[3] Si-Yu Tian,[3] Wen-Ting Fan,[3] Yan-Ling Liu,[3] Irina Svir,[1] Alexander Oleinick,[1] Wei-Hua Huang[3]

[1] *PASTEUR, Chemistry Department, Ecole Normale Superieure, CNRS, PSL Research University, Sorbonne University, 24 rue Lhomond, Paris 75005, France.*
[2] *State Key Laboratory of Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China.*
[3] *College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, P. R. China.*
e-mail address: christian.amatore@ens.psl.eu

Macrophages are an important class of immune innate cells that typically act as a first-line of defense against disease as they engage in phagocytosis, viz., in a series of complex mechanisms by which the macrophage engulfs and digests pathogens and damaged or non-functional cells. Phagocytosis is performed within intra-cytoplasmic organelles known as phagolysosomes, in which the engulfed pathogen or cellular debris are submitted to intense fluxes of reactive oxygen and nitrogen species (ROS and RNS, respectively) which eventually breaks them down into their molecular components. However, it is clear that the amount of produced ROS and RNS has to be proportioned to their consumption while engaged in the digestion of what has been trapped inside phagolysosomes. In the opposite case either the macrophage action is not fully efficient or, worst, may alter its own intracellular components [1]. This raised the hypothesis of ROS/RNS homeostasis within the performance of immune function, although this could never be demonstrated. Hence, the possibility to quantitatively and individually monitor the four corresponding primary ROS/RNS (ONOO-, H2O2, NO, and NO2-) with sub-millisecond resolution at the single cell level was clearly warranted to elucidate the still unclear mechanisms of their rapid generation [2,3] and to track their concentrations variations over time inside phagolysosomes. To achieve this goal, a novel nanometric cylindrical electrode was specifically designed for this purpose [4]. Its fabrication involved covering a commercial silicon carbide (SiC) nanowire with a dense monolayer of 3 nm platinum nanoparticles whose high electro-catalytic performances allowed the characterization and individual continuous measurements of each of the four primary ROS/RNS. This allowed for the first time a quantitative, selective and statistically robust determination of the individual amounts of ROS/RNS initially present in single phagolysosomes and of their differential kinetic production while they are consumed, a process that mimics the physiological homeostasis. Indeed, the sub-millisecond resolution of the nanosensor allowed the kinetic measurement of the rapid ability of phagolysosomes to generate each of the four primary ROS/RNS and evidenced that they do so by adjusting differentially their enzyme pools of NADPH oxidases (NOX, generating superoxide) and inducible nitric oxide synthases (iNOS generating NO) as a function of time to finely regulate their homeostasis. This work has revealed an unsuspected but essential point, key of our immune responses and precious for the development of immunotherapies by demonstrating and rationalizing the biomolecular basis of homeostasis inside macrophages undergoing phagocytosis.

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Keynote Lecture

Sensors for Sustainable Agriculture & the Environment

Alan O'Riordan

Nanotechnology group, Tyndall National Institute, University College Cork, Dyke Prade, Cork, Ireland
e-mail address: alan.oriordan@tyndall.ie

With the global population expected to grow to over 9.6 billion by 2050 it is a projected that a 50-60 % increase in food production will be required. A key challenge then, going forward, will be to sustainably close the food gap. This must be achieved against the backdrop of climate change & desertification, labour shortages and competition for energy, land & resources. It is clear then, that addressing this challenge will require the development of more efficient and sustainable food production techniques and processes. To this end, new digital technologies, that are fit for purpose, are urgently required to digitise the entire food chain. This convergence between the Internet of Things (IoT) and the agri-food industry requires sensor systems and technologies that provide real time data to producers and processers; required for rapid, but informed, decision making. This talk will provide an overview on current problems in agriculture and demonstrate application of digital technologies developed within our group can address the sustainability issues currently being experienced in this sector.

Keynote Lecture

Design of Aerogel-based Electrocatalysts for Oxygen Reduction Reaction in Fuel Cells

L. Elbaz

Department of Chemistry, Bar-Ilan University, Ramat-Gan 529002, Israel
e-mail presenting author: lior.elbaz@biu.ac.il

Great advancements have been made in the past couple of decades in the development of platinum group metal-free (PGM-free) oxygen reduction reaction (ORR) catalysts based on earth-abundant elements such as nitrogen, carbon, and first-row transition metals (usually Fe or Co, but also Cu and Mn). This work has been mostly inspired by biological systems where some of the catalytic centres are composed of complexes of metallo-porphyrins and phthalocyanines. These molecular catalysts show fair, but not exceptional ORR activity and stability. In order to increase the performance of transition-metal complexes, a new class of high temperature-treated (HT-treated) catalysts, composed of the same elements, i.e., a transition metal, carbon and nitrogen, has been developed. Although some improvements were made, the performance of HT-PGM-free ORR catalysts remains inferior to PGM catalysts, calling for further improvements in order to make them a viable alternative to the state-of-the-art materials. One such direction is the increase of the active site density, and catalyst utilization to mitigate their intrinsically low turnover frequency (TOF).

In this work, we designed, synthesized, and characterized ORR catalysts based on iron and/or copper, carbon and nitrogen in a well-defined, high surface-area covalent framework (COF) of aerogels. Aerogels are ultralight, porous materials, with ultra-low density, and high void volume (> 97%), also known for their unique physicochemical properties such as high porosity, controllable pore size and surface area, just to name a few. The variety of precursors used for aerogel synthesis makes them promising candidates for a wide range of applications in catalysis, capacitors, insulators, absorbents, and many more. In the context of electrocatalysis of fuel cells' reactions, carbon-aerogels have been mostly used so far as catalysts' supports for PGM and PGM-free catalysts.

In their inorganic form, aerogels can have ultra-high catalytic site density, high surface area, and tuneable physical and chemical structures - all very important features for a heterogeneous catalyst. In this talk, I will discuss the synthesis and electrocatalytic properties of several transition metal-based aerogels developed in my research group. For example, at the beginning of our work on this topic, we synthesized an aerogel based on 5,10,15,20-(tetra-4-aminophenyl)porphyrin (TAPP) and Fe(II), which was later heat-treated at 600°C to enhance its electronic conductivity and catalytic activity while preserving its macro-structure. The resulting material has a very high concentration of atomically dispersed catalytic sites (4.01·1019 sites cm-3), capable of catalyzing the ORR in alkaline solution very well (Eonset = 0.93 V vs. RHE, TOF = 0.2 e- site-1 s-1 at 0.8 V vs. RHE). I will present the work we conducted on this topic and include some of our most recent unpublished results with bi-metallic complexes which show exceptional performance.

Keynote Lecture

Electrochemical characterization of shape memory steels in aqueous solutions

C. Pérez, A. Collazo, B. Díaz, R. Figueroa, X.R. Nóvoa

ENCOMAT Group, CINTECX, Universidade de Vigo, Campus Universitario As Lagoas,
36310 Vigo, Spain
e-mail presenting author: cperez@uvigo.es

The Fe-based Shape Memory Alloys (Fe-SMAs) are smart materials with shape memory effect, which is based on the stress-induced martensite transformation from α(fcc)-austenite to ε(hcp)-martensite by the action of stress, and the reverse transformation (ε → α) by heating. The Fe-SMAs have great potential in civil engineering structures, mainly for constrain recovery applications such as pipe joins, rails couplings, or pre-stressing reinforced elements [1]. Most of the studies are focused on the structural and thermomechanical characterization of these Fe-SMAs, and only a few addressed their electrochemical characterization. This aspect is important to understand the corrosion behaviour under different conditions.

The present work is focused on the electrochemical behaviour of two types of Fe-SMAs, with nominal composition of Fe28Mn6Si5Cr and Fe17Mn5Si10Cr4Ni1(VC). An artificial oxide film was generated by cyclic voltammetry in 0.1 M KOH + 0.1M NaOH (pH=13) solution. The film was characterized by Electrochemical Impedance Spectroscopy (EIS) technique, and the thickness was assessed by means of X-ray Photoelectron Spectroscopy (XPS) technique. The Mott-Schottky approach was used to assess the semiconducting character of the generated films. For comparative purpose, the same measurements were carried out in B500 SD steel and AISI 304L. Figure 1 illustrates the 6th cycle in all samples. Significant differences are observed that should be related to the presence of the alloying elements [2].

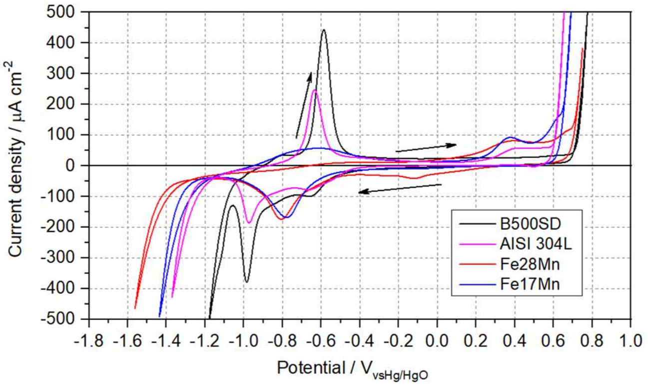

Figure 1: Cyclic voltammograms (6th cycle) for the studied samples performed at 5mV·s^{-1} scan rate in 0.1 M NaOH + 0.1 M KOH solution.

The behaviour of passive film in aggressive conditions, namely the presence of chlorides or the loss of alkalinity (decrease in pH) was also evaluated by cyclic voltammetry technique. The results confirm the best behaviour of the AISI 304L followed by Fe17Mn and Fe28Mn. The most sensitive to these aggressive conditions was the mild carbon steel (B500 SD sample).

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Keynote Lecture

Electrochemical interfaces to produce renewable fuels and chemicals

M. Escudero-Escribano

ICREA and Catalan Institute of Nanoscience and Nanotechnology, UAB Campus, 08192 Bellaterra, Barcelona (Spain)
maria.escudero@icn2.cat

Tailoring the structure of electrochemical interfaces and active sites at the atomic and molecular levels is key to elucidating the design principles for the development of advanced materials for renewable energy conversion, as well as the production of green fuels and chemicals. This talk will focus on our recent work on electrified interfaces and advanced materials for electrochemical energy conversion reactions, such as oxygen and carbon dioxide/carbon monoxide electrocatalysis.

First, I will present our work toward understanding and tuning the structure-activity-stability relations for oxygen reduction [1,2] and oxygen evolution [3] for the production and utilisation of green hydrogen in fuel cells and water electrolysers. Then, I will show our model studies on well-defined Cu-based surfaces to understand structure-properties relations for CO_2 reduction [4-6]. We have investigated the effect of pH, specific anion adsorption and potential dependence for CO reduction on Cu single crystals [4,5] as well as methods to evaluate the distribution of domains on Cu-based catalysts [7]. Finally, I will discuss some strategies for selective oxidation reactions such as formic acid oxidation [8] and partial oxidation of methane to methanol [9].

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Structural and electrochemical characterization of cellulose derived Carbon aerogels

P. Atanasio,[i] F. A. Scaramuzzo,[i] M. Pasquali,[i,] M. Rossi[i, z]

[i] *Department of basic and applied science for engineering SBAI, Sapienza Univeristy of Rome, Via Antonio Scarpa 14/16, 00161, Italy*
[j] *Interdepartmental research center on nanotechnologies applied to engineering of Sapienza CNIS, Sapienza Univeristy of Rome, Piazzale Aldo Moro 5, 00161, Italy*
e-mail presenting author: pierfrancesco.atanasio@uniroma1.it

Carbon aerogels (hereinafter CAs) are unique porous solids made of a network of interconnected carbon structures. Thanks to properties as low density, electrically conductive frameworks, chemical stability, high surface to volume ratio and continuous porosities, they have been widely studied for applications in many fields, e.g. hydrogen adsorbents, supports for catalyst, energy storage [1].

CAs can be fabricated from a wide spectrum of starting materials, such as organic monomers, polymers or biomasses. Regardless of precursors, the production process always involves three fundamental steps: gelation, drying and carbonization [2].

The aim of this work is to study the structural, morphological, and electrochemical properties of light and stable CAs obtained by cellulose purified from Rice Husk (hereinafter RH). RH is the outer covering of rice and it is a green, economical, abundant, nontoxic, and biodegradable source of carbon. It is mostly made of cellulose, lignin and hemicellulose, but also of inorganic components as silica [3].

Purification of cellulose occours with a two step pretreatment with sodium chlorite in acetic acid and sodium hydroxide. The gel is obtained dissolving cellulose in a solution of sodium hydroxide and urea in water and regenerated with pure water, freeze dried and carbonized in Ar atmosphere at 800°C.

A full characterization of the thus obtained CAs has been performed by using different analytical techniques, aimed at understanding behaviour and best potential applications. Morphology, composition, and dimensions have been evaluated by scanning electron microscopy, X-ray tomography and energy dispersive X-ray spectroscopy. X-ray diffraction and Raman spectroscopy have been used to investigate structures and graphitization. Pores dimension and distribution have been observed by BET analysis. Electrochemical behaviour has been studied with cyclic voltammetry and ciclations in order to further evaluate CAs performance as electrodes.

This study represents a first step to fully understand the potential of rice husk as a green source for carbon aerogels and its most promising applications, and it paves the way to additional investigations towards the valorization of a low value agricultural waste.

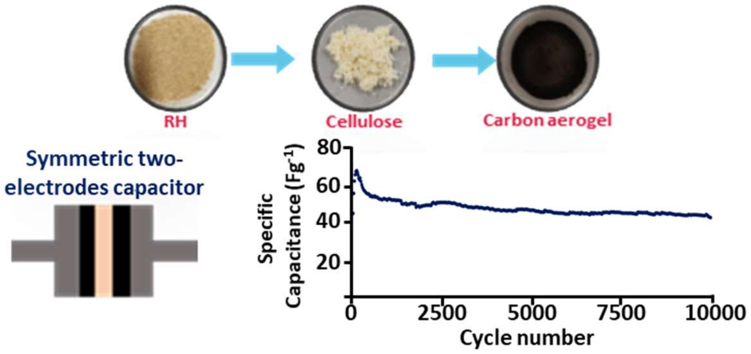

Figure 1: CAs production synthetic pathway, scheme of a two electrodes symmetric supercapacitor and Cycle life of a CAs supercapacitor at a charge/discharge current density of 0.1 Ag-1 for 10000 cycles

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Differences between graphite and disordered carbon anodes for high-power Li-ion batteries

M. Lagnoni,[a] S. Ahn,[b] D. Chernyshov,[b] A. Bertei[a]

[a] *Dept. of Civil and Industrial Engineering, University of Pisa, Largo Lucio Lazzarino 2, IT 56126-Pisa, Italy*
[b] *HE Carbon Supercap Ltd, 32 Telford way, GB W3 7XS-London, United Kingdom*
e-mail presenting author: marco.lagnoni@unipi.it

The increasing demand for Li-ion batteries necessitates the development of batteries capable of fast-charging in low time. However, limitations in mass transport and kinetic factors within battery electrodes, especially at the anode, bottlenecks fast-charge performance and induces parasitic processes (e.g., lithium plating), which can significantly reduce battery capacity. Graphite, the most widely used anode material, exhibits suboptimal fast-charge performance due to phase separation during lithium intercalation, leading to capacity degradation [1]. Disordered carbon anodes have emerged as a potential alternative to graphite, offering high capacity retention and resistance to lithium plating. However, a comprehensive understanding of the physical processes underlying their improved performance compared to graphitic electrodes is still lacking.

In this study [2], we employ electrochemical analysis and a validated multi-physics model [1,3-4] to identify and quantify the chemical and physical origins of performance differences between state-of-the-art graphite and nanocluster carbon (a disordered carbon) anodes during fast-charging. Our model, validated against galvanostatic intermittent titration techniques (GITT) and charge/discharge curves, predicts the Li concentration distribution at the particle scale, revealing the effects of various intercalation mechanisms on fast-charge performance (Figure 1). By quantifying the contributions of activation, concentration, and diffusion overpotential losses to the electrochemical response, we elucidate how the active material influences charge transfer kinetics and solid-state lithium diffusion. Unlike graphite, nanocluster carbon enables lithium insertion without phase separation, facilitating faster lithium diffusion, improved volume utilization, and reduced charge transfer resistance. Consequently, nanocluster carbon demonstrates enhanced performance and higher capacity retention during fast-charge than graphite. To demonstrate the practical implications of these material phenomena, we fabricate multi-layer pouch cells with nanocluster carbon anodes, which withstand over 5,000 fast-charge cycles at 2C without significant degradation (Figure 2).

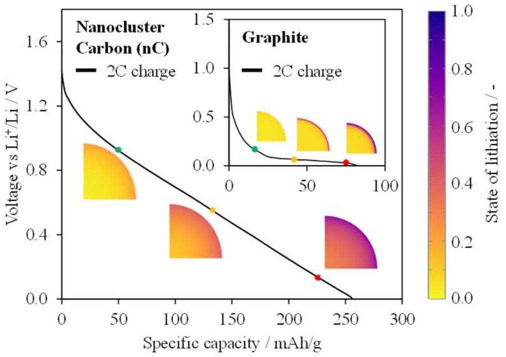

Figure 1: model prediction of Li-concentration during high-rate charge

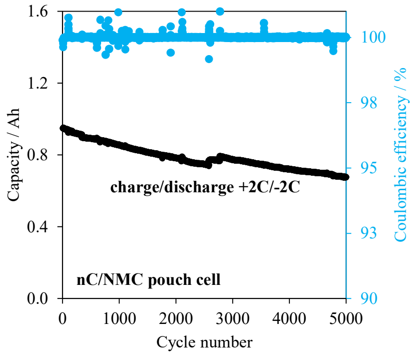

Figure 2: nC/NMC multi-layer pouch cell performance cycled at 2C charge/discharge

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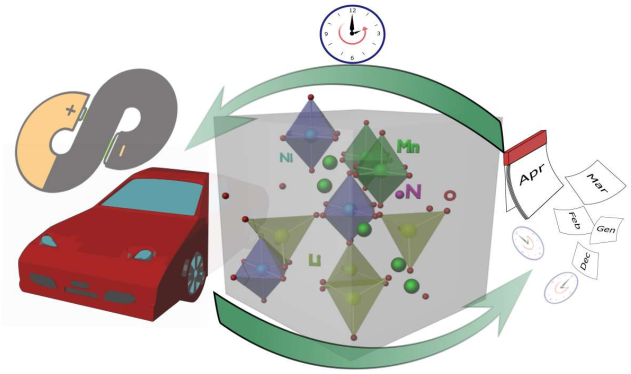
Enhancing the stability of LNMO high-voltage cathode by Mg and Zr dual modification

L. Balducci[a], H. Darjazi[b], F. Nobili[a,c]

[a]*School of Science and Technology - Chemistry Division, University of Camerino, Via Madonna delle Carceri, ChIP, 62032 Camerino, Italy*
[b]*GAME Lab, Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi, 24, 10129, Torino, Italy*
[c]*GISEL—Centro di Riferimento Nazionale per i Sistemi di Accumulo Elettrochimico di Energia, INSTM, via G. Giusti 9, 50121 Firenze, Italy.*

Energy transition philosophy is moving toward the synthesis of green, suistainable and long-life energy storage systems. $LiNi_{0.5}iMn_{1.5}O_4$ (LNMO) cathode material attracts great interest form research field as cobalt-free and high voltage material for LIBs[1]. Despite the high number of studies on this cathode the perfomance degradation still lacks of investigation and suitable solutions, especially at high temperature. Thanks to its high voltage and high theoretical energy density of 650 Wh Kg^{-1} and 4.7 V (vs Li/Li^+) , respectively, LNMO is regarded as a promising candidate as high voltage cathode material[2]. Despite these proprieties LNMO suffer from capacity fading that associated with Mn dissolution into the electrolyte and multiple phase transition upon charge and discharge processes, especially at high rates and temperatures, thus limiting its commercialization[3]. Herein we propose a structural modification by combined Mg and Zr to limite these drawbacks. This modication strategies greatly ehnance the cycling stability up to 1000 cycle at both 25°C and 50°C. Finally, we shed light on the electron and ion transport behaviours during oxidation and reduction by electrochemical impedence spectroscopy. The low cost modifications coupled with the demonstrated performance are encouraging for fostering industrial applications of LNMO material.



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Functionalised Alumina nanoparticles for HF scavenging and transition metal ions trapping in NMC and LNMO-based lithium batteries

D. Callegari,[1,2] M. Canini,[1,3] M. Coduri [1,3], S. Davino,[1,3] E. Quartarone [1,2]

[1] *Department of Chemistry, University of Pavia, Via Taramelli 16, 27100 Pavia, Italy*
[2] *GISEL - Centro di Riferimento Nazionale per i Sistemi di Accumulo Elettrochimico di Energia, INSTM, via G. Giusti 9, Firenze 50121, Italy*
[3] *INSTM, National Inter-University Consortium for Materials Science and Technology, Via G. Giusti 9, 50121 Florence, Italy*

e-mail presenting author: daniele.callegari01@universitadipavia.it

One of the challenges in the field of high-energy-density lithium ion batteries is to prevent the leaching of transition metal ions (TM) from the cathode active materials caused by the presence of even small traces of hydrofluoric acid (HF), coming from the water-induced decomposition processes of the LiPF6-based electrolytes. The attack by HF is consequently responsible for the rapid cell failure [1]. One of the methods to mitigate this phenomenon consists of coating the cathode with oxides such as Al_2O_3 or ZrO_2 [2, 3]. However, this approach leads to the formation of a double interface, wich could potentially hinder the diffusion of the Li^+ ion.

This study was focused on the production of chitosane-functionalised alumina nanoparticles (ANP) with scavenger properties towards HF as filler for the composite cathode. The scavenging behaviour is triggered by the presence of protons and consequently by pH changes. Two different chemistries were investigated, namely NMC ($LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$) and LNMO ($LiNi_{0.5}Mn_{1.5}O_4$). The scavenger activity was evaluated by screening different loadings of ANP in LNMO- and NMC-based cathodes, dipped in a commercial LP30 electrolyte. The solutions were analized by ICP-OES to evaluate the amount of dissolved transition metal ions after a 5-day treatment at 55°C to accelerate and promote HF formation.

The effect of the scavenging ANPs on the functional performance was evaluated on coin cells including LP30 and LP30 enriched with 120 ppm of water. Cells with scavenger-free cathodes were also investigated for sake of comparison. After the electrochemical characterization, the loss of transition metals was evaluated by ICP-OES. Concernig the scavenger properties, ANP proved outstanding efficiency in mitigating the effects of acid attack, as confirmed by a significant reduction of the transition metal dissolution rate in case of scavenging cathodes.

The presence of ANP has also benefical effects on the electrochemical performances of the cathode that exhibited remarkably lower capacity loss and higher specific capacity than the scavenger free systems after 200 cycles @1C, especially in presence of water contamination.

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Innovative hybrid high voltage electrodes based on LMNO/LFP materials for lithium-ion batteries

Daniele Versaci,[i] Roberto Colombo,[i] Giorgio Montinaro,[i] Julia Amici,[i] Mihaela Buga,[j] Carlotta Francia,[i] Silvia Bodoardo[i]

[i] Electrochemistry Group, Department of Applied Science and Technology (DISAT), Politecnico di Torino, Corso Duca degli Abruzzi, 24, 10129 Torino, Italy
[j] National Research and Development Institute for Cryogenic and Isotopic Technologies – ICSI Rm. Valcea, 240002, Romania

e-mail presenting author: daniele.versaci@polito.it

Electrochemical energy-storage systems, such as lithium-ion batteries (LiBs), have turned out to be the most prevalent technology for a wide range of devices, from small electronics to stationary energy storage applications, and electric mobility. However, to meet the ever-increasing market demand, significant effort is still needed in order to develop batteries with better performance in terms of power and energy density.

In this frame, cathode materials completely cobalt-free and operating at high voltage (e.g. 4.75 V), such as LNMO (lithium nickel manganese oxide – $LiNi_{0.5}Mn_{1.5}O_4$) are particularly interesting and potentially able to increase the electrochemical performance of next-generation high-energy-density LiBs [1].

Unfortunately, LNMO still suffers of some drawbacks such as easy cation leaching during cycling (in particular at high C-rate) and electrolyte decomposition at high voltage. Therefore, one possible approach to mitigate these issues, increasing the safety of the system, the lifetime, and limiting the cost, is using blended electrodes, containing multiple types of active materials.

In the present work, within HYDRA H2020 project, the influence of LFP (lithium iron phosphate – $LiFePO_4$) physically mixed with LMNO was studied both from morphological and electrochemical point of view. LFP was chosen because of its outstanding thermal and electrochemical stability, and its influence on the electrochemical performances of the cathodes, such as cycling performances, lifetime and safety. The role of LFP was studied changing its amount inside the cathode formulation and the electrochemical properties were evaluated both in half-cell and full-cell configuration.

In particular, the simple and up-scalable physical blending, by resonant acoustic mixing (RAM) technique, provided a good distribution of LFP and LNMO particles, resulting in increased electrochemical performances. The blended LNMO/LFP cathode was able to deliver a specific capacity higher than 125 mAh g^{-1} at C/10 and a capacity retention higher than 80% after 1000 cycles at 1C vs. lithium. Analogously, the blended electrode shows a capacity retention close to 74% after 100 cycles in full-cell configuration (vs. graphite), almost 30% higher than the pure LNMO cathode.

Acknowledgments: Authors kindly acknowledge Hydra project (Horizon 2020 innovation program under Grant agreement number: 875527) for funding.

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Development of high-capacity electrode materials for Li-ion batteries based on a sustainable approach

A.Celeste,[a,b] G. Spanu,[b] M. Tuccillo,[a] F. Bozza,[b] P. Reale,[c] S. Brutti[a] and L. Silvestri[b]

[a] *Department of Chemistry, University Sapienza of Rome, p.le Aldo Moro 5, 00185-Roma, Italy*
[b] *Department of Energy Technologies and Renewable Sources, ENEA C.R. Casaccia, via Anguillarese 301, 00123-Roma, Italy*
[c] *Department of Fusion and Technology for Nuclear Safety and Security Department, ENEA C.R. Frascati, via Enrico Fermi 45, 00044-Frascati, Italy*

e-mail presenting author: laura.silvestri@enea.it

Since their first commercialization in 1991, Lithium-Ion Batteries (LIBs) have ruled the secondary battery market becoming the main energy source for today's portable electronics and electric vehicles. However, the increasing of global battery demand is putting high pressure in battery supply chain. Among the limiting factors of LIBs, there are the costs, raw materials supply and the gravimetric-specific capacity limits. In this context, the development of advanced materials is a key factor to improve battery performance but it is also a key element determining the cost, the environmental impact and recyclability of batteries.[1]

Here, we propose two examples of advanced electrode materials for Li-ion batteries developed in our laboratories: i) Co-free Li-rich layered oxide (LRLO) as high voltage positive electrode and ii) doped calcium ferrite (CFO) as high capacity negative electrode.

LRLOs are a valuable alternative to current commercial cathode materials, thank to their higher specific capacities (>250mAhg^{-1}), larger operating voltage (>3.6V) and high energy density (900 WhKg^{-1}). Compared to other layered oxides, i.e. NMC or Ni richThey can be considered a more economically alternative due to the higher content of manganese in their formula .[2]

While, regarding CFOs, iron-based materials are considered as potential anode materials for lithium-ion batteries thanks to their low cost, abundancy, non-flammability, good safety, environmental benignity, and high specific capacity (600-1000 mAhg^{-1}).[3] Specifically, CFO reacts in lithium cells through a conversion mechanism and compared to the binary systems, i.e., Fe_2O_3, theoretical calculations proved that the Ca incorporation could plays an important role to expand the lattice distance, facilitating the Li-ion transfer. [4]

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A design of experiment approach to the upscaled synthesis of NMC materials for Li ion batteries

Federico Barbon,[a] Luca Campagnaro,[a] Marco Bersani,[b] Daniele Versaci,[c] Silvia Bodoardo,[c] Alessandro Martucci[d] and Silvia Gross[a,e]

[a]Dipartimento di Scienze Chimiche, Università degli Studi di Padova, Padova, Italy
[b]Particular Materials srl, Cadoneghe(Padova), Italy
[c]Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Torino, Italy
[e]Dipartimento di Ingegneria Industriale, Università degli Studi di Padova, Padova, Italy
[f]Institute for Chemical Technology and Polymer Chemistry (ITCP) – Karlsruhe Institute of Technology (KIT), Germany
e-mail presenting author: federico.barbon@studenti.unipd.it

Production of materials for Li-ion batteries has surged dramatically in recent years. In particular, the cathodic component is considered the most critical part, both from the cost and energy density aspects. Therefore, a crucial improvement to the connection between the research and the industrial prospects is needed.[1] In this regard, continuous hydrothermal flow synthesis (CHFS) has been successfully employed to produce $LiFePO_4$, but its potential for other cathode chemistries is still largely unexplored.[2] Only very recently the synthesis of NMC-like materials ($LiNi_{1-x-y}Mn_xCo_yO_2$) was carried out,[3] but no systematic study on the influence of the synthesis parameters on the final product was performed. A rational approach to the fine optimization of a specific composition is often overlooked in academic research, favouring a “trial and error” approach where only one variable at time in changed. However, an evident issue emerges when this view is transferred to the industrial world, where a very limited number of trials is allowed and a commercially viable product is often the target.

An ideal solution, also highlight in the field of inorganic chemistry,[4] is represented by the “Design of Experiment” (DoE), in which the experimental results are statically analysed with a multi-variable approach. In this way, a reduced number of experiment and, at the same time, a wider investigation of the factors’ influences can be performed, also by taking into consideration the combined influence of the single parameters to the result. Moreover, this powerful tool can predict the conditions to meet a specific set of synthesis requirements and can be employed both at the screening level and for the final optimization.

In this work, a plethora of NMC compositions, from 111 to the more industrially relevant 532 and 622, were synthetized with the CHFS setup and different synthetic conditions (synthesis temperature, calcination temperature, calcination time and cooling time) were selected to study the influence on the final particles both at the structural and morphological level. Surprisingly, even if the compositions between the samples are similar, a different dependence on the conditions was evidenced. These results were then related to the electrochemical performances and allowed to identify the most relevant factors in each of these sets saving a considerable amount of time and materials.

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(Invited) Why Metallic Zinc is Inefficient as Anode in Aqueous Zn-Ion Batteries: the Role of the Hydrogen Evolution

G. Zampardi [a]

[a] *University of Bremen, Energy Storage and Energy Conversion Systems, Bibliothekstraße 1, 28359, Bremen (DE)*
e-mail presenting author: zampardi@uni-bremen.de

Mild acidic aqueous Zn-ion batteries (ZIBs) are among the most promising aqueous-based post-Li energy storage technologies for stationary applications thanks to their high volumetric energy and power density, high environmentally friendliness and low costs [1]. Such batteries are usually constituted of a positive electrode, which is able to (de-)insert Zn^{2+} in/from its lattice and a negative electrode based on metallic zinc.

Unfortunately, the commercialization of rechargeable aqueous ZIBs remains hindered mostly because of the non-efficient zinc electrodeposition caused by: (I) the non-homogeneous deposition of metallic zinc, and (II) the parasitic evolution of gaseous H_2 [2]. Metallic zinc offers clear advantages as anodes in aqueous ZIBs, due to its intrinsic high reservoir of Zn^{2+} ions. However, despite hindered the parasitic hydrogen evolution reaction is not completely suppressed onto the surface of metallic zinc and its occurrence produces a local alkalinization of the pH in proximity of the electrode. This results in the irreversible loss of Zn^{2+} ions and in the entombment of the metallic zinc surface because of the accumulation of electronically insulating Zn-oxides/hydroxides species.

Here, the role of the parasitic hydrogen evolution reaction on the Zn electrodeposition/dissolution efficiency will be discussed. The electrodeposition of zinc on different metallic substrates has been evaluated by means of galvanostatic cycling on porous electrodes resembling realistic charge/discharge conditions of an aqueous ZIB. In addition, morphological and compositional analysis has been performed onto the pristine and cycled substrates to assess the Zn deposits over prolongued cycling and *in operando* differential electrochemical mass spectrometry (DEMS) has been performed to quantify the amount of parasitic H_2 evolved during the cycles.

It will be shown how the major contribution to a low Zn electrodeposition efficiency as defined in aqueous ZIBs is not simiply given by the Coulombic efficiency of the zinc electrodeposition/dissolution reaction but rather by the formation of dead zinc deposits.

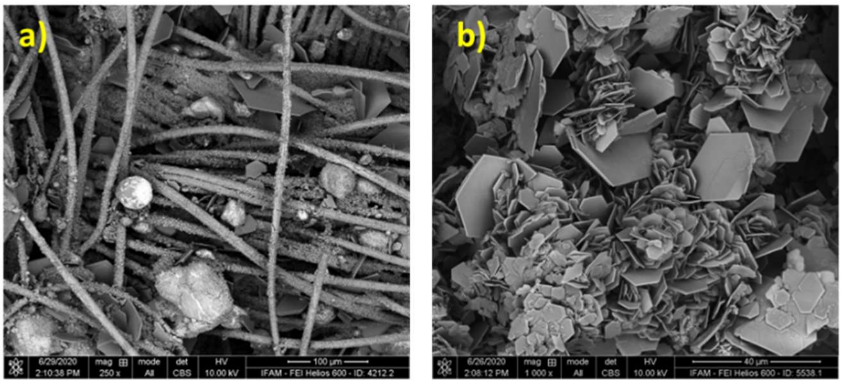

Figure 1: C SEM image of: a) Bi-In powder substrate after 200 cycles, b) Zn powder electrode after 90 cycles.

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New materials for secondary Na-ion batteries targeting at sustainability and high performances

A. Piovano[1,2], S. Porporato[1,2], H. Darjazi[1,2], M. Milanesi[1,2], M. Bartoli[1,2], G. Meligrana[1,2], G. A. Elia[1,2], C. Gerbaldi[1,2]
[1]GAME Lab, Department of Applied Science and Technology, Polytechnic of Torino, Corso Duca degli Abruzzi 24, 10129, Torino, Italy
[2]National Reference Center for Electrochemical Energy Storage (GISEL) - INSTM, Via G. Giusti 9, Firenze 50121, Italy
e-mail presenting author: alessandro_piovano@polito.it

Nowadays, the wordwidely ongoing energy transition has pointed out the pressing need for new energy storage technologies based on abundant and low-cost materials, to satisfy the exponentially increasing market demand and to overcome the current scarcity of some key and critical elements, such as lithium and transition metals (Co and Ni, primarily).

In this respect, secondary sodium-based batteries display great advantages in terms of high-energy density, low-cost, and simple manufacturing. In this work, different cathode and anode materials were explored in lab-scale Na-metal cells. These materials include high entropy oxides (HEO) and Prussian Blue analogues (PBAs) as cathodes, and carbon-based materials as anodes. On one side, HEO are innovative materials where multiple cations within the same crystal phase contribute to the overall behavior, while PBAs have attracted wide attention due to low cost, easy and tunable synthesis, and high versatility [1]. On the other side, carbonaceous materials can be obtained from the pyrolysis of waste materials, such as biomasses or disposed face masks, which are so repurposed into high-value applications [2].

All of these electrode materials were tested in combination with standard electrolytes (based on organic solvents), but also with electrolytes based on room-temperature ionic liquids (RILs), with great advantages in terms of safety, low toxicity and flammability [3]. Lab-scale Na-metal and Na-ion cells were fully characterized by means of electrochemical impedance spectroscopy, cyclic voltammetry and galvanostatic charge/discharge cycling. Materials exhibited relatively high specific capacities with high coulombic efficiency (above 98% even after prolonged cycling, up to 1000 cycles).

Furthermore, many efforts are also dedicated in the frame of SUNRISE European project to the recycle of polyvinyl butyral (PVB), which is used as polymeric interlayer into laminated glass for construction and automotive. Up to now, most of the post-consume PVB from laminated glass is incinerated or landfilled, causing the loss of 125000 tons per year. Our goal is to apply in energy storage systems the fraction of recycled PVB that does not fulfill the optical and mechanical requirements for being reused into the original glass manufacturing process. Particularly, the recycled PVB can be used as a binder in the electrode preparation and/or as a separator. In order to be competitive with conventional binders and separators (such as CMC and PP/PE, respectively), the costs of the whole recycling process have been targeted at 10 $/kg for the binder and 60 $/kg for the separator [4].

In conclusion, the independent optimization of each component of the energy storage systems will thus contribute to improve the whole value chain and foster the broadly coveted energy transition.

Acknowledgments

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Characterising the Ionic Transport and Thermodynamic Properties of Potassium-ion Electrolytes

S. Dhir,[i] B. Jagger,[i] A. Maguire,[i] and M. Pasta[i]

[i] *Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK*
e-mail presenting author: shobhan.dhir@materials.ox.ac.uk

The lithium price has increased more than sevenfold since the start of 2021 (as of May 2022), reaching unprecedented price levels and demonstrating significant challenges for the security of supply of lithium for lithium-ion batteries (LIBs) [1]. With forecasts showing a potential significant lithium supply deficit by 2030 [1], the case for alternative chemistries based on abundant minerals which can fulfil some LIB functions has never been stronger. Sodium-ion batteries (NIBs) and potassium-ion batteries (KIBs) are emerging as promising complementary technologies to lithium-ion batteries (LIBs) due to the availability and low cost of sodium and potassium, and the minerals comprising their leading electrodes [2,3]. KIBs have a significant advantage over NIBs as K^+ can reversibly intercalate into the graphite electrodes used in LIBs, thus one of the primary components of KIBs is already available at commercial scale, unlike for NIBs [2]. The lower charge density of K^+ compared to Li^+ has also been suggested to result in superior ion transport in the electrolyte with KIBs potentially able to deliver superior rate capability and low-temperature performance. However, a comprehensive characterisation of the ionic transport and thermodynamic properties of nonaqueous K-ion electrolytes, critical to the development of KIBs, has not yet been reported. Here, for the first time, we fully characterise the ionic transport and thermodynamic properties of a nonaqueous K-ion electrolyte (Figure 1) [4], potassium bis(fluorosulfonyl)imide (KFSI) in 1,2-dimethoxyethane (DME) and compare it with its Li-ion equivalent (LiFSI in DME) over the concentration range 0.25–2 m. This was realised by developing a K metal preparation protocol enabling sufficient K metal stability for electrolyte characterisation. Our results demonstrate that the K-ion electrolyte indeed displays significantly higher salt diffusion coefficients and transference numbers than the Li-ion electrolyte, evidencing the potential for high-power applications of KIBs.

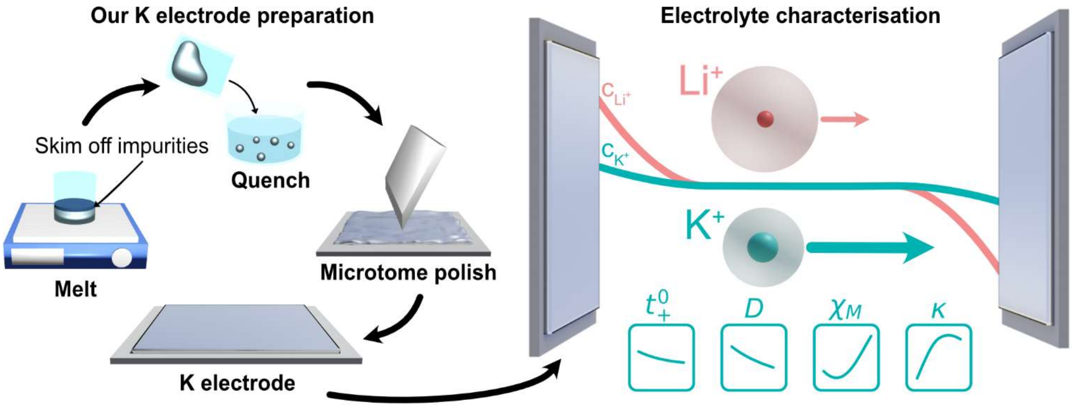

Figure 1: Schematic of our K preparation protocol enabling K-ion electrolyte transport and thermodynamic property characterisation.

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Solid State Hybrid Inorganic Organic Polymer Electrolytes for Advanced Sodium Secondary Batteries

K. Vezzù, F. Brombin, G. Pagot, V. Di Noto

Section of Chemistry for Technology, Department of Industrial Engineering, University of Padova,
Via Marzolo 9, 35131 Padova, Italy
e-mail presenting author: keti.vezzu@unipd.it

The large-scale rollout of electric vehicles, smart grids and portable electronics is expected to require an amount of energy storage devices that the Li-ion technology alone will not be able to satisfy. In this concern, a quest for novel electrochemical energy storage technologies has started [1]. Sodium secondary batteries appear to be a good choice due to: (i) the high availability of raw materials; (ii) the low cost of sodium; (iii) the low sodium standard reduction potential; and (iv) the similarity between the chemistries of sodium and lithium, which facilitates the transition between the two technologies. Up to date, the best-performing electrolytes for the reversible deposition of sodium are based on organic solvents, which suffer from safety concerns and a poor stability towards sodium metal. Thus, research activities in this field are devoted to the development of safe and stable solid state electrolytes able to efficiently transport Na^+ ions.

A new family of hybrid inorganic-organic polymer electrolytes (HIOPEs) for advanced solid state sodium secondary batteries is presented. The pristine HIOPE is obtained through the reaction between zirconium ethoxide and polyethylene glycol (PEO). The resulting material is doped with sodium perchlorate as source of Na^+ ions. In this system a 3D network is obtained, where inorganic zirconium metal nodes are interconnected by means of PEO chains. The latter ensure flexibility to the overall structure. After doping with the poly(ethylene glycol) dimethyl ether plasticizer, a room temperature conductivity higher than 10^{-4} S cm^{-1} is demonstrated.

An advanced study of the thermal and structural properties of the proposed materials is presented, with a particular focus on the interactions established between the different chemical species and complexes composing the HIOPEs. The conduction mechanism is elucidated starting from the results obtained in a wide range of temperatures from broadband electrical spectroscopy studies.

Taking all together, this study offers insights on the application of non-traditional solid state electrochemical functional components as replacements for conventional solvents in the emerging field of sodium secondary batteries.

Acknowledgments

The project "Interplay between structure, properties, relaxations and conductivity mechanism in new electrolytes for secondary Magnesium batteries" (Grant Agreement W911NF-21-1-0347-(78622-CH-INT)) of the U.S. Army Research Office. The project "ACHILLES" (prot. BIRD219831) of the University of Padua. The project "VIDICAT" (Grant Agreement 829145) of the FET-Open call of Horizion 2020. The project TRUST (protocol 2017MCEEY4) of the Italian MIUR funded in the framework of "PRIN 2017" call.

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Beneficial Effect of Conductive Polymers in Aqueous Zinc-Ion Batteries

M. Baghodrat,[a] G. Zampardi,[a] F. La Mantia[a, b]

[a] Energy Storage and Energy Conversion Systems, University of Bremen, Wiener Str. 12, 28359 Bremen, Germany
[b] Fraunhofer Institute for Manufacturing Technology and Advanced Materials – IFAM Wiener Str. 12, 28359, Bremen, Germany.
e-mail presenting author: mo_ba@uni-bremen.de

Aqueous Zin-ion batteries (A-ZIBs) have become an attractive choice for stationary storage applications because of their high specific power and reversibility in aqueous solutions, as well as their low cost, environmental friendliness, and abundance of metallic zinc [1]. Despite the promising advantages, their commercialization remains limited due to the lack of suitable Zn-insertion materials for the positive electrode. Among the possible candidates, copper hexacyanoferrate (CuHCF) has attracted significant attention as an active material for the positive electrode in A-ZIBs thanks to its high cell working potential of about 1.7 V vs. Zn^{2+}/Zn, high power-rate capability, non-toxicity, and simple and inexpensive synthesis route that can be easily scaled up to an industrial level. However, CuHCF suffers from a relatively short cycle life [2]. A promising strategy to prolong the cycle life of the battery active materials is to coat the particles with conductive polymers [3,4].

Here, the electrochemical performance of CuHCF coated with Polypyrrole (PPy) and Poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS) was investigated in flooded three-electrode cells. Initially, the thermal stability of CuHCF was evaluated in order to increase the polymers electrical conductivity via thermal treatment at the highest temperature possible. CuHCF particles were then coated with different amounts of PPy or PEDOT:PSS. Galvanostatic cycling of the coated CuHCF demonstrated a significant prolongation of the electrode cycle life. Uncoated CuHCF exhibited a cycle life of ca. 250 cycles when cycled in an aqueous solution of 0.1 M $ZnSO_4$ at a current rate of 1C. In comparison, the cycle life of the coated CuHCF increased significantly when coated with PPy reaching 600 cycles, and up to 700 cycles when PEDOT:PSS was used. Compositional, morphological, and structural analysis has been carried out together with the electrochemical analysis in order to understand the effect of the nature of the polymer used for the coating, its optimal amount and the underlaying mechanisms on the electrochemical performance of CuHCF.

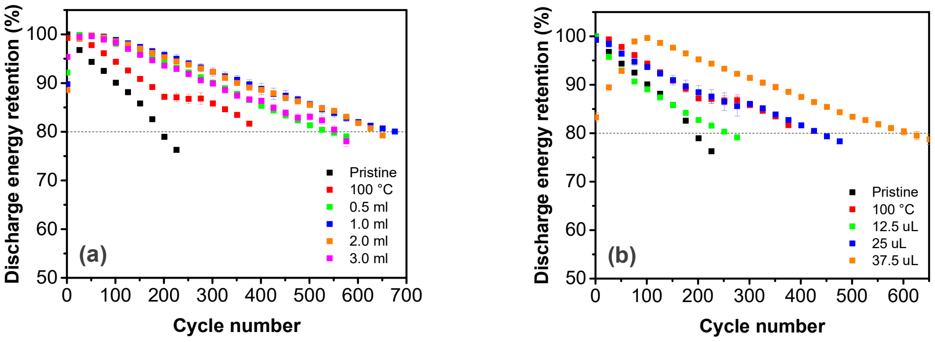

Figure 1: Discharge energy retention of CuHCF-based electrodes coated with a) PEDOT:PSS and b) PPy cycled at 1C.

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Ionic Liquid Electrolytes for Sodium-Ion Battery Systems

G. Maresca [a,b], *A. Petrongari* [c], *M. Ottaviani* [d], *K. M. Ryan* [d], *S. Brutti* [c], *G.B. Appetecchi* [a]

[a] *ENEA, Materials and Physicochemical Processes Technical Unit (SSPT-PROMAS- MATPRO), Via Anguillarese 301, 00123, Rome, Italy*
[b] *La Sapienza University of Rome, Department of Basic and Applied Sciences of Engineering, Piazzale Aldo Moro 5, 00185, Rome, Italy*
[c] *La Sapienza University of Rome, Department of Chemistry, Piazzale Aldo Moro 5, 00185, Rome, Italy*
[d] *Materials and Surface Science Institute and the Department of Chemical and Environmental Sciences, University of Limerick, V94 T9PX Limerick, Ireland*
e-mail presenting author: giovanna.maresca@uniroma1.it

Sodium-ion batteries (SIBs) are considered a promising alternative technology to lithium-ion ones for the coming-soon electrochemical energy storage systems. Sodium has attracted remarkable attention for its larger natural abundance, lower cost, and in particular, for its similar chemical characteristics with respect to lithium [1].

Similarly, to Li-ion devices, the use of volatile and flammable organic liquid electrolytes represents a remarkable safety drawback. A strategy for overcoming this issue is replacing conventional organic electrolytes with ionic liquids (ILs) [2-3], thanks to their properties such as flame suppression, negligible vapor pressure, thermal-chemical-electrochemical stabilities, and good ionic conductivity.

In this study, different ILs based on the 1-ethyl-3-methyl-imidazolium (EMI) and trimethyl-butyl-ammonium (N_{1114}) cations coupled with the bis(fluorosulfonyl)imide (FSI) anion were studied as electrolyte materials in Na-ion batteries [6-7], using the NaTFSI salt. The sodium-intercalation process of hard-carbon (HC) anodes and α-$NaMnO_2$ cathodes in EMIFSI and N_{1114}FSI-based electrolytes were investigated by cyclic voltammetry tests at different scan rates combined with impedance spectroscopy measurements. The electrochemical performance of these systems, in Na-half cell, were evaluated by galvanostatic charge/discharge measurements. Spectroscopy measurements were carried out to get information on the surface chemistry (SEI growth-up) at the electrolyte/electrode interface.

We demonstrated that EMIFSI and, in particular, N_{1114}FSI-based electrolytes are good candidates for novel NIB formulations for their ability to reversibly intercalate sodium ions in both hard-carbons and α-$NaMnO_2$ electrodes, with a controlled degradation of the electrolyte. This is likely due to a stable SEI layer promoted by the FSI anion. Furthermore, both ILs show good performances in terms of cyclability in Na-half cells. Therefore, EMIFSI- and N_{1114}FSI-based electrolytes are of interest for the realization of highly safe, reliable, and advanced sodium-ion electrochemical energy storage devices.

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Electrospun spinel-structured high-entropy (Cr,Mn,Fe,Co,Ni), (Cr,Mn,Fe,Co,Zn) and (Cr,Mn,Fe,Ni,Zn) oxides as electrocatalysts for oxygen evolution in alkaline medium

Claudia Triolo,[a,d] Simon Schweidler,[b] Ling Lin,[b] Gioele Pagot,[c,d] Vito Di Noto,[c,d] Ben Breitung,[b]
Saveria Santangelo[a,d]

[a] Dipartimento di Ingegneria Civile, dell'Energia, dell'Ambiente e dei Materiali (DICEAM),
Università Mediterranea di Reggio Calabria, 89122 Reggio Calabria, Italy
[b] Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
[c] Section of Chemistry for the Technology (ChemTech), Department of Industrial Engineering,
University of Padova, Via Marzolo 9, 35131 Padova (PD), Italy
[d] National Reference Center for Electrochemical Energy Storage (GISEL), Consorzio
Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), 50121 Firenze, Italy
e-mail presenting author: saveria.santangelo@unirc.it

The slow kinetics of the oxygen evolution reaction (OER) still strongly limits the broad market penetration of electrochemical water splitting as a sustainable technology for large-scale hydrogen production. Spinel-structured transition metal (TM) oxides are in focus due to their great potential as low-cost OER electrocatalysts [1–4]. Among them, high-entropy spinel oxides (HESOs) with multiple TM-cation sites lend themselves to engineering of the octahedral redox-active centres to enhance the catalyst reactivity [5].

This work deals with the preparation of electrospun HESO nanofibers (NFs), based on (Cr,Mn,Fe,Co,Ni), (Cr,Mn,Fe,Co,Zn) and (Cr,Mn,Fe,Ni,Zn) combinations, and their evaluation as OER electrocatalysts in alkaline medium, together with (Cr,Mn,Fe,Co,Ni) HESO nanoparticles (NPs) prepared via the sol-gel method.

Electrochemical measurements are performed in 1 M KOH solution using a three-electrode setup (Pt spiral counter electrode; Ag/AgCl reference electrode; HESO-based working electrode).

(Cr,Mn,Fe,Co,Ni) HESO NFs and NPs (Tafel slopes: 49.1 and 51.3 mV dec^{-1}, respectively) outperform not only (Cr,Mn,Fe,Co,Zn) and (Cr,Mn,Fe,Ni,Zn) NFs (62.5 and 59.6 mV dec^{-1}, respectively), but also IrO_2 reference electrocatalyst (52.9 mV dec^{-1}). The higher concentration of oxygen vacancies on their surface and the higher occupation of octahedral sites by redox-active Co^{2+} and Ni^{2+} centres are responsible for their behaviour.

Electrospun HESO NFs have great potential as ink-jet printable electrocatalysts.

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Highly active Pt@ZrO2/FTO electrodes for Hydrogen Evolution Reaction

S. Minelli[a], Irene Casale[a], Xiufang He[a], A. Vertova[a,b], C. Lenardi[b], C. Piazzoni[b], *and* A. Minguzzi[a,b]

Department of Chemistry – The University of Milano – Via Golgi 19 20133 Milano, Italy.
INSTM Consorzio Interuniversitatio Nazionale per la Scienza e Tecnologie dei Materiali, Via G. Giusti 9, 50121 Firenze, Italy
CIMAINA and Department of Physics Aldo Pontremoli - The University of Milano – Via Celoria 16 20133 Milano, Italy.
e-mail presenting author: simone.minelli@unimi.it

Hydrogen has rapidly acquired the role of energy vector, thanks to its elemental abundance on earth and to the environmental and energetic issues at the basis of its production and usage as molecular H_2. Water as hydrogen source certainly adds appeal to the process because of its general availability as base material, the possibility of tuning the product quality, and the well-assessed reaction paths according to the adopted methodologies and conditions. In this work, we focus on the alkaline electrolytic hydrogen production, which is considered more environmental friendly and economical respect to acid one[1], when a greater efficiency is achieved. In turn, the electrolyte governs the choice of the electrode materials and the relevant reactions[2], hence the energy consumption, the costs and the H_2 quality. We present the use of a class of electrode materials which exhibit specific electroactivity[3] for HER/HOR with extended lifetime and reasonable costs. We specifically focus on Pt, with the aim of compare the interaction of Pt to ZrO_2 respect to Pd [4], supported on ZrO_2, a ceramic oxide, compatible with human tissues[5], whose role here is to enhance the electroactivity of classic Platinum Group Metals (PGM). To carefully control the electrocatalyst composition and morphology, the electrodes are prepared by ion-beam sputtering deposition on FTO supports, thus obtaining ordered depositions of ceramic and electrocatalyst (Figure 1).

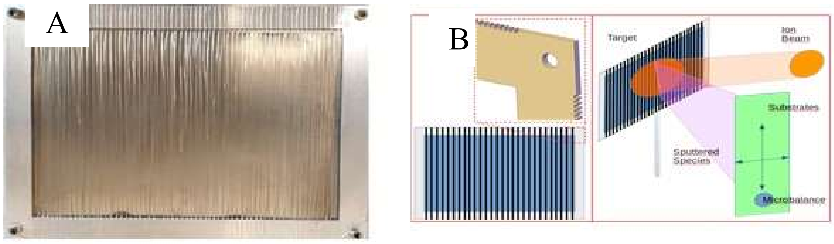

Figure 2. **A:** the target; **B:** schematic drawing of the composite target: Pt foil (blue) fixed on the target holder through an aluminium frame (grey) that, in turn, hosts the Zr wire (black); **B left up**: detail of the frame with hooking grooves for the Zr wire

The outcomes point to the synergistic effects between the precious metal catalyst and the ceramic support, not only in terms of chemical stability of the layer, but also of enhancement of the reaction rates. The electroactivity and stability of this novel electrocatalyst structure has been investigated by Cyclic Voltammetry and Electrochemical Impedance Spectroscopy for selected thicknesses (25-200 nm) of the active layer, deposited by ion beam sputtering. Finally, an effective enhancing of the electroactivity, as evidenced by the drastic reduction of the charge transfer resistance, has been evidenced, thus allowing the parallel reduction of catalyst load even at increasing current densities.

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Improved activity and stability of Pt NPs supported on CeO_2/C as electrocatalysts for oxygen reduction reaction: novel insights in the synthesis and physico-chemical characterization

Mattia Parnigotto,[a] Marco Mazzucato,[a] Maria Chiara Dalconi[b], Luca Gavioli[c], Gregorio Dal Sasso[b], and Christian Durante[a]

[a] Department of Chemical Sciences, University of Padova, Via Marzolo1, 35131, Padova, Italy
[b] Department of Geoscience, University of Padova, Via Gradenigo 6, 35131 Padova, Italy
[c] Department of Mathematics and Physics, Università Cattolica del Sacro Cuore, via della Garzetta 46, 25133 Brescia, Italy
e-mail presenting author: mattia.parnigotto@phd.unipd.it

One of the critical actions against climate change is the necessary transition to a renewable energy supply. Proton Exchange Membrane Fuel Cells (PEMFC) could be the best candidates to replace the traditional combustion engines used in the automotive sector. The main hindrances of PEMFC commercialization lie first in the prohibitive costs of platinum, second in the slow Oxygen Reduction Reaction (ORR) at the platinum-based cathode, and finally in the short-term durability associated with degradative mechanisms, which cause the loss of cell performance during its working.

There have been many strategies to improve these last aspects, one of them being the use of a metal oxide support, as demonstrated by Du et al. which deposited Pt on six metal oxide supports, TiO_2, MoO_3, SnO_2, Nb_2O_5, Ta_2O_5, WO_3 to develop the most durable catalyst, demonstrating a higher dissolution of Pt/C compared to Pt/SnO_2, as confirmed by ICP-MS analysis [1]. On the other hand, Ceria has been incorporated in the anodic side of PEM fuel cells of several vehicles, such as the Toyota 2017 Mirai, since it can act as a radical scavenger during the operating conditions of the device [2]. Despite all these benefits for the anodic and cathodic PEMFC compartments, in-depth studies have not been conducted to optimize the synthesis of the PtMO_2/C ORR catalyst, nor to gain a clear understanding of catalytic activity and stability under operative conditions.

With the aim of synthesizing a novel and efficient ORR catalyst through an easy and sustainable method, we define the synthesis of monodimensional and well-dispersed Pt nanoparticles (Figure 3 a). Pt NPs were synthesized under mild thermal conditions and without reducing agents, taking advantage of the contribution that CeO_2 or SnO_2 provides to Pt nucleation. The improved activity (Figure 1 b) and stability because of the addition of CeO_2 or SnO_2 are verified, respectively, by characterisations at Rotating Disk Electrode and the Gas Diffusion Electrode. The use of XPS, HRTEM, and XRD characterizations provides an in-depth investigation of the improved metal-support interaction.

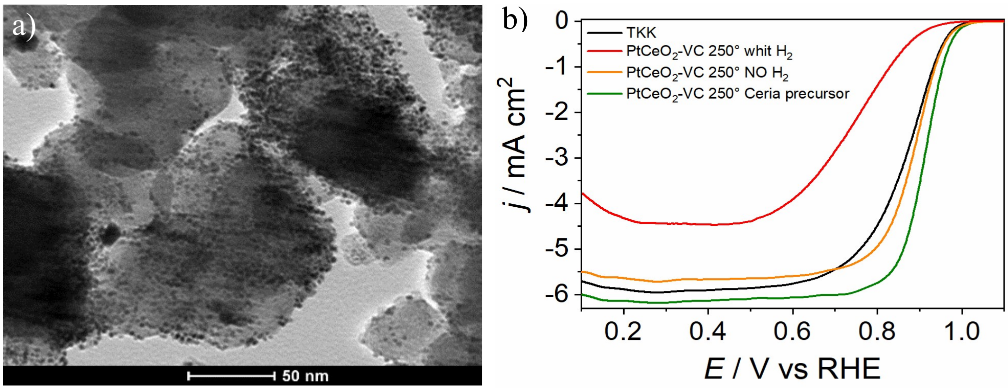

Figure 1: a) TEM image and b) RDE characterisation in oxygen-saturated 0.1 M HClO4 Pt nanoparticles (2-3 nm) obtained by solid state synthesis with CeO_2 nanoparticles on Vulcan XC72

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Single nickel atoms on carbon nitride as efficient oxygen evolution catalyst: Structural and functional characterization

L. Calvillo,[a] N. Rossetti,[a] A. Ugolotti,[b] G. Dražić,[c] C. Di Valentin[b]

[a] Department of Chemical Sciences, University of Padova, via F. Marzolo 1, 35131 Padova, Italy.
[b] Materials Science Dept. U5, University of Milano-Bicocca, via Cozzi 55, 20125 Milano, Italy.
[c] Department of Materials Chemistry D10, National Institute of Chemistry, Hajdrihova 19, p.p. 660, SI-1001, Ljubljana, Slovenia.
e-mail presenting author: laura.calvillolamana@unipd.it

In this work, we present an OER electrocatalyst based on nickel single atoms stabilized on carbon nitride (CN). The use of single atom catalysts (SACs) allows a 100% atomic efficiency; however, their high surface energy makes them highly unstable, specially under catalytic conditions. Therefore, the development of support materials able to stabilize them is crucial for their commercial use. We propose the use of CN since it contains a high amount and uniform arrangement of nitrogen species able to coordinate the Ni atoms. In addition, it presents well defined cavities that can confine the metal atoms avoiding their agglomeration [1]. CN has been chemically synthesised from melamine and cyanuric chloride at low temperature, in order to control the polymerization process and obtain a highly ordered structure [2]. Subsequently, nickel atoms were introduced into the polymeric matrix through an impregnation method. The Ni-CN samples were characterized by ICP, XRD, XPS, HR-TEM and EXAFS. The experimental characterization was combined with DFT calculations to define the structure of the catalysts (Figure 1a). The HRTEM and EXAFS results confirmed the presence of Ni single atoms (Figures 1b-1c). An accurate OER study as a function of the Ni content was performed both on the Ni-CN samples (Figure 1d). The catalytic stability of the materials was studied by subjecting the catalyst to an accelerated ageing treatment, while the structural stability was determined by HR-TEM and EXAFS. Once the stability of the Ni-CN material was confirmed, it was used to prepare and hybrid catalyst with carbon nanotubes. The resulting Ni-CN/CNT hybrid material showed a much higher activity than the corresponding components.

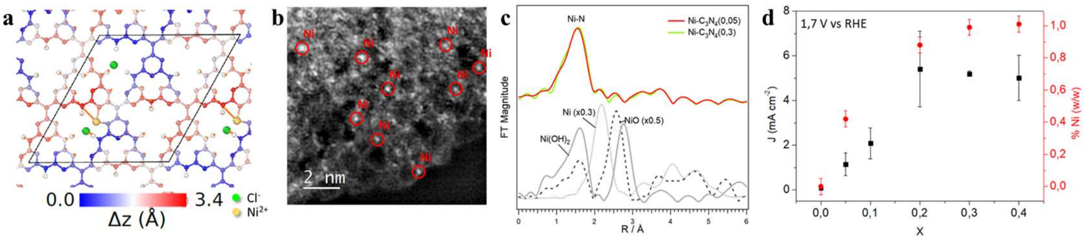

Figure 1: (a) Molecular structure of Ni-CN(x), x is the synthesis molar ratio Ni/CN; (b) HAADF-STEM image of Ni-CN(0.2); (c) FT-EXAFS spectrum; (d) current density (J) generated at 1.7 V vs RHE for x=0-0.4, red axis and red values are referred to the ICP-MS characterization.

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Exploring the use of bioethanol to aid the electrolysis of water at high temperatures

M. Lo Faro[a], F. Berto Ometto[b], S. Campagna Zignani[a], S. Vecino-Mantilla[a], J. Perez[b], and E. Ticianelli[b]

[a] Institute of Advanced Energy Technologies (ITAE) of the Italian National Research Council (CNR),
Via Salita S. Lucia sopra Contesse 5, 98126 Messina, Italy
[b] Instituto de Quimica de São Carlos - USP, Av. Trab. São-carlense, 400, Brazil
e-mail presenting author: lofaro@itae.cnr.it

A growing need for green hydrogen as an energy vector or chemical intermediate poses a challenge to its production. There is therefore a keen interest in improving current technologies and developing new approaches to reduce energy consumption when producing pure H_2. Using solid oxide electrochemical cells, we devised an innovative cell that could simultaneously reduce water and oxidize bioethanol, and as a result, produce green hydrogen with very low electric power energy. A symmetrical electrolyte-supported architecture was used to achieve this result. In both the anode and cathode, we used an exsolved perovskite (Lanthanum strontium cobaltite doped with Ni - LSCN), while we used a lanthanum gallate-based electrolyte (LSGM) as a supporting electrolyte. Figure 1 shows an overview of the architecture and reactions that occur at each electrode.

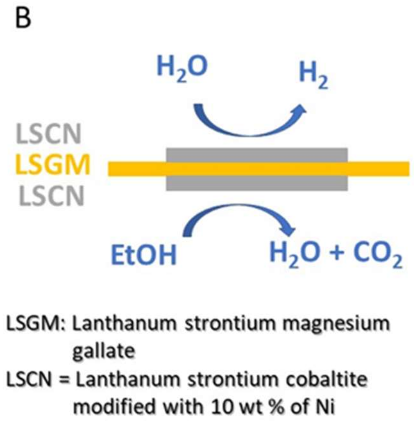

Figure 1: Features of the fully perovskite electrolyte-supported cell used in this experiment and expected reactions

The purpose of this communication is to describe electrochemical experiments, gas chromatographic analysis of outlet gases from both sides, and physicochemical characterization of both electrodes and cells. With a current density of 0.8 A cm^{-2} at 0.25 V, this cell showed excellent stability and low power consumption during 450 hours of testing. Our study also led to the development of a fully reversible cell based on perovskites, which required no additional H_2 to maintain the H_2O electrode in a reduced state, in contrast to commercial solid oxide electrochemical cells.

Acknowledgements

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The authors affiliated with IQSC-USP thanks to the Fapesp/Shell project Proc 2020/15230-5 - BG E&P Brasil (Shell)-CPE "Research Centre for Greenhouse Gas Innovation - RCG2I"

Direct evidence of thin amorphous layer formation on polycrystalline $LaNiO_3$ electrocatalyst for OER by XAS

G. De Amicis,[a] A. Testolin,[b] F. D'Acapito,[c] A. Vertova,[d] A. Minguzzi,[d] P. Ghigna.[a]

[a] *Department of Chemistry, University of Pavia, Viale Taramelli 16, 27100, Pavia, Italy*
[b] *Industrie De Nora S.p.A., Via Leonardo Bistolfi 35, 20134 Milan, Italy*
[c] *CNR-IOM-OGG, LISA-CRG, c/o ESRF, 71 Avenue des Martyrs, Grenoble, France*
[d] *Department of Chemistry, University of Milan, Via Golgi 19, 20133, Milan, Italy*

e-mail presenting author: giuditta.deamicis01@universitadipavia.it

The continuous increase in energy demand and concerns about environmental pollution caused by fossil fuel extraction and consumption, has raised the necessity to develop clean and sustainable energy sources. In this context, *green hydrogen* act as a main character. This term is applied to hydrogen produced by electrochemical water splitting (*ws*) linked to renewable energy sources, such as solar, wind and geothermal ones [1]. *Ws* is mainly limited by slowelectrode kinetics associated with the Oxygen Evolution Reaction (OER) at the anode, a sluggish four electrons/four protons coupled reaction, which requires, highly efficient electrocatalytic materials. For now, IrO_2 is the most efficient catalyst for OER, but it is extremely expensive [2]. Operating in alkaline conditions permits the use of non-noble and low-cost metal electrocatalysts, leading to the possibility of cheaper hydrogen production [3].

In this work, we studied $LaNiO_3$ perovskite as anodic catalytic material for Alkaline Water Electrolysis (AWE). Perovskite oxides have an ideal cubic structure with stoichiometry ABO_3 in which lanthanides or alkaline earth cations occupy the A-site, and transition metal cations the B-site. Lanthanides and transition metals are highly abundant elements, which allows the purchase of bulk materials for industrial processes. Their flexible crystal and electronic structure provide them ideal candidates to study the correlations between OER activity and structure [4].

In this study, $LaNiO_3$ was synthesized by a co-precipitation method with subsequent calcination at 700 °C [5]. Structural and morphological analysis followed by electrochemical characterization allow a proper assessment of $LaNiO_3$ for industrial electrode manufacturing. The material shows excellent OER activity, comparable with IrOx commercial catalyst and the most active non-noble metal catalysts for OER [6]. We also studied the OER mechanisms on $LaNiO_3$ based anodes via *operando* X-ray Absorption Spectroscopy (XAS) which allowed to assume that, under cathodic conditions, a layer of a Ni(II) compound, forms at the catalyst surface, and it is subsequently re-oxidized under anodic potentials. The fresh Ni(III) sites at the surface are possibly the active sites for adsorption and for the OER reaction (Figure 1). The formation of the amorphous layer is 10% *ca.* of the total Ni atoms.

The combined effect of the formation of the thin amorphous layer and the robustness of the bulk $LaNiO_3$ catalyst, provide it as excellent electrocatalyst for OER under alkaline conditions. $LaNiO_3$ turns out to be a polycrystalline material potentially very stable, but also very active for the OER.

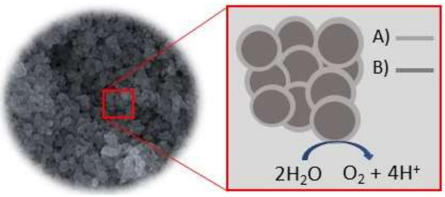

Figure 1: Schematic representation of surface amorphization of $LaNiO_3$: A) amorphous layer B) crystalline layer

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(Invited) Equivalent Electrical Circuit modeling of electrode-brain interface

L. Iannucci[1]

[1]*Department of Applied Science and Technology, Politecnico di Torino,*
Corso Duca degli Abruzzi 24, 10129-Torino, Italy
e-mail presenting author: leonardo.iannucci@polito.it

Recent advances in neural recording and neurostimulation allow physicians to monitor human brain activity and intervene in many neurodegenerative diseases. For this purpose, innovative neural implants are developed, which are able to inject the correct charge into the brain for a safe and efficient therapy. In order to correctly design the electronic circuitry in neural implants, equivalent electrical circuits are required to model the electrode/brain interface. Often, circuit parameters are considered stationary over time, even though many studies have shown that interfacial impedance varies significantly after electrode implantation, both in the first days after electrode insertion and in the following months.

This contribution will present the results from the ex-vivo experiments carried out to derive the appropriate equivalent electrical circuit models to describe the electrode-brain interface. The tests were carried out using Pt/Ir microelectrodes, inserted in ex-vivo porcine brain samples. The impedance measurements were carried out every 24 hours and the total duration of the experiments was 6 days [1].

Results showed a significant reduction in the measured electrode impedance after few days from the beginning of the test. At the same time, the number of time constants present in the spectra increased from one (at the beginning of the test) to three (after 72 hours from the electrode insertion). Thanks to morphological characterizations of the electrodes tip performed at the end of the test by electron microscopy, this phenomenon was associated with the biofilm attachment to the electrode surface. For this reason, different electrical circuits were used (reported in Figure 1) and the values of the circuit parameters during the experiment were computed. As neural recording and neurostimulation are deeply affected by the magnitude of the electrodes' interfacial impedance, the present study is of great importance to support the design of neural implants and thus allow an efficient therapy.

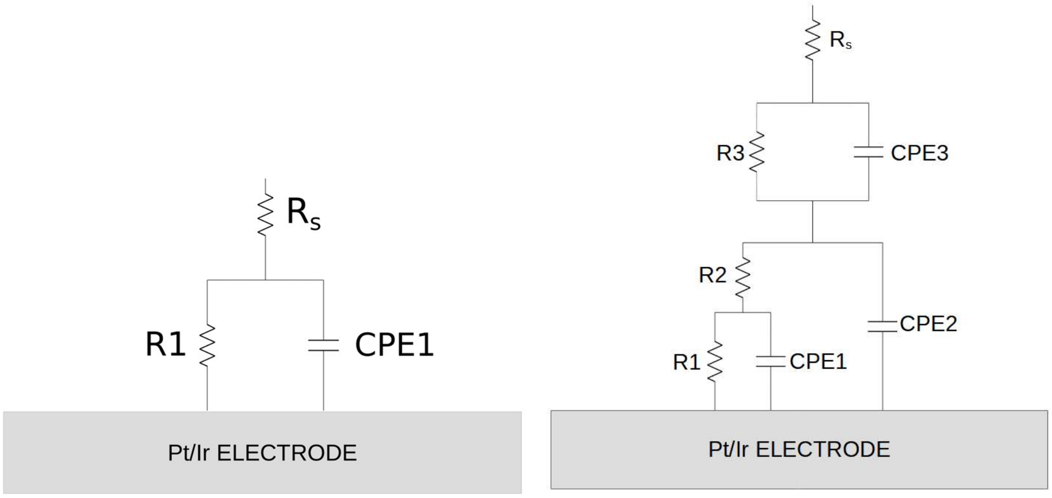

Figure 1: Equivalent electrical circuits used to model the electrode/brain interface. On the left, the circuit used in the first part of the experiment (up to 48 hours from the insertion in the porcine brain). On the right, the circuit used in the second part of the experiment.

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Unraveling the mechanism of hydrogen reversible reaction in buffer solutions by means of dynamic impedance spectroscopy

F. La Mantia,[1] J. Mugusa,[1] R. Chukwu,[1] D. Brogioli,[1]

[1] *Production Engineering, University of Bremen, Bibliothekstr. 1, 28359-Bremen, Germany*
e-mail presenting author: lamantia@uni-bremen.de

Hydrogen evolution and oxidation reactions are playing an increasingly important role in the energy transition, as molecular hydrogen becomes more popular as future energy carrier. Moreover, hydrogen is also very important as a paradigm electro-catalytic reaction, and therefore it is well-suited as standard for investigating specific effects, such as the influence of a buffer in the kinetics of reaction. In particular, we have investigated the effect ofn the concentration of phosphate buffer with pH value close to neutrality (1:1 KH_2PO4:K_2HPO) on the reaction mechanism and kinetics. In order to unravel the reaction mechanism, we have acquired dynamic impedance spectra during a cyclic voltammetry using dynamic multi-frequency analysis (DMFA). By combining cyclic voltammetry and a multi-sine wave, this methodology allows investigating the frequency response of the electrochemical systems far from the steady state condition [1]. The frequency response can be used to obtain information on the system itself and, if a model is available, it is possible to fit it to the experimental data, as in the classic electrochemical impedance spectroscopy.

The response of the hydrogen reversible reaction to the cyclic voltammetry has shown that both hydrogen evolution as well as hydrogen oxidation changes almost linearly with the concentration of the buffer, thus underlining that the buffer plays an active role. We postulated that in this case the Volmer and Heyrowsky steps proceed through the buffer itself

$H_2PO_4^- + e^- \rightleftharpoons= H_{ad} + HPO_4^{2-}$ (1)

$H_{ad} + H_2PO_4^- + e^- \rightleftharpoons= H_2 + HPO_4^{2-}$ (2)

In addition to this, we used the dynamic impedance spectra to gather information on the reaction path (Volmer-Tafel or Volmer-Heyrowsky) and the reaction kinetic constants based on the variation of the charge transfer resistance and desorption resistance with the electrode potential.

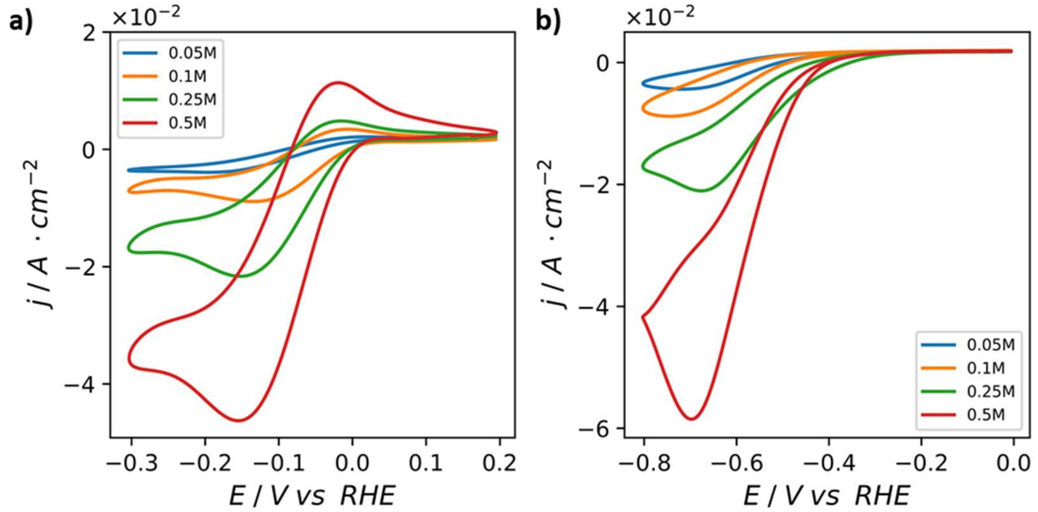

Figure 1: Cyclic voltammetry of hydrogen reversible reaction on (a) platinum and (b) gold at different phosphate buffer concentrations

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Development of ultra-microelectrodes for SECM high-spatial resolution sensing of living cell microenvironment

F. Falciani,[1] M. Malferrari,[1] Gabriele Tullii,[2] Camilla Galli,[3] Elisa Di Pasquale,[3] Maria Rosa Antognazza,[2] S. Rapino[1]

[1]*Department of Chemistry "Giacomo Ciamician", University of Bologna, via F. Selmi 2, 40126,Bologna, Italy.*

[2]*Center for Nano Science and Technology@Polimi, Istituto Italiano di Tecnologia, 20133, Milano, Italy*

[3]*Humanitas Clinical and Research Center-IRCCS, 20089, Milano, Italy*

e-mail presenting author: francesco.falciani4@unibo.it

The study of cellular microenvironment is important for understanding differences of phenotypically different cells, such as healthy cells and cancer cells. The tumor microenvironment (TME) plays a key role in tumor cell progression and cell resistance to therapy[1]. Two of the main factors that afflict tumor microenvironment are extra-cellular pH (pHe) and oxygen consumption by cells. Hypoxia and high glycolytic activity are common characteristics of cancer cells leading to increased production and secretion of lactate and an associated release of H^+ to the extra-cellular space [2].

Due to its non-invasive character and high-spatial resolution Scanning Electrochemical Microscopy (SECM) is a powerful technique for investigating and characterizing single living cell microenvironment [3,4,5]. In this work, we developed an electrochemical method for the study of single cell respiration, also evaluating the cell morphology contribution on the measurements, of healthy and cancer cells. Furthermore, we employed the method to study the oxygen consumption of cardiomyocytes in specific metabolic conditions.

By bringing the electrode close to the cell body, it was possible to disentangle the current signal component related to oxygen concentration from the one due to the topological contribution of the cell. In the near proximity of the cell, the impact of the probe functioning on oxygen availability have been evaluated. We also developed micro-electrochemical sensor to be used as probe in Scanning Electrochemical Microscopy for high-spatial resolution sensing of pH of cell microenvironment.

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A novel voltammetric immunosensor for the POC detection of salivary MMP-8 as a biomarker of periodontitis

R. Antiochia[1], C. Tortolini[2], V. Gigli[2], A. Angeloni[2], F. Tasca[3], N.T.K. Thanh[4,5]

[1]*Department of Chemistry and Drug Technologies, University of Rome "La Sapienza", P.le Aldo Moro 5, 00185, Rome, Italy*
[2]*Department of Experimental Medicine, University of Rome "La Sapienza", Viale Regina Elena 324, 00166 Rome, Italy*
[3]*Faculty of Chemistry and Biology, Department of Materials Chemistry, University of Santiago of Chile, Av. Libertador Bernardo O΄Higgins 3363, 8320000, Estacion Central, Santiago*
[4]*Biophysics Group, Department of Physics & Astronomy, University College London, Gower Street, London WC1E 6BT, U.K.*
[5]*UCL Healthcare Biomagnetic and Nanomaterials Laboratories, Royal Institution of Great Britain, 21 Albermarle Street, London W1S 4BS, U.K.*

e-mail presenting author: riccarda.antiochia@uniroma1.it

Periodontitis is a disease found in the oral cavity which consists of a chronic inflammation of the periodontal tissues, due to the accumulation of dental plaque [1]. Periodontitis starts as a normal gingivitis and can progress onto a chronic and aggressive disease, with periodontal tissue destruction, leading to tooth mobility and tooth loss. Matrix metalloproteinase-8 (MMP-8) was demonstrated to be the most prevalent MMP in diseased periodontal tissue, gingival crevicular fluid (GCF) and saliva, whose concentration correlates with disease severity [2]. Various methods have been reported in literature for quantifying MMP-8 in oral fluids, such as enzyme-linked immunosorbent assay, time-resolved immunofluorescence assay and lateral-flow immunoassays. The only POC devices for salivary detection of MMP-8 available on the market are PerioSafe ® and Implant Safe ® dipstick immunotests, which combine lateral flow technology with ELISA detection.

Voltammetric immunosensors represent interesting alternatives, as they are low cost, fast, easy to use with possibility of POC analysis.

This work describes the development of a novel voltammetric immunosensor for the detection of salivary MMP-8. The electrochemical platform is based on a graphene screen-printed electrode (GPH/SPE) functionalized by gold-nanospheres (AuNSs) [3] and antibodies against MMP-8 protein (anti-MMP-8). The very good performances exhibited by the proposed biosensor allowed its use in real saliva samples, where it showed comparable results to the conventional ELISA method. Therefore, the anti-MMP-8/AuNSs/GPH/SPE based immunosensor may represent a promising tool for non-invasive screening of periodontitis at the POC.

To the best of our knowledge this is the very first time that a voltammetric immunosensor has been developed and applied for MMP-8 detection.

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Carbonaceous slurries for advanced semi-solid redox flow batteries

[1,2]Francesco Capodarca, [3]Alessandro Brilloni, [3,4]Davide Mesto, [1,3]Jaqueline Goldmann, [1,2,3]Francesca Soavi.

[1]Dept. of Chemistry, Giacomo Ciamician, via Selmi 2, 40126, Bologna, Italy
[2]National Reference Center for Electrochemical Energy Storage (GISEL) - INSTM, Via G. Giusti 9, 50121 Firenze, Italy
[3]Bettery Srl , Via Pisacane 56, 74016 Massafra, Italy
[4]Dept. Of Chemistry, Università degli studi di Bari "Aldo Moro", Via Orabona 4, 70125 Bari, Italy

e-mail presenting author: francesco.capodarca@studio.unibo.it

Among the different kinds of energy storage devices, the redox flow battery (RFB) systems have received much attention due to the decoupling between energy and power and their flexibility in design. In this kind of systems, the electrodes are current collectors and their role is to intercept the flowing active solutions and provide higher surface area to increase the contact with the dissolved redox active species, leading to enhanced current density.

A recent approach that has been exploited to boost the RFB performance, is represented by the use of slurry electrodes in the so-called semi-solid RFBs. The slurry electrodes are composed of an electrolyte and carbonaceous particles. Depending on the RFB chemistry, electroactive species are dissolved in the electrolyte or consists in active particles dispersed in the slurry. The great advantage in using non-soluble active materials is to overcome the solubility limit that decreases the maximum energy storable. By exploiting this approach, different kinds of semi-solid RFBs have been exploited, from Vanadium-RFBs up to Li-ion, Li/S and Li/O_2 cells. For all the above mentioned semi-solid RFBs, it is of paramount importance the development of an efficient carbonaceous percolating network that is required to fully exploit the active materials and enhance the kinetics of the faradaic reactions.

The conductive behaviour of the slurries is much affected by the carbon content, the morphology of particles and on the elctrolyte formulations. In turn, these features affect agglomeration or sedimentation in the dispersion media over time.

Here we report about an electrochemical impedance spectroscopy study that has been carried out to evaluate the conductivity of acqueous or organic semi-solid slurries based on different carbons. Specifically the properties of suspensions based on commercial carbon black and CO_2-derived nanoparticles are compared.

Aknowlendgement

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Electrolyte tuning for an effective copper deposition-stripping process in all copper redox flow batteries

Rossella Petruzzelli[1], Giampaolo Lacarbonara[1], Declan P. Casey[2], Stefania Porcu[3], Pier Carlo Ricci[3], James F. Rohan[2], Catia Arbizzani[1]

[1]University of Bologna, Department of Chemistry “Giacomo Ciamician”, Via F. Selmi, 2, 40126, Bologna, Italy
[2]University College Cork , Tyndall National Institute, Lee Maltings, T12R5CP Cork, Ireland
[3]University of Cagliari, Department of Physics, SP 8 Km 0.700, 09042 Cagliari, Italy

e-mail presenting author: rossella.petruzzell2@unibo.it

For large energy applications, redox flow batteries (RFBs) are systems able to store and provide energy with relatively low cost and long cycle life and efficiency in comparison to other electrochemical energy storage devices. They are also interesting systems since energy and power are decoupled, with the possibility to tailor them according to the need [1].

RFBs typically exhibit redox couples at high concentrations in aqueous or organic media, which are stored in two external tanks and pumped into a stack, where oxidation and reduction of the two redox couples occur for charging and discharging the device [2].

All-copper chemistry involves three oxidation states of copper (Cu^0, Cu^+, Cu^{2+}), where Cu^+ and Cu^{2+} are dissolved species in a solution of high chloride concentration and Cu^0 is metallic copper deposited on the substrate surface. In the charging process, electrodeposition of copper takes place at the negative electrode, while reversed reactions are observed during discharge, when the stripping of the deposited copper occurs [3]. The formation of chlorocomplexes assure the solution stability [4]

The Cu deposition requires initial nucleation and subsequent layer growth. The optimal condition requires a high nucleation density on a certain substrate and low overpotential for the deposition. A high nucleation density leads to a more compact and homogeneous deposit that will grow in a controlled manner, minimizing side reactions with impurities and giving a controlled layer growth [5].

The aim of this work is to tune the electrolytes using additives to obtain a homogeneous copper deposit that allows a more effective deposition-stripping process and an increase in the coulombic efficiency of the system.

Acknowledgements

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Towards Sustainable Energy: Progress in Redox-Free Reverse Electrodialysis with Carbon-Based Capacitive Electrodes

A.Aixalà-Perelló,[1,2] P. Zaccagnini, [1] A. Pedico[1], A. Lamberti[1,2]

[1]Politecnico di Torino, Dipartimento di Scienza Applicata e Tecnologia (DISAT), Corso Duca Degli Abruzzi, 24, 10129 Torino, Italy
[2]Istituto Italiano di Tecnologia, Center for Sustainable Future Technologies, Via Livorno 60, 10144 Torino, Italy
e-mail presenting author: anna.aixala@iit.it

This work presents redox-free reverse electrodialysis (R-RE) as a novel approach for sustainable energy conversion. Carbon-based capacitive electrodes are used instead of conventional redox couples, eliminating the need for redox species and enhancing environmental compatibility. Composite electrodes, consisting of active carbon; carbon black, which provided high electrical conductivity; and PTFE binder, which enhances mechanical stability. Titanium grids were incorporated to reduce electrode resistance. Electrode compression was proposed to enhance interfacial contact and reduces ion diffusion path, minimizing parasitic resistances.

The electrodes characteristics were studied by means of electrical impedance spectroscopy and cyclic voltammetry to analyze both the diffuse layer resistance and their capacitive behaviour. Promising results include a maximum capacity of almost 80 F/g and a minimum resistance of around 35 Ohm. The study's findings represent a significant advancement in redox-free reverse electrodialysis, contributing to sustainable energy conversion technologies and environmentally friendly electrochemical systems. The combination of composite electrode materials, titanium grids, and compression techniques improved their performance and reduced parasitic resistances. Accurate dimensioning of the electrodes, facilitated by impedance spectroscopy and cyclic voltammetry, ensured suitability for handling required currents. The research showcases the potential of carbon-based capacitive electrodes in R-RE, addressing the demand for sustainable energy solutions and promoting eco-friendly electrochemical systems.

Ammonium chloride: an unusual electrolyte for promising applications

[i] Andrea Stefano Grassi,[i] Edoardo Guerrini, [i] Massimo Maccagni

[i] Engitec Technologies S.p.A.,via Borsellino e Falcone 31, 20026 Novate Milanese (MI), Italy
e-mail presenting author: a.grassi@engitec.com

Electrowinning is the oldest industrial electrolytic process that involves the electrodeposition of a metal from a solution that leaches it from ores or secondary sources such as wastes or recycled materials. Its first industrial application dates back to 1883 and numerous improvements have been made since then. Nowadays, obtaining high-purity metals using only renewable resources, electricity, and avoiding conventional pyrometallurgy is attracting increasing interest. In 1995 Engitec Technologies began the study of an electrolysis process based on a relatively unusual electrolyte: ammonium chloride[1].

In the electrowinning industry, chlorides always played a controversial role; while they are able to leach and maintain high concentrations of metal cations in the solution their presence inevitably generates chlorine gas at the anode (1). The presence of chlorine gas requires a dedicated abatement system and special care in the choice of electrodes and building materials. Ammonium chloride solves these problems due to the reaction that occurs when chlorine gas is generated in presence of ammonia. Chlorine evolved at the anode reacts immediately with ammonia to produce nitrogen and chlorides (2). Ammonium chloride is not without its complications: mono, di, and trichloramines can be formed depending on the pH of the electrolysed solution [2], and the oxidation of ammonia produces acidity, shifting the pH of the system towards more acidic values. To keep the pH of the solution in the range where the formation of chloramines is avoided, continuous pH monitoring and constant ammonia injection are required.

Engitec's commitment to research has led to the development of two technologies for recovering zinc from electric arc furnace and lead from secondary sources like zinc-rich electric arc furnace dust and lead paste from recycled lead acid batteries. Ammonium chloride is very effective in leaching zinc oxide due to the formation of a stable zinc- chloride-ammonia complex, while in the case of lead, the metal cation is stabilised by the formation of a tetra-chloride complex. While zinc is solubilised as a positively charged complex and is easily electroplated in the form of compact cathode sheets (3), lead is negatively charged and is repulsed by the cathode, leading to the formation of a weakly adherent, spongy deposit. Taking advantage of these two behaviours, Engitec has developed two hydrometallurgical technologies named EZINEX® (Engitec Zinc Extraction) and F.A.S.T. (Flakes Auto-Stripping Technology), both tested on a pilot scale and ready to be commercialised. The overall reaction cell reaction, in the case of the EZINEX® technology, results in the production of metallic zinc, and generation of nitrogen that can be freely released into the atmosphere, avoiding the need for a dedicated abatement system. Ammonia is consumed as a reagent and ammonium chloride is regenerated (4) and reused to close the plant cycle meeting the requirements of a zero liquid discharge plant. This is a very concrete example of the industrial application of electrochemical research.

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{1}$$

$$Cl_2 + {}^2/_3\, NH_3 \rightarrow 2HCl + {}^1/_3\, N_2 \tag{2}$$

$$Zn(NH_3)_2\, Cl_2 \; + 2e^- \rightarrow Zn + \; 2NH_3 + 2Cl^- \tag{3}$$

$$Zn(NH_3)_2\, Cl_2 \; + {}^2/_3\, NH_3 \rightarrow Zn + {}^1/_3\, N_2 + 2NH_4Cl \tag{4}$$

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Tunable all-solid-state wire-shaped high power device

Mara Serrapede[a,b], Francesco Seller[a,b], Pietro Zaccagnini[a,b], Micaela Castellino[b], Ignazio Roppolo[a,b], Felice Catania[b], Jennifer Tata[c], Tiziano Serra[c], Stefano Bianco[b], Andrea Lamberti[a,b]

a Istituto Italiano di Tecnologia, Center for Sustainable Future Technologies, Via Livorno 60, 10144, Turin, Italy
b Politecnico di Torino, Dipartimento di Scienza Applicata e Tecnologia (DISAT), Corso Duca Degli Abruzzi, 24, 10129, Turin, Italy
c MARTUR Italy Srl, Via Stefano Scoffone 3, 10095 Grugliasco T

e-mail presenting author: mara.serrapede@polito.it

Energy storage devices integrated into textiles have emerged as relevant strategy for electronic applications. In this context, herein novel flexible devices were developed, in which the control of both the electrode characteristics and the solid-electrolyte properties allows to build all-solid-state wire-shaped supercapacitors that can be integrated and waved. The proposed class of devices was assembled using modified CNT yarns as electrodes and a blend of ionic liquid, Li salt and poly(ethylene glycol) acrylate to fabricate the solid-polymeric electrolyte. Excellent performance in terms of both electrochemical parameters and stability were obtained. These achievements are possible thanks to the coupling of asymmetric CNT yarns, following an optimization of the activation procedure together with the improvement of the polymeric electrolyte. The results show a capacitance as high as 1.8 mF/cm, energy density of 1.3 µWh/cm and a capacitance retention higher than 100 % over 1200 cycles. [1-3]

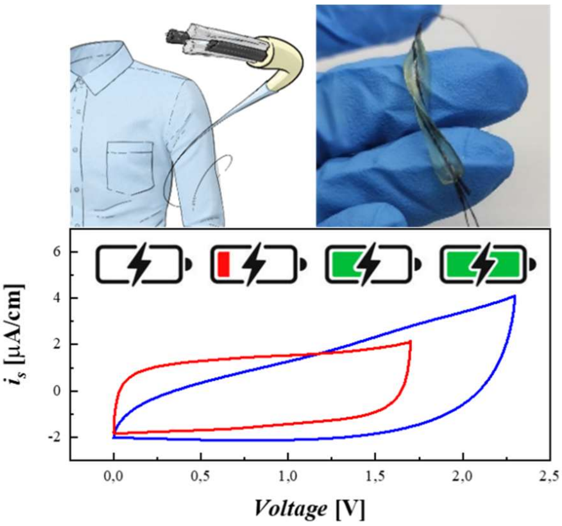

Figure 1 sketch and photo of the wire shaped solid state device and cyclic voltammetries of the symmetric (red) and asymmetric (blue) device.

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Improved specific capacitance of WO_3 nanostructures obtained by hydrothermal synthesis for energy storage applications.

G. Mineo[a,b], M. Scuderi[c], S. Mirabella*[a,b], E. Bruno[a,b]

[a] *Dipartimento di Fisica e Astronomia "Ettore Majorana", Università degli Studi di Catania, via S. Sofia 64, 95123 Catania, Italy.*

[b] *CNR-IMM (Catania Università) via S. Sofia 64, 95123 Catania, Italy.*

[c] *IMM-CNR, VIII strada 5, 95121 Catania, Italy*

e-mail presenting author: giacometta.mineo@dfa.unict.it

Critical raw materials are largely employed in the current technology applications. Their partial or total substitution is challenging for the development of a green and sustainable economy. Nanotechnology represents a strategic route to reduce their use, while continuing to take advantage by their properties. Among them, WO_3 represents a promising material for energy storage applications, thanks to its wide capability of small positive ions (H^+ and Li^+) intercalation and the use of nanotechnology allows to reduce the used total amount of WO_3. The high surface-to-volume ratio of WO_3 nanostructures allows a high rate of charge transfer in supercapacitors with hexagonal crystal structure confirmed by XRD investigation and drop coated onto an appropriate substrate. A careful protocol for electrode realization, controlling mass, thickness and morphology of WO_3 based nanostructures (nanorods and urchin-like nanostructures, 0.5–1 µm long and 50 nm large and 3 µm respectively), is proposed. An extensive electrochemical study (employing cyclic voltammetry and galvanostatic charge-discharge analysis) is performed to evaluate the WO_3 charge storage capability (632 F/g at 5 mV/s and 466 F/g at 0.5 A/g) [1] and to describe and model the storage process in terms of surface and diffusion-controlled mechanisms. The good pseudocapacitive characteristics of the realized WO_3 nanostructures are hence proved by realizing an asymmetric supercapacitor (ASC) in which the as tested WO_3 electrode acts as cathode and a graphene paper (GP) electrode is used as anode, thus obtaining the high energy density (90 W × h/kg) at a power density of 90 W × kg^{-1} and the high-power density (9000 W/kg) at an energy density of 18 W × h/kg [1]. All the data are obtained with a very low mass loading of 2 mg/cm^2, opening the way to use this material in green and sustainable economy.

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Exploitation of Green Supercapacitors to boost RFB performance

Monica Giovannucci[1,2], Elisabetta Petri[1,2], Francesca Soavi[1,2]

[1]Department of Chemistry "Giacomo Ciamician",
Alma Mater Studiorum University of Bologna, Via Selmi 2,40126, Bologna, Italy

[2]Center for the Environment, Energy, and Sea - Interdepartmental Centre for Industrial Research in Renewable Resources, Environment, Sea and Energy (CIRI-FRAME), Alma Mater Studiorum University of Bologna, Viale Ciro Menotti 48, 48122, Marina di Ravenna (RA), Italy

e-mail presenting author: monica.giovannucci2@unibo.it

Designing a Hybrid Energy Storage System (HESS) concerns coupling technologies with complementary characteristics. Several specifications must be taken into account during the feasibility analysis of the HESS: energy density, power density, and discharge time are often considered in this stage. If other characteristics such as cost, lifetime, shelf life, storage duration, ecologic impact safety, and design flexibility are taken into consideration, one of the best technologies couplings appears to be the one made up of Redox Flow Battery (RFB) and a Supercapacitor (SC) [1].

Here we report on a HESS consisting of a direct parallel connection of a Vanadium Redox Flow Battery (VRFB) and a SC. Firstly, the VRFB and the SC have been tested separately with a short time (5 s) discharge protocols; then the two systems have been connected in parallel and tested using the same discharge protocol. After testing, an electrical simple model was created to explain what happens during the discharge of the direct parallel system: the model consists in a parallel R-C circuit that allows to predict the transient behaviour of the coupling. The tests highlighted that the VRFB ohmic drop is mitigated by the SC thanks to the transient behaviour of the R-C circuit; in addition, the hybrid system delivers higher energy at currents that are much higher than those that can be sustained by the VRFB alone. This behaviour is explained by the model that we propose.

Testing and modelling aim to get insights into the behaviour and the benefits of the VRFB-SC HESS. Moreover, the model permits to properly size the SC in relation to the VRFB performance and to select the SC components for such application. Indeed, this work demonstrates that green, aqueous-based SC represent an economic and eco-friendly solution to boost VRFB power at the short discharge times [2] [3].

Acknowledgments

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Dye-doped silica nanoparticles as enhanced luminophores for ECL-based biosensors

M. Difonzo,[i] Y.A. Alemu[i], E. Rampazzo[i], G. Valenti[i], L. Prodi[i], F. Paolucci[i]

[i] *Department of Chemistry "Giacomo Ciamician", Alma Mater Studiorum - University of Bologna,*
Via Francesco Selmi 2, 40126-Bologna, Italy , Institute, Address, ZIP code-City, Country
e-mail presenting author: marinella.difonzo2@unibo.it

Electrochemiluminescence (ECL), consisting of a luminophore generating light as a result of an electrochemical reaction, is a largely exploited technique for bioanalytical applications [1]. The first ECL emitters were organic molecules, which gradually left the way to inorganic complexes [2]. Indeed, ECL-based biosensors are widely employed to quantify biomarkers, such as nucleic acids, proteins, antibodies, small molecules, or even bacteria [1].

One of the most common types of ECL biosensors implies the construction of antibody sandwich assays, through which analytes are captured and revealed. Replacement of single molecules of emitters by dye-doped nanoparticulated systems for the labeling of detection antibodies would enable to improve luminophores' solubility and stability in aqueous media, ameliorate the efficiency of ECL signal generation, and increase biosensors' sensitivity.

Here we show how silica nanoparticles covalently doped with ruthenium derivatives (DDSNPs) increase the ECL signal 8.5 times compared to the $Ru(bpy)_3^{2+}$ complex [3]. However, many parameters, not only the doping degree, are affecting the final ECL intensity and the latter cannot only be improved by a mere increase in the amount of encapsulated dye. Aiming at the individuation of DDSNPs' optimal characteristics for the implementation of a more effective ECL-biosensor, we recently focused on the analysis of the variation of ECL signal according to nanoparticles size and charge of the encapsulated dye [$Ru(bpy)_3^{2+}$ or $Ru(bpy)_2(bps)$].

ECL signal intensity increases with smaller particle size. This is probably due to the larger amount of embedded luminophore accessible to the radical cations that initiate the ECL reaction because of the greater surface area that smaller particles have compared to bigger ones. Nanoparticles doped with a neutral dye rather than a positively charged one exert a higher ECL intensity, as the interaction between the luminophore and the positively charged radicals may be favored by a decrease in the dye's positive charge.

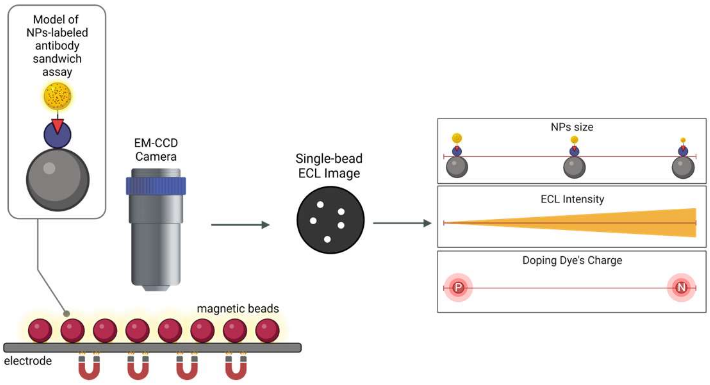

Figure 1: schematic representation of ECL microscopy of DDSNPs conjugated to magnetic microbeads and the relations particles size-ECL intensity and doping dye's charge-ECL intensity observed.

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(Invited) Enhancing sensing and electrocatalysis in NiO microflowers decorated with mono and bimetallic nanoparticles

Salvo Mirabella,[i,ii] Luca Bruno [i,ii], Sergio Battiato [i,ii], Mario Scuderi [iii], Luigi Falciola [iv]

[i] *Dip. di Fisica e Astronomia, Univ. of Catania, Via Santa Sofia 64, Catania, Italy*
[ii] *CNR-IMM, Catania Università, Via Santa Sofia 64, Catania, Italy*
[iii] *CNR-IMM, VIII Strada 5, Catania, Italy*
[iv] *Dip. di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy*
e-mail presenting author: salvo.mirabella@dfa.unict.it

Surface decoration by means of metal nanostructures is an effective way to locally modify the electronic properties of materials. Bimetallic decoration of semiconductor electrodes typically improves catalytic and sensing performances because of a well-claimed synergistic effect. A microscopic and quantitative investigation of such an effect on energy bands of semiconductor can be really useful for further exploitation.

Au, Pd and Au@Pd (core@shell) nanoparticles (10–20 nm in size) were synthesized through chemical reduction method and characterized with scanning and transmission microscopy, Rutherford backscattering spectrometry, cyclic voltammetry electrochemical impedance spectroscopy and Mott–Schottky analysis. The nanoparticles have been used to decorate Ni-based nanostructured electrodes with the aim to quantitatively investigate the effect of decoration with mono or bimetallic nanoparticles. Decorated electrodes show higher redox currents than bare ones and a shift in redox peaks (up to 0.3 V), which can be ascribed to a more efficient electron transport and improved catalytic properties. These effects were satisfactorily modeled (COMSOL) employing a nano Schottky junction at the nanoparticle–semiconductor interface, pointing out large energy band bending (up to 0.4 eV), space charge region and local electric field (up to 108V/m) in bimetallic decoration. Sensing test of glucose and H2O2 by decorated Ni oxide electrodes were performed to consolidate our model. The presence of bimetallic nanoparticles enhances enormously the electrochemical performances of the material in terms of sensitivity, catalytic activity, and electrical transport. The modification of energy band diagram in semiconductor is analyzed and discussed also in terms of electron transfer during redox reactions. [1]

Electrochemical water splitting represents a promising alternative to conventional carbonbased energy sources. The effect of ultra-low Pt decoration on hydrogen evolution reaction (HER) in alkaline media has been modelled through energy band bending supported by electrochemical analyses. A full cell for alkaline electrochemical water splitting has been built, composed of Pt decorated NiO microflowers as cathode and bare NiO microflowers as anode, showing a low potential of 1.57 V to afford a current density of 10 mA cm2 and a good long-term stability [2]. The reported results pave the way towards an extensive utilization of Ni based nanostructures with ultralow Pt content for efficient electrochemical water splitting.

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Atomically Precise Gold Nanoclusters Connected by a Ruthenium(II) Complex Bridge

Mattia Reato, S. Antonello, S. Bonacchi, F. Maran

Department of Chemistry, University of Padova, Via Francesco Marzolo 1, 35131, Padova, Italy
mattia.reato@phd.unipd.it

Understanding and controlling the properties of atomically precise thiolate-protected gold nanoclusters (NCs) is an important research target in current nanoscience. Ultrasmall NCs, with diameters of less than 1.6 nm, are known to exhibit molecular behavior with versatile properties that make them interesting building blocks for fabricating hierarchical structures with customized electronic, electrochemical, optical, and magnetic properties [1-4]. This work describes a novel triad system where two $Au_{25}(SR)_{18}$ clusters are bridged by a Ru(II) complex coordinated to three bipyridines, one of which containing two -CH_2SH groups (Figure 1A). The formation of this new system was confirmed by UV-vis absorption spectroscopy, ESI mass spectrometry, nuclear magnetic resonance, and electrochemistry. The multi-component system exhibits a multiredox-response, and differential pulse voltammetry measurements (Figure 1B) point to some electronic communication between the two NC cores. This work represents an important first step in the quest for making complex electroactive materials using NCs as building blocks.

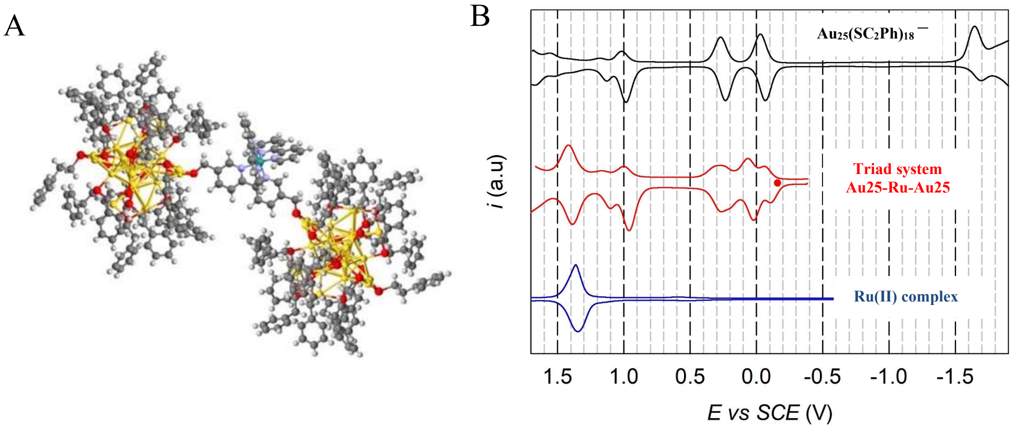

Figure 1: A) Molecular model of the triad system; **B)** DPV curves of the triad and reactants used in the synthesis.

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Oxygen Reduction Reaction at Fe Phthalocyanine Modified Electrodes. The Effect of Ligands (-F, -Cl, -Br, -I, -ClO_4, -NO_3), Ions, and pH on the Electrocatalysis. Ab initio Molecular Dynamics Simulation in Electrolyte Media and Experimental Analysis

Federico Tasca[i], Walter Orellana[ii], César Zúñiga Loyola[ii], Angélica Gatica Caro[ii], Nicolas Troncoso[ii], Soledad Ureta[ii], Jose H. Zagal[ii],

[i]*Facultad de Química y Biología, Universidad de Santiago de Chile, Santiago, Chile.*
[ii]*Departamento de Ciencias Físicas, Universidad Andrés Bello, Sazié 2212, 837-0136 Santiago, Chile.*
e-mail:Federico.tasca@usach.cl

Iron macro cycles are among the most promising non precious metal catalysts for the oxygen reduction reaction (ORR). Nevertheless, those catalysts perform very poor in acidic media. To understand the reasons that cause the impossibility to use those catalysts in acid, graphite electrodes were drop-coated with inks of iron phthalocyanine adsorbed on carbon nanotubes (FePC-CNT) and the electrocatalytic behaviour of the catalyst was studied in various supporting electrolytes (i.e., HF, HCl, HBr, HI, H_2SO_4, $HClO_4$, CH_3COOH, HNO_3 and NaOH) by the mean of cyclic voltammetry, polarization curves, and electrochemical impedance spectroscopy. Water, cations and anions were simulated by ab initio molecular dynamic simulations to explain and visualize the occurring physical adsorption phenomena. The demetallation of the catalyst could be excluded because more than 3.6 eV would be necessary for this process to occur. On the other hand, we found that the absorption of the anion of the specific acid at the Fe centre, would compete with the coordination of oxygen and prevent the catalytic process, modifying the ORR rate-determining step and the final product of the reaction. Electrochemical analysis, Tafel slope analysis, as well as impedance spectroscopy corroborate this process.

Oxygen reduction reaction mechanism in Calcium-doped double perovskite as reversible electrode for solid oxide cells

A. Barbucci[1], A. Maria-Asensio[1], F.R. Bianchi[1], L. Cardona[1], D. Clematis[1], B. Bosio[1]

[1] *Department of Civil, Chemical and Environmental Engineering (DICCA), University of Genoa, Via All'Opera Pia 15, Genova, Italy*
e-mail presenting author: barbucci@unige.it

Solid oxide cells (SOC), electrolysers and fuel cells, represent a promising technology able to fulfil the goals of energy transition [1]. The market penetration of such devices needs the development of high-performing materials, and a rising interest is focused on double perovskites. These mixed ionic electronic conductors can be tuning by chemical composition and electrode morphology to reach high chemical stability and high electrochemical performance. They are excellent oxygen electrodes in solid oxide cell technology used as fuel cells, steam/CO_2 electrolysis cells and electrochemical air separation units.

$SmBa_{1-x}Ca_xCo_2O_{5+\delta}$ co-doped double perovskite is here considered as a promising reversible oxygen electrode, and a deeper analysis about the optimal composition ($SmBa_{0.8}Ca_{0.2}Co_2O_{5+\delta}$) is discussed. The goal of the analysis is the identification of kinetic path for oxygen reduction and oxidation reactions by coupling different electrochemical techniques (EIS, I-V curve), (Figure 1-a). The electrochemical characterization has been performed in a wide range of operation conditions (temperature, oxygen partial pressure) to evaluate the electrode reversible behaviour, and the relationship between phenomena governing the overall electrode kinetics has been established by using distribution of relaxation times (DRT), equivalent circuit analysis (ECM) and physically-base modelling (Figure 1-b).

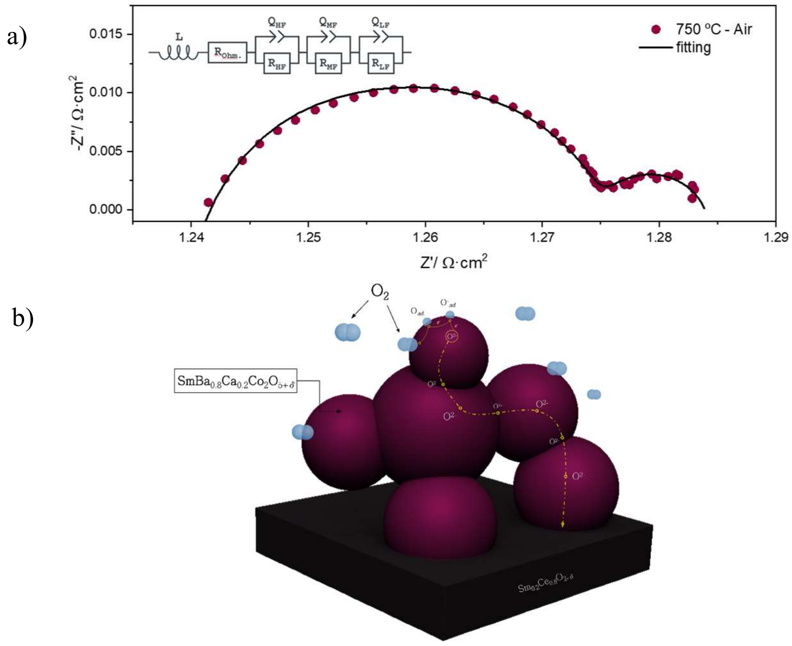

Figure 1: **a)** Electrochemical Impedance Spectroscopy of symmetrical half-cell of $SmBa_{0.8}Ca_{0.2}Co_2O_{5+\delta}$ at 750 °C, in air. **b)** Sketch of the kinetic mechanism for oxygen reduction reaction

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Study of the Oxygen Reduction Reaction on Electrocatalysts in Conditions Mimicking Fuel Cell Operation by High-Temperature *“Ex-Situ”* Cyclic Voltammetry

A. Brega,[1] A. Nale,[2] S. Brimaud,[1] E. Negro,[2] L. Joerissen,[1] G. Pagot,[2] S. Boudjelida,[2] P. J. Kulesza,[3] I. A. Rutkowska,[3] V. Di Noto[2,4]

[1] ZSW - Center for Solar Energy and Hydrogen Research Baden – Württemberg, Helmholtzstraße 8, 89081 Ulm, Germany
[2] Section of Chemistry for Technology, Department of Industrial Engineering, University of Padova, Via Marzolo 9, 35131 Padova, Italy
[3] Faculty of Chemistry, University of Warsaw, Pasteura 1, PL-02-093, Warsaw, Poland
[4] National Interuniversity Consortium of Materials Science and Technology, Via Marzolo 9, 35131 Padova, Italy

e-mail presenting author: vito.dinoto@unipd.it

The most widespread *“ex-situ”* approach to screen developmental ORR ECs involves the use of a rotating (ring) disk electrode (R(R)DE) setup. Though very practical and accurate, conventional R(R)DE experiments are able to study the ORR features of an EC only in quite a narrow set of operating conditions (T = 30-60°C; P = 1 bar). These latter are different from those that are most commonly adopted at the cathode of a LT-FC (T = 80-100°C; P = 2 – 3 bar). As a result, the information obtained on the ORR features of an EC by means of conventional R(R)DE studies may not be fully representative of the behavior of the EC in an operating LT-FC.

To address this shortcoming herein we present an innovative setup able to elucidate the ORR features of both benchmark and innovative ECs in experimental conditions that are very close to those found in operating low-temperature FCs. Specifically, the setup consists of a homemade channel flow electrode (CFE) cell operated in a rather simple closed system with a controlled oxygen concentration and maintaining a high level of cleanliness.

The modeling, materials selection, design, and testing of a versatile CFE cell developed from scratch is presented. The cell is compatible with commercially-available RDE components and special care is devoted to ease the overall assembly of the experimental setup. The cell is characterized by a well-defined hydrodynamics, a low dead volume, a high mass-transfer rate and a high signal/noise ratio. The cell also allows to measure accurately the pressure and the temperature in close proximity of the working electrode. It is demonstrated the possibility to study the ORR features of ECs up to a temperature of 80°C and a pressure of 3 bar. Both benchmark and innovative ECs are taken into consideration. The latter exhibit features that are very different in comparison with the conventional Pt/C ECs, especially in terms of: (i) chemical composition of the active sites, that typically includes more than one element; and (ii) morphology of the support, that is based on different carbon nanostructures. The proposed setup is implemented to determine crucial ORR features of the ECs, including the kinetically-controlled current, the activation energy and the accessibility of O_2 to the active sites.

Acknowledgements

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(Invited) Hybrid electrolyte membranes for high temperature PEM fuel cells

I. Nicotera,[i] C. Simari,[i] E. Lufrano,[i] A. Enotiadis[j]

[i] *Department of Chemistry and Chemical Technology, University of Calabria, Via P. Bucci, Rende (CS) 87036, Italy*
[j] *National Center for Scientific Research "Demokritos", 15310, Athens, Greece*

e-mail presenting author: isabella.nicotera@unical.it

Nanocomposites membranes based on hydrophilic nanostructured materials are of great interest for PEMFC applications due to significant gains in thermal stability, mechanical and barrier properties. Layered doubled hydroxide, Graphene Oxide (GO) or Nanoscale Ionic Materials (NIM), were properly synthesized and organo-functionalized to interact with the ionomer in order to prepare advanced hybrid electrolytes membranes. Such materials can modulate the nature of water confined in the nanosized ionic channels of Nafion (perfluoro sulfonic acid - PFSA - ionomer), and, as a result, hybrid membranes show high proton mobility and water retention in dehydrating state.[1-3]

Non-fluorinated aromatic polymers have clear advantages over PFSA membranes for fuel cell applications, including higher mechanical strength, thermal and chemical stability, oxidation resistance and ease of processing. Its low cost, mechanical and thermal resistance, reduced fuel crossover and ease of preparation make polysulphone (PSU) a potential candidate to replace the Nafion electrolyte in proton exchange membrane fuel cells (PEMFCs).

Novel nanocomposite proton exchange membranes based on sulfonated Polysulfone were successfully fabricated via scalable, cost-effective, and ecofriendly solution casting method.[4-5] The formation of highly connected ion channels promotes an effective Ghrotthus-type mechanism for the proton transport also under dehydrating environment. Such features allowed proton conductivity values and electrochemical performances in single cell PEMFC distinctly higher than the Nafion recast, demonstrating the possibility to prepare cost-effective and high performing sPSU-based membranes able to operate under very harsh conditions, that is low-humidification and high temperatures.

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Triggering the electrode multi-catalytic activity for reversible symmetric solid oxide cells

Anna Paola Panunzi, Leonardo Duranti, and Elisabetta di Bartolomeo

Department of Chemical Science and Technologies, University of Rome Tor Vergata, Via della Ricerca Scientifica, 00133-Rome, Italy
e-mail presenting author: anna.paola.panunzi@uniroma2.it

The intermittent nature of renewables requires efficient systems capable of storing excess energy and supplying it during the consumption peaks. Among innovative technologies, reversible solid oxide cells (r-SOC) combine the concepts of solid oxide electrolyser cell (SOEC) and solid oxide fuel cell (SOFC) in a single device. R-SOCs can alternatively switch between power-to-fuel mode (turning energy into storable fuels) and fuel-to-power mode (converting back the stored fuels into electrical energy) with high intrinsic efficiency resulting from high temperature operation [1].

The pursuit of newly designed materials has recently been oriented towards the tailoring of a multi-purpose catalyst, both for anodic and cathodic applications. To this extent, the concept of reversible symmetric solid oxide cells (r-SSOCs) minimizes mechanical and thermo-chemical compatibility issues to a single type of electrode/electrolyte interface, reducing fabrication/maintenance costs and favoring large-scale production [2], as well as withstand antipodal pO2 conditions at high temperature [3].

Together with redox resistance, the electrode material of a r-SSOC must ensure both mixed ionic-electronic conductivity and versatile activity towards all the reactions involved: ORR, OER, oxidation of various fuels and H_2O/CO_2 reduction. Low cost, earth-abundant iron-based perovskite oxides are ideal candidates as multi-tasking electrode materials. B-site substitution on Sr-doped lanthanum ferrites $La_{1-x}Sr_xFe_{1-y}M_yO_{3\pm\delta}$ has been extensively explored, aiming at increasing structural stability under highly reducing environment (M = Ti, Cr, Mn) [4], or electronic/ionic conductivity and catalytic activity (M = Co, Ni, Cu) [5].

A valuable solution in terms of electrocatalytic performance is the substitution of B-site iron with a small amount (< 5 mol%) of platinum group metals (PGMs). Such quantities of PGMs can be profitably harvested from secondary sources, such as spent automotive three-way catalysts (TWCs) or more recently, from electrode membrane for hydrogen production [6]. Recycling is an economically and ecologically convenient PGMs source, alternative to localized low-grade ores extraction.

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Innovative ceria nanoparticles decoration for composite Aquivion® proton exchange membranes with improved lifetime

D. Stucchi[1], A. R. Ferrari[1], T. Caielli[1], G. Stucchi[1], A.G. Di Tolla[1], P. Mustarelli[1]

[1] *Material science dept., Università degli Studi di Milano Bicocca, Via Cozzi 55 Milano, 20125, Italy*
e-mail presenting author: d.stucchi7@campus.unimib.it

Almost all the energy we consume is produced from fossil fuels with the subsequent production of CO_2 that is the main cause of the ongoing climate crisis. The most promising alternative is a hydrogen-based circular economy where green H_2 is produced in renewable electricity-powered water electrolyzers, and electrochemically combined with oxygen to power all our everyday activities in fuel cells. The only commercially available technology in this field are of proton exchange membrane fuel cell (PEMFC) where the ion conducting membrane is based on a perfluorosulfonated polymer (e.g. Nafion® and Aquivion®). The main limit of this technology is related to the relatively low lifetime of the device caused by the degradation of the polymeric chains [1] caused by radical species (•OH •OOH) created, as byproducts of the complicated oxygen reduction reaction, at the cathode.

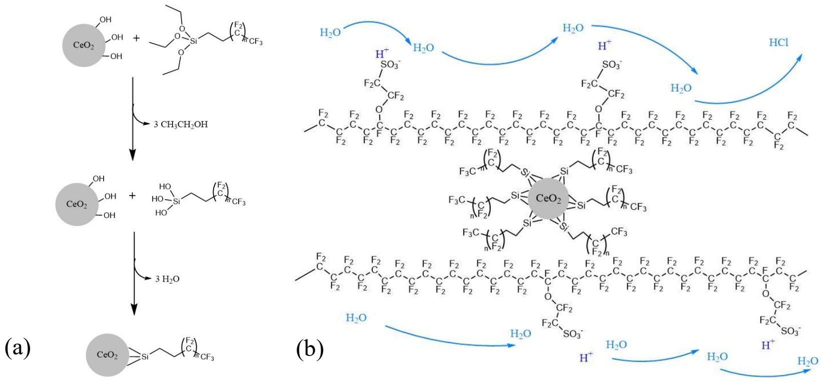

Figure 1: schematic representation of the decoration procedure (a) and of the resulting composite membrane (b)

The best strategy to improve the device's lifetime is the introduction of radical scavenger species in the membrane electrode assembly (MEA). The most promising radical scavengers are cerium oxide nanoparticles embedded either in the polymeric membrane [2], or in the catalyst layer [3]. To improve the compatibility between the inorganic filler and the organic polymeric matrix we synthesized CeO_2 NPs decorated with a perfluoroalkyl chain trough a silanization process of the nanoparticles surface (figure1). This is expected to increase the compatibility of the filler with the membrane thus allowing for higher scavenger loads without significant losses in conductivity: the perfluorinated pendant on the oxide NP is expected to anchor it in the hydrophobic domain of the membrane; thus, hopefully, not disrupting the delicate ionic channel network. Furthermore, the decoration is expected to reduce the migration effect that have been highlighted in long-term studies [4] of composite MEAs and improve the mechanical properties of the membrane acting as a physical cross-linker between different polymeric chains. Both the decorated NPs and the composite membrane have been characterized with thermal analysis (TGA, DSC), mechanical measurements (DMA, tensile strength) morphological studies (XRD and SEM) and spectroscopies (IR, ss-NMR). The resulting membranes were also electrochemically characterized with IEC and conductivity measurements as well as with Fenton for durability assessment.

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Valorization of forestry-waste as electrode materials for Na-ion batteries

Luca Bottoni,[i] H. Darjazi,[i] L. Sbrascini,[i] A. Staffolani, L. Balducci,[i] L. Minnetti,[i] F. Nobilii,[i,j]

[i] School of Science and Technology, Chemistry Division, University of Camerino, Via Madonna delle Carceri, Camerino, 62032, Italy
[j] GISEL, Centro di Riferimento Nazionale per i Sistemi di Accumulo Elettrochimico di Energia INSTM, Via Giuseppe Giusti 9, Firenze (FI) 50121, Italy
e-mail presenting author: luca.bottoni@unicam.it

Nowadays, sodium-ion batteries (SIBs) represents a potential alternative to lithium-ion batteries (LIBs) in large-scale energy storage applications due to the low cost and large distribution of sodium resources [1]. Recent improvements in SIBs have been obtained by the utilization of Hard Carbon at anode side, which can be obtained by renewable feedstock such as lignocellulosic materials coming from agricultural and forestry by-products [2]. In addition, the selection of a bio-based binder is crucial to break down the impact on the environmental sustainability and costs reduction of electrodes [3]. In this context, five different local forestry plants waste collected from Central Apennines (Italy) were used as precursor for both fabrication of Hard Carbon and extraction of their components (i.e. cellulose and lignin) that were used as binders. The Hard Carbons were obtained through a pyrolysis at 1000 °C in N_2 atmosphere with different yields % according to the lignin and cellulose contents. The cellulose was isolated with a mild bleaching process with H_2O_2 and then converted to the sodium salt of carboxymethylcellulose (Na-CMC), while the lignins were extracted through an organsolv methods combining Cyrene or γ-Valerolactone in a mixture with H_2O. In Figure 1 are reported the charge-discharge cycling and rate capabilities of holm-aok and willow-derived hard carbons combined with the two binders in anode and compared with commercial-CMC. The best electrochemical performances were obtained with Holm oak-derived HC using lignin as binder: it delivers specific capacity higher than 200 mAh g^{-1} at 1C (300 mA g^{-1}) with promising capacity retentions (around 76 % after 1000 cycles) and superior rate capabilities. Similar results were obtained for Willow-derived HC, where the binder lignin guarantee a very high stability upon cycling (capacity retention of 87 % after 1000 cycles) as well as good rate capability. The long cycle life, the cell stability and the capacity retention using lignin as binder can be related to the robust adhesiveness given by the highly crosslinked structure of lignin.

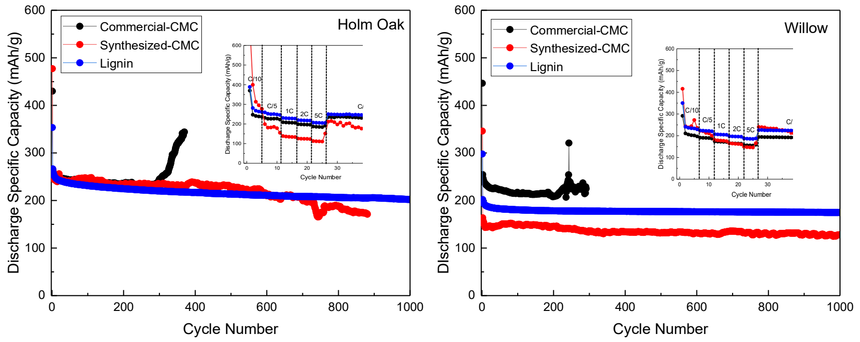

Figure 1: Specific Capacities and Rate Capabilities with different binders of Holm oak and Willow-HCs;

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Effect of Presodiation Additive on Structural and Interfacial Stability in $Na_{0.66}Mn_{0.75}Ni_{0.2}Mg_{0.05}O_2$/Hard Carbon Full Cell

L. Sbrascini,[a] A. Sarapulova,[b] C. Gauckler,[c] M. Marinaro,[c] F. Nobili,[a,d] S. Dsoke,[b]

[a] *School of Science and Technology – Chemistry Division, University of Camerino, Via Madonna delle Carceri – ChIP, Camerino 62032, Italy*
[b] *Institute for Applied Materials (IAM), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany*
[c] *Zentrum Für Sonnenenergie Und Wasserstoff Forschung Baden-Württemberg (ZSW) Helmholtzstraße 8, 89081, Ulm (Germany)*
[d] *GISEL – Centro di Riferimento Nazionale per i Sistemi di Accumulo Elettrochimico di Energia, INSTM, Firenze, Italy*
e-mail presenting author: leonardo.sbrascini@unicam.it

Due to the limited availability of Li resources on the Earth's crust, the transition from Li- to Na-ion batteries is progressively becoming a more and more important research topic, especially when considering the stationary energy storage. For full cell applications, Ni- and Mn-based P2-layered oxides have demonstrated to be suitable cathode materials to achieve high working potentials and cyclic stability while still maintaining environmental benignity [1]. On the other hand, porous hard carbons derived from waste biomass are the mostly explored anode materials in SIBs because of their ability to store Na^+ ions through intercalation and surface adsorption; however, they generally suffer from high irreversible capacity loss at the first cycle due to the formation of SEI [2]. Pre-sodiation agents for practical application on a larger scale are therefore required [3]. The present work proposes the study of sacrificial $Na_2C_4O_4$ as a pre-sodiating agent in a cell employing a layered $Na_{0.66}Mn_{0.75}Ni_{0.2}Mg_{0.05}O_2$ cathode and a corn cob-derived hard carbon anode with high loadings. The chosen anode/cathode combination is found to be in principle suitable for full cell application, with good stability and reversibility after the first cycles. The use of $Na_2C_4O_4$ to address the SEI formation successfully provided a higher initial specific capacity, though a progressive worsening of reversibility and stability is also displayed. Changes in the structural evolution upon cycling, in the surface morphology of the electrode and in the electrolyte decomposition, as well as in the SEI/CEI interphases formation are deeply studied through in-situ and ex-situ techniques upon presodiation, evidencing a polarization of the P2-to-OP4 phase transition and a thickening of SEI/CEI with the presence of carbonate species, eventually leading to increased resistances.

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On the structural evolution of air-exposed layered oxide cathodes for sodium-ion batteries: the example of Sodium Manganese Nickel Oxide

N. Pianta,[a] G. Brugnetti,[a] C. Triolo,[b,d,e] A. Massaro[c,d], I. Ostroman[a], C. Ferrara[a,d,e], D. Sheptyakov[f], A. B. Muñoz-García[d,g], M. Pavone[c,d], S. Santangelob,d,e, R. Ruffo[a,d,e]

[a] Dipartimento di Scienza dei Materiali, Università di Milano Bicocca, Milano 20125, Italy.
[b] Dipartimento di Ingegneria Civile, dell'Energia, dell'Ambiente e dei Materiali (DICEAM), Università "Mediterranea", Via Zehender, Loc. Feo di Vito, 89122 Reggio Calabria, Italy.
[c] Dipartimento di Scienze Chimiche, Università di Napoli Federico II, Napoli 80126, Italy.
[d] National Reference Center for Electrochemical Energy Storage (GISEL), Via G. Giusti 9, Firenze 50121, Italy
[e] Consorzio Interuniversitario per la Scienza e Tecnologia dei Materiali (INSTM), Via G. Giusti 9, Firenze 50121, Italy
[f] Laboratory for Neutron Scattering and Imaging, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland
[g] Dipartimento di Fisica "E. Pancini", Università di Napoli Federico II, Napoli 80126, Italy.
e-mail presenting author: nicolo.pianta@unimib.it

As the interest on Sodium-ion batteries (SIBs) grows not only in research but also in the industrial landscape, so does the necessity for systematic and exhaustive studies on the active materials that compose them. Layered oxides (Na_xTMO_2) are a typical choice for cathode fabrication due to their good properties in terms of achievable capacity and operating potential[1,2]. Several of them are, unfortunately, unstable towards air and tend to change their structure upon water insertion[3,4]. Despite the impact it would have on a battery's performance, their structural evolution during air exposure is currently not known.

The example here proposed concerns the properties of Sodium Manganese Nickel Oxides (NMNO), a well-known class of cathodes for Sodium-Ion Batteries[5,6]. The structural evolution from a layered P2 to a monoclinic birnessite one was evaluated by subsequent X-ray diffraction analyses, together with exhaustive studies of the electronic features both on the pristine and on the final material. The electrochemical properties of both structures of NMNO were deeply evaluated in half cells vs metallic lithium, showing similar potential-electric charge profiles but with differences in both average potential and diffusion coefficients. Sodium insertion mechanism was also studied by means of ex situ X-ray synchrotron diffraction and Raman analyses so to correlate electrochemical and structural properties together. Finally, DFT calculations were used to unveil the role of intercalated water molecules on the electrochemical and structural properties of air-exposed NMNO, clarifying how the birnessite phase maintains very good stability.

Apart from giving a clearer view on the processes and timescale of layered oxide reaction with atmospheric water (particularly useful when dealing with alkali-ion batteries), the study of this aging process can be used as an important tool to theorize new highly scalable syntheses, alternative to wet and solid-state ones for birnessite phases, opening new windows towards other uses of transition metal oxides in water-based environments (e.g., aqueous Sodium-Ion Batteries).

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Tuning the energy storage properties of pseudocapacitive Manganese Oxides obtained via electrochemical synthesis.

P. Zaccagnini,[1,2] M. Sperti,[1] M. Serrapede,[1,2] L. Baudino,[1] M. Reina,[1,2] A. Pedico,[1] S. Bianco,[1] A. Lamberti[1,2]

[1] Department of Applied Sciences and Technologies, Polytechnic of Turin, Corso Duca degli Abruzzi 24, 10129-Turin, Italy
[2] Centre for Sustainable and Future Technologies, Italian Institute of Technology, Via Livorno 60, 10144-Turin, Italy
e-mail presenting author: pietro.zaccagnini@polito.it

Electrodeposition of manganese oxides can be achieved through cathodic and anodic processes. In the cathodic process, manganese deposition occurs initially, followed by oxidation in an oxidizing atmosphere [1]. The anodic processes, as documented in the literature, involve the direct synthesis of primarily hydroxide structures [2,3].

Based on a proposed synthesis method [4], a recent work under review [5] introduces an additional assumption. We propose the incorporation of sodium ions from the supporting electrolyte into doped manganese oxide phases. This concept was further explored in our study, where we investigated the influence of the supporting salt cation on the storage capacity of the synthesized manganese oxides. Figure 1 presents preliminary analyses, depicting gravimetric capacitances plotted against the size of the supporting cation radius of sulfate salts (C_2SO_4, C=Li, Na, K). The measurements were performed at 1 mV s^{-1} in an aqueous 1M Na_2SO_4 electrolyte. It is hypothesized that the doped layered structures may exhibit distinct structural properties [6].

This result is part of a project that has received funding from the European Research Council (ERC) under the European Union's ERC Starting Grant Grant agreement No. 949916

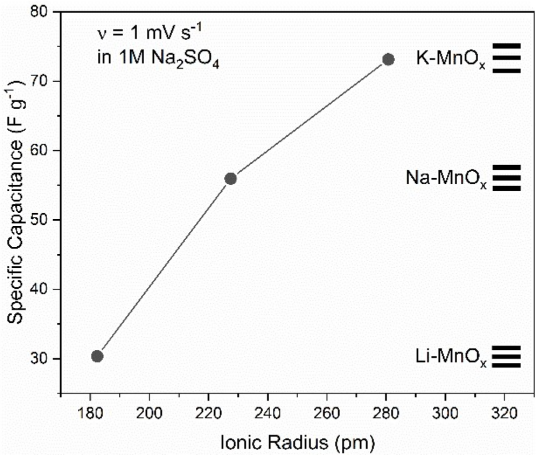

Figure 1: measured gravimetric capacitances vs the cationic radiuses of the different supporting salts. These values were calculated out of CV recorded at 1 mV s-1 in the same aqueous electrolyte of 1M Na_2SO_4.

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Phase-separating active materials in lithium-ion batteries: a modelling overview with application to carbon-based anodes

A. Bertei,[a] M. Lagnoni,[a] X. Lu,[b] S. Ahn,[c] D. Chernyshov[c]

[a] Dept. of Civil and Industrial Engineering, University of Pisa, Largo Lucio Lazzarino 2, IT 56126-Pisa, Italy
[b] School of Engineering and Materials Science, Queen Mary University of London, Mile End Road, GB E1 4NS-London, United Kingdom
[c] HE Carbon Supercap Ltd, 32 Telford way, GB W3 7XS-London, United Kingdom
e-mail presenting author: antonio.bertei@unipi.it

Some active materials used in lithium-ion battery (LIB) electrodes undergo phase separation into Li-rich and Li-poor phases upon lithium intercalation. Typical examples are $LiFePO_4$ (LFP) at the cathode and graphite at the anode. While phase separation enables useful features, such as a constant equilibrium potential as a function of state-of-charge, such behaviour is too complex to be modelled as solid-solution materials and necessitates a different approach.

In this study we present a modelling framework, based on the phase-field approach and non-equilibrium thermodynamics principles [1], which reproduces phase separation at the particle scale in LIB electrodes. We discuss how the data obtained with classical techniques used to estimate solid-state diffusion coefficients, such as the galvanostatic intermittent titration technique (GITT) [2], must be revisited for this class of materials. In particular, simulations show that the relaxation behaviour of a phase-separating active material upon current interruption is not only a function of solid-state diffusion properties, but its time-scale depends also on the dynamics of moving interfaces between Li-rich and Li-poor phases. This has significant implications on the distribution of lithium within secondary particles because, upon fast lithiation, the Li-rich phase grows at the particle surface and prevents further lithiation. This is especially critical for graphite anodes, since the Li-rich phase (also known as stage I) at the particle surface promotes the plating of metallic lithium outside the particle [3]. On the other hand, experiments and simulations of a disordered carbon, which does not undergo phase separation, reveal an effectively faster solid-state diffusion and a more significant resistance to lithium plating even at high C-rate [4]. We finally discuss how these insights can guide researchers to improve battery materials and to design more efficient fast-charging protocols.

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Insights into the Development and Performances of Ionogel-based Electrolytes for Solid-State Lithium-based Batteries

Y. Zhang[1,2], C. Gerbaldi[1,2], G. A. Elia[1,2]

[1]Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129-Turin, Italy
[2]National Interuniversity Consortium of Materials Science and Technology (INSTM), Via G. Giusti 9, 50121-Florence, Italy
e-mail presenting author: ying.zhang@polito.it

Among different types of solid-state electrolytes (SSEs), the ionogel systems, in which polymer electrolytes are doped with room-temperature ionic liquids (RTILs), are amongst the most attractive choices to reach ionic conductivity values comparable to those of liquid electrolytes, ensuring better safety and electrode/electrolyte interface stability [1]. In our previous studies, several ionogel samples were prepared by in-situ UV-curing [2]. Here, we present the results of newly optimized methacrylate-based solid-state electrolyte systems conceived for ambient temperature cycling with high-energy cathodes. We characterized the electrolyte formulations using various physico-chemical and electrochemical methods, and the focus is particularly on the influence of using two different RTILs as reaction media on the properties of the resulting materials and their electrochemical behaviours. The achieved results indicated that viscosity affects the polymerization kinetics of the ionogels, which in turn affects their thermal stability and galvanostatic cycling behavior. Lithium lab-scale cells were assembled with ionogel-polymerized-on-NMC-cathodes for galvanostatic cycling measurements, and they demonstrated initial discharge capacities of around 180 mAh/g at low C-rate in the voltage range of 3.0-4.3 V at room temperature. Furthermore, motivated by the demand of increasing the overall performance of the SSEs, different types of composite electrolytes are now under our investigation and further development, including the utilization of active and inert inorganic fillers. For example, we introduced LLZO ceramic microparticles into ionogel systems for fabricating composite SSEs via *in-situ* photopolymerization. So far, the best achieved preliminary cycling results showed enhanced and more stable cycling behaviour at higher C-rates up to 0.2C at room temperature, which demonstrates the promising prospects of our composite SSEs and their potential contribution to the fabrication of solid-state, high-energy lithium-based batteries.

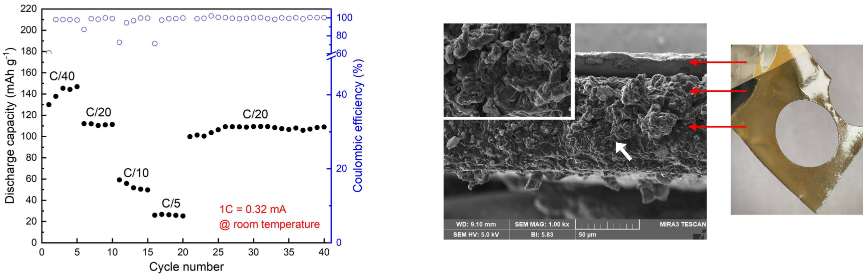

Fig. 1. Galvanostatic cycling results (left) and FESEM cross-sectional image (right) of composite electrolyte fabricated through in-situ polymerization on the surface of NMC-532 cathodes.

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Innovative electrode chemistry in ionic liquid electrolytes for sodium-less battery systems

Giovanni Battista Appetecchi,[a] Andrea Cioffi,[a,b] Angelica Petrongari,[b] Sergio Brutti[b,c]

[a]ENEA, Materials and Physicochemical Processes Technical Unit (SSPT-PROMAS-MATPRO)
Via Anguillarese 301, 00123, Roma, Italy
[b]La Sapienza University of Rome, Department of Chemistry, P.le Aldo Moro 5, 00185, Rome, Italy
[c]GISEL-Centro di Riferimento Nazionale per i Sistemi di Accumulo Elettrochimico di Energia,
INSTM, Via G. Giusti 9, 50121 Firenze, Italy
gianni.appetecchi@enea.it

Sodium as well as lithium metal anodes are affected by severe passivation phenomena by the electrolyte, leading to unwelcome surface growth up of passive layers and/or dendrites which deplete the performance and safety of the electrochemical device [1]. Silica-gel based electrode substrates (SGESs), able of hosting sodium within their porouos structure, were proposed in the place of conventional Na° metal anodes because of their capability of allowing very homogeneous sodium plating, thus remarkably reducing dendritic formation [2]. Therefore, SGESs were addressed to sodium-less battery systems where the Na° anode is initially missing.

In this work, the behaviour of SGESs was investigated in innovative electrolytes based on salts molten at room temperature, called ionic liquids (ILs). ILs, highly retardant fluids with negligible vapor pressure, are proposed as alternative solvents to volatile and hazardous alkyl carbonates, commonly used in sodium batteries, for enhancing the safety and reliability level of the electrochemical device.

The SGESs were prepared by blending the active material (Sodium silica-gel) with the electronic conductor (carbon) and a polymer binder (PEO or PVdF). Trimethyl-butyl-ammonium bis(fluorosulfonyl)imide ($N_{1114}FSI$), synthesized and purified in our labs, was selected as the ionic liquid [3] in combination with the NaTFSI and NaFSI salts. XRD, Raman and SEM-EDX analysis were carried on SGESs for investigating their chemical structure whereas galvanostatic cycling tests were run to examine the electrochemical performance. Tests in organic electrolyte were carried out for comparison purpose.

The data show a coulombic efficiency equal to 100 % starting from the 1st cycle and for more than 500 cycles in conjunction with very low cell voltage (3-30 mV), highlighting for efficient and reversible Na° stripping/plating process. These results are likely ascribable to an optimal electrode/electrolyte interphase due to the good film-forming ability of the FSI anion. SEM-EDX analysis, carried out after prolonged cycling tests (> 500 cycles), evidences stronger degradation for the FSI anion with respect to the TFSI one and a thicker passive film in the PVdF-containing SGESs. The $N_{1114}FSI$ ionic liquid shows a better compatibility with SGESs and Na° electrodes with respect to the organic solvents. The best performances were found in the NaFSI-based electrolyte.

To summarize, this work demonstrated the feasibility of ionic-liquid electrolytes in sodium-less batteries, enhancing the safety/reliability and, at the same time, the electrochemical performance (as compared with organic electrolytes).

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Evaluating the impact of processing on argyrodite-based thin solid electrolytes

L. Mezzomo,[a-b] J. Li,[b] S. Kim,[b] Y. A. Chart,[b] M. Pasta,[b] R. Ruffo[a]

[a] Dipartimento di Scienza dei Materiali, Università di Milano Bicocca, via Cozzi 55, 20125-Milano, Italy
[b] Department of Materials, University of Oxford, Parks Road, OX1 3PH-Oxford, United Kingdom
e-mail presenting author: l.mezzomo@campus.unimib.it

Inorganic solid-state electrolytes (ISEs) are playing a major role in the implementation of solid-state lithium metal batteries. Among them, argyrodite sulfides (Li_6PS_5Cl) result particularly promising thanks to their high ionic conductivity. However, the poor ductility of ceramic materials, further encumbered by sulfides incompatibility with moisture, greatly limits SSE processability and performance [1]. To facilitate this task, one interesting approach consists in the encompassment into the ISE of small contents of polymer binder which endow an improved flexibility to the system, enabling the production of thin solid electrolytes (TSEs). Such TSEs benefit of reduced thickness and of better electrodic contact which, in turn, induce a reduced overall impedance. Similar systems can also be produced exploiting roll-to-roll or casting processes, industrial techniques that can pave to way to a scalable manufacturing which goes beyond the thick ceramic pellets conventionally employed on the lab-scale.

A complete understanding of different TSEs' processing techiques results therefore pivotal. Consequently, this work investigates two different scalable approaches suitable to produce argyrodite-based TSEs with small amounts of rubbery binder. Firstly, an industrially relevant technique such as tape casting permitted a facile production of flexible TSEs from a toluene mixture containing nitrile-butadiene rubber (NBR) (Figure 1a). Conversely, the use of carboxylated NBR (XNBR) enabled a wet roll-to-roll approach based on cold-calendering (Figure 1b) [2]. Mechanical, morphological and electrochemical properties of the resulting electrolytes were investigated employing several techniques such as PFIB, PEIS and tensile testing. Overall, better mechanical properties linked to an improved binder distribution were observed in tape-casted samples. Conversely, calendered TSEs displayed improved ionic conductivity, also demonstrating higher values of critical current density and good performances during cycling. The effects of different densification pressures, required to assure an intimate interparticle contact in the ISE, and of increasing binder loadings were also studied to determine the optimal tradeoff between ionic conductivity and ease of processing.

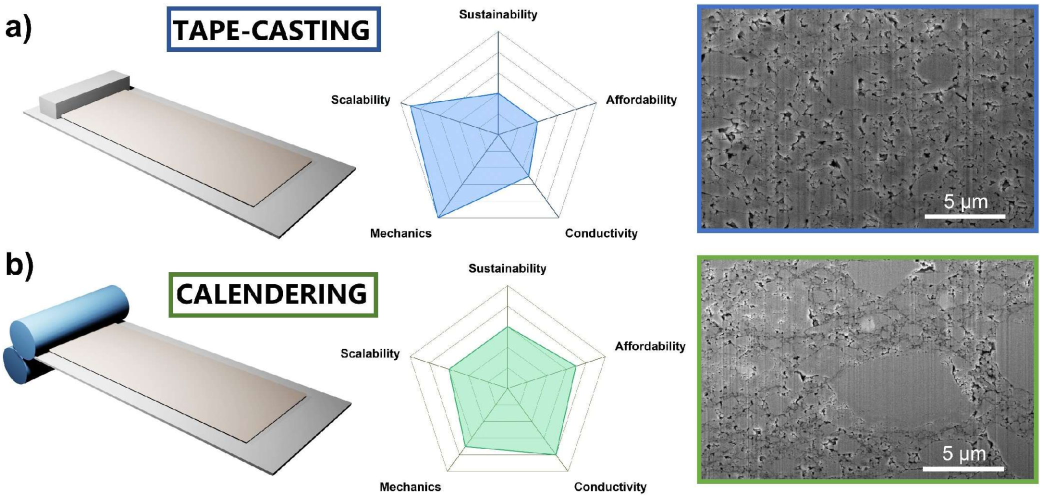

Figure 1: Schematic showing the two different TSEs' manufacturing techniques with the relative properties.

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Effect of the synthesys conditions on the electrochemical properties of lithium-rich Li1.2Ni0.2Mn0

P. Prosini,[i] A. Aurora,[i] L. Della Seta [i], C. Paoletti [i]

[i] *ENEA, Energy Department, C.R. Casaccia, Santa Maria di Galeria, 301, 00123 – Roma e-mail presenting author: pierpaolo.prosini@enea.it*

Cobalt-free lithium-rich cathode materials have recently attracted attention for their high specific capacities. These materials contain a combination of a Li_2MnO_3 layered structure and a Li_2NiMnO_4 spinel structure and can be described as $xLi_2MnO_3 \cdot yLiNi_{1/2}Mn_{1/2}O_2$. Among the various compositions, the one with $x = y = 0.4$ has given excellent results in terms of capacity and cyclability. In addition to the composition, also morphology influences the material properties. By using different synthesis routes, it is possible to deeply modify the morphology and, as consequence, the properties of the material. In this work, different types of synthesis have been examined among which solid state and sol-gel methods. The sol-gel method using citric acid as complexing agent gave the best results. The material thus prepared showed capacities of approximately 200 mAh g^{-1} when cycled at 10 mA g^{-1}. The capacity is still held at 125 mAh g^{-1} when the current is raised to 100 mA g^{-1}. The capacity drops to 75 mAh g^{-1}, doubling the current. Further increasing of current leads to a rapid decline in capacity, until to 25 mAh g^{-1}, at 300 mA g^{-1}. For low discharge currents there is a slight increase in capacity with the progress of the cycling while for high discharge currents the capacity tends to decrease. The material is able of discharging just under 600 Wh kg^{-1} for specific powers of 30 W kg^{-1}. When the power is increased up to 1000 W kg^{-1} the specific energy is reduced to only 10 Wh kg^{-1}. The presentation will show the structures, morphologies and electrochemical characteristics of the materials prepared using the different synthesis methodologies.

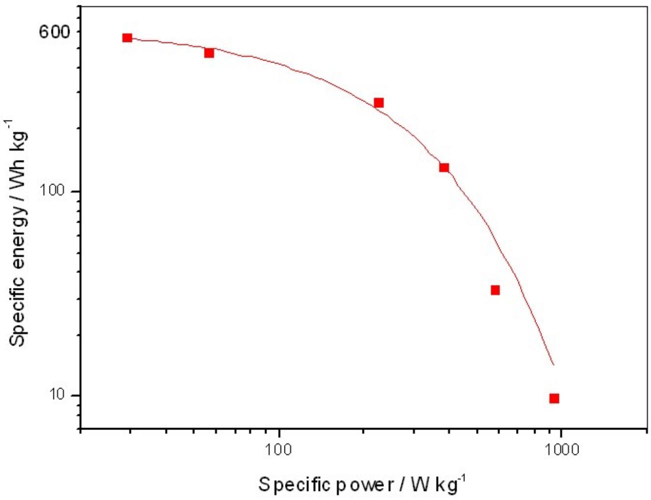

Figure 1: Ragone plot for the $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ prepared in presence of citric acid and thermally treated at 900°c for 6 h.

Bio-based separators for sustainable battery technology

A. De Marco[1], L. Bargnesi[1], N. Albanelli[1], C. Arbizzani[1]

[1] *University of Bologna, Chemistry Department "Giacomo Ciamician",*
Via F. Selmi, 2, 40126, Bologna, Italy
antonio.demarco8@unibo.it

Rechargeable energy storage devices had a fundamental impact on the society thanks to their capability to reversibly store and release electrical energy. Since their invention, batteries have changed significantly in architecture, chemistry and performance and, nowadays, they are even more important, both for the increased use of renewable sources of energy and for transport electrification [1].

The separator is a critical component of batteries since it prevents electrical short circuits, being a physical barrier between the anode and the cathode, but it also serves for ion transportation. Traditional polyolefin-based separators are widely used in lithium-ion technologies thanks to their price and chemical stability [2]. However, this stability determines a high resistance to biodegradation [3]. Consequently, the use of these technologies increases the plastic pollution that is a formidable threat to the sustainable development of human society. To overcome this problem, the use of a bio-based separator is needed.

The aim of this project is the realization of a bio-based separator by means of a green process. After a deep evaluation of several natural polymers, sodium alginate (SA) has been chosen to realize a composite separator for Li-ion and Li metal technologies. SA is a cell wall component of brown algae, and it is the salt of alginic acid whose conversion allows the solubility in water. Alginates have a liquid-gel behaviour in aqueous solution and for this reason they are processable in water. In presence of divalent cations (especially calcium), the low viscosity solution is turned immediately into a gel. SA was selected thanks to its thermal and chemical stability that make it a promising candidate for the realization of a new generation separator [4]. The technique used for the preparation of the membrane is the phase inversion, which is one of the most used industrial strategies for the realization of nowadays separators, using ethanol (EtOH), a green antisolvent.

Bio-based separators represent an important opportunity for next-generation sustainable batteries, and, in the next years, it will become fundamental to investigate more in details these systems to guarantee the best performance of energy storage devices.

Acknowledgements

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Graphite Silicon composites for Li-ion batteries: beneficial effect of metal carbide additives

J. Piñuela-Noval(1), A. F. Valdez(1), S. Brutti(2), M. A. Navarra(2), M. Agostini(3)

(1) Nanomaterials and Nanotechnology Research Center (CINN-CSIC), Universidad de Oviedo (UO), Principado de Asturias (PA), Avda. de la Vega, 4-6, 33940, El Entrego, Spain
(2) Department of Chemistry, "Sapienza" University of Rome,
P.le Aldo Moro 5, 00185 Rome, Italy
(3) Department of Chemistry and Technology of Drugs, "Sapienza" University of Rome,
P.le Aldo Moro 5, 00185 Rome, Italy

marco.agostini@uniroma1.it

The pathway for improving lithium-ion batteries' energy density strongly depends on finding materials with enhanced performance. Although great efforts have been done, on the anode-side, graphite is still the best choice. In the last decade, silicon elements are attracting growing attention as anode since their use can theoretically increase specific capacity of the negative electrode side. However, as the electrochemical mechanism involves the alligation of a large amount of Li, the silicon electrode experiences huge volume changes (more than 300% of its initial volume), leading to fracture and pulverizations of the electrode.

Recently, composite of silicon/wolfram carbide@graphene with a particular microstructure has been reported to maintain high initial Coulombic efficiency and long cycle life, alleviating structural changes [1]. Also, metal carbides (Mo_2C, Cr_2C_3, etc.) in the form of Si–Cr_3C_2@few-layer graphene and Si–Mo_2C@few-layer graphene electrodes were also reported with good electrochemical performance [2]. Carbides, in general, can provide an excellent conductive skeleton to improve the electronic conductivity of Si, thanks to the presence of nano-conductive channels that reduce electron transfer resistance [3,4].

In this contribution we report on the using of carbides (Mo and Cr based) in graphite-silicon composites for lithium-ion batteries. A simple to scale two-step process, consisting first in the formation of metallic carbides (molybdenum or chromium) in the matrix of graphite using spark plasma sintering technology and then in mixing graphite/carbides with Si nanoparticles (< 250 nm) by ball milling is proposed. Electrochemical performances are investigated and compared with standard graphite/Si nanoparticle electrodes. The results demonstrated how the presence of Carbides stabilizes the electrochemical performance regarding Coulombic efficiency and cycling stability.

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Innovative Polymeric Separators from recycled PVB for both Li- and Na-ion Batteries

Silvia Porporato[1,2], Matteo Gastaldi[1,2], Hamideh Darjazi[1,2], Alessandro Piovano[1,2],
Giuseppina Meligrana[1,2], Giuseppe A. Elia[1,2], Claudio Gerbaldi[1,2]
[1]*GameLab Group, Department of Applied Science and Technology, Polytechnic of Turin, Corso Duca degli Abruzzi 24, 10129, Turin, Italy*
[2]*National Reference Center for Electrochemical Energy Storage (GISEL) - INSTM, Via G. Giusti 9, 50121, Firenze, Italy*
silvia.porporato@polito.it

Large-scale energy storage systems are becoming fundamental for the modern society, particularly to fully exploit major advantages from renewable energy sources. In this respect, secondary sodium-based batteries may represent the key technology since they possess high-energy density, low-cost, simple design and easiness in maintenance. Nevertheless, the state of art materials are rather far from a mass commercialization. An essential role is played by electrolytes and separators, which are deepened in this work. Indeed, many factors must be considered while selecting the best separator, including electronic insulation, low ionic resistance, mechanical stability and chemical resistance to degradation[1].

In this context, we prepared polyurethane-based membranes starting from polyvinyl butyral (PVB) and diisocyanate, by means of a coagulation bath [2,3]. The choice of PVB as polymer is related to the European project SUNRISE, which aims to find different recycling pathways for this material, normally used as polymeric interlayer into laminated glasses. Nowadays, the PVB fraction collected after disposal, that lacks of optical and mechanical requirements for its original purpose, is incinerated or landfilled, causing annually tons of losses [4].

After preparation, our PVB-based membranes were characterized from a physico-chemical perspective by means of thermal analysis, dynamic mechanical analysis (DMA), infrared spectroscopy (IR) and field-emission scanning electron microscopy (FESEM). Successively, they were tested as separating membranes inside both lithium- and sodium-metal cells, wetted with the following electrolyte solutions: 1) lithium exafluorophosphate (LiPF6) 1M in EC:DMC, 2) sodium exafluorophosphate (NaPF6) 1M in EC:DMC. Ionic conductivity, plating and stripping processes, cyclic voltammetry and galvanostatic cycling were evaluated, to demonstrate the practical application of the developed materials in laboratory scale Li- and Na-based electrochemical cells at various conditions of current rate, temperature and aging. Preliminary results are highly encouraging and pave the way to the development of more sustainable separators from waste products for safe, low-cost energy storage devices.

Acknowledgments

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Biobased solvents electrolytes for Li-ion batteries

M. Melchiorre,[1,2] K. S. Teoh,[3] J. L. Goméz Urbano,[3] F. Ruffo,[1] A. Balducci[3]

[1] Dipartimento di Scienze Chimiche, Università degli Studi di Napoli Federico II, Complesso Universitario di Monte S. Angelo, via Cintia 21, 80126 Napoli, Italy
[2] ISusChem S.r.l., Piazza Carità n.32, 80134 Napoli, Italy
[3] Friedrich-Schiller-University Jena, Institute for Technical Chemistry and Environmental Chemistry and Centre for Energy and Environmental Chemistry Jena (CEEC Jena) Philosophenweg, 7a, 07743 Jena, Germany
e-mail presenting author: massimo.melchiorre@unina.it

One of the main challenges of this century is the energetic transition from fossil-based feedstocks to fully renewable energy sources (RESs). Within this framework, energy storage devices like lithium-ion batteries or electric double layer capacitors (EDLC) can play a major role on alleviating the intermittent and unstable nature of RESs [1]. These two devices have a common component, the electrolyte, which is formed by the combination of an appropriate conducting salt (e.g. lithium salts for Li-ion batteries, and tetraalkylammonium salts for EDLCs) and non-aqueous solvents. On this regard, organic solvents are mostly used at industrial level due to their wider electrochemical stability window compared to most water-based electrolytes [2]. However, common organic dipolar solvents are fossil-based and present high ecotoxicological and risk profiles. Therefore, their drop-in replacement with biobased, benign, and performing solvents is a relevant topic of general concern [3].

Ketals of a-hydroxy acids (AHA) and g-valerolactone (GVL) can be both prepared from biobased feedstocks and they already showed promising performance in EDLCs devices [4, 5]. Herein, we report the introduction of these solvents in Li-ion batteries by a detailed investigation of their transport properties, thermal behavior, and electrochemical performances. As-described sustainable-based electrolytes (Figure 1) show promising performances either for conventional cathodes (lithium iron phosphate – LFP) or anode materials (graphite – GE), clearly demonstrating their suitable application for advanced Li-ion batteries.

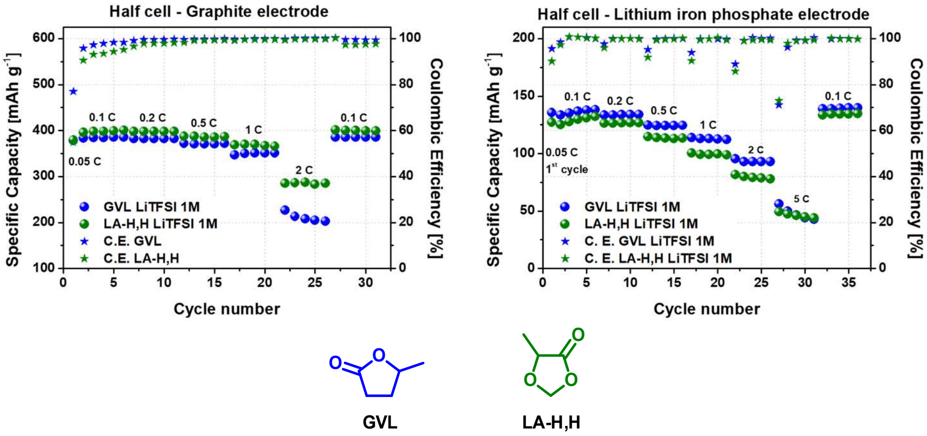

Figure 1: C-rates of GE and LFP half-cells employing g-valerolactone (GVL) and 5-methyl-1,3-dioxolan-4-one (LA-H,H). A 2%wt and 10%wt of vinylene carbonate (VC) was used as additive, respectively.

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Development of thin layer electrocatalytical architectures: a microelectrodic approach

Enrico Berretti[a], Maria Vincenza Pagliaro[a], Francesco Bartoli[a], Hamish A. Miller[a], Francesco Vizza[a] and Alessandro Lavacchi[a]

[a] *Italian National Research Council (CNR), Institute for the chemistry of organometallic compounds (ICCOM), Via Madonna del Piano 10, Sesto Fiorentino (Florence), 50019, Italy*
enrico.berretti@iccom.cnr.it

In recent times, great effort has been put in developing efficient and stable electro-catalytical surfaces for Fuel Cells (FCs) applications. The majority of the reactions of interest for this topic still rely on the adoption of costly and scarce elements, like Platinum Group Metals (PGMs) for the catalysts production. Consequently, much research effort has moved to the minimization of rare metals loadings; this is attempted by alloying PGM materials with more available elements, or by changing the geometrical design of the catalytical entities in order to maximize electroactive surfaces. Moreover, cutting-edge electro-catalysts for medium to low temperature FC applications are still adopted in form of nanoparticles dispersed in electro-chemically inert yet conductive powders. This production procedure could hinder accessibility for a vast array of surface characterization techniques, which are used to study the whole range of phenomenon which take place during FC duty-cycles.
In this context, geometrically defined surfaces mimicking the electrochemical behavior of the catalysts could represent a great step forward for the comprehension of the phenomenon taking place at the interface between the fuel solutions and the catalysts. Such surfaces, in form of microelectrodes with precise and predetermined exposed areas, could help to assess many issues occurring on the catalyst during the electrochemical reactions, thus helping to develop strategies to overcome their deactivation/dissolution and to increase their efficiency.

This contribution will describe the activities for the production of multilayered model catalytical surfaces, to be used mainly for the study of alcohols electro-oxidation reaction in alkaline media. The aim of this work is to develop a robust procedure to prepare geometrically defined surfaces which could be easily tailored for the production of a vast array of different electroactive surfaces. Multilayered microelectrodes were produced by Physical Vapor Deposition (PVD) and shaped by a mix of Electron Beam Lithography and Focused Ion Beam Milling techniques. Obtained working electrodes were characterized structurally and compositionally by SEM, STEM, EDX, XRD XPS and XAS. A final functional characterization was performed by electrochemical methods, to assess effective catalytical capability of the produced electrodes toward the oxidation of different organic molecules (EtOH, Formate, etc..).

Characterization of $LiNi_{0.5}Mn_{1.5}O_4$ Sputtered Thin Films as High-Voltage and High-Performance Cathode for Li-Ion Batteries

Darjazi H.[a,b] , Madinabeitia I.[c], Zarrabeitia M.[d], Gonzalo E.[e], Acebedo B. [e], Rezvani S. J.[f], Fernández-Carretero F. J. [c], Nobili F.[b,g] , García-Luis A. [c], Muñoz-Márquez M. Á.[e,g]

[a]Group for Applied Materials and Electrochemistry - GAME Lab, Department of Applied Science and Technology - DISAT, Politecnico di Torino, Torino, 10129, Italy.

[b]GISEL—Centro di Riferimento Nazionale per i Sistemi di Accumulo Elettrochimico di Energia, INSTM, via G. Giusti 9, 50121 Firenze, Italy.

[c]TECNALIA, Basque Research and Technology Alliance (BRTA) Parque Científico y Tecnológico de Gipuzkoa, Mikeletegi Pasealekua 2, 20009 Donostia-San Sebastián, Spain

[d]Helmholtz Institute Ulm (HIU), Helmholtzstrasse 11, 89081, Ulm, Germany - Karlsruhe Institute of Technology (KIT), P.O. Box 3640, 76021, Karlsruhe, Germany.

[e]Centre for Cooperative Research on Alternative Energies (CIC energiGUNE), Basque Research and Technology Alliance (BRTA), Alava Technology Park, Albert Einstein 48, 01510 Vitoria-Gasteiz, Spain.

[f]School of Science and Technology - Physics Division University of Camerino Via Madonna delle Carceri 9B, 62032 Camerino, Italy.

[g]School of Science and Technology - Chemistry Division, University of Camerino, Via Madonna delle Carceri, ChIP, 62032 Camerino, Italy.

To develop Li-ion batteries (LIBs), a good choice of cathode materials plays a vital role in terms of performance, cost, and safety. $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) attracts great research interests as high voltage Co-free cathodes in LIBs since it has a high theoretical energy density of 650 Wh kg^{-1} with an operating voltage of ~ 4.7 V (vs Li/Li^+) and theoretical specific capacity around 147 mAh g^{-1} [1]. However, a more detailed study is required for the LNMO interface, since its stability plays an important role on the overall electrochemical performance impact.

In this work, we pioneer the use of MF-AC magnetron sputtering method in different Ar-N_2 gas mixtures ratios to prepare various LNMO thin films with high control of the morphology, size and crystal particle growth, which results on a synergic effect over electrochemical cycling and rate performance (see Fig. 1). The nitridation process has been considered in the past to enhance electrical conductivity as well as electrochemical behaviour [2]. The thin films are studied by physicochemical, structural, morphological, and electrochemical characterization techniques.

The specific discharge capacity values and rate capability were improved by increasing the Ar/ N_2 ratio to 50% and 75%. This optimization can be correlated to the morphological and structural characteristics, improved conductivity, and increase of the partial cation ordering. Eventually, aiming at promoting the practical applications of LNMO, we end up this work by evaluating electronic ionic transport properties and insights into the intricate phase transition during the initial charging process. The EIS results show nitridation had a significant effect on improving electronic and electrochemical performances and on limiting the phase transitions.

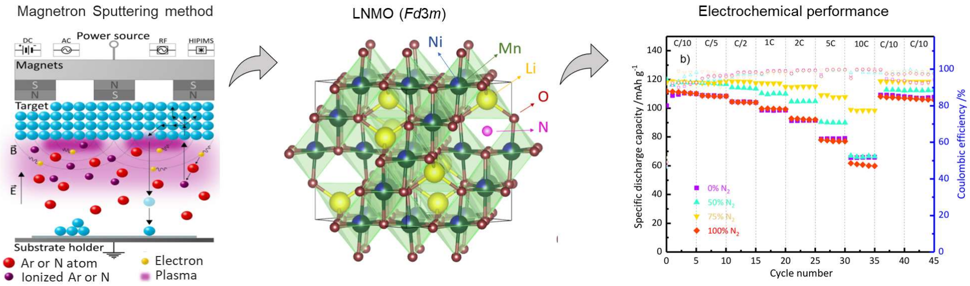

Fig. 1. Synthesis and characterization of LNMO thin films grown under different Ar-N_2 gas flow mixtures.

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Performances' enhancement ensured by the addition of filler in PVDF-HFP-based electrolytes for lithium metal batteries

E. Carena,[i] L. Mezzomo, [i] S. Mostoni, [i] N. Vallana, [i] C. Ferrara, [i,j] R. Ruffo, [i,j] P. Mustarelli [i,j]

[i] Department of Materials Science, University of Milano-Bicocca, via R. Cozzi 55, 20125-Milano, Italy
[j] National Reference Center for Electrochemical Energy Storage (GISEL), Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), via Giusti 9, 50121-Firenze, Italy

e-mail presenting author: e.carena1@campus.unimib.it

To win the energetic challenges of the future, it is mandatory to invest in technologies able to grant better employment of alternatives to fossil fuels. Electric vehicles and renewable energies request energy storage devices able to deliver higher specific capacity and energy density. Although metallic lithium-based rechargeable batteries could ensure these characteristics, their employment is still in the research stage as it is necessary to overcome some issues, the first and foremost the uncontrolled dendritic growth. A possible solution is to replace commercial liquid electrolytes with solid-state electrolytes (SSEs) constituting a physical barrier, opposing mechanically to the dendrites' continuous growth; also, the dispersion of inert filler inside the SSEs could be employed in order to additionally increase the mechanical reinforcement.

The project here developed is based on the synthesis of PVdF-HFP-based nanocomposite electrolyte membranes through a simple and cost-effective solvent casting method, dispersing the polymer, which forms the matrix, lithium bis(fluorosulfonyl)imide (LiFSI) and a new functionalized filler in a binary solvent mixture (DMF:THF) [1]. Novel hybrid nanoparticles (NPs) were synthesized by grafting short chains of poly(ethylene glycol) (PEG_x) with different molecular weights (x=750,5000 g mol^{-1}) on silica, that was previously synthesized and functionalized with APTES molecules [2]. The NPs mechanically reinforce the solid electrolyte to inhibit the dendritic growth and reduce crystallinity to raise the ionic conductivity, which is also achieved through the coordination of Li^+ performed by ethers groups on PEG_x chains; at the same time, polymers grafted on silica NPs promote the obtaining of homogeneous systems by increasing the degree of compatibility between the polymeric matrix of the electrolyte and inorganic filler. The obtained nanocomposite membranes (~150 µm), previously characterized through NMR and SEM-EDX, were first tested to determine their ionic conductivity, then in symmetric lithium cells subjected to increasing current densities: this confirmed that nanocomposite electrolytes can withstand metal deposition during stripping and plating analysis, differently from the membrane without dispersed filler. In particular, the most promising sample (realized dispersing 5 wt% of $SiO_2@PEG_{750}$) registered 0.1 mS cm^{-1} at room temperature and more than 250 hours of stripping and plating analysis. This encouraging result opens to the possibility to test this SSE also in LMB with $LiFePO_4$ as cathodic material, to verify its behaviour in real working conditions.

Overall the nanocomposite PVdF-HFP membranes are able to provide adequate mechanical reinforcement against dendrite perforation, excellent chemical and electrochemical stability, good ionic conductivity, and promising electrochemical performances; at the same time, they solve the problems of toxicity and leakages that make liquid electrolytes commonly used in commercial batteries unsafe.

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Design and characterization of high-performance water-based electrolytes for lithium-ion batteries

I. Pellini[i], S. Khalid[i], R. Ruffo[i]

[i] *Department of Material Science, University of Milano Bicocca, Via Cozzi 55, 20125 Milano (Italy)*
e-mail presenting author: i.pellini1@campus.unimib.it

The most used electrolytes in lithium-ion batteries (LIBs) present serious problems of flammability and environmental impact, due to the organic carbonates (such as EC, DMC, PC, DEC…) that they contain. One of the most promising current research lines about LIBs electrolytes is focused on the replacement of these solvents with water-based electrolytes. The use water as solvent for electrolytes gives several benefits because it is a very environmentally friendly, safe, cheap, and high conductive medium. However, water also presents an important limit: its electrochemical stability window (ESW) of only 1.23 V. In order to overcome this limit, one promising possibility is the use of superconcentrated solutions, called water-in-salt electrolytes (WISEs), in which the salt:water weigh and volume ratio is greater than one [1]. In this solutions ESW is broader because the greater part of the water molecules are locked in the solvation shells and cannot react.

Another problem related to the absence of organic substances is the difficulty in the formation of a Solid-Electrolyte Interphase (SEI) layer, which prevent electrode/electrolyte destructive reactions while allowing the Li^+ ion passage through the interface. The addition of a non-flammable solvent to a WISE makes it easier to form the SEI layer, without reducing the safety of the solution. Sulfolane (Figure 1) is a great candidate to create a bisolvent-in-salt (BSIS) aqueous electrolyte because it is miscible with water, inflammable and low toxic.

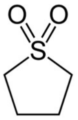

***Figure 4**: sulfolane*

Of course, also the choice of the salt is crucial in the design of an electrolyte. The salt employed in this work is lithium (fluorosulfonyl)(trifluoromethanesulfonyl)imide, LiFTFSI (Figure 2), that was chosen because of two main features: (1) the high fluoride content, that helps the formation of the SEI layer and (2) the asymmetric anions, that can extend the battery life, by hinder salt crystallization[2].

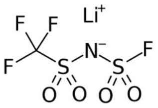

***Figure 5**: LiFTFSI*

The focus of this work are the physicochemical and electrochemical characterizations of two BSIS electrolytes, constituted of sulfolane, water and LiFTFSI, in the molar ratios of 3:1:2 and 3:1:3 (called 3S:H_2O:2L and 3S:H_2O:3L respectively). Thanks to different techniques, a full investigation of the properties of these electrolytes, such as solvation structure, conductivity and ESW, was performed. Moreover, the electrolytes were tested in a full cell with Gravimetric Charge Discharge (GCD) measurements, using the standard $LiMn_2O_4$ and $Li_4Ti_{15}O_{12}$ as positive and negative electrode respectively, managing to obtain a 2.4 V battery (Figure 3) with a coulombic efficiency greater than 99.5% in the best case, that lasted more than 700 cycles (Figure 4).

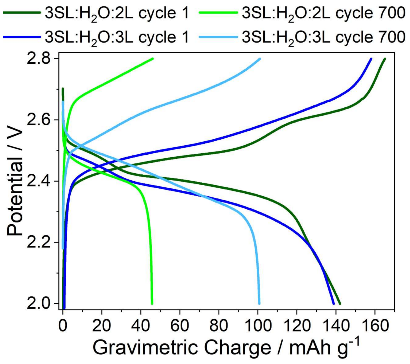

***Figure 6**: GCD curves*

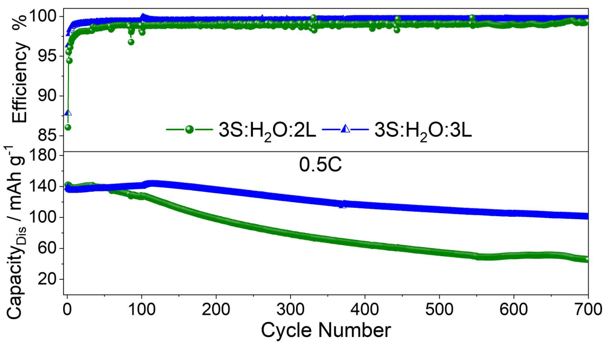

***Figure 7**: long cycling GCD performances*

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A new prospective in the development of bio-based polymer coatings from discarded tomato peels and the role of electrochemistry

Mirko Magni[a], Beatrice Tagliabue[b], Valentina Re[b], Rita Nasti[a], Giangiacomo Beretta[a], Raffaella Suriano[b]

[a]*Department of Environmental Science and Policy, Università degli Studi di Milano, 20133 Milano, Italy*

[b]*Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, 20133 Milano, Italy*

Keywords: bio-waste, circular economy, electrochemical impedance spectroscopy, corrosion protection, accelerated cyclic electrochemical technique

One of the biggest issues that global policies have to face, and solve, is the satisfaction of the ever-growing demand for materials in a less impacting fashion. A largely impacting sector is that of resins and polymer coatings devoted to the corrosion protection of metal and alloys. Considering the strong dependence by petrochemical industry for the supply of raw materials, the environmental regulatory and the socio/economic scenarios is already forcing the sector to turn to more sustainable supply chains. Accordingly, there is an urgency for identifying the most industrially relevant strategies that can realize this green transition as quick as possible. Among the available solutions, the valorization of bio-waste is one of the most virtuous as it does not create the socio and etic conflicts concerning the exploitation of soil and fertilizers to grow biomass (edible or not) to be then directly processed for chemicals and materials production. Besides the technological aspects to valorize bio-waste, the need for creating a solid and profitable production chain among all the involved industrial realities is mandatory to bring the scientific innovation into the real word, that one of the production at large scale.

Starting from an analysis of the Italian agro-food compartment, and guided by considerations on the chemical composition of the different kinds of vegetable waste, the project focused on tomato waste deriving from the transformation sector of this fruit. The project aims at the valorization of tomato peels, a bio-waste that is largely produced by Italian canning industry and that is currently exploited only in few low added-value chains. Specifically, we propose a novel approach to produce precursor(s), of know and constant purity and composition, for the formulation of fully bio-based epoxy resins for the corrosion protection of metal and alloys. After presenting the innovation with respect to the few analogous examples in the literature, we will show how electrochemical impedance spectroscopy (as part of a series of technological tests) resulted a powerful technique to investigate the barrier properties and other key features of a series of coatings obtained through different formulations.

Acknowledgments

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Development of High Entropy Alloys Coatings by Electrodeposition

M. Fedel [a], D. Ascani [a], D. Ahmadkhaniha [b], C. Zanella [a,b]

[a] *Department of Industrial Engineering, University of Trento, via Sommarive 9, Trento, TN 38123, Italy*
[b] *Department of Materials and Manufacturing, Jönköping University, box 1026, Jönköping 55111, Sweden*
e-mail presenting author: michele.fedel@unitn.it

The present work explores the feasibility of applying electrodeposition to produce high entropy alloys (HEAs) coatings on steel substrate from a single aqueous bath. The set of electroplating systems was constituted by: NiCoCuMoW, NiCoCuW, and NiCoMoW, respectively. The five-element coating was the targeted HEA, while the four-elements coatings were produced for benchmarking. By applying a direct current to the electrolytic cells, it was possible to reduce the different metal ions in the form of compact and dense coatings. EDS data confirmed the presence in the deposits of all the elements with a quite homogeneous distribution. The configurational entropy of the obtained deposits was computed according to the Boltzmann equation. Combining SEM and EDS results, it was possible to analyze the surface morphology and chemical composition of the samples. SEM surface analysis reveals that HEA deposits consist of nodular morphology in which the systems differ from each other in terms of nodule size. Micrographs also reveal the presence of diffuse cracks over the surface because of internal stresses or hydrogen embrittlement. The NiCoCuW seems to have a less cracked microstructure than the other systems. All HEA coatings prepared show the typical XRD patterns of amorphous microstructure.

A preliminary DSC study pointed out the presence of intense exothermic peaks comprised between 600-700 °C in all three types of coatings, probably related to the crystallization transformations. Polarization curves carried out in NaCl (0.1 M) and Na2SO4 (0.01 M) show weak passivity for NiCoCuMoW and NiCoMoW deposits. On the other hand, the polarization curves of the NiCoCuW coating have the typical trend of active materials. The mechanical properties of the coatings were highlighted through a nano hardness indentation test. HEA coatings exhibit a remarkable hardness which stands at 5.35 ± 1.30 GPa in the NiCoCuMoW deposit, 6.92 ± 0.73 GPa in the NiCoCuW deposit, and 5.74 ± 1.21 GPa in the NiCoMoW deposit. The hardness results contrast the “high entropy effect” that usually affects HEA properties because the NiCoCuW system characterized by the lowest configurational entropy simultaneously has the best hardness value. This result could open a debate on the effectiveness of the electrodeposition process in providing metastable structures capable of enhancing the coating properties in a more significant way than complex alloy systems.

On the use of in-situ techniques for the study of metals corrosion

L. Casanova,[i] M. Menegazzo,[j] A. Brenna,[i] M. Ormellese,[i] and G. Bussetti[j]

[i] Dept., of Chemistry Materials and Chemical Engineering "G. Natta", Politecnico di Milano, via Mancinelli 7, 20131 Milan, Italy
[j] Dept., of Physics, Politecnico di Milano, Piazza Leonardo Da Vinci, 20133 Milan, Italy

e-mail presenting author: luca.casanova@polimi.it

Electrochemical techniques are unvaluable tools for the study of many technological processes like corrosion, battery science and generally materials science. In particular, electrochemical impedance spectroscopy (EIS) deserves attention thanks to its widespread use and the plethora of information which can be extracted from a single experiment. However, data interpretation is sometimes misleading and research is active to establish a correct interpretation of the multitude relaxation events manifesting during the spectroscopic acquisition. Following this idea, in-situ techniques as atomic force microscopy (AFM) and Raman spectroscopy, carried out in an electrochemical cell, can help to confirm valuable physical parameters. In the following, three cases related to Ti, Mg and carbon steel are provided.

In particular, the electrochemical behavior of Ti [1], when the metal passes from a passive to an active state, provides a Nyquist representation (Figure 1a) with capacitive loops and negative real impedances, justified by the formation of concentration cells responsible for the flowing of huge anodic currents.

Mg corrosion in a simulating body fluid solution (SBF) generally presents complex EIS spectra, according to the corrosion mechanism which involves the presence of adsorbed intermediates. Here surface techniques permit to relate the low frequency capacitive loop to the presence of surface films.

The effect of the application of a cathodic current, when a carbon steel sample is immersed in a solution held at pH 13 is studied by means of EIS coupled to in-situ AFM and Raman spectroscopy. The applied reducing condition involves important structural and topographical modifications of the electrode surface correlated to a sensible modification of the cell impedance (Figure 1b).

Those are only few examples of the power of in-situ techniques applied to the study of electrochemical processes as corrosion of common technologically relevant metals, also permitting a deep understanding of the surface state of carbon steel when subjected to cathodic protection.

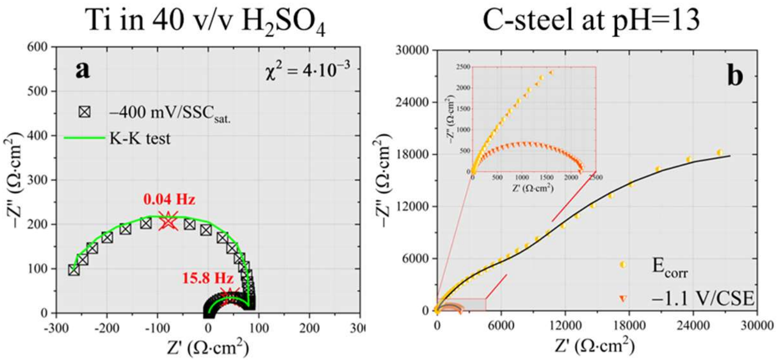

Figure 1: **a)** Nyquist representation of Ti collected in H_2SO_4 ; **b)** Nyquist representation of C-steel at the corrosion potential (E_{corr}) and at −1.1 V/CSE.

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EC-STM exploration of Pt nano-clusters nucleation and growth under the effect of Au(111) support and implications on the reactivity for Oxygen Reduction Reaction

A. Facchin, L. Litti, F. Cazzadori, M. Cattelan, C. Durante,

University of Padova, Department of Chemical Sciences, via Marzolo 1, 35131, Padova, Italy
e-mail: christian.durante@unipd.it

Oxygen reduction reaction (ORR) is a vital reaction, not only for all biological systems on earth, but also in the emerging field of fuel-cells and metal-air batteries and electrochemical sensors. In these devices, O_2 is entailed at the cathode, and it undergoes reduction, with H_2O or H_2O_2 being produced. Unfortunately, ORR kinetics is sluggish and needs to be catalyzed [1]. Though platinum group materials (PGM) should be avoided due to scarcity and high costs, they still represent the most performing catalysts for ORR. EC-STM can be conveniently employed as an advanced in situ characterization technique, which provides information on a sample surface at the solid/electrolyte interface. Indeed, the sample is probed by STM and at the same time is polarized as working electrode. This means that EC-STM can record the dynamic of an electrocatalytic process at the atomic scale [2,3]. This ability was exploited to characterize a series of platinum-based molecular complexes, as shown in Figure 1a. The peculiarity is that each complex carries a different number of coordinating nitrogen atoms, and the resulting electrochemical activity towards ORR significantly differs among different complexes. All the complexes have no redox behaviour, but in presence of O_2, a relevant catalytic behaviour emerged, in particular after repetitive potential scanning by cyclic voltammetry (Figure 1b). We employed Raman and XPS characterizations, along with EC-STM images, to study modifications in the surface morphology during potential cycling (see Figure 1b,c). The results indicate that small gold clusters are formed exclusively in the presence of Pt-N complexes. These complexes subsequently decompose, resulting in the formation of Pt-Au active sites with high intrinsic selectivity towards the two-electron reduction of O_2 to H_2O_2. The reduction process was analyzed through cyclic voltammetry, and the selectivity was measured using the rotating ring and disk electrode technique (Figure 1d). It was found that both the activity and selectivity depend on the Pt complex precursors and, most likely, their redox stability. The potential influence of nitrogen-containing ligands on the activity and selectivity of the ORR process is currently being investigated.

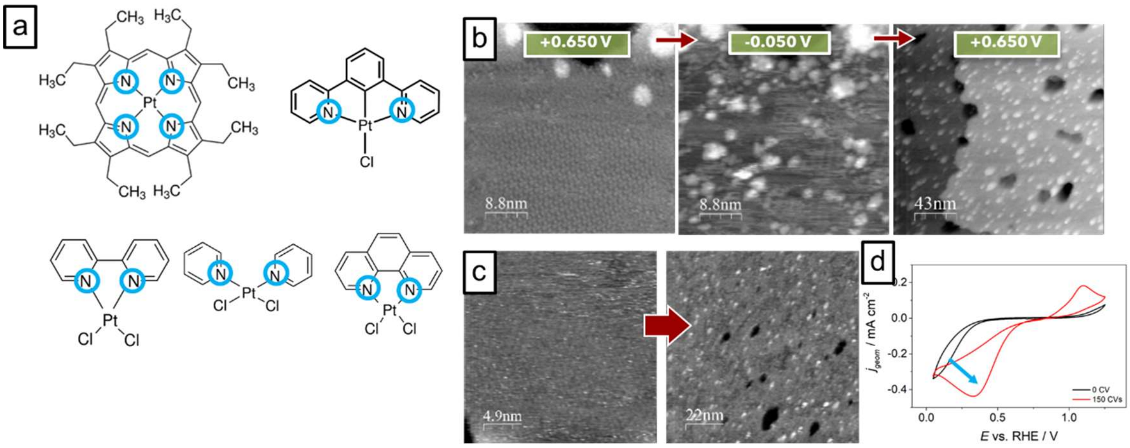

Figure 1: a) examples of Pt-N complexes employed in the investigation; b) EC-STM images in $HClO_4$ 0.1 M of Au(111) functionalized by Pt-N complexes and surface evolution upon electrochemical cycling; d) evolution of the Pt-N@Au(111) electrochemical response in $HClO_4$ 0.1 M upon electrochemical cycling.

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Towards scaling up in sustainable electrode production

E. Ravesio[a], D.Versaci[a], Montinaro G.[a] and S.Bodoardo[a]

[a] *Dip. Applied Science and Technology (DISAT), Politecnico di Torino, C.so Duca degli Abruzzi 24, 10029 Torino, Italy*
elisa.ravesio@polito.it

The maturity of a technology can be well described by the Technology Readiness Level (TRL) which is a scale to estimate how far a technology is from commercialization. Frith et al. proposed a specific TRL for Li-ion Batteries (LIBs) that highlights the gap between the laboratory studies and the industrial level [1]. This gap is considered one of the most important bottlenecks in the commercialization of new technologies and it is strictly related to the absence of pilot lines at laboratory levels. When cells production is concerned, to scale-up the production process is challenging and it is strongly depending on the chemical composition of the electrode, the interphase with the electrolyte and its composition and the chemical-physical properties of the slurry, which is influenced by the final rheological properties.

The electrode production starts with the mixing of the electrode components (active material, conductive additive, binder and solvent). The used techniques can be very different depending if this is performed at laboratory scale (commonly with a simple magnetic stirrer) or industrial level with bigger slurry amount (e.g. in a planetary mixer). The use of this technology permits to increase the slurry stability, in particular for more environmental friendly water-based production, so avoiding unwanted phenomena such as aggregation and sedimentation, often due to hydrogen bonding. The increase of the solid content of the slurry can limit the sedimentation phenomena, even if it can lead to the increase of the viscosity which can create problems during the coating step [2].

The coating is the core step of the electrode production strongly affected by the scale of production (from lab to industrial scale): at the laboratory scale, the process is discontinuous while the high yield needed at the industrial level requires a process fully automated and continuous [3]. In particular, at the laboratory level, the main instrument chosen for the deposition is the tape casting (doctor blade), while at the industrial level the technology switch to different types of technologies (slot die coater) [3].

Our research aims to better understand how innovative active materials and aqueous binders perform at different TRL levels to anticipate and propose new solutions to overcome the challenges that the industry will face.

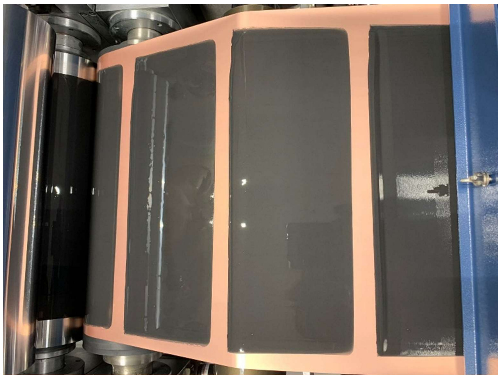

Figure 8 *– Anode coating on roll-to-roll machine*

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Efficient electroreduction of CO_2 to CO and HCOOH in a gas-liquid buffer layer flow cell employing carbon cloth electrodes functionalized with a fac-Mn(apbpy)$(CO)_3$Br complex as gas diffusion cathodes

J. Filippi,[1] L. Rotundo,[2] H.A. Miller,[1] R. Rocca,[2] A. Tiozzo,[2] R. Gobetto,[2] C. Nervi,[2] F. Vizza[1]
[1] Italian National Research Council (CNR) Institute for the chemistry of organometallic compounds (ICCOM) Via Madonna del Piano 10, Sesto Fiorentino (Florence), 50019, Italy
[2] Università degli Studi di Torino, Torino, Italy
jonathan.filippi@virgilio.it

The electroreduction reaction of CO_2 is one of the most challenging strategies for excess renewable energy storage into carbon-neutral fuels. Particular interest is aroused by the production of CO, as it is a fundamental building block for many industrial processes including Fisher-Thropsch and methanol synthesis. An innovative approach is to use organometallic complexes as electrocatalyst allowing, in principle, a higher metal utilization efficiency compared to metal-nanoparticle-based electrocatalyst. Furthermore, anchoring the complex on electro-conductive supports helps to overcome the mass transport limitations of the electroactive species from the bulk to the electrode surface allowing also much higher electrocatalyst stability. Among many types of electro-conductive supports, carbon cloth has excellent properties for the fabrication of gas diffusion layer cathodes for gas-electrolyte buffer layer interface. Herein we describe the use of a manganese Lehn-analogue complex (fac-Mn(apbpy)$(CO)_3$Br) grafted on carbon cloth support by diazonium salt reduction, as electrocatalyst in aqueous media for the reduction of CO_2 to CO. The electrocatalyst, supported in carbon cloth working as a gas diffusion cathode, was tested in a gas-flow cell fed with pure CO_2 operating at atmospheric pressure. In this condition, the supported Mn complex was able to convert CO_2 into CO and formic acid at -0.67V vs RHE with a faradaic efficiency higher than 75% (>95% initial) and 11% for CO and HCOOH respectively. In addition a productivity rate higher than 350NlCO min-1 gMn-1, and turnover numbers up to 82000 and 12000 for CO and HCOOH in 14h of were observed.

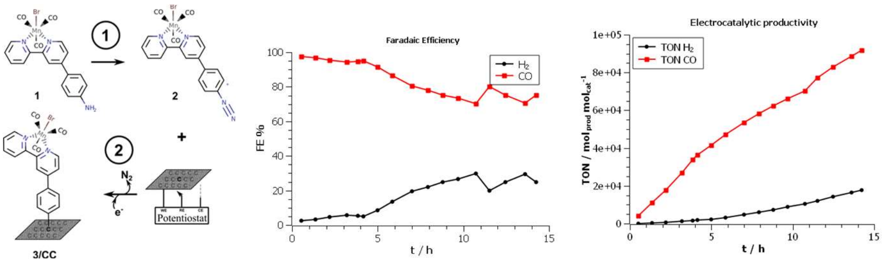

Figure 1. left) fac-Mn(apbpy)$(CO)_3$Br grafting process on carbon cloth; middle) CO-faradaic efficiency and; right) electrocatalyst turnover number (TON) time profiles.

Acknowledgements

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Conversion of CO_2 to sustainable fuels by using a zero-gap cell with Cu-based cathode

A. Salanitro,[i] S.C. Zignani [i], *V. Chiodo [i], S. Maisano [i], A. Carbone [i], A. Aricò [i]*

[i] *Institute of Advanced Energy Technologies (ITAE) of the Italian National Research Council (CNR)*
e-mail presenting author: salanitro@itae.cnr.it

In order to achieve energy and environmental sustainability, electrochemical CO_2 reaction reduction (CO2RR) is an important method of converting CO_2 to evaluate products. As a result of electrochemical reduction of CO_2, fuel additives and chemical feedstocks such as alcohol can be produced. Our proposal is the utilization of copper based oxide as a cathode for CO2RR prepared by the oxalic synthetic method [1]. Figure 1 shows the XRD spectrum of fresh CuOx used as a cathode in electrochemical experiments. There are typical crystal reflections of cuprite (Cu_2O - JCPDS card n° 05-0667), tenorite (CuO - JCPDS card n° 05-0661), and metallic copper (Cu - JCPDS 04-0836). A semi-quantitative determination of the weight fraction of each constituent was performed using native software on XRD equipment. As a result, 85.4 wt.% of cuprite, 4.9 wt.% of tenorite, and 9.6 wt.% of metallic copper were found.

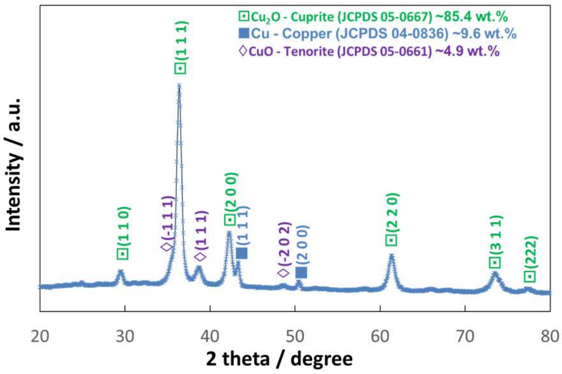

Figure 1: XRD pattern of the cathode electrocatalyst prepared by the oxalate method

First, anode and cathode inks had to be prepared. The anode for all electrochemical experiments was NiFeOx. These materials were dispersed in ethanol and sonicated to manufacture electrodes by spray coating technic. Gas diffusion layer (GDL) purchased from Sigracet was used as support for the cathode and nickel felt purchased from Bekaert for the anode. This procedure resulted in a total catalyst loading of 2 mg cm^{-2} for the anode and 1 mg cm^{-2} for the cathode. A Fumatech (FAA3-50) anion exchange membrane was used as a polymer electrolyte. A final step was membrane electrode assembling (MEA) using cold press anode and cathode electrodes. Experimental results showed that the oxalate method is promising method to prepare CuOx catalyst to CO2RR, we were able to achieve a mixture of Cu-based structures having oxidizing states from 0 to 2. A combination of electrochemical tests and liquid effluent analysis confirmed some results reported in the literature regarding the promotion of intermediates that may result in secondary reactions producing gases like H_2, CO, C_2H_4, as well as carbonaceous fuels like Et-OH, Pr-OH, Allyl-OH, Acetal-H and Propion-H.

Acknowledgements
The authors acknowledge the financial support provided by EU H2020 GREEN DEAL “ECO2FUEL” project “Large-scale low-temperature electrochemical CO_2 conversion to sustainable liquid fuels” Grant Agreement number: 101037389.

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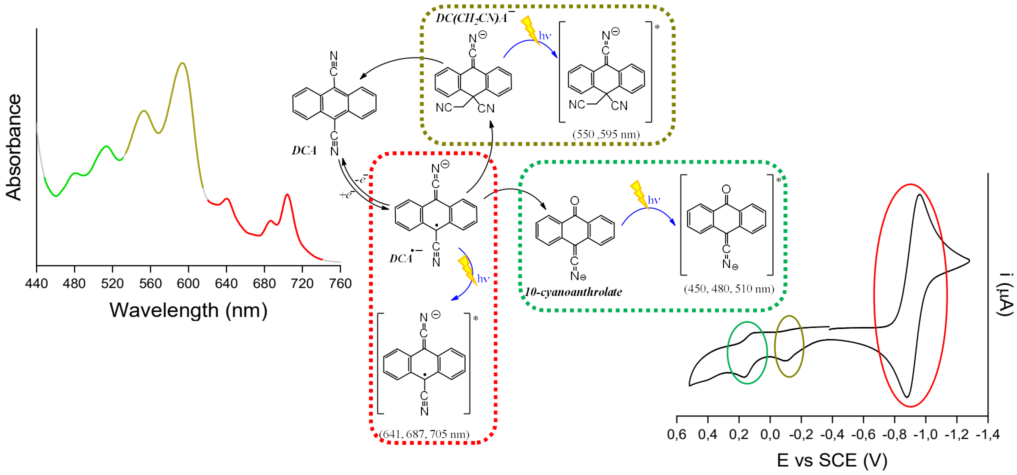
Mechanistic insights into the electrochemical reduction of 9,10-dicyanoanthracene for electrophotocatalysis

Daniel Morales-Martinez, L. Rizzo, L. Dell'Amico, S. Antonello, S. Bonacchi

Department of Chemistry, University of Padova, Via Francesco Marzolo 1, 35131, Padova, Italy
daniel.morales@unipd.it

In recent years, electrophotocatalysis (e-PC) has gained more attention because it drives the activation of molecules with high reduction potentials using not aggressive conditions such as room temperature and low overpotentials thus, allowing the formation of different products in a selective way [1]. In particular, the active form of the photocatalyst (PC) is achieved upon its electrochemical reduction or oxidation to generate $PC^{\cdot-}$ or $PC^{\cdot+}$ respectively, followed by an appropriate UV-Vis irradiation to get $*PC^{\cdot\pm}$. The so obtained $*PC^{\cdot\pm}$ quickly carries out the intermolecular electron transfer with the substrate, initiating thus the chemical reaction. Among the different photocatalysts used in this approach, the 9,10-dicyanoanthracene (DCA) is one of the most used compounds for different reactions due to its chemically reversible behavior and excitation wavelength to excite $DCA^{\cdot-}$ (510 nm) [2–4]. The present work is focused on the analysis of the electrochemical reduction mechanism of DCA. A combination of electrochemistry and UV-Visible spectroscopy was exploited to get insights into the electro-photocatalytic mechanism enabling optimization of the yield and timing of the borodechlorination of 1-chloronaphthalene as a prototype reaction. This study paves the way for the design of highly performing electro-photocatalysts enable to unlock the production of useful drugs and feedstocks.



Scheme 1: Products generated during the electrochemical reduction of DCA in acetonitrile.

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Electro-photo-catalysis: Merging One Photon and One Electron in the Same Reaction Pathway

A. Piccoli, A. A. Isse, M. Fantin

Department of Chemical Sciences, University of Padova,
Via Marzolo 1, 35131, Padova, Italy
marco.fantin@unipd.it

In this contribution, we describe the combination of the energy of one photon and one electron in the same reaction pathway. The integration of a photocatalytic system inside an electrochemical cell allows the selective generation of reaction intermediates, addressing one of the main problems of synthetic organic electrochemistry.

Our findings demonstrate that the injection of one photon and one electron (or hole) into a molecular photocatalyst leads to the formation of excited state species with remarkably high energy levels. These species can participate in highly demanding chemical reactions.

The process was followed by voltammetric techniques, recorded in the dark or under illumination (Figure 1). Remarkably, we could electrogenerate at a glassy carbon electrode the radical anion of naphthalene imide at the excited state. This was achieved by irradiation of the electrode surface during the potential scan. This excited state acted as an exceptionally potent photoreductant, enabling the cleavage of resilient carbon-halogen bonds.

The development of this novel technology carries significant implications. Firstly, it advances our understanding of the interaction between electrons and photons within a shared reaction pathway. Secondly, it facilitates the efficient synthesis of organic compounds and materials. Lastly, it offers a promising approach for the removal of polluting compounds, such as PCBs.

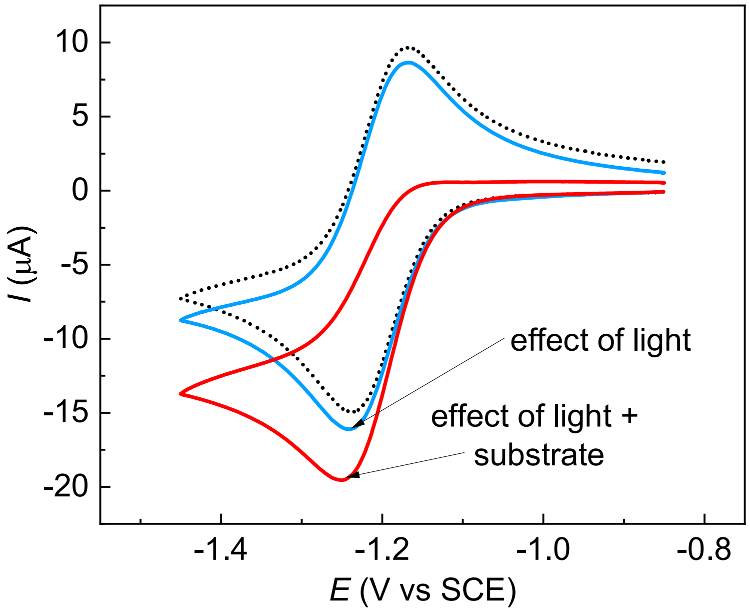

Figure 1: Cyclic voltammtry of 10^{-3} M napthtalene imide in the dark (dotted line) and under 440 nm light irradiation (solid lines) in DMF + 0.1 M n-Bu_4NBF_4. The red curve was recorded in the additional presence of 2×10^{-2} M chlorobenzene (substrate) under irradiation.

Embedded nanomaterials in electrocatalysis for energy

Alessandro Lavacchi, Francesco Bartoli, Marco Bellini, Enrico Berretti, Laura Capozzoli, Yanxin Chen, Hamish Miller, Maria Vincenza Pagliaro, Francesco Vizza.

Italian National Research Council (CNR)
Institute for the chemistry of organometallic compounds (ICCOM)
Via Madonna del Piano 10, Sesto Fiorentino (Florence), 50019, Italy
Alessandro.lavacchi@iccom.cnr.it

Nanomaterials rise concerns in terms of safety and electrocatalysts make no exception. Indeed, most electrocatalysts consist of nano-powders easily dispersible into the environment and the working places. While the formulation of inks out of these powders include binder that fix them, such fixing does not guarantee safety against the release of nanoforms into the environment. These aspects have been seldom covered in the scientific literature, however they deserve a deeper focus. Recently, while reviewing the application of titanium dioxide nanomaterials in electrocatalysis, we introduced the classification of electrocatalysts in embedded and powdery nanostructure [1]. This classification highlights the potential to release nanoforms at any stage of the life cycle of the devices. Embedded nanostructures limit this risk as they consist of nanoforms that are strongly anchored to macroscopic support. Accordingly, they are easy to handle and make device fabrication and dismantling easier and safer.

In this talk, I will describe our recent investigations on the quest of supports for the fabrication of embedded electrocatalysts, with a special emphasis on titanium dioxide supports. The talk will highlight the main issue in the development of embedded nanostructure, with a focus on mass and charge transport and the achievement of a high electrochemically active surface area. The former two aspects are particularly relevant in gas fed fuel cells and electrolysis in neutral media, where the ionic conductivity across the electrode must be provided by the catalytic layer itself, imposing severe constraints on the thickness of catalyst.

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(Invited) Biotechnology meets electrochemistry: examples of emerging applications of Microbial Electrochemical Technologies

Marianna Villano, Marco Zeppilli, Mauro Majone

Department of Chemistry, Sapienza University of Rome, P.le Aldo Moro 5, 00185-Rome, Italy
e-mail presenting author: marianna.villano@uniroma1.it

Microbial Electrochemical Technologies (METs) are promising approaches for converting the organic matter contained in wastewater into electrical power or a variety of value-added compounds (e.g., biofuels, organic acids, and alcohols) [1]. Specifically, METs merge traditional principles of microbiology (or, more in general, biotechnology) with those of applied electrochemistry, and rely on the ability of the so-called "electro-active" microorganisms to exchange electrons with a solid-state electrode, which can be used as an electron acceptor or donor for their metabolism [2]. METs have attracted considerable attention over the last few years and a plethora of applications have been developed with the systems being generally classified depending on the electrolytic or galvanic scenarios [3]. As an example, microbial fuel cells (MFC) and microbial electrolysis cells (MEC) couple wastewater treatment to electricity or reduced compounds as final products, respectively; whereas microbial electrosynthesis cells (MES) are typically not related to wastewater treatment and aim at producing multi carbon organic compounds from carbon dioxide sequestration and reduction.

Here, an overview of emerging METs applications will be presented and discussed based on results collected in our laboratory as well as on data reported in the literature. Particular attention will be dedicated to the analysis (primarily by means of cyclic voltammetry) of the electro-activity of the biofilm established at the anode of two-chamber MECs, which is crucial to the overall process performance since it partially provides the energy required to sustain the desired cathodic reaction. Also, MECs configuration and operating conditions (e.g., type of membrane, electrode materials, and applied potential) on the efficiency of hydrogen or methane generation will be analyzed. With specific reference to biomethane production, METs are also being investigated as downstream technology to conventional anaerobic digestion systems for biogas purification and upgrading along with possible recovery of nutrients (such as ammonium). Additionally, a novel MET application, referred to as"electro-fermentation" (EF), will be presented and discussed [4]. EF consists of the use of a polarized electrode to steer product distribution in traditional fermentation processes with both pure and mixed microbial cultures. In EF the electrode can, in principle, act as an electron acceptor or donor, or simply as a means to alter the oxidation-reduction potential of the fermentation broth and, in turn, the intracellular redox state (i.e. $NADH/NAD^+$ balance). Even though the molecular and biochemical basis underlying the EF approach are still largely unknown, it represents an extremely appealing strategy to gain great control over fermentation processes.

Overall, all examined METs applications perfectly fit with the development of the circular economy concept.

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Coupling green hydrogen and poly-generation

G. Squadrito, A. Nicita, G. Maggio

Consiglio Nazionale delle Ricerche - Istituto di Tecnologie Avanzate per l'Energia "Nicola Giordano" (CNR-ITAE), via Salita S. Lucia sopra Contesse 5, 98126 Messina, Italy
e-mail presenting author: gaetano.squadrito@itae.cnr.it

The current main issues for humanity are related to pollution and global warming. To face these issues, a shift towards renewable energy technologies is currently running in the world. Renewable electricity share is growing. Nowadays it represents 28% of the world's electricity production from just 15% in 2016, and reached the 13.8% of the global energy consumption. The progressive increase of the power share of renewable energy sources (RES) in the electric grid introduces problems related to the natural discontinuity and fluctuations of RES, that are the object of an increasing number of investigations, and require energy storage systems to mitigate them. Although there are different possible technologies for energy storage, hydrogen is considered the most suitable choice for massive and long-term storage of RES power. This is because hydrogen is an energy vector (fuel) and also a commodity gas and a feedstock for many industrial applications, so that it can also strongly contribute to decarbonisation of a number of sectors defined "hard to abate".

Nowadays, almost all hydrogen is produced by steam methane reforming (SMR) and gasification of fossils fuels. According to the IEA Global Hydrogen Review 2022, about 82% of the hydrogen produced is directly derived from methane, oil and carbon. while, hydrogen produced by low-emission technologies is about 0.7%, with the majority of this coming from fossil fuels with CCUS and only 0.04% coming from renewable electricity via water electrolysis. In 2021, the emissions associated with hydrogen production were more than 900 Mt CO2. Hydrogen production costs by these processes are low, \$1-2/kg H2 for SMR and \$1-1.5/kg H2 for gasification, respectively. Consequently, the main challenge is how to produce hydrogen at costs that are competitive with these traditional production methods, but without emitting CO2 into the atmosphere. The two approaches currently able to meet this challenge generate the so-called "blue hydrogen" and "green hydrogen". But the most important game is played on green hydrogen, the production of which does not entail CO2 emissions, as only renewable energy is used.

Green hydrogen can be produced by various methods, but the most suitable and well developed technology is based on electrochemical water splitting (electrolysis), then "green hydrogen" is usually defined as "hydrogen made via electrolysis using renewable electricity". This concept has shaped the policies of Europe and other developed countries, concentrating investments in this direction and forgetting other production pathways of green hydrogen. However, focusing the attention on electrolysis, some new issues involving geopolitical and social aspects are coming up like, for example, the water issue. This is due to the necessity of having huge amounts of high purity water for running electrolysis to produce large amounts of hydrogen. Electrolysis is not the only green path for hydrogen production, but also the other available and foreseen technologies present a number of limitations.

In recent years, the authors conducted a number of studies demonstrating that by coupling green hydrogen production with other goods or energy productions it is possible to strongly reduce the green hydrogen production cost. Moreover, coupling the green hydrogen production with poly-generation approach opens a number of new opportunities that introduce new economic and/or social value to the green hydrogen.

In this work, an overview of the applicable technologies, with a focus on electrolysis, and possible advantages of coupling green hydrogen production and poly-generation is carried out. This, with the purpose of supplying to hydrogen value chain actors an overview of possible solutions and of suggesting them a holistic perspective looking at all the possible technologic options instead of an approach focused on a single technology and product.

Modelling Single Atom Electrocatalysts

G. Di Liberto[a], I. Barlocco[a], G. Pacchioni[a]

[a] *Dipartimento di Scienza dei Materiali, Università degli Studi di Milano Bicocca, Milano, Italy*

giovanni.diliberto@unimib.it

Single Atom Catalysts (SACs) are emerging as a relatively new frontier in the field, bridging the classical worlds of homogeneous and heterogeneous catalysis. Computational chemistry offers a valid and viable framework to access the atomistic details of electrocatalytic processes and to rationalize of even predict novel systems. Recently, a lot of attention has been dedicated to the reactions of evolution and conversion of molecular hydrogen and oxygen from or to liquid water.[1] The activity of SACs for water splitting is usually rationalized or predicted using the seminal model proposed by Nørskov and co-workers, where the free energy of key intermediates adsorbed on an extended metal surface is used to explain the catalytic activity.[2]

In this presentation we discuss the key ingredients to model electrocatalytic processes on SACs. SACs differ substantially from metal surfaces and can be considered analogues of coordination compounds. In coordination chemistry, at variance with metal surfaces, stable complexes of hydrogen and oxygen can form.[3,4] We show that the same can occur on SACs and their formation may change the kinetics of the process.[5,6] This can be estimated by extending the original kinetic obtaining a multi- dimensional volcano plot for the HER and OER on SACs. DFT numerical simulations of dozens of models demonstrate that the formation of the suggested complexes may lead to different conclusions about the activity of SACs in the water splitting reaction. The results are validated against selected experimental cases. This work provides an example of the important analogies between the chemistry of SACs and that of coordination compounds, and underlines the key ingredients to be accounted when attempting to provide predictions with computational frameworks.

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Alkaline water electrolysis based on non-critical raw materials

S. Campagna Zignani [i], A. Salanitro [i], G. Monforte [i], A. Carbone [i], A. Arico [i]

[i] *Institute of Advanced Energy Technologies (ITAE) of the Italian National Research Council (CNR)*
e-mail presenting author: zignani@itae.cnr.it

One of the most widely used electrolytic technologies at a commercial level is alkaline electrolysis for hydrogen production up to the megawatt range. A large impact of this technology can be attributed to the fact that these devices can be adapted to a variety of scales for distributed energy needs, as well as the fact that pure hydrogen generated through liquid-electrolyte water electrolysis is not expensive. A catalyst based on a Ni structure with a high surface area can enhance the HER activity but it would still be limited by the intrinsic catalytic activity of metallic Ni. Thus, it is appropriate to modulate the chemical environment of Ni by alloying it with other metals while taking advantage of the high surface areas of Ni-based nanostructures.

Specifically, this study investigates the development of non-critical raw material (CRM) cathode catalysts for water alkaline zero-gap cells for the production of green hydrogen. NiCu, NiCuMo and NiMo electrocatalysts were studied in a zero-gap cell configuration coupling a commercial alkaline membrane and an anode based on NiFe. The best behaviour was observed for NiCu at 70°C (Figure1). We have used the oxalate method allowing the formation of NiCu alloy with phase impurities lower than 3 %, crystallite size of approximately 7nm and total surface area of 160 m^2g^{-1}..

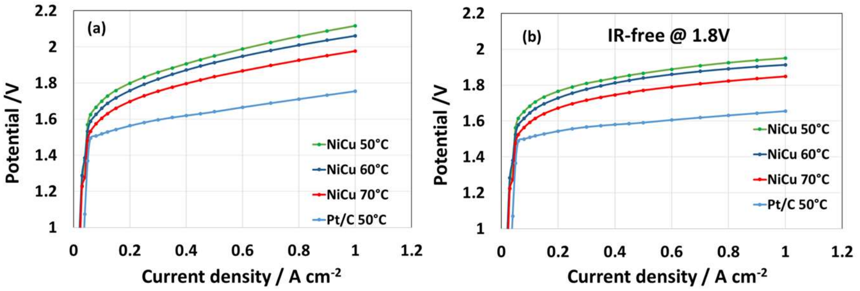

Figure 1: Polarization curves comparing the Banchmarck and NiCu cathodes (a), IR-free (b)

The electrochemical results concerned the evaluation of overpotential to H_2 evolution, performance compared to benchmark materials, achieving a promising current density of 1 A cm^{-2} @ 1.85V at 70 °C IR-free (Figure1, b), stability towards chronopotentiometric test. These demonstrate as the NiCu is a promising substitute for Ni, commonly used as cathode for alkaline electrolysers, although the stability is still an open issue.

Acknowledgements

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Study of a new approach for the treatment of iodinated contrast media in wastewater using electrochemical deiodination

F. Vitulano,[1] L. Sorti,[1] C. F. Morelli,[1] F. Uggeri,[2] A. Minguzzi,[1]
A. Vertova[1]

[1] *Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, 20133, Milano, Italy*
[2] *Bracco S.p.A., Via Caduti di Marcinelle 13, 20134, Milano, Italy*
fiammetta.vitulano@unimi.it

The environmental concern about active pharmaceutical ingredients (APIs) is drawing increasing attention as these substances are resistant to degradation treatments, persistent in aqueous medium and able to have a negative impact on aquatic organisms and human health [1]. Among APIs, iodinated X-ray contrast media (ICM) have been detected in municipal wastewater at relatively high concentrations (up to 100 µg L^{-1}) and in drinking water as well, as a result of their stability and resistance to common biological wastewater treatments [2]. ICM compounds themselves should not impose high risk for human health owing to their low ecotoxicity, but the role of degradation products formed during treatment processes is still unclear. For this reason, it is highly desirable to develop an effective degradation method. In this scenario, the electrochemical reductive deiodination of ICM is examined in this study as a green technique that, through the cleavage of C-I bonds, makes the transformation products more biodegradable and less bioaccumulative [3,4], allowing at the same time the recovery of the valuable iodine. In this work, cyclic voltammetry (CV) was used to study the electrochemical behavior of iodinated compounds like 4-iodoanisole, 4-iodotoluene and 4-hydroxyisophthalic acid derivatives, in aqueous and non-aqueous systems, comparing different cathode materials. In particular, CV performed in acetonitrile on 4-iodoanisole and 4-iodotoluene allowed to identify silver (Figure 1) and gold as the most promising cathodes.

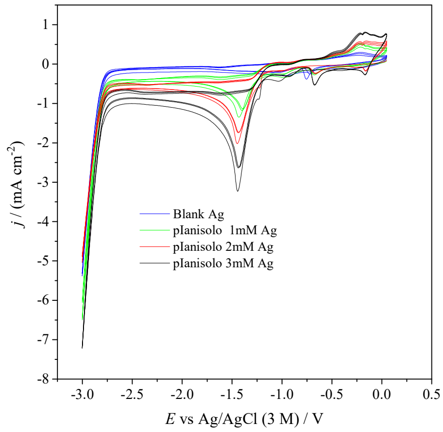

Figure 9: CVs of blank and different concentrations of 4-iodoanisole on silver electrode in a solution of acetonitrile and tBu_4NClO_4 0.1 M

After CV studies, preliminary electrolysis on different ICM showed that reductive electrochemical deiodination is an efficient process and likely occurs *via* radical iodine formation [5]. This study provides more insights into the mechanisms of ICM degradation in reductive processes.

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(Invited) State-of-the-art and Developmental Trends in Platinum Group Metal-free Catalysts

Plamen Atanassov

Department of Chemical & Biomolecular Engineering, Materials Science & Engineering and Chemistry,
National Fuel Cell Research Center, University of California, Irvine, CA 92697

Platinum group metal-free (PGM-free) catalysts have been targeted as possible Earth Abundant Elements solution to many electrochemical energy conversion technologies. Special attention has been given to PGM-free electrocatalysis with atomically dispersed (AD) transition metal moieties decorated over nitrogen-doped carbonaceous materials (a.k.a. M-N-C catalysts). Major applications for M-N-Cs are in cathode catalysts for oxygen reduction reaction (ORR). [1] These materials are employed across the pH-range: in proton exchange membrane fuel cells (PEMFC), biological (microbial) fuel cells (MFC) and alkaline, including anion/hydroxyl exchange membrane fuel cells (AFC, AEMFC/HEMFC). We have successfully introduced M-N-C catalysts synthesized by sacrificial support method (SSM) as a hard template approach based on high temperature pyrolysis.[2] In most cases a secondary pyrolysis is being performed to promote AD display of the transition metal.[3]

This talk will address structure-to-property correlations for M-N-C catalysts in ORR based on electrochemical activity obtained in rotating ring-disk electrodes (RRDE) with those spectroscopic and microscopic observations and density functional theory (DFT) calculations of oxygen binding on AD transition metal. We will discuss the role of the AD transition metal, participation of the surface N-groups as co-catalysts/alternative active sites and the possible role of surface oxides as co-catalysts or hydrophilic/hydrophobic properties descriptor. M-N-C catalysts performance in single membrane electrode assembly (MEA) fuel cells will also be discussed in the context of its surface chemistry and materials structure/morphology. We will focus on local hydrophobicity of SSM-based M-N-C electrocatalysts and its impact on the MEA performance.

A broad spectrum of AD transition metal decorated MNCs have been synthesized and evaluated for catalytic activity in ORR (and other processes). The use of such materials as "active supports" for highly dispersed platinum or platinum alloy nanoparticles will be discussed. New developments in synthesis protocols enabling "green chemistry" scalable solutions will be discussed.

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Pitch presentations

Electrochemical synthesis of new possible nanoscaled gadolinium-based contrast agents

C.Carbone,[i] M. Minardi,[i] A.Stöeckle,[j] F. Uggeri,[k] A. Vertova,[i] A. Minguzzi[i]

[i] *Department of Chemistry, Universty of Milan, Via C. Golgi 19, 20133, Milan, Italy*
[j] *Institute of Physical Chemistry and Electrochemistry, Leibniz University Hannover, Callinstr 3A, 30167 Hanover, Germany*
[k] *Bracco Imaging SpA, Via E. Folli 50, 20134, Milan, Italy*
claudia.carbone@unimi.it

Magnetic Resonance Imaging (MRI) is a widely used imaging technique for the diagnosis, staging and evaluation of response of many types of cancer, exploiting the differences in spin relaxation times of water protons. The admininsration of Gadolinium-Based Contrast Agents (GBCAs) is required to obtain high-contrast images for the detection of some diseases; they have influence on the relaxation time of water protons, allowing the enhancement of their relaxivity, and so the signal intensity [1]. Currently, nine gadolinium complexes are clinically approved and widely used as GBCAs.

In the present research, the advantages of electrochemistry are exploited for the synthesis of a new possible GBCA. The project was inspired by the research on metal-ion batteries, and in particular by Prussian blue analogs (PBAs), which are among the most promising cathodic materials [2]. Thanks to their simple synthesis, non-toxicity, stability, biocompatibility and their capacity for the reversible insertion of variety of ions, they have been recently considered also in the medical field [3]. Two different sized particles of Zinc Hexacyanoferrate (ZnHCF), have been prepared by co-precipitation [4][5]. As the medical interest lies in monodispersed nanoparticles with average diameter of about <100 nm, the current focus is on nanometric spherical s-ZnHCF. A known amount of ZnHCF has been deposited on the surface of the conductive material FTO (Fluorine-doped Tin Oxide) and used as working electrode (WE) in a close reactor, immersed in an aqueous solution of gadolinium ions Gd^{3+}.

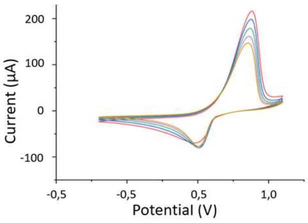

Figure 1: Cyclovoltammetry in $Gd(CH_3CO_2)_3$ 0.1 M, WE: s-ZnHCF deposited on FTO

Cyclovoltammetries show the oxidation and reduction of iron atoms, whose peaks fall at different potentials depending on the electrolyte (and so on the intercalating cation), due to the different chemical environment. CVs in gadolinium acetate (Figure 1), allowed to understand the potential for the intercalation of Gd^{3+}. With the application of the reductive voltage in chronoamperometries, it was possible to create gadolinium-rich particles which could ideally work as contrast agents. The proposed mechanism implies that Fe^{3+} atoms are reduced to Fe^{2+} and induce the intercalation of Gd^{3+} into the 3D open framework structure of ZnHCF. By adopting our approach, it would be possible to finely control the amount of Gd^{3+} pushed in the structure, and so tuning their ability in enhancing MRI signal.

Preliminary investigation indicate that the Gd-modified ZnHCF is particularly stable, a needed requirement of a GBCA for avoiding free-Gd^{3+} leaks into the human body.

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Thiolate Protected Gold Nanoclusters and the Hydrogen/Deuterium Puzzle

A. Conte,[a] S. Antonello,[a] M Reato,[a] and F. Maran[a,b]

[a] *Department of Chemistry, University of Padova, Via F. Marzolo 1, 35131-Padova, Italy*

andrea.conte.5@phd.unipd.it

[b] *Department of Chemistry, University of Connecticut, 55 North Eagleville Road, Storrs, Connecticut 06269, United States*

Electrochemical methods have been successfully employed to study substituent effects, a field pioneered by the late Petr Zuman.[1] So far, however, substituent effects have never been studied by changing a *very large* number of identical substituents. This kind of study obviously requires the use of very special molecules where this kind of substitution is indeed possible.

Ultrasmall thiolate (SR) protected gold nanoclusters, such as $Au_{25}(SR)_{18}$, are prepared with atomic precision and exhibit molecular properties. Their electrochemical and, more generally, electron transfer (ET) behavior can be tuned by acting on both the metal and organic components.[2-4] $Au_{25}(SR)_{18}$ molecules, therefore, provide the opportunity to test the combined effect of changing 18 identical ligands.[5]

We prepared the first fully deuterated gold nanocluster, $Au_{25}(SC_4D_9)_{18}$, and compared its electrochemical, ET, solid-state, photophysical, and singlet-oxygen photosensitizing behaviors in comparison with those observed for the corresponding $Au_{25}(SC_4H_9)_{18}$ cluster.[2-7] The deuterated molecule exhibits a number of unexpected differences, such as: The diffusion coefficient is smaller, consistently with a larger hydrodynamic radius; The rates of heterogeneous ET and, particularly, intercluster ET in films are lower, pointing to a thicker monolayer; The rate by which two deuterated clusters react in films to form Au_{38} is significantly lower than for $Au_{25}(SC_4H_9)_{18}$; Single crystal X-ray crystallography evidences important differences between the structures of $Au_{25}(SC_4D_9)_{18}$ and $Au_{25}(SC_4H_9)_{18}$. These and further results indicate that deuterated thiolates are far from being noninnocent ligands.

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Electropolymerization of poly(1,3-dioxolane) for solid state batteries application

N. Albanelli, F. Capodarca, M. Zanoni, G. Lacarbonara, C. Gualandi, M. L. Focarete, C. Arbizzani

Dept. of Chemistry "G. Ciamician", Università di Bologna , Via Selmi 2, 40126, Italy
e-mail presenting author: nicolo.albanelli2@unibo.it

Batteries are crucial for a wide range of applications, from consumer electronics and automotive to stationary systems for electricity generated from intermittent renewable sources, such as wind and solar energy [1]. At present, the most exploited chemistry is based on lithium, in which the electrolyte usually consists of lithium salt and carbonate-based organic solvent. This poses some serious safety concerns about the toxicity and the low ignition point of such electrolytes. The narrow working temperature, decomposition under high voltage, and the inability to suppress lithium dendrite growth make the traditional liquid electrolyte no longer satisfactory for the expected high-energy battery of the future [2]. Advances in active chemistry are left to the solid-state chemists' creativity and innovation in the design and elaboration of new intercalation electrodes and solid electrolytes [3]. In fact, solid electrolytes and, in particular, the ones based on polymers are safer than liquid electrolytes as they do not have leakage problems and because of their nontoxic, low-vapor pressure, and non-flammable properties [4]. The majority of dry solid polymer electrolytes reported so far is based on high molecular weight poly(ethylene oxide) (PEO) complexed/dissolved with different Li^+ salts, in which the Li^+ conduction occurs via the complexation of the ions at different coordination sites, which are the O atoms in the chain [5].

An interesting polymer is poly(1,3-dioxolane) (PDOL), since it contains a higher content of O atoms (43.2 wt%) than PEO (36.4 wt%), indicating more interaction sites exist in PDOL-based electrolyte, which could lead to a higher ionic conductivity [6]. PDOL has been already employed as a protective layer both for sulfur electrodes and high-voltage cathodes, in which DOL was electrochemically polymerized [7], and also as an artificial SEI for lithium metal anode [8]. In this work PDOL was electropolymerized starting from a solution of DOL-LiTFSI 1.7m, which was added to a dry electrospun poly(acrylonitrile) (PAN) scaffold. The physico-chemical characterization of the polymer system has been carried out exploiting several techniques, including TGA and DSC for the thermal properties, DMA to investigate the mechanical properties, SEM to understand the morphology and FTIR. The conductivity of the electropolymerized PDOL has been investigated at different temperatures in a stainless-steel symmetric cell employing electrochemical impedance spectroscopy measurements. Furthermore, the use of the PAN-PDOL-LiTFSI system as a polymer solid-state electrolyte has been evaluated in a full cell, with lithium metal employed as the negative electrode.

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Sn/Ti oxide from $Ti_3Al_{(1-x)}Sn_xC_2$ MAX Phases (x=0.4, 0.7, 1) as Negative Electrode for Lithium Ion Batteries: three Sides of a Coin

N. Vallana[1], A. Gentile[2], C. Ferrara[1], D. Cerrone[2], I. Ostroman[1], S. Marchionna[2], R. Ruffo[1]

[1] *Dipartimento di Scienza dei Materiali, Università degli Studi di Milano Bicocca, Via Cozzi 55, Milano 20125, Italy*
[2] *Ricerca sul Sistema Energetico - RSE S.p.A., Via R. Rubattino 54, Milano 20134, Italy*
e-mail presenting author: n.vallana@campus.unimib.it

Batteries are electrochemical devices that have characterized society and its development in recent decades. Moreover, to improve the use of renewable energy sources and electric vehicles, and with the continuous growth of the demand for portable electronics, the demand for batteries that can meet global needs has increased. Currently, the most widely used type of them is the lithium-ion battery (LIB), which is reliable and provides satisfying electrochemical performances[1]. However, the most used anode in this system is the graphite anode (theoretical capacity of 370 mAh g^{-1}), which suffers from aging and becomes unsafe with high currents. So, it is important to investigate other types of materials as possible and promise anode that could give better properties. MAX phase (where M is a transition metal cation, A is a metallic or metalloid element and X is C, N or B) are a class of 3D materials, with layered hexagonal crystal structure (space group $P6_3/mmc$) consisting of several layers of MX, alternated with layers of pure A-elements along the c cell parameter[2]. One of the most common of this class of materials is the Ti_3AlC_2 MAX phase. However, it shows poor energy storage performances as active electrode (capacity of 60 mAh g^{-1}).

One compound well-known as active material is titanium oxide (TiO_2). This has been shown to be a well-established and particularly stable material for applications in ion batteries. However, it has a lower capacity than graphite[3].

One interesting material as electrode is tin oxide (SnO_2): this is a very promising material due to its high specific capacity, but it suffers from poor stability due to the high volume change it undergoes during charge and discharge cycles[4].

A possible strategy to improve the long-term stability of this oxide is to use the stable titanium oxide with it: is reported that by adding it, making a solid solution of Sn/Ti oxide, the total system achieves less volume change during cycling and so gains a stability improvement.

Here, a promising strategy to obtain a new active electrode material based on the MAX-phase system, combined with titanium/tin oxide to improve its specific capacity, is proposed. First, MAX-phase $Ti_3Al_{(1-x)}Sn_xC_2$ are obtained via spark plasma sintering, with x equal to 0.4, 0.7 and 1. After that, the material is oxidized by a thermal treatment in air to obtain a nanostructured layer based on tin oxide and titanium oxide. To better understand their structure and composition, these materials are investigated by morphological and structural analysis, like x-ray diffraction (XRD), scanning electron microscopy (SEM), and Raman spectroscopy. Then, their electrochemical properties are studied, versus lithium in coin cell setup and versus a working positive electrode in pouch cell setup, demonstrating their possible availment as promising negative electrode in LIB.

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The influence of electrolyte composition and current collector morphology on the properties of anodeless lithium metal batteries

I. Ostroman,[i] L. Mezzomo,[i] S. I. Ince,[i] F. Zaglio,[i] R. Ruffo[i]

[i]*Department of Materials Science, University of Milano-Bicocca, via Roberto Cozzi 55, 20125 Milano, Italy*
e-mail presenting author: i.ostroman@campus.unimib.it

Among all the possibilities for next-generation rechargeable batteries, lithium metal is still craved as the Holy Grail of negative electrode materials, for the high theoretical specific capacity and lowest redox potential. Moreover, lithium metal batteries have a superior energy density with respect to currently used Li-ion batteries, and such energy density can be further increased by studying the anodeless configuration: the cell setup consists of a bare copper current collector where the lithium is plated directly from the cathode. Unfortunately, lithium plating/stripping on high-area surfaces displays a series of well-known problems: unstable SEI, dendrites formation that leads to cell short-circuit, and dead-lithium formation that causes severe capacity fading. In this respect, a lot of interesting strategies have been proposed; the ones adopted in this study are the electrolyte design and the employment of engineered current collectors.

For this research, in the first part the effect of three different liquid electrolytes was studied on symmetrical Li|Li coin cells: commercial LP30 (1.0 M $LiPF_6$ in EC/DMC), a Deep Eutectic Solvent "DES" (TFA:$LiPF_6$ (80:20) with 10% EC and 5% FEC) [1], and a Dual Salt "DS" (LiDFOB 1M and $LiBF_4$ 0.2 M in DEC/FEC) [2]. The comparison has been carried out at equal charge by increasing the current (0.5, 1, 2, 4 mA cm^{-2}) and lowering the plating/stripping time (2, 1, 0.5, 0.25 h), and in all the configurations the electrolyte showing the best performances is the DS: while using the commercial LP30 and the DES the cell overpotential escalates as the cycles increase (respectively to ±0.1 and ±0.3 V), with the DS the cyclic potential profile remains stable between ±0.02 V even after 200 cycles, confirming the validity of such electrolyte in the formation of a stable SEI. Moreover, this stabilizing effect and its repercussions on the lithium morphology have been also detected by SEM measurements of the plated lithium surfaces.

In the second part, the DS performance has been measured in a non-symmetrical configuration to study the effect of the current collector: Cu|Li coin cells have been used for anodeless plating and stripping (1 mA cm^{-2} current and 1 h for half cycle). As preliminary measurements, both the smooth and the rough sides of a plain Cu foil have been tested; the coins with rough Cu have displayed the most stable potential profiles and the highest Coulomb efficiencies (Figure 1). This is believed to be a hint of the positive effect of an irregular Cu surface: to further explore it, the employment of dendritic Cu as current collectors has been set as the following step of this research, and it is currently under investigation.

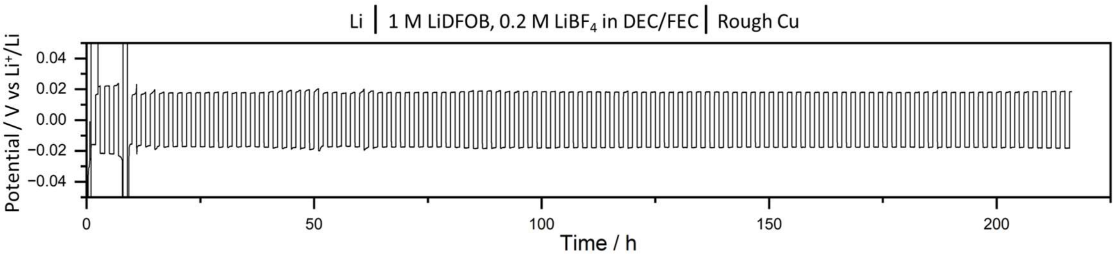

Figure 1: GCPL profile of anodeless LMB with rough side of Cu as current collector and dual salt as electrolyte.

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Poly(aryl piperidine)-based Ion-Solvating Membranes for water electrolysis

T. Caielli[i,j], S.C. Rajappan[j], D. Aili[j], J.O. Jensen[j], P. Mustarelli[i]

[i] *Chemistry, Università degli studi di Milano Bicocca (UNIMIB), Via cozzi 55, 20125, Italy*
[j] *Energy Conversion and storage, Denmark Technical University (DTU), Electrovej 375, 2800, Denmark*

t.caielli@campus.unimib.it

One of the main limitations to the realization of efficient, pressurizable, and in the meantime durable Water Electrolyzers (WE) is the lack of a proper separator/membrane. The vast majority of commercial alkaline WEs adopt a Zifron diaphragm, a state-of-the-art and very durable commercial separator. However, high gas crossover and high area-specific resistance limit the maximum current density of Zirfon-based WE and don't allow a pressurization of the system. Anion Exchange Membranes (AEM) are a promising alternative, that could ultimately allow for operation with a pure water feed. AEM research has achieved impressive results in the last 5 years. AEMs of different chemistries with high conductivity (> 100 mS/cm), small thickness (< 40 µm), and alkali stable polymeric backbones are now produced at lab scale and available as commercial products. Anyhow, degradation of the quaternary ammonium cationic moieties employed in AEMs causes a conductivity decrease and reduce the durability of AEMs WE. Despite quaternary ammonium with unprecedented stability towards alkali are being successfully incorporated in AEMs [1, 2] their durability is still not sufficient.

Ion-Solvating Membranes (ISM) have been recently proposed as a promising alternative for WE separators [3]. ISMs anion conduction mechanism is not based on fixed cationic groups like AEMs but relies on the uptake of electrolyte (both OH^- and K^+) attained by the high overall polarity of the polymer matrix. The absence of cationic groups in ISM widens the choice of possible chemistries with good stability towards alkali. ISMs for alkaline WE, which have been studied in detail, are based on polybenzimidazoles, achieving high conductivities in 20-30 wt.% KOH. However, these polymers undergo hydrolysis in alkaline environment, with loss of mechanical properties and cell failure. It is indeed not trivial to find a polymer with a suitable balance between KOH uptake and conductivity on one hand, and mechanical robustness and alkaline stability on the other.

Topic of the presented work is the synthesis and testing of ISM based on of Poly(aryl piperidine)s (PAP). PAPs are polymers with alkali stable backbone that, in the quaternized form, are receiving strong interest for AEM application. However, no scientific paper employing PAPs as ISM matrix has been published. Poly(biphenyl piperidine) (PBP), the simplest amongst PAPs, resulted to have low electrolyte uptake, and therefore low conductivity. In order to increase the electrolyte uptake, casting process parameters as well as modifications to PBP chemical structure were performed. A complete characterization of the polymer was performed with spectroscopic and thermal techniques. Electrochemical tests were carried out to determine membrane conductivity at different KOH concentrations and temperature. Ageing tests were performed in KOH solutions and electrochemical cells.

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Coupling desalination electrodialysis technology with green hydrogen production

G. Campisi, A. Pellegrino, F. Proietto, A. Tamburini, G. Micale, O. Scialdone

Dip. di Ingegneria, Università degli studi di Palermo, Viale delle scienze, 90128 Palermo, Italy
e-mail presenting author: giovanni.campisi02@unipa.it

The ICCP (Intergovernmental Panel on Climate Change) in its last report [1] estimated a worldwide temperature increase ranging between 2.2 and 3.5 degrees by the end of the century, with a dramatic effect on the environment. European Union is strongly promoting sustainable policies to avoid global warming, trying to reduce CO_2 emissions and fund a transition from fossil fuel to hydrogen. Green hydrogen production will be crucial in the following years. A boundary topic concerning hydrogen production through electrolysis is the need for pure water. Stoichiometrically, for 1 kg of hydrogen, about 9 litres of water are needed, and studies suggest almost 2.3 Gt of hydrogen are required in the future hydrogen-based society [2], as consequence, the amount of water required becomes abnormally large. Unfortunately, United Nations have identified the scarcity of water as another issue of crucial importance for people living on earth. With this respect, coupling hydrogen production with seawater desalination might be a promising and sustainable option. Electrodialysis (ED) [3] is a well-known electro-membranes technology able to desalinate salty waters by consuming electric energy. The technology consists in the repetitions of ionic exchange membranes (cationic CEM and anionic AEM), separated by spacer-filled channels hosting the salty solution to be desalinated. The system is stacked with several cell pairs (i.e. repetitive unit constituted by a CEM and an AEM and the 2 spacer-filled channels). The cell package so assembled is completed by two end-compartments where two electrodes are present. Here the electricity supplied by an external load is converted into ionic flux by suitable red-ox reactions. When water is fed also to these electrode compartments hydrogen and oxygen evolution occur at the cathode and anode, respectively.

In this work, multi-ED units are adopted in order to investigate the simultaneous production of water and hydrogen. Alshebli et al. [4] studied a similar experimental system (using a Na_2SO_4 solution), to prove the technical feasibility of this coupling, but no economic analysis was performed to demonstrate its convenience. In particular, a techno-economic model for multi ED-units is developed to estimate the process main variables, and suitable profitability indexes (such as the Levelized Cost of Hydrogen LCOH). The simulation campaign is carried out considering a fixed number of cell pairs, able to treat a given amount of seawater. The total number of cell pairs is divided up between multiple electrodes (mimicking the classical electrolysers) in order to maximise the hydrogen productivity and reduce its cost. Preliminary analyses show that the proposed idea can be profitable for the case of some design features and operating conditions. Results suggest that this technology might be a promising option to produce green hydrogen without any water footprint.

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An experimental investigation on the green hydrogen production through Electrodialysis with Bipolar Membranes process

A. Pellegrino, G. Campisi, F. Proietto, A. Cipollina, A. Tamburini, O. Scialdone, G. Micale

[i] *Dipartimento di Ingegneria, Università degli Studi di Palermo, viale delle scienze ed. 6, 90128 Palermo, Italy*
e-mail presenting author: alessandra.pellegrino01@unipa.it

In the last decade, the increasing temperatures in the world represents the biggest problem the mankind faces, as global warming causes environmental disasters that can permanently change the life on the planet. In order to solve or at least mitigate this problem as much as possible, the major world leaders have established that the use of fossil fuels, the main producers of greenhouse gases, needs to be stopped and the path to renewable sources promoted [1]. In this framework, the hydrogen has been identified as the energy carrier under which renewable energy can be stored. The hydrogen is the lightest and most abundant element in the universe, and it has the highest gravimetric energy density of all known substances, i.e., the lower heating value is 120 MJ kg^{-1} and the higher heating value is 141 MJ kg^{-1}. Hydrogen can be produced with zero emissions and in a totally sustainable way by coupling the electrolysis of water with the renewable energy resources and, in this case, it is called green hydrogen. The focus of the international community is strongly on hydrogen, just consider that in 2021 more than 200 MW of electrolyzers became operational, including 160 MW in China and more than 30 MW in Europe to produce green hydrogen [2]. The most well-known electrolyzers in the state-of-the-art are [3]: (i) Alkaline Electrolyzers, the most studied and mature; (ii) Proton Exchange Membrane Electrolyzers, the most promising; (iii) Anion Exchange Membrane Electrolyzers, under development; and (iv) Solid Oxide Electrolysis Cells, high temperature electrolyzers under development. In this context, new types of electrolyzers were also developed, enabling the production of green hydrogen in an electro-membrane process, all in one technology.

The electro-membrane process that has been investigated in the literature, although not in detail, is Reverse Electrodialysis (RED), in which the energy produced from the salt gradients is consumed in the system itself in hydrogen production [4]. An earlier study has also been carried out on Electrodialysis (ED), for the simultaneous production of hydrogen and the water desalination [5]. The literature study, however, clearly shows that the main limitation of these technologies is the current density, which is two orders of magnitude lower than the values of conventional electrolyzers. To overcome this limitation, the present work proposes to combine the membrane process known in literature as Electrodialysis with Bipolar Membranes (EDBM) with the hydrogen production, resulting in the Hydrogen - Electrodialysis with Bipolar Membranes Electrolyzer (H-EDBM). The EDBM is a technology that can support much higher current densities (i.e., 0.1 A cm^{-2}) than ED/RED, and it is comparable to that used in state-of-the-art electrolyzers. Through a current applied to the system, the EDBM is able to desalinate the salt stream fed, producing acid and base, due to the presence of the bipolar membranes. The aim of this work is to characterize for the first time the cathodic and anodic compartments in which hydrogen and oxygen are produced, and from simple 'by-products' of the process, they are brought to the leading role. In particular, a comprehensive experimental campaign of H-EDBM has been carried out studying different configurations and testing different operating conditions, obtaining maximum faradic efficiencies for both hydrogen and oxygen, and achieving hydrogen productivity of up to 18 mol h^{-1} m^{-2}.

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Poster presentations

p-01

Realtime analysis of electrochemical reactions in batteries: the OpMetBat project

Sergio Brutti[1], Leonardo Suraniti[1], Paola D'Angelo,[1] Burkhard Beckhoff,[2] Maria Assunta Navarra[1], Marco Agostini[3]

[1]Dipartimento di Chimica, University of Rome La Sapienza, P.le Aldo Moro 5 00185 Roma (IT)
[2] Physikalisch-Technische Bundesanstalt, 2-12, 10587 Berlin, Germany
[3]Dipartimento di Chimica e Tecnologie del Farmaco, University of Rome La Sapienza, P.le Aldo Moro 5 00185 Roma (IT)
Presenting author email: Sergio.brutti@uniroma1.it

The development of new battery materials is key to improving the performance, lifetime, safety and cost of energy storage technologies like Li-ion batteries for electric vehicles. However, innovation is hampered by the inability of industry to reliably characterize their structure and chemistry in an operating environment.

The OpMetBat project will build a metrological framework supporting traceable operando characterization of state-of-the-art battery materials under dynamic charge / discharge conditions. This includes advancement and validation of ex situ methods, establishing new protocols, cells and a best practice guide for operando approaches and developing new instrumentation enabling hybrid, multiparameter measurement to inform new materials development.

The project aims to develop operando techniques and hybrid (multi-modal) instrumentation, supported by quantitative and validated ex situ analysis and electrochemical measurements methods, to enable beyond state-of-the-art materials characterization for high-capacity energy storage technologies.

The good practice guide developed within this project will benefit the scientific community by improving reliability, repeatability/reproducibility and fidelity of operando measurements. The project will pioneer operando metrology for battery research at several European synchrotron radiation facilities and the transfer into laboratories to support industry and researchers.

Acknowledgements: The 21GRD01 OpMetBat project has received funding from the European Partmership on Metrology Participating States and from the European Union's Horizon 2020 research and innovation programme..

p-02

Biobased gel polymer electrolyte for Li-air batteries

M. Longo,[a] M. Gandolfo,[a] J. Amici,[a] C. Francia,[a] S. Bodoardo[a]

[a] *Electrochemistry Group, Dept. of Applied Science and Technology, Politecnico di Torino,*
C.so Duca degli Abruzzi 24, 10128, Torino, Italy
mattia.longo@polito.it

The necessity to cut the CO_2 emissions, with the goal to mitigate the rising global temperatures, has led to a profound interest in batteries optimization and alternative electrochemical storage systems. Due to their extremely high energy density, Li-O_2 batteries are considered a promising alternative electrochemical system to the commercial Li-ion batteries [1].

However, their commercial application is limited by the system's poor cycle stability and low reversible capacity which is heavily dependent on the electrolyte properties.

In order to eliminate the drawbacks due to the liquid electrolyte, a gel polymer electrolyte (GPE), consisting of a biobased methacrylated gelatine (GelMA) matrix and a DMSO based liquid electrolyte, has been developed and characterized [2].

The curing of the GelMA monomers was carried out through a fast and cheap UV mediated radical photopolymerization [3].

These electrolytes combine the high mechanical strength and the thermal stability of the polymer matrix with the liquid electrolyte electrochemical properties.

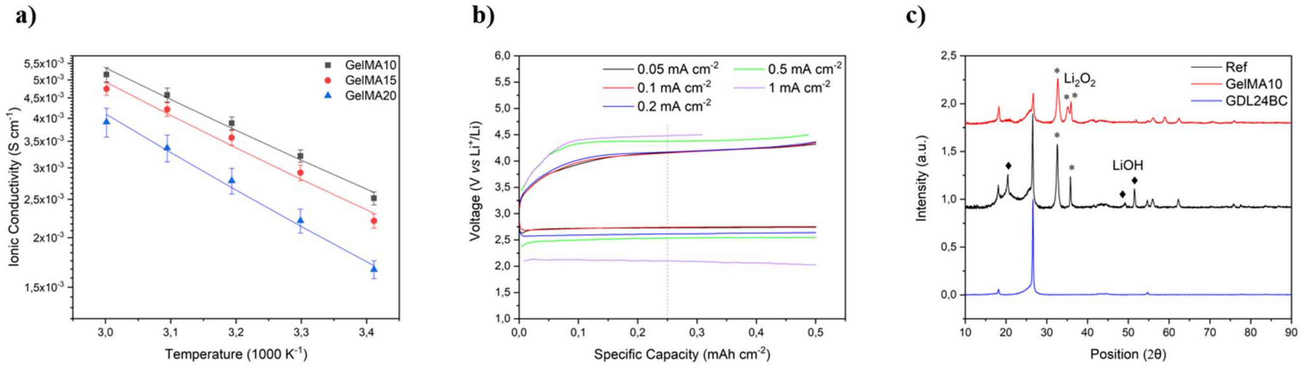

Figure 10. a) Arrhenius plot of the GPEs. b) Galvanostatic charge and discharge curves for GelMA10 at different current densities. c) Diffractograms of the cathodes of cells containing GelMA10 and the reference electrolyte after discharge compared with a pristine cathode.

The cured membranes display a high room temperature ionic conductivity (Figure 1.a), as well as a good interfacial stability against Li metal and reversible cycling in a wide range of current densities (Figure 1.b).

Furthermore, the cathodes of the discharged cells were investigated by XRD, and it was observed that the GelMA presence slows down the decomposition of the DMSO, thus increasing the reversibility of the electrochemical reactions (Figure 1.c).

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p-03

Structured catalyst for indirect internal reforming (IIR) of biogas in a solid oxide fuel cell (SOFC)

Elisabetta Di Bartolomeo, A. Prioriello, L. Duranti, C. Larosa, M.L. Grilli,[a] I. Luisetto[a]

Department of Chemical Science and Technology, University of Rome Tor Vergata, Via della Ricerca Scientifica 1, 00133 Rome, Italy
[a]Department of Energy Technologies, Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA) Casaccia RC, Via Anguillarese 301, 00123 Rome, Italy
e-mail presenting author: dibartolomeo@uniroma2.it:

The production of biogas from anaerobic digestion of different biomass sources (e.g. waste from the agro-food industry, sewage sludge, or landfills) is among the EU- promoted environmental policies. Biogas is composed of two major greenhouse gases: methane (50-65 %) and carbon dioxide (35-50 %) and their relative composition depends on the source of organic material. An efficient valorization of biogas is crucial in the perspective of counteracting the increasing global warming. Dry reforming of methane (DRM) is an efficient way to convert methane and carbon dioxide into valuable chemical products. It is a strongly endothermic reaction favored at high temperatures ($\geq$ 800 °C) and low pressure and produces a mixture of H2 and CO (syngas) with a molar ratio close to unity. In this work is the development of a structured catalyst for the dry reforming of biogas to be used as a pre-reformer in indirect internal reforming configuration (IIR) solid oxide fuel cells (SOFCs). The structured catalyst is based on NiCrAl foams coated with Ruthenium (nominal loading 3.0 wt %) supported on CaZr0.85Sm0.15O3 (CaZrSmO) perovskite oxide. The powder is produced by solution-combustion synthesis and deposited on metallic foams by the wash-coating method. Catalytic tests for dry reforming of methane (DRM) reaction are carried out at 850 °C, 700 °C and 550 °C for an overall 50 h with CH4/CO2 = 1 and P = 1.3 bar at different gas hourly space velocities (GHSV). . The carbon amount on spent structured catalysts is evaluated. The final goal of the paper is the proof-of-concept of the process: a laboratory validation of an IIR-SOFC fed by biogas.

p-04

Co-electrolysis of CO_2 and H_2O at intermediate temperatures using coated commercial cells

M. Lo Faro, S. Campagna Zignani, S. Vecino-Mantilla, G. Monforte, and A. Aricò

Institute of Advanced Energy Technologies (ITAE) of the Italian National Research
Council (CNR), Via Salita S. Lucia sopra Contesse 5, 98126 Messina, Italy
e-mail presenting author: lofaro@itae.cnr.it

As a result of climate change, environmental threats are on the rise in advanced countries. A number of actions have been taken to address this issue, including the rational use of energy, the adoption of a circular economy, and the restoration of the environment [1, 2]. In this context, the song's theme "what goes around comes around" is more relevant than ever as a point of action for scientists, policymakers, and societies [3]. As part of research, capturing, reusing, and valorizing CO_2 produced by numerous industries could be an option. Combined with the need to store renewable electricity, this action can lead to a sustainable vision. The fuels produced by this process can therefore be labeled as "green" [4]. In order to achieve this goal, hydrogen and carbon dioxide can be converted into syngas at intermediate temperatures using solid oxide electrochemical cells (SOECs) [5, 6]. The ability of SOECs to reduce both H_2O and CO_2 is one of their key characteristics, and they represent one of the most effective methods to store renewable energy today. Because commercial cells are adapted from those made for power generation (i.e. SOFCs), they are not suitable for generating gas of higher quality than syngas. Another disadvantage of commercial cells is their low reversible cathode and high carbon deposition risks. Therefore, their use is limited, as well as their overall performance and durability. Commercial cells can be effectively overcome to this problem by adopting a coating layer on their cathodes, as it has already been extensively demonstrated. The results obtained with cermets and an exsolved perovskite are compared in this communication. To determine whether SOEC cells could improve gas quality, electrochemical analyses and gas chromatography were performed. By adding a functional layer to the cathode, we achieved a complementary effect between electrochemical mechanisms at the cathode and catalytic mechanisms that involve CO_2 and CO methanation. According to the results obtained, this approach demonstrated the potential for CO_2 and H_2O coelectrolysis to produce fuels with a higher added value than syngas.

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p-05

Development of advanced next generation solid-state batteries for electromobility applications: presentation of the ADVAGEN project

J. Amici,[i] D. Dessantis,[j] D. Ferrero,[j] M. Santarelli,[j] C. Francia,[i] S. Bodoardo[i]

[i] *Electrochemistry Group, DISAT, Politecnico di Torino, c.so D.ca degli Abruzzi 24, 10129 Torino, Italy*
[j] *STEPS Group, DENERG, Politecnico di Torino, c.so D.ca degli Abruzzi 24, 10129 Torino, Italy*
e-mail presenting author: julia.amici@polito.it

To date, the battery market is dominated by lithium-ion (Li-ion) chemistries, as the energy density has more than doubled and their costs have dropped by a factor of at least 10. However, conventional Li-ion batteries are reaching their performance limits in terms of energy density and additional features are needed to ensure safe batteries. Therefore, new battery generations are required, such as Solid-State Batteries (SSBs), as well as the creation of a new industry value chain in Europe towards their commercialization. To do so, the development and deployment of new manufacturing technologies, enabling the large-scale production of SSBs, is crucial.

Thus, it is key to develop next solid-state battery generations with innovative and scalable manufacturing techniques to accelerate cost reduction, energy savings, and enhanced safety and enable its implementation in commercial applications

The ADVAGEN project is doing so by developing a novel lithium metal (LiM) battery cell technology, based on high performing hybrid solid-state electrolyte (oxide-sulfide based), which will be safer and more reliable. Therefore, the aim is to gain a technological advantage over the current world market, especially Asian competition, hence sustainably strengthening the EU as a technological and manufacturing leader in batteries.

The main objective of ADVAGEN is to develop, manufacture and validate the most performant, stable, and safe 10Ah solid-state pouch cells, by developing novel materials for each of the parts that constitute a battery (i.e., the electrolyte, anode and cathode). In particular, the focus is on an innovative hybrid oxide-sulfide ceramic electrolyte to be integrated with a lithium metal anode and a high Ni-rich content-based cathode.

Given that the ADVAGEN consortium covers the full battery value chain, it is in an excellent position to successfully conceive significant battery developments, as well as to adequately produce and test these results in a small scale and ramp up to production to find a use case in the EV industry. Moreover, the recycling process developed for the ADVAGEN solid-state batteries aims at developing a circular economy approach.

The developed technology within the ADVAGEN project aims to have impacts at different levels.First, towards increasing global competitiveness of the European battery ecosystem through generated knowledge and leading-edge technologies in battery materials, cell design, manufacturing and recycling. Then, towards accelerating the growth of innovative, competitive, and sustainable battery manufacturing industry in Europe, and speeding up the spreading of electrified mobility through increased attractiveness for citizens and businesses, offering lower prices, better performance and safety. Last but not least, towards increasing grid flexibility, increasing share of renewables integration, and facilitated self-consumption and participation in energy markets by citizens and businesses, as well as increasing the overall sustainability and improved Life Cycle Assessment of each segment of the battery value chain.

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p-06

Bio-renewable gel polymer layers as lithium metal protection for Li-O_2 batteries

J. Amici,[i] G. Banaudi, [i] M. Longo, [i] M. Gandolfo, [i] C. Francia, [i] S. Bodoardo [i]

[i] *Electrochemistry Group, DISAT, Politecnico di Torino, c.so D.ca degli Abruzzi 24, 10129 Torino, Italy*
e-mail presenting author: julia.amici@polito.it

The growing need for clean energy production, due to global warming, has addressed the research towards the study of cleaner and more performing energy storage solutions and electric vehicles technologies. One of the most promising technologies currently being studied is the lithium - air battery, thanks to its high theoretical energy density of the order of 11000 Wh kg^{-1}. This extraordinary value is explained by the use of a metallic lithium anodes but, above all, by the use of porous carbon cathodes (GDL) where the active material, oxygen, flows from the outside. The use of metallic lithium anodes, however, results in many drawbacks that limit the stability and cycling of these batteries. For this reason, in this work, two biorenewable polymer gel membranes have been studied for lithium protection. The membranes, based on chitosan, a polysaccharide obtained from the deacetylation reaction of chitin, second biopolymer most present in nature, has shown very promising results.

The study is based on membranes with low molecular weight chitosan (<100 kda) and medium molecular weight chitosan (190 - 310 kda), methacrylated, cross-linked and subjected to the process of swelling in LiTFSI 0.5 M in DMSO. Both membranes showed excellent ionic conductivity values at room temperature, of the order of 3 mS cm^{-1}, excellent interfacial stability in contact with lithium metal, electrochemical stability windows up to 4.5 V vs Li/Li^+, stability for more than 500 hours in lithium plating and stripping tests and, above all, a lithium transference number of 0.88 for medium molecular weight chitosan, and 0.76 for low molecular weight chitosan, which, in fact, make chitosan methacrylate a promising gel polymer electrolyte. Finally, the membranes were used in Li-O_2 cells with a lithium metal anode, a carbon gas diffusion layer cathode and a bilayer electrolyte composed by a chitosan membrane for anode protection and a glass fiber separator soaked with LiTFSI 0,5M in DMSO against the cathode. Such cells have shown a good discharge capacity, with values greater than the one with liquid electrolyte alone. In addition, they proved to have an excellent cycling stability with a coulombic efficiency tending to 100% for more than 30 cycles (Figure 1.b and c) while the cell with liquid electrolyte alone failed after 15 cycles (Figure 1.a). These results make the biorenewable chitosan membranes a promising lithium anode protection system for the development of energy storage technologies with higher energy density such as lithium – air batteries.

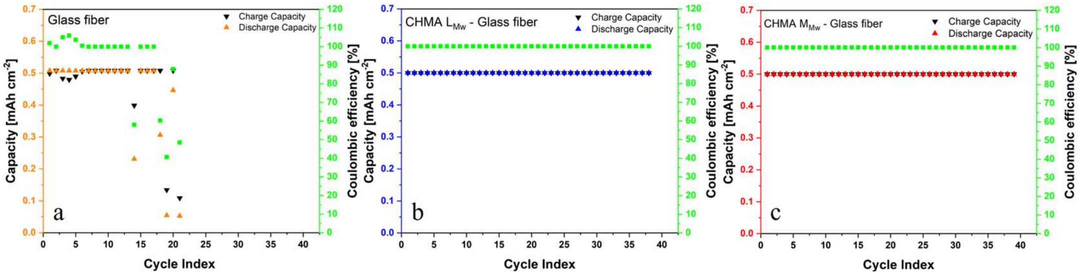

Figure 11: Cycling performances at a current density of 0.1 mA cm-2 and a fixed capacity of 0.5 mAh cm-2 of a cell containing the liquid electrolyte alone (a), a cell containing the glass fiber electrolyte and the low molecular weight chitosan based membrane (b) and cell containing the glass fiber electrolyte and the medium molecular weight chitosan based membrane (c)

p-07

Nanocomposite Metal Oxides: An Innovative Catalyst for CO_2RR

Alessia Pollice,[i] Miriam Moro,[i] Giovanni Valenti,[i] Michele Melchionna,[z] Paolo Fornasiero,[z] Maurizio Prato,[z] and Francesco Paolucci,[i]

[i] Dept. of Chemistry "Giacomo Ciamician", Alma Mater Studiorum - University of Bologna, Via Selmi 2, 40126 - Bologna, Italy.
[j] Instituto per l'Energetica e le Interfasi (IENI)-CNR, C.so Stati Uniti 4, 35127 Padova, Italy.
[z] University of Trieste, Dep. of Chemical Science, Center of Excellence of Nanostructured Material (CENMAT), Trieste, Italy.

alessia.pollice4@unibo.it

Nanoparticles have shown great promise in electrochemistry, particularly in the CO_2 reduction reaction (CO_2RR).

The Nanomaterials show a wide range applicability thanks to their features:

- *(i)* The high surface area-to-volume ratio of nanoparticles.
- *(ii)* The possibility of tailor the surface properties of nanoparticles, such as their composition and morphology, to enhance the selectivity of the CO_2RR towards specific products.
- *(iii)* The ability to integrate nanoparticles into various electrode architectures, such as nanowires, nanotubes, and thin films, to further improve the performance of CO_2RR.

To be a solution for our future energy requirements and to meet the industrial demand, the materials must be readily available and cheap. Among them, carbon-based nanomaterial could improve the selectivity and the efficiency of the reaction and provide high current densities, when combined with metal oxides. Cerium Oxide (CeO_2) is an optimum catalyst support because is able to form strong metal-support interactions with metals as copper, which allows the formation of a partially charged metal at the metal–CeO_2 interface [1].

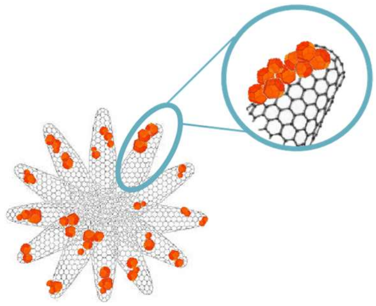

Figure 12: Nanoflower of CNHs@CeO_2

Particularly the selectivity on Cu–CeO_2 shows a wide range in CO_2RR products, depending on the sizes, the compositions, and the synthetic method of the material. In this research the focus is the study of the correlation between the synthetic method of a material made of CeO_2 supported on Carbon Nanohorns (with or without copper on it) with the selectivity in CO_2RR. Overall, nanoparticles offer a promising avenue for developing efficient and selective electrocatalysts for CO_2RR and could potentially contribute to mitigating the carbon footprint.

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p-08

Redox-mediated electrochemiluminescence enhancement for bead-based immunoassay

Alessandro Fracassa,[a] C. I. Santo,[a] E. Kerr,[b] S. Knezevic,[c] D. J. Hayne,[b] P. S. Francis,[d] F. Kanoufi,[e] N. Sojic,[c] F. Paolucci[a] and G. Valenti*[a]

[a] *Department of Chemistry Giacomo Ciamician, University of Bologna, via Selmi 2, Bologna 40126, Italy.*
[b] *Institute for Frontier Materials, Deakin University, Geelong, Victoria 3220, Australia.*
[c] *Univ. Bordeaux, CNRS, Bordeaux INP, Institut des Sciences Moléculaires, 33607 Pessac, France.*
[d] *Deakin University, Centre for Sustainable Bioproducts, Faculty of Science, Engineering and Built Environment, Geelong, Victoria 3220, Australia.*
[e] *Université Paris Cité, ITODYS, CNRS, F-75013 Paris, France.*
e-mail presenting author: alessandro.fracassa2@unibo.it

Electrochemiluminescence is a leading bioanalytical technique because of its high signal-to-noise ratio and analytes detection in very low concentrations [1].

To make ECL viable for clinical diagnostics, Roche Diagnostic started to produce fully automated analyzers that exploit the bead-based immunoassay technology. This system employs biotinylated and dye-functionalized antibodies that specifically recognize a given antigen. When the analyte is present the classical sandwich assay is formed. In this way, the ECL signal achieves proportionality to the analyte concentration. Commercialized ECL-based immunoassays typically exploit tris(2,2'-bipyridine)ruthenium(II) ($[Ru(bpy)_3]^{2+}$) and tri-*n*-propylamine (TPrA) as ECL luminophore and coreactant, respectively. The beads-based immunoassay is based on the heterogeneous co-reactant ECL mechanism where the Ru(II) complexes are not directly oxidized. Therefore, in order to produce the emitting $[Ru(bpy)_3]^{2+*}$, the $[Ru(bpy)_3]^{2+}$ labels are first reduced by $TPrA^{\bullet}$ and then excited by the electrogenerated $TPrA^{\bullet+}$ via homogeneous eT (Fig. 1a) [2].

To date, there is a lack of straightforward methods to enhance the ECL signal of commercial bead-based immunoassays without further modifications (i.e., by employing novel luminophores with higher quantum yield compared to $[Ru(bpy)_3]^{2+}$ or by introducing nanomaterials).

Herein, we investigate the reaction mechanism underlying the modulation of the ECL signal of $[Ru(bpy)_3]^{2+}$ labels anchored to magnetic beads (Fig. 1b). Specifically, we utilise ECL microscopy to analyse the emission of Ru(II) labels on single beads upon interaction with three different Ir(III) complexes with different photochemical and electrochemical properties (i.e., excitation and emission wavelengths, redox potentials, charge, etc.) [3].

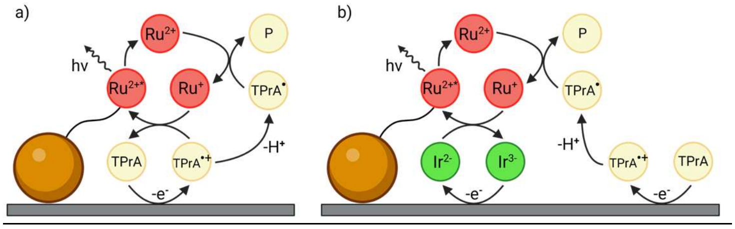

Figure 13. *Schematics of (a) the conventional heterogeneous ECL pathway and (b) the enhanced 'redox mediated' pathway in a heterogeneous beads-based immunoassay. The magnetic microbead is represented by the orange sphere while the* $[Ru(bpy)_3]^{2+}$ *luminophore and the* $[Ir(sppy)_3]^{3-}$ *complex are labeled as* Ru^{2+} *and* Ir^{3-}*, respectively.*

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p-09

Investigation of the electrochemical performances of nanocomposite TiO_2/polymer electrolyte with self-standing cathode synthesized with an innovative scalable approach

[a] Asia Patriarchi,[a] Hamideh Darjazi, [a] Francesco Nobili, [a] Miguel Ángel Muñoz Márquez [a]

[a] School of Science and Technology; Chemistry division, University of Camerino, Via Madonna delle Carceri- ChIP, Camerino(MC) 62032, Italy
E-mail: asia.patriarchi@unicam.it

Li-ion batteries (LIBs) are the most developed electrochemical energy storage technology, and they are widely utilized not only in portable electronics such as smartphones and computers, but also in electric vehicles and stationary storage systems [1]. LIBs have been very successful thanks to their remarkable properties such as good cyclability, high energy density, low self-discharge and long cycle life [2] However, there are safety concerns and practical drawbacks related with the use of liquid electrolytes, such as flammability of organic solvents, thermal stability, lithium dendrite growth, insufficient structural strength and risk of electrolyte leakage [3].

Thus, solid electrolyte seems a great choice to meet the requirements of safety and energy density. In particular, polymer-based electrolytes have attracted considerable attention owing remarkable properties such as low cost, non-flammability, good thermal stability, high flexibility and excellent mechanical properties. Unfortunately, solid polymer electrolytes present some disadvantages related to their low ionic conductivity at room temperature (10^{-8}–10^{-7} S cm^{-1}) and poor interfacial contact that currently limit their performance [4], [5].

To overcome these drawbacks, herein we present a three-component solid poly(ethylene oxide) (PEO)/lithium bis(trifluoromethanesulfanyl) imide (LiTFSI)/titanium dioxide (TiO_2) composite electrolyte that outperforms standard PEO-based solid electrolytes. The electrolyte properties are further enhanced by combining it with a self-standing $LiFePO_4$ catholyte made with a novel, simple and easily scalable approach.

The structural, morphological and compositional properties of this system EW fully characterized by means of infrared spectroscopy (FT-IR), thermalgravimetric analysis (TGA), differential scanning calorimetry (DSC), scanning electron microscope (SEM) and x-ray diffraction (XRD). Then, the electrochemical properties of the system are investigated by cyclic and linear voltammetry, galvanostatic cycling and electrochemical impedance spectroscopy.

The results show that adding controlled concentration of TiO_2 considerably improves the electrochemical performance of solid composite electrolyte, and the tests performed with LFP catholyte underlines a good cyclability of the system confirming the success of the new synthetic path used for the self-standing electrode.

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p-10

From Lab to Market: The Journey of Electrochemiluminescence based biosensors

Chiara Mariani [i], Claudio Ignazio Santo [i], G. Valenti [i], F. Paolucci [i]

[i] *Department of Chemistry “Giacomo Ciamician”, University of Bologna, Via Selmi 2, 40126, Bologna, Italy*
e-mail: chiara.mariani16@unibo.it

Accurate quantification of biomarkers is crucial for controlling the current pandemic situation and preventing future outbreaks. With its high sensitivity, electrochemiluminescence (ECL) has emerged as a leading technique in the field of immunoassay-based biomarker detection and biosensor development. The electrochemically induced signal generation enables the development of sensors characterized by minimal background interference, precise temporal and spatial resolution, adaptability, and cost-effectiveness [1]. Based on that, over the past two decades, the ECL research evolved from being an academic curiosity to achieving industrial success. One of the most successful ECL-based diagnostic platforms is the Elecsys® analyser from Roche Diagnostics, which utilizes ECL technology for the detection of a broad range of analytes. Elecsys® is based on Ru (II) coordination complexes (tris(2,2′-bipyridine) ruthenium (II) $[Ru(bpy)_3]^{2+}$) and the so-called “oxidative-reduction” sacrificial coreactant (tri-n-propylamine TPrA) [2][3]. The detection of biomarkers occurs through a labelled sandwich immunoassay that is attached to a magnetic microbead. Once the biomarkers have undergone immunorecognition, the magnetic beads are drawn to the working electrode surface with the use of a magnet, and the ECL signal is detected after potential application. This system has been extensively used in clinical laboratories worldwide and has become an industry standard for diagnostic testing.

Nevertheless, it remains a lack of understanding regarding the key elements that influence the mechanism for the signal generation. Our recent efforts have exploited the synergy between ECL and microscopy to attain a deeper comprehension and optimization of the overall ECL mechanism [4]. To achieve this optimization, several factors need to be considered. Here, we are implemented the instrumentation deigned to enhance spatial resolution and utilizing a fast and precise fluidic system that combines workflow automation with trigger signals to achieve advanced synchronization. By continuously refining these elements, we are paving the way for the application of the whole system with the Elecsys® instrumentation in collective-bead experimental condition, ultimately improving its sensitivities and diagnostic capability.

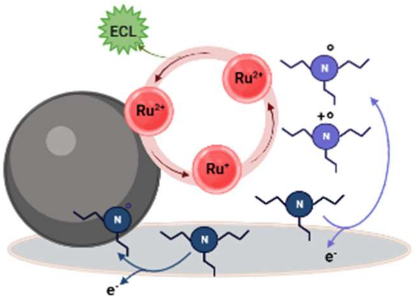

Figure 14 Schematic representation of the “oxidative-reduction” heterogeneous ECL mechanisms for the couple $Ru(bpy)_3^{2+}$/TPrA.

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p-11

An Exudate Gum as Suitable Aqueous Binder for High Voltage Cathode Material

Daniele Versaci[i], Davide Dessantis[j], Julia Amici[i], Marco Minella[z], Carlotta Francia[i], Silvia Bodoardo[i]

[i] Electrochemistry Group, Department of Applied Science and Technology (DISAT), Politecnico di Torino, Corso Duca degli Abruzzi, 24, 10129 Torino, Italy
[j] STEPS, Department of Energy, Politecnico di Torino, c.so Duca degli Abruzzi 24, 10129 Torino, Italy
[z] Department of Chemistry and NIS Inter-Departmental Centre, University of Torino, via P. Giuria 5, Torino, 10125, Italy

e-mail presenting author: daniele.versaci@polito.it

The improvement of future generations of lithium-ion batteries should not solely focus on performance, but also consider aspects such as cost and environmental sustainability of the manufacturing processes [1]. While the study and development of new active materials have enhanced key battery parameters like energy and power density, a significant challenge lies in enhancing the electrochemical performance of batteries by utilizing "non-active" materials (binder, current collector, separators) that are cost-effective, environmentally friendly, and easily recyclable. Specifically, in the case of the binder, the primary objective is to replace current fluorinated compounds with water-soluble materials [2]. Starting from these considerations, in this study we evaluate, for the first time, tragacanth gum (TG) as suitable aqueous binder for the manufacturing process of cobalt-free, high-voltage Lithium Nickel Manganese Oxide (LNMO) cathode.

TG-based LNMO cathodes, incorporating a low binder content of 3 wt%, exhibit favorable thermal and mechanical properties. Notably, they demonstrate exceptional cycling stability with 60% capacity retention after more than 500 cycles at 1C, impressive-rate capability of 72 mAh g-1 at 15°C, and a coulombic efficiency close to 99%. Moreover, the TG-based electrode exhibits good mechanical properties and minimal degradation, even after more than 1000 cycles at a high cut-off voltage of 4.9 V and elevated cycling temperature (50 °C).

Additionally, TG exhibits important recovery and recycling properties, making it an environmentally friendly and multifunctional binder for next-generation lithium-ion batteries. These combined benefits of electrochemical performance, mechanical stability, and sustainability position tragacanth gum as a promising binder option for the future development of lithium-ion batteries.

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p-12

Electrochemical Generation of Radicals to Trigger a Controlled Polymerization Process

Giovanni Lissandrini, Francesca Lorandi, Abdirisak A. Isse, Marco Fantin

Department of Chemical Sciences, University of Padova
Via Marzolo 1, 35131, Padova, Italy
marco.fantin@unipd.it

Enabling precise chemical transformations requires the smooth generation of radicals on an electrode surface. This is especially important for electrochemically-mediated radical polymerizations, where a continuous and controlled production of radicals at the electrode surface is necessary to sustain the polymerization process in the bulk of the solution.

In recent decades, the field of radical polymerization has undergone a significant transformation with the advent of the reversible-addition fragmentation radical polymerization (RAFT) method. This technique allows for the creation of polymers with controlled properties such as molecular weight, structure, and functionalities. Consequently, RAFT polymers have found wide-ranging applications in areas such as dispersants, elastomers, rheology modifiers for mining applications, drug delivery systems, and more. However, there is currently no established procedure for initiating a well-controlled RAFT polymerization using electrochemical methods [1]. The development of such a protocol could unlock numerous additional applications for these polymers in fields such as electrochemical sensors, batteries, and supercapacitors.

In this contribution, we present a method for achieving a controlled and adjustable generation of radicals on an electrode surface to initiate a RAFT polymerization (see Figure 1). The process involves three steps: first, a redox mediator (Med) is reduced at the working electrode; second, the mediator transfers its excess electron to a thiocarbonyl compound, causing C-S bond cleavage and the release of a radical ($P_n^\bullet$); third, the radical propagates and engages in reversible exchange with the thiocarbonyl compound, resulting in a well-controlled polymerization.

The selection of the mediator, applied potential, and thiocarbonyl compound will be discussed, revealing the principles behind achieving a precisely controlled electrochemically-mediated RAFT polymerization.

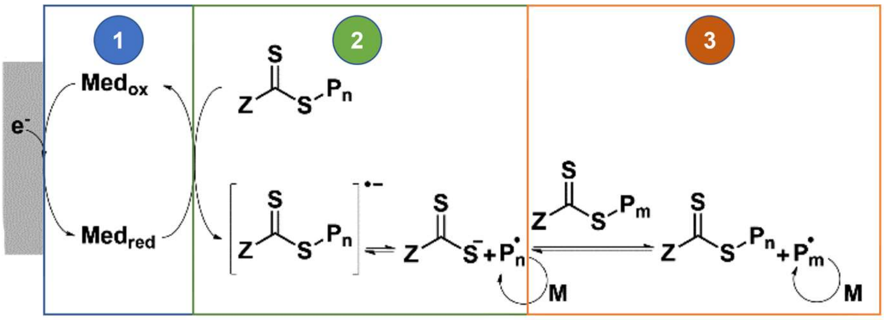

Figure 15. Electrochemically mediated RAFT polymerization

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p-13

Manufacturing of Lithium-ion battery electrodes by using carbon nanomaterials (CNM) as conductive additive produced via CO_2 reduction process

N. Albanelli, S. Mojtahedi, A. Gregucci, C. Arbizzani, F. Soavi

Dept. of Chemistry, Giacomo Ciamician, via Selmi 2, 40126, Bologna, Italy

e-mail presenting author: nicolo.albanelli2@unibo.it

The extraction of valuable carbon-based products from CO_2 reduction represents a promising route to reduce greenhouse gas emissions, promote circular economy practices, and facilitate the integration of energy storage sources such as Li-ion batteries and supercapacitors [1]. Using such extremely valuable sustainable products obtained from the CO_2 capture process can solve not only the global warming problems but also the high demand of the battery industry to provide graphite and highly conductive additives, like carbon nanotubes, carbon nanofibers, and carbon nanospheres [2][3]. In this current work, a multi-wall carbon nanotube (MWCNT) extracted from CO_2 reduction treatment was introduced as the conductive additive into the graphite and lithium iron phosphate anode and cathode of a lithium-ion battery cell.

MWCNTs (UP Catalyst®) were produced by a proprietary electrochemical process. The electrodes were produced by casting, using both the conventional poly(vinylidene fluoride) binder, dissolved in N-methyl-2-pyrrolidone, and sodium alginate as a greener, water soluble alternative binder. The electrochemical performance of the MWCNT-based electrodes, were compared to that of lithium-ion battery cathodes and anodes produced with a commercial carbon additive (SuperC65 or SuperC45, Imerys). The electrodes featuring MWCNT offer comparable electrochemical performance to conventional ones in which commercial conductive additives were utilized.

Aknowledgements

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p-14

Electrochemical CO_2 reduction inspired by the theory of emergence of life

Francesco Panico,[a] Alessandro Minguzzi,[a,b] Michael J. Russell,[c] Alberto Vertova,[a,b]

[a] *Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, 20133, Milano, Italy*
[b] *Consorzio Interuniversitario di Scienze e Tecnologia dei Materiali, Via San Giusti 9, 50121, Firenze, Italy*
[c] *Dipartimento di Chimica, Università degli Studi di Torino, 10125 Torino, Italy*
e-mail presenting author: francesco.panico@unimi.it

The dilemma about how does life emerged from inanimate matter keeps scientists awake for centuries, including L. Pasteur, J.B.S. Haldane, A. Oparin, S. Arrhenius, E.Schrödinger [1]. Since the 70s, after the discovery of Oceanic Hydrothermal Vent fields, the Alkaline Hydrothermal Vent (AHTV) theory for the emergence of life gained attention, since the AHTV seems to be plausible cradles where the first organisms may have arisen [2]. Today new insight about the behaviour of these geological system comes from electrochemistry [3]; electrochemical phenomena act in a well-ordered manner, dealing with interfaces, difference in electrical and redox potentials, diffusion and vectoral movement, with evident parallelisms to the metabolism of living cells.

In the Archean era, Alkaline Hydrothermal Vents were generated by the reaction between alkali, metal and hydrogen, rich the fluid coming from the geological process of serpentinization of oceanic crust with a slightly acidic and CO_2 rich ocean; here a mineral barrier precipitate dividing the inside from the outside, this membrane was made mainly from iron oxide and hydroxide, green rust, iron sulphide together with Ni, Zn ,Co, Mn ions [4][5]. The surface of this material and the structure of the vent itself can act as efficient promoter for coupling CO2 reduction reaction (to simple organic molecules) with hydrogen oxidation [6].

On the other hand, material scientists and chemists worldwide are frantically searching for an effective material capable of performing CO_2RR at affordable prices; could mineral that performed carbon dioxide reduction 4.4 billion years ago used in today's industry to face environmental challenges of the new millennium? Here is the idea of "emergence of life inspired material" for CO_2 conversion.

The purpose of our research is to study the behaviour of AHTV using the instruments and "way of thinking" of an electrochemist: the geological system is modelized as a fuel cell where continuous supply of carbon dioxide and hydrogen is given, the electrode material is made of the vent's mineral, anode and cathode are short-circuited in a configuration that recall a corrosion process. The system, capable of coupling CO_2RR and HOR, is powered ultimately by the pH difference between the two compartments (the simulated inner vent fluids and the oceanic waters). We performed many experiments with this setup, concluding that formic acid can be produced and proving that the geological system behaves according to Evans diagram expectation.

This research configures as an emblematic example of technological transfer, that is to say that the demand about the fundamental questions of science fuels technological development [7].

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Lignin-Derived Vacuum Pyrolysis Hard Carbon for Sodium Ion Batteries

Claudia Paoletti, Annalisa Aurora, Pietro Colucci, Livia Della Seta, Elisabetta Borsella,
Margherita Moreno, Pierpaolo Prosini, Davide Tedeschi, Mauro Falconieri

ENEA, Italian National Agency for New Technologies, Energy and Sustainable Economic Development, Casaccia Research Centre, Via Anguillarese 301, 00123 Santa Maria di Galeria, Rome, Italy
claudia.paoletti@enea.it

Relying on more abundant materials, Sodium Ion Batteries (SIBs) provide a promising alternative to Lithium Ion Batteries (LIBs) for energy storage applications where the energy density is not crucial.

Despite the substantial similarities between SIBs and LIBs, many challenges remain to be addressed, brought in by their chemistry differences. One of them is related to the anode materials, which is Hard Carbon (HC) in SIBs, instead of graphite as in LIBs as necessary since Na^+ ions do not intercalate into graphite due to their size and solvation shell [1]. HC is a disordered carbonaceous material that is non-graphitizable and is normally obtained from the pyrolysis of organic precursors at temperatures above 1000°C under inert atmospheres. HC offers advantages such as low working electrochemical potential, a high specific capacity, and thus a high specific energy density [2]. The electrochemical properties of HC rely heavily on the processing conditions and carbon source used. If the pyrolysis process is not properly optimized, it may result in low yield and/or a high surface area of the HC, leading to a significant capacity loss during the first cycle and reduced coulombic efficiency. This is partly attributed to the instability and high solubility of the passivation layer that forms at the HC electrode/electrolyte interface (SEI) in an SIB, which also accelerates electrolyte decomposition, reducing cycle life.

In this study, a set of HCs have been produced from lignin [3], as carbon source, using a vacuum pyrolysis process at high temperature. The produced materials wer characterized with the aim of optimizing the synthesis conditions to obtain high quality anode material for SIBs. If compared with pyrolysis processes in the atmospheric environment , the oxygen-free environment and high temperatures conditions in a vacuum chamber increase the compactness of the produced HC, allowing to obtain a higher energy density anodic material. Moreover, by testing different vacuum pyrolysis conditions, it has been possible to tune the material structural properties in terms of interplanar distance, graphitization degree, porosity and surface area. [4] The HC were characterized by X-ray diffraction and Raman spectroscopy, physisorption and thermal analysis, and by SEM for the morphological characterization; finally they were tested as anode material for SIBs by galvanostatic cycling. The experimental results for samples obtained at short pyrolisis time present the best electrochemical performances due to the better graphene-graphene interlayer distance. On the contrary, by increasing the pyrolysis time, an increase in the graphitization degree is evident examining the Raman spectra. The interplanar distance is a parameter which depends on both the pyrolysis conditions and the purity and characteristics of the precursor used; therefore, the use of highly purified and selected precursors as lignin can help to obtain a shorter interplanar distance.

This work aims at contributing to the development of sustainable and cost-effective anode materials for SIB promoting the utilization of lignin as a valuable renewable resource.

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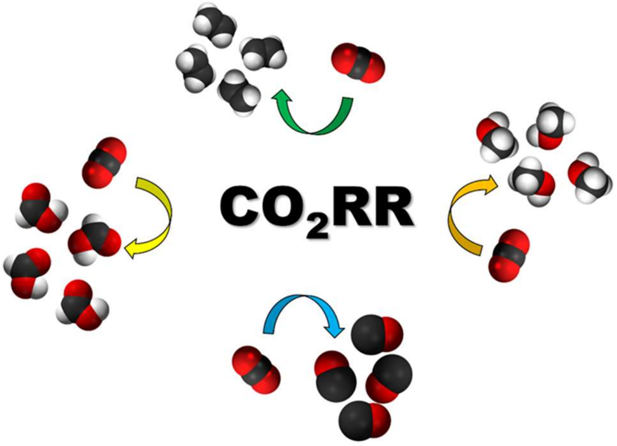
Copper Nanocrystals Synthesis and Their Application as Electrocatalysts for CO2 Conversion

Andrea Conte, Diego Vaccarin, Marco Baron, Alessandro Aliprandi, Sabrina Antonello, Sara Bonacchi

Department of Chemistry, University of Padova, Via Francesco Marzolo 1, 35131, Padova, Italy
andrea.conte.5@phd.unipd.it

The increment in global temperature is leading to dramatic changes in Earth's ecosystems.[1] As reported by IPCC (Intergovernmental Panel on Climate Change) assessments, climate change is mostly due to the uncontrolled emission of greenhouse gasses during the last two centuries.[2] CO2 plays a significant role in this context as the main greenhouse gas. In this framework, the conversion of CO2 to renewable feedstocks is one of the main goals to achieve for building a net zero human society. Copper is the only metal able to convert CO2 directly to multi-carbon products[3] thanks to its ability to bind the intermediates strongly enough to carry out carbon-carbon coupling.[4] However, achieving selectivity toward a well-determined product is still an unsettled issue. Recently, it was reported that specific copper crystal facets enhance dramatically the selectivity toward C2 hydrocarbons.[5,6] We synthesized copper nanocrystals using green reagents and a water medium via hydrothermal methods. These nanostructures were characterized by SEM (scanning electron microscopy), XRD (X-ray diffraction), and electrochemistry. In addition, these nanocrystals were tested as electrocatalysts. The results showed that this material is a promising catalyst to produce C1 and C2 hydrocarbons with high faradic efficiency.



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Integrated wire-shaped supercapacitor for texile energy storage

Mara Serrapede[a,b], Francesco Seller[a,b], Pietro Zaccagnini[a,b], Andrea Lamberti[a,b]

a Istituto Italiano di Tecnologia, Center for Sustainable Future Technologies, Via Livorno 60, 10144, Turin, Italy
b Politecnico di Torino, Dipartimento di Scienza Applicata e Tecnologia (DISAT), Corso Duca Degli Abruzzi, 24, 10129, Turin, Italy

mara.serrapede@polito.it

Flexible and lightweight energy storage devices have become increasingly important for the development of wearable and portable electronics. In this work, we present a novel wire-shape supercapacitor based on carbon nanotube (CNT) yarns and an ionic liquid based electrolyte. The combination of these materials offers high surface area, high conductivity and excellent flexibility, making them a promising candidate for flexible energy storage. The CNT yarns were characterized in a three-electrode configuration by means of electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) either in water-based electrolytes and ionic liquids. The separator was prepared by non-solvent induced phase separation and then the device was soaked in ionic liquid.
The devices exhibited high specific capacitance for a waterless system, additionally, they maintained their performance even under extreme deformation: the flexibility of the devices were tested by bending at different angles.
Overall, this work highlights the advantages of using CNT yarns and ionic liquid electrolytes for the development of flexible and high-performance supercapacitors. The wire-shape design of the device offers additional advantages for integration into wearable or flexible electronics, providing a promising path towards the development of highly efficient and adaptable energy storage systems. [1-3]

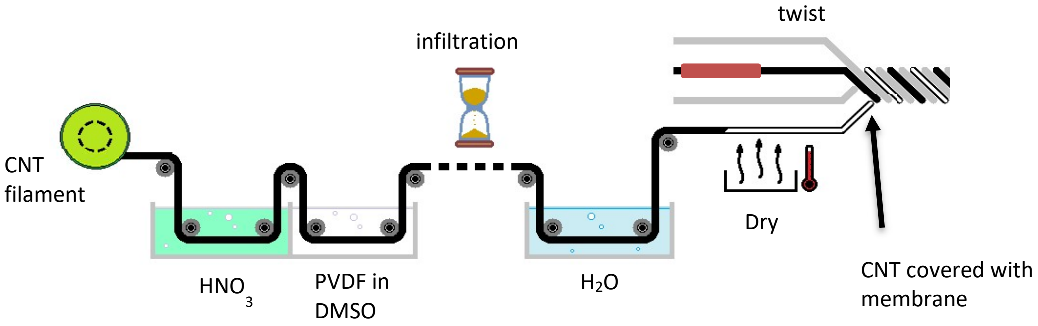

Figure sketch of wire-shaped supercapacitor fabrication.

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p-18

Deep eutectic solvents for high efficient and sustainable metals recovery from spent lithium ion batteries

R. Morina,[i] N. Pianta,[i] P. Mustarelli,[i] C. Ferrara[i]

[i] *Department of Materials Science, University of Milano Bicocca, via Cozzi 55, 20125 Milano, Italia*

e-mail presenting author: r.morina@campus.unimib.it

One of the most important challenges for European Union (EU) is to reduce the CO_2 emissions by 55% within 2030 and to zero within 2050. For this reason, the electrification of road transport is fundamental, and the European Commission identified the lithium-ion battery (LIB) value chain as strategic element to achieve EU goals in terms of climate neutrality and competitiveness of the EU industry [1]. LIBs embodied various critical raw materials (CRMs) such as Li, Mn, Co, Ni, graphite, that are not geologically available as massive and primary resources in Europe. The methods for the recovery of Co, Li, Ni metals at industrial scale from LIBs waste are thermal/chemical methods like pyro- and hydrometallurgy. However, these processes are highly energy-consuming, require harsh conditions and produce toxic materials. In addition, they do not lead to easily recoverable elements [2].

In our work we propose a new green, cheap and safe approach for the degradation of LIBs waste and subsequent recovery of CRMs by using a new type of organic solvents as lixiviant, the Deep Eutectic Solvents (DES). DESs are obtained by simply mixing two or more safe components (cheap, renewable, and biodegradable, solid at room temperature), which are capable of forming a hydrogen bond and hindering the crystallization thus forming a liquid system at room temperature. Tho most common hydrogen bond acceptor (HBA) is choline chloride (ChCl) while several hydrogen bond donors (HBD) have been proposed ranging from organic acid, alcohol, to ammine [3]. Here we report a systematic investigation of several DESs compositions; the DESs have been characterized with TGA-IR and DSC to evaluate their stability, IR, and NMR to investigate their structure. The leaching experiments have been performed exploring the effect of time, temperature, and rate between DES and the active material. We study the degradation of the most common cathodic materials such as NMC ($LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$), LCO ($LiCoO_2$), LMO ($LiMnO_2$) and LFP ($LiFePO_4$). ICP measurements were performed to investigate the leaching efficiency of the DES.

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Gravure printing for printed batteries manufacturing: the influence of the printing quality on the LFP based cathode functionality

Maria Montanino[1], Claudia Paoletti[2], Anna De Girolamo Del Mauro[1] and Giuliano Sico[1]

[1]ENEA Italian National Agency for New Technologies, Energy and Sustainable Economic Development,
Portici Research Centre, 80055 Portici, Italy;
[2]ENEA Italian National Agency for New Technologies, Energy and Sustainable Economic Development,
Casaccia Research Centre, 00123 Roma, Italy;
e-mail presenting author: maria.montanino@enea.it

Thanks to their high customizability, printed batteries are more and more involved in our daily life to feed portable electronics, biomedical devices and IoT [1]. Among the printing techniques, gravure is the most appealing for the low cost manufacturing of functional layers since its unique capability to provide both high resolution and high production speed, but is few investigated because of the necessity of diluted ink. The required low viscosity inks make difficult to obtain the desired functionality and an adequate mass loading resulting challenging, especially in the production of composite layers such as electrodes for lithium-ion batteries. Aimed by the growing interest for printed batteries, recently we investigated the gravure printing for lithium-ion batteries electrodes manufacturing, obtaining very good results in term of capacity, reproducibility and long life cyclability [2,3]. Our research highlighted the necessity to rule the ink formulation for boosting the possible use of such printing technique for the low cost industrial production of printed batteries. For such propose, as driver for the ink formulation, we decided to use a methodology mainly based on the Capillary number approaching the unity, which is able to provide a good printing quality. For such research we used Lithium Iron Phosphate as study case for the cathodic layer manufacturing. Such research allowed to investigate if a good printing quality is sufficient to guarantee the desired layer functionality and how printing quality could eventually influence the layer performances.

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p-20

Study of LiTi$_2$(PO$_4$)$_3$/Electrolyte interface in a mixed cation water-in-salt electrolyte (WISE) for Na-ion battery applications

S. Khalid ,[i] R. Ruffo. [i]

[i] *Dept., Materials Science, Via Roberto Cozzi 55, 20126 Milan, Italy*
e-mail presenting author: s.khalid3@campus.unimib.it

Aqueous electrolytes, particularly highly concentrated solutions, present a compelling alternative to organic counterparts as battery electrolytes. Their notable advantages include low flammability, reduced toxicity, cost-effectiveness, and abundant availability, while maintaining wide potential windows[1]. In this study, we explore the characteristics of a half-cell containing lithium titanium phosphate (LTP) in a highly concentrated aqueous mixed cation (27 molal Na$^+$/K$^+$-CH$_3$OOH) electrolyte, with the aim of establishing it as a highly promising anode material for sodium-ion batteries. Our comprehensive characterization involves constant current measurments and static electrochemical impedance spectroscopy, which yield valuable insights into the thermodynamic and kinetic properties of the system. Through these careful experiments, we extract crucial information pertaining to the system's thermodynamics, such as the activation energy of processes, diffusion coefficient, as well as the kinetics, including the evolution of process parameters. The highly concentrated electrolyte demonstrated a room temperature conductivity of 21.2 mS cm^{-1}, enabling currents up to 5 C. Cycling the LTP electrode in the WISE electrolyte at 1 C (Fig 1a) yields an average anodic specific capacity of 68 mAh g^{-1}, with a remarkable average charge efficiency of 99.0%. The low activation energy of 0.12 eV or 11.58 KJ mol^{-1} (Fig 1b), in line with that of other electrode/aqueous electrolyte systems[2,3] proves the very good kinetic properties of the interface between the NASICON electrode and the electrolyte. The impedance to charge transfer between the liquid electrolyte and electrode is predominantly influenced by two key factors: the de-solvation process and the diffusion within the Solid Electrolyte Interphase (SEI). In the case of water-in-salt electrolytes, these contributions are expected to be minimized owing to the limited availability of water molecules capable of forming a hydration shell and the absence of a well-defined SEI. The value of the diffusion coefficient “D” at room temperature (around 10−13 cm^2 s^{-1}) is in line with other reports in the literature[4]. The low activation energy of 0.48 eV (Fig 1c) suggests that the diffusion can be easily improved by increasing the temperature. These findings significantly contribute to advancing our understanding of the performance and potential applications of NASICON based electrode materials in highly concentrated WISE electrolytes.

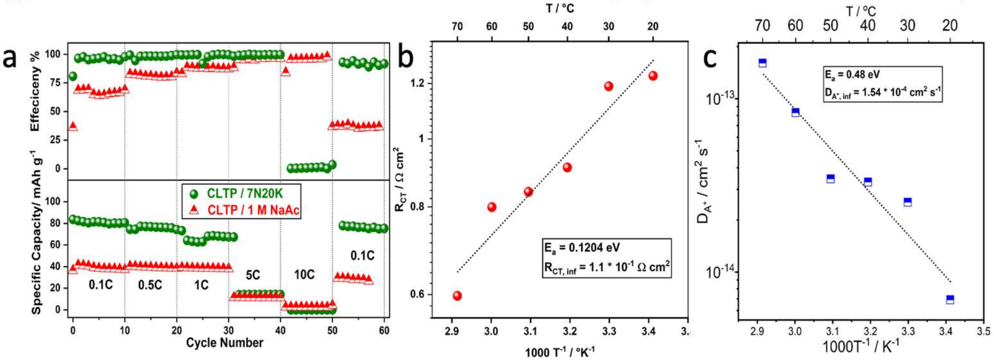

Figure 16:(a) Rate test of LTP half cells high concentrated (green) and diluted sodium acetate (red), (b) Arrhenius plot of charge transfer resistance in concentrated electrolyte. (C) Arrhenius plot of the diffusion coefficient of LTP in highly concentrated mixed cation WISE .

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Electrochemical Shaping of Polymer Chain-Ends: Application to Polymers Prepared by Atom Transfer Radical Polymerization

Marco Fantin,[a] Alessandro Zampieri,[a] Felix Schnaubelt,[a] Khidong Kim,[b] Krzysztof Matyjaszewski,[b] Christian Durante,[a] Abdirisak A. Isse[a]

[a]*Department of Chemical Sciences, University of Padova, Via Marzolo 1, 35131, Padova, Italy*
[b]*Center for Macromolecular Engineering, Carnegie Mellon University, Pittsburgh, PA, USA*
abdirisak.ahmedisse@unipd.it

The chain end of polymers produced by reversible deactivation radical polymerizations (RDRPs) is the most versatile and reactive group of the macromolecules. Although the chain end fidelity is crucial during polymerization as it allows good control over molecular weight and dispersity, and the possibility of chain extension in block copolymerizations, the presence of the chain end in the final polymeric material is undesirable in many applications, because untreated end groups can cause problems such as undesired color or decomposition to malodorous or toxic compounds. Therefore, for many applications, the chain end should be either modified or removed.

Electrochemistry can provide a general tool to modify the chain end in a diverse array of controlled radical polymerization processes, such as atom transfer radical polymerization (ATRP) and reversible-addition-fragmentation radical polymerization (RAFT), among others (Figure 1). Often the chain end contains an electroactive moiety such as a carbon-halogen or a carbon-sulfur bond which readily undergoes reductive cleavage. Therefore, direct or mediated electrolysis with an appropriate catalyst can be used to selectively modify the polymer chain ends (R-X, where X is the chain-end group or atom). Possible electrochemical modifications of the chain end include (i) reductive hydrogenation, (ii) reductive coupling of polymer chains with doubling of molecular weight, and (iii) incorporation of an electrochemical probe or a chromophore.

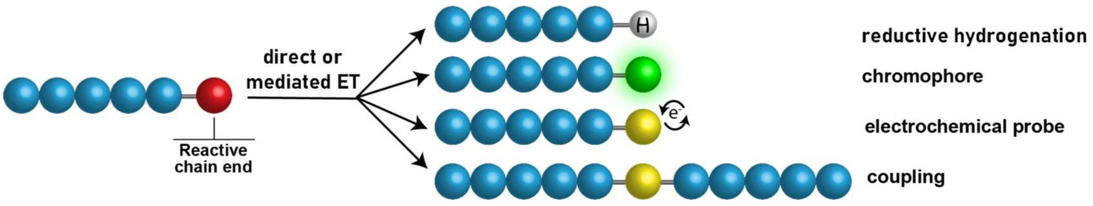

Figure 1. Electrochemical transformation of polymer chain ends.

This contribution will discuss the results of the application of this technology platform to the removal of chain end groups from polystyrene and polyacrlates prepared by ATRP. The role of reaction medium, electrode material (or catalyst), applied potential (or current), and starting polymer molecular weight on product distribution will be discussed.

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Low temperature hydrothermal synthesis of quaternary ferrites as anode for Li-ion batteries

Davide Vendrame[a], Keti Vezzù[b,c], Vito di Noto[b,c], Silvia Gross[a,c]

[a] Dipartimento di Scienze Chimiche (DiSC), University of Padova, Via Marzolo 1, Padova, 35131, Italy
[b] Section of Chemistry for the Technology (ChemTech), Department of Industrial Engineering, University of Padova, Via Marzolo 9, 35131 Padova, Italy
[c] National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence, Italy
[c] Karlsruher Institut für Technologie (KIT), Institut für Technische Chemie und Polymerchemie (ITCP), Engesserstrasse 20, Karlsruhe, 76131, Germany

e-mail presenting author: davide.vendrame@phd.unipd.it

Lithium-ion batteries (LIBs) with outstanding energy and power density have been extensively investigated in recent years. The currently commercialized graphite anode is limited by its relatively low theoretical capacity (372 mAh g^{-1}) and the sluggish lithium-ion diffusivity.[1]

As superior alternatives to the graphite anode, transition-metal oxides display higher theoretical capacities; unfortunately, they suffer from drastic structural degeneration associated with volume expansion and low inherent electronic/ionic conductivity, resulting in inferior cycling stability and poor rate performance.[1,2] Therefore, the development of new electrode materials with high lithium-ion storage capacity, superior structure stability, and excellent conductivity for LIBs is urgently needed.

Iron-based spinel oxides like with general formula AFe_2O_4 (A= Ni, Co, Zn, Mn) have been explored for their Li-cyclability.[3,4] Among various ferrites, $NiFe_2O_4$ can electrochemically react with 8 mol of Li providing a theoretical capacity of 915 mAh g^{-1}; in addition, both nickel and iron are abundant elements on earth and relatively nontoxic.[5]

The present Ph.D. project focuses on synthesizing quaternary metal-based ferrite materials ($NiFe_{2-x}Cr_xO_4$, $NiFe_{2-x}Mn_xO_4$ where x = 0.25, 0.50, 1.0), since the partial substitution of Fe with another metal cation leads to improved ion transportation and electric conductivity,[4] and investigating their electrochemical properties as anode active materials for LIBs. These materials were synthesized using a subcritical hydrothermal approach,[6] resulting in nanoparticles (10-30 nm) with excellent crystallinity and purity, determined by TEM, XRD and ICP analysis, showing the successful incorporation of the dopant cations within the lattice structure of $NiFe_2O$. The materials were tested as anode active materials for LIBs exhibiting high specific capacities (> 230 mAh·g^{-1}) and good stabilities within 50 cycles of charge/discharge. Further studies will be carried out to evaluate the structural rearrangement of the anode active material over 50 cycles, expanding the knowledge of the stability of the synthetized samples.

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Low-temperature co-pyrolysis process to recover valuable metals from spent cathode materials

E. Carena,[i] R. Morina,[i] M. Vergani,[i] C. Ferrara [i,j]

[i] *Department of Materials Science, University of Milano-Bicocca, via R. Cozzi 55, 20125-Milano, Italy*
[j] *National Reference Center for Electrochemical Energy Storage (GISEL), Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), via Giusti 9, 50121-Firenze, Italy*

e-mail presenting author: e.carena1@campus.unimib.it

Global warming and increasingly urgent climate tragedies clearly demand a change of course from contemporary society, in the direction of avoiding the use of fossil fuels in favour of renewable energy instead. For this to happen efficiently, the use of systems capable of storing energy, such as lithium-ion batteries (LIBs), must be considered. Such devices are widely exploited both in electric mobility and in portable devices. While LIBs may represent a solution to the environmental problem, they at the same time constitute a ticking-time bomb: the growing number of LIBs that are accumulating poses a staggering danger, if one considers the presence of flammable liquid electrolytes and heavy metals that risk accumulating in soils. In addition, the continually increasing demand that forces growth in production steadily depletes the Planet of certain raw materials critical for cathodes, that are being extracted laboriously and without the slightest safety for the workers involved, who come from areas of high political and social disruption [1,2].

One possible solution to these problems is to recycle these end-of-life devices, to limit the disposal of waste batteries into landfills (with inevitable hazardous environmental consequences) and to reduce the demand for new mining, re-assigning value to raw materials. There are several viable recycling options, such as hydrometallurgical, exploiting the leaching process with the use of inorganic acids However, this brings problematic issues: the production of such acids is itself a polluting process, and wastewater management is a demanding problem. Another industrially pursued route is pyrometallurgy, which involves thermal treatments at very high temperatures to recover valuable metals. The alternative explored in this project is based on the idea of lowering pyrolysis temperatures, exploiting the reducing activity of waste bio-organic materials that drive the carbothermic reduction; the biomass waste are previously characterized through thermogravimetric analysis and X-ray fluorescence spectroscopy. [3] Exploiting lower temperatures is suitable to provide an economic and environmental advantage, and at the same time ensures that the lithium contained in the cathodes can also be recovered, easily separated from cobalt and put back into the market as carbonate. The products obtained in nitrogen atmosphere processes are extensively characterized by SEM and XRD analysis, a leading technique in identifying the phases present to adjust the main parameters: temperature (range explored: 200-800 °C), isotherm time (30 minutes - 2 hours), and mass ratio between the cathode ($LiCoO_2$) and reducing materials. This method makes it possible to minimize energy consumption while utilizing waste LIBs, avoiding their dangerous accumulation, and at the same time to take advantage of green reducing agents, which would otherwise have to be disposed of, in an ethical and fully sustainable approach.

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p-24

Composite Janus membranes as multifunctional separators for safer Li metal batteries

D. Callegari,[1,2] S. Davino, M.M.-Llamas [1,4], L. Malavasi [1,3], M. Parmigiani [1], E. Quartarone [1,2]

[1] Department of Chemistry, University of Pavia, Via Taramelli 16, 27100 Pavia, Italy
[2] GISEL - Centro di Riferimento Nazionale per i Sistemi di Accumulo Elettrochimico di Energia, INSTM, via G. Giusti 9, Firenze 50121, Italy
[3] INSTM, National Inter-University Consortium for Materials Science and Technology, Via G. Giusti 9, 50121 Florence, Italy
[4] Unidad Académica Preparatoria, Plantel II, Universidad Autónoma de Zacatecas, Zacatecas, Zac 98068, México

e-mail presenting author: daniele.callegari01@universitadipavia.it

Battery failure due to internal shorting is extremely difficult to detect and mitigate. This issue can be induced by external causes such as mechanical deformation, overcharging and also unstable Li electrodeposition leading to dendrite growth witch penetrate the separator [1]. A widely explored route to overcome such drawbacks is the use of a ceramic filler (alumina o zirconia) to engineering a robust composite separator. However, the resulting film often only delays the dendrite penetration, resulting in an even more violent and dangerous failure subsequent to the shorting event [2].

Here, a PVdF-HFP -based Janus separator (JS) in A-and-B configuration is proposed, where A is a layer composed of an ionically inorganic conductor (Al-LLZO, $Li_{6.24}La_3Zr_2Al_{0.24}O_{11.98}$), facing the anode, and B is a composite film including N-doped carbon quantum dots (N-CQDs), facing the cathode. The rationale behind such choice is the use of a robust inorganic system (Al-LLZO) as physical barrier against the dendrite penetration and the use of ultra-small structures such as the quantum dots capable to reduce the solvation of the Li-ions and to boost uniform Li deposition. Different loadings of the N-CQDs were explored in order to evaluate the influence of the partially conducting behavior of the layer on the shorting processes. To this aim, a comparison between N-CQDs and CNTs in the JSs was also discussed. The multifunctional separator was investigated in terms of wettability, electrolyte uptake, thermal (TGA, DSC), mechanical (DMA) and morphological properties in order to understand the role played by membrane asymmetry on the functional behaviour. The electrochemical performances were evaluated by means of potentiodynamic electrochemical impedance spectroscopy (PEIS) and galvanostatic cycling (GCPL) carried out on NMC811| *Separator* | Li(M) coin cells with a standard liquid electrolyte. Accelerated rate calorimetry (ARC) analysis was finally performed to demonstrate the robustness of the Janus separator also in terms of cell thermal stability**.**

A neat PVdF-HFP and a Single Layer (PVdF-HFP:Al-LLZO) separators were also characterised for sake of comparison. The performance of neat PVdF-HFP separator showed a stable cycling at a current density of 200 mA g^{-1} (1C) but a significant discharge capacity loss of about 30%. In contrast, the Single Layer separator exhibited an internal self-discharge after only 114 cycles due to short circuit events. In contrast, no sudden voltage drops or presence of undesired phenomena in the charge/discharge profile were recorded for the JS, that showed significantly enhanced performance and stability up to at least 130 cycles with a final discharge capacity of 146 mAh g^{-1} and capacity fading lower than 10%.

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p-25

Microwave-Assisted Growing of MoS_2 Nanoflowers on Functionalized Mesoporous Carbon for Enhanced Alkaline Hydrogen Evolution Reaction

M. Mazzucato,[a] E. Campedelli,[a] M. Parnigotto,[a] M. Nardi,[b] C. Durante[a]

[a] Dept. of Chemical Science, University of Padova, Via Marzolo 1, 35131, Padova, Italia
[b] IMEM-CNR, Via alla Cascata 56/C, 38123, Trento, Italia
e-mail presenting author: marco.mazzucato@unipd.it

In the pursuit of economically viable alkaline water electrolysis implementation, a fundamental requirement is the development of highly active and stable electrocatalysts made from crustal abundant metals. In recent years, transition metal dichalcogenides (TMDs) have gained intensive attention due to their fascinating structure, catalytic properties, chemical stability, and low cost. Since it is well known that molybdenum disulfide is a potential candidate to replace Platinum-based catalysts toward alkaline HER [1], our research is focused on 2D-MoS_2 grown on functionalized mesoporous carbon (FMC).

MoS_2 is a layered material where active sites for hydrogen evolution reaction are located at the layer edges and the exfoliation and the fracture into nanometric "particles" to enhance edges exposition are not easy to achieve with a top-down approach starting from commercially available crystals. Therefore, here we considered a bottom-up approach starting from Mo and S precursor using a microwave-assisted synthesis while utilizing functionalized carbon support to facilitate the nucleation and growth of small MoS_2 clusters [2]. As a matter of fact, carbonaceous materials can effectively prevent the migration and aggregation of NPs, while the presence of heteroatoms can promote nucleation and/or synergistically enhance the activities of catalysts based on metallic compounds.

Molybdenum sulfide nanosheets have been synthesized on carbon supports functionalized with nitrogen and sulfur functional groups employing a green and fast method (Figure 1 left). We verify that, compared to commercially available nanosheets dispersed on carbon, MoS_2/FMC consists of a well-exfoliated and small sheet with a flower shape, that results in higher activity toward HER (η_{10} = 350 mV vs. 500 mV, see Figure 1 right). Both RDE and electrolysis were conducted on the material to evaluate the activity, selectivity, and durability of materials under operative conditions in both undivided and divided cells. The material was fully exanimated combining XRD, XPS, Raman, and TEM analysis to ensure the formation and dispersion of the nanometric sheet of MoS_2, which permit obtaining a higher edge exposure.

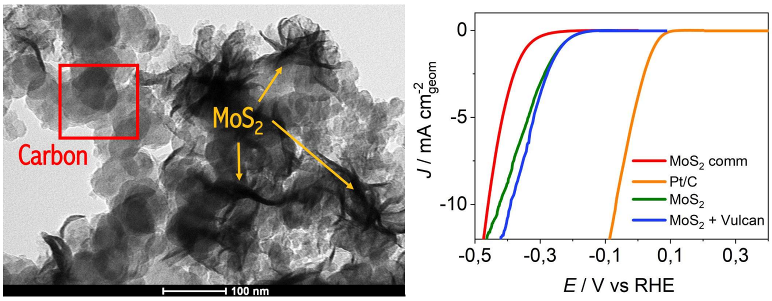

Figure 1: left) TEM image of MoS_2@C obtained in a microwave reactor and right) comparison between Pt, commercial MoS_2 and homemade MoS_2

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p-26

Effect of Innovative Carbon Additives in Positive Active Mass of AGM Lead Acid Battery on Dynamic Charge acceptance

M. Mazzucato,[a] M. Cattelan,[a] D. Zamboni,[a] N. Milani,[a] M. Parnigotto,[a] G. Daniel,[b]
D. Fabris,[b] S. Cazzanti,[b] C. Durante[a]

[a] Department. of Chemical Sciences, University of Padova, Via Marzolo 1, 35131, Padova, Italy
[b] FIAMM Energy Technology S.P.A., Viale Europa 75, 36075, Montecchio Maggiore (VI), Italy
e-mail presenting author: marco.mazzucato@unipd.it

Lead-Acid Battery (LAB) is a mature but still a competitive technology for the energy economy of the next future, also thanks to their high rate of recyclability. However, ongoing investments are needed to improve production and performance. LABs have gained success thanks to their stability, reliability, recyclability, and low cost of raw materials. A well-known problem is the limited charge efficiency and cyclability, due to an important degradation of electrodes during the discharging-charging process. Already in the 80s it was observed that in percentage spanning from 0.5 to 2.0 wt.%, carbon black, carbon fiber, cellulose, and other related materials added to the positive mass were sufficient to improve the performance, mechanical strength, and conductivity of LAB [1].

Here we selected a series of carbon-based materials, which were screened on the bases of physicochemical and electrochemical properties such as surface area, porosity, graphitization degree, conductivity, contact angle (wettability), and the overpotential versus the hydrogen evolution reaction [2] (**Figure 1a**). The best candidates were mixed and tested at different loadings in the positive active mass to prepare positive plates from scratch. A 1+/2– test cell was developed for the electrical, electrochemical, and chemical characterization of the novel electrodes in AGM configurations (**Figure 1c**). The prepared cells were tested under standard charge-discharge **(Figure 1b**) protocol and then tested with a homemade protocol for water loss using coupled electrochemical polarization and gas analysis [3] adapted for the AGM configuration in accumulation mode instead of flux mode. The incorporation of certain carbonaceous materials is evaluated as impact in the charge/discharge performance of the LAB cell under test, when compared to commercial plates. Studies of increasing the carbon concentration to determine the optimal percentage for maximum efficiency was also considered.

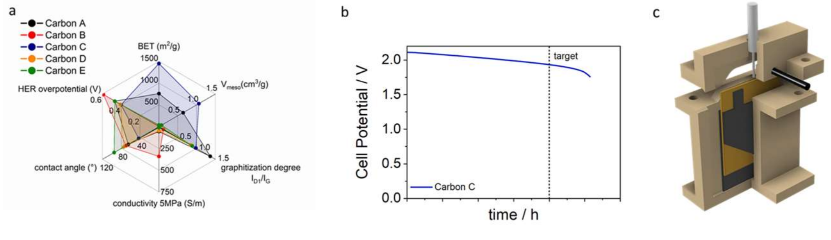

Figure 1: a) radar graphs illustrating an overview of the chemical and physical properties analyzed for commercial carbon materials and b) discharging current profiles. c) Possible prototype for AGM cell with a reference electrode on top.

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Porphyrin/sPEEK Composite Membranes for PEMFC Technology

A. Sorrenti[1] A. Carbone[2], M. Castriciano[1], A. Romeo[1], I. Gatto[2]

1 Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, University of Messina, V.le F. Stagno D'Alcontres 31 - 98166 Messina, Italy.
2Istituto di Tecnologie Avanzate per l'Energia "Nicola Giordano" (ITAE-CNR), Via S. Lucia sopra Contesse 5 - 98126 Messina, Italy,

e-mail presenting author: adriano.sorrenti@studenti.unime.it

The use of fossil fuels is one of the main causes of the global warming, so the use of renewable sources is one of the priority of European governments. In this context, hydrogen is considered the greenest vector for energy production. Polymer electrolyte membrane fuel cells (PEMFCs) technology have been identified as the most efficient and eco-friendly energy-conversion device for different applications. The key components of PEMFC is Nafion membrane, based on perfluorinated polymer. Recently, the European commission has added the fluorine in the Critical Raw Materials list, so an alternative should be realized. In this contest, the polyaromatic membranes based on sulphonated polyetheretherketone (sPEEK), due to its properties such as high thermal and chemical stability, excellent mechanical properties, good proton conductivity, can be considered as an alternative and good candidate to conventional membranes. In order to enhance a proton path for the conduction mechanism and improving the characteristics of the sPEEK material, opportunely selected porphyrins able to specifically interact with the polymeric matrix and/or to aggregate into ionic domains, were added [1, 2]. The presence of porphyrins in their monomeric, dimeric, and/or aggregated forms into the membrane ionic domains have been observed using porphyrins with different chemical structure. In particular, we succeeded in modulating the percentage of the different porphyrin species present into the proton-conducting channels acting on the dye load in the range 0.35−5 wt % porphyrin/polymer.

Physico-chemical characterizations in terms of UV-Vis and Fluorescence emission, ion exchange capacity, water retention, dimensional variations and swelling, proton conductivity were carried out to verify both the insertion and interaction between the polymeric matrix and porphyrin. Single cell electrochemical tests in a PEMFC configuration were carried out to verify the performance in different operative conditions. The electrochemical results highlight a correlation between the performance and the composition of the system polymer/porphyrin.

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Single Lithium-Ion Conducting Polymer Electrolytes based on Nafion for Lithium Sulfur batteries

I. Nicotera,[i] E. Lufrano,[i] C. Simari,[i] M. Tuccillo,[j] S. Brutti,[j] M. Nojabaee,[z] B. Sievert,[z]

[i] *Department of Chemistry and Chemical Technology, University of Calabria, Via P. Bucci, Rende (CS) 87036, Italy*
[j] *Department of Chemistry, University of Rome La Sapienza, P.le A.Moro 5, Rome 00185, Italy*
[z] *Institute of Engineering Thermodynamics, German Aerospace Center, Pfaffenwaldring 38-40, 70569 Stuttgart, Germany*

e-mail presenting author: isabella.nicotera@unical.it

Rechargeable batteries with the lithium–sulfur (Li–S) chemistry has attracted great interest as one of the most promising candidates for next generation electrochemical energy storage systems. One of the biggest obstacles for practical applications of Li-S batteries is caused by the soluble nature of the highly ordered lithium polysulfides (Li2Sn) in the organic electrolytes and induce a so-called “shuttle effect”. A solid-state electrolyte (SPEs) could be a valid alternative in terms of reducing the polysulfides dissolution and shuttle, as well as to protect the lithium metal anode and to minimize dendrite formation, which is beneficial for improving the safety and cycle life of Li−S batteries.

Polymer electrolytes based on ionomers (e.g., Nafion) with easily ionizable groups (e.g., sulfonic groups covalently bonded to the polymer side-chains, −CF2SO3−) are promising thanks to the high concentration of weakly coordinating anions (counterions). In this work, lithiated Nafion membranes were synthesized, and their ionic conductivity and lithium transference number were investigated in common nonaqueous organic solvents (EC/PC and Glymes).

Ionic conductivities and lithium transference number display significant values, with σ ≈ 5×10−4 S cm−1 at 25 °C and t_{Li^+} close to unity. The absence of solvent leaching on thermal cycles is also noteworthy. The description at molecular level of the lithium transport mechanism has been carefully tackled through a systematic study by 7Li-NMR spectroscopy (Pulsed Field Gradient-PFG and relaxation times), while the mechanical properties of the film electrolytes have been evaluated by dynamic mechanical analysis (DMA) in a wide temperature range.

The electrochemical studies have been conducted both in Li/Li symmetric cell and in secondary Li-S cells. The preliminary results are very interesting in terms of stability window and stability of the lithium stripping.

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Functionalized graphene oxide for energy harvesting from salinity gradient

A. Pedico,[a] D. Molino,[a] P. Zaccagnini,[a,b] S. Bocchini,[a,b] A. Lamberti.[a,b]

[a] *Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 - Turin, Italy*
[b] *Center for Sustainable Future Technologies, Italian Istitute of Technologies, Via Livorno 60, 10144 - Turin, Italy*
e-mail presenting author: alessandro.pedico@polito.it

Graphene oxide functionalized with a novel positively charged monomer is proposed for application in energy harvesting from salinity gradients. The capacitive mixing technique has been selected to harvest energy. This technique requires a supercapacitor-like device, in which the electrolyte solution can be continuously replaced, switching between high salinity and low salinity solutions. Doing so, it is possible to obtain a spontaneous voltage raise and convert the mixing chemical energy into electrostatic energy that can be easily recovered. Cyclic performing charge and discharge steps, it is possible to have a net energy income. The functionalized graphene oxide has been obtained by a simple and scalable method. The material obtained in this way has been mixed in organic solvent with activated carbon and hydrophobic polymeric binder to obtain a stable dispersion. The as prepared slurry has been coated on a metallic current collector by doctor blade method and then dried at 50 °C in order to obtain the final electrode. The counterpart is obtained by coating the activated carbon with a thin film anion exchange membrane. The final device, exploiting high surface area asymmetric electrodes with opposite charges, is obtained juxtaposing a pair of these electrodes inside a homemade cell specifically designed for capacitive mixing application. The inlets are connected to gear pumps. To simulate seawater and freshwater, artificial NaCl solution are used. Material characterization techniques such as electron microscopy and infrared spectroscopy are employed to study the physical and chemical structure of the proposed materials. Thermogravimetric analysis is used to investigate the effectiveness of the functionalization procedure. Electrochemical methods are chosen to investigate the performance of the proposed materials.

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Exploring the lithium-mediated nitrogen reduction reaction into ammonia

F. Bella, A. Mangini, L. Fagiolari, J. Amici, C. Francia, S. Bodoardo

Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129-Turin, Italy
e-mail presenting author: federico.bella@polito.it

The lithium-mediated (Li-m) nitrogen reduction reaction (NRR) represents the most promising electrochemical process for renewable-driven and delocalized NH_3 production. Finding a complementary pathway to the Haber-Bosh (HB) process allows a step forward to the net-zero carbon emission policy, essential to contrast the climate crisis. Indeed, HB causes a global average of 2.86 tons of CO_2 emitted per ton of NH_3 [1].

The reducing power of lithium has been applied in different strategies; it is possible to distinguish between continuous processes and step-by-step systems. In the first case, N_2 is reduced simultaneously to the protonation into NH_3, while, in the second option, the Li nitridation is conducted in the absence of H^+ to avoid the competitive hydrogen evolution reaction (HER). Among the continuous processes, the most promising one employed a batch cell at 20 bar of N_2 with a fluorinated Li salt in tetrahydrofuran and with ethanol addition as the proton donor. Indeed, these systems reached a Faradaic efficiency approaching 100% [2], as well as a commercially relevant ammonia production rate of 153.28 $\mu g/h{*}cm^2$ at a current density of 1 A/cm^2_{geo} [3].

The step-by-step technology presents the intrinsic advantage of water exploitation as the proton donor in a separate environment and or time of the process, ensuring greater stability. Therefore, this pathway avoids organic molecule degradation, as well as H_2 feedstock need and consumption [4]. Moreover, the Li–N_2 reaction in a completely aprotic environment could maximize Li exploitation, enhancing scalability. Indeed, Li reduction, essential for the mediator recirculation, is the most energy-requiring step [4].

Li nitridation has been studied both in a direct thermochemical reaction [4] and with promising Li–N_2 galvanic cells [5]. In similarity with metallic Li–gaseous batteries (e.g. Li-O_2 devices), Li-N_2 devices have been recently tested both for NH_3 production and for energy storage. Even if this technology is still in its infancy, a proof-of-concept of Li_3N formation has been verified [5].

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A lignin-based potassium battery

F. Bella,[i] S. Trano,[i] G. Pascuzzi,[ii] F. Corsini,[ii] M. Armandi,[i] L. Fagiolari,[i] J. Amici,[i] C. Francia,[i] S. Bodoardo,[i] S. Turri,[ii] G. Griffini[ii]

[i] Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129-Turin, Italy
[ii] Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133-Milan, Italy
e-mail presenting author: federico.bella@polito.it

Rechargeable batteries are a key technology in the world rush toward the energy transition. Li-ion batteries (LIBs) have reached unprecedent targets of performance and safety, nevertheless it is not logical thinking that the LIB technology alone is able to provide for the whole world electrification, given lithium scarcity (0.0017 wt% in the Earth crust) and its uneven distribution.

In this scenario, it is not surprising the increasing attention coming from the research community on potassium-based batteries. Potassium is abundant on Earth (2.09 wt%), evenly distributed and characterized by a very low standard equilibrium potential (-2.93 V vs. SHE with respect to -3.09 V vs. SHE of Li^+/Li) and Lewis acidity (smaller solvated ions and thus faster conduction). Nonetheless, K-ion batteries have lower volumetric and gravimetric energy density with respect to LIBs, but this makes them perfectly suitable for stationary application. In light of this consideration, it is logical to already design potassium-batteries for large scale commercialization to be sustainable and low cost.

Looking at this goal, our groups have carried out the preparation of two main components of this battery (i.e., anode and electrolyte) starting from a widely abundant and sustainable biosourced precursor: lignin.

On one side, we have worked on the design, synthesis and characterization of a lignin-based membrane by crosslinking a pre-oxidized Kraft lignin matrix with poly(ethylene glycol) diglycidyl ether [1]. Once the membrane was activated by soaking a liquid electrolyte, the as obtained gel polymer electrolyte was fully characterized, showing suitable ionic conductivity, excellent chemical compatibility and tremendous ability at suppressing the formation of metal dendrites.

In parallel, a carbonaceous anode was prepared from the synthesis of a carbon powder obtained starting from Kraft lignin. The latter underwent a precarbonization process at 250 °C, to be then mixed with a KOH aqueous solution and urea. Once it resulted dried, the chemical activation of the carbon material was completed by heating it up to 700 °C under nitrogen. Not only the chemical activation requires lower activation temperature, but it also provides a material with a turbostratic disordered structure with very low graphitization degree (i.e., ideal for K-ion insertion) and higher specific surface area. The biobased anode was able to cycle with capacity values comparable to commercial ones and even more promising cycling stability.

The resulting lignin-based potassium prototype cell is the answer to the quest of an exponentially increasing electrification and large stationary storage demand, but it also fulfills the responsibility for sustainable and low-cost industrial production.

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Highly Stable, Crosslinked Polymer Membranes for Batteries

K. Vezzù, G. Crivellaro, G. Pagot, P. Sgarbossa, E. Negro, V. Di Noto

Section of Chemistry for Technology, Department of Industrial Engineering, University of Padova, Via Marzolo 9, 35131 Padova, Italy
e-mail presenting author: keti.vezzu@unipd.it

Long-term energy storage is a crucial stepping stone for the introduction of renewable sources in the energy mix due to their intermittent nature. Non-aqueous Flow Batteries (NFBs) are expected to operate at higher potential differences in comparison to conventional aqueous systems, thus yielding an improved power density. However, among the several issues of NFBs, it is pivotal to develop ion-conducting separators stable in organic solvents.

Here we present a new family of ionomers which proved promising as candidates to implement this crucial function. The ionomers are founded on the strong ionic interactions between the functionalities of a polyamide-based material (P) and a perfluorosulfonic acid macromolecule (N). The latter interactions establish crosslinks between the two starting macromolecules. Consequently, the polymeric structure of the final ionomer is reorganized, improving the mechanical properties and curtailing the swelling upon immersion in organic solvents.

The membranes obtained in this studies show a swelling < 7% after 1000 hours of immersion both in acetonitrile (ACN) and in a 1:1 vol./vol. mixture of ethylene carbonate and propylene carbonate (EC:PC). Upon exchanging the P-N_x membranes with: a) tetraethylammonium (TEA^+) cations, a common benchmark mobile specie for NFBs, it is shown that P-$N_{0.95}$ shows a conductivity at 25°C of 1.5 $mS\cdot cm^{-1}$ and 0.5$\cdot mS\cdot cm^{-1}$ at 25°C in 0.1 M TEA^+ in ACN and 0.1 M TEA^+ in EC:PC and b) $LiPF_6$, a common benchmark for lithium batteries, P-$N_{0.91}$ present a conductivity up to 0.84 mS cm^{-1} at 25°C in 0.1 M $LiPF_6$ in EC:PC.

These results suggest that the proposed materials are suitable for application in NFBs and solid state batteries, opening the door to development of new systems.

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Electrodic structure optimisation for Anion Exchange Membrane Fuel Cell Application

I. Gatto,[i] A. Patti,[i] A. Saccà,[i] A. Carbone[i]

[i] *Istituto di Tecnologie Avanzate per l'Energia "Nicola Giordano" (ITAE-CNR), Via S. Lucia sopra Contesse 5 - 98126 Messina, Italy*
e-mail presenting author: irene.gatto@itae.cnr.it

Energy is today responsible for more than 75% of the EU's greenhouse gas emissions and the transition towards climate neutrality assumes a central role. It must drastically increase the share of renewable energy sources and clean energy carriers, and improve energy efficiency [1]. The European Green Deal is a set of policy initiatives proposed by the European Commission with the overall goal of achieving climate neutrality in Europe by 2050. In this context, the green power generation based on reneawable sources such as Fuel Cells (FC) and in particular polymer electrolyte fuel cell (PEFC) play a key role due to high efficiency and low environmental impact [2]. In recent years, FCs based on anion exchange membrane (AEM) are becoming a valid alternative to proton exchange membrane (PEM), due to the possibility to use non-platinum-group metal catalysts, that are considered critical raw materials (CRM), and to allow less expensive metal hardwares that use alkaline exchange polymeric membrane as an electrolyte [3-4]. In any case, the use of AEM as an electrolyte requires a development and optimization of the electrode structures and membrane electrode assembly (MEA). In this work, MEAs, based on a commercial FAA3-50 membrane, were developed and electrochemically characterized in a single cell configuration. Starting from previous results [5], it was evaluated the electrodic structure in terms of ionomer content in presence of microporous layer (MPL) in the GDL. Physico-chemical chracterizations to verify the hydrophobicity/hydrophilicity of the catalyst layer as a function of the ionomer loading were carried out. The developed MEAs were characterized in a 25 cm^2 single cell and the electrochemical results were related with the physico-chemical data.

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Revolutionising the Fabrication of Gas Diffusion MoS_2 Electrodes to Advance New Generation Electrolyzers

E. Campedelli[a], M.Parnigotto,[a] Marco Mazzucato,[a] M. Timpel,[b] M. V. Nardi,[b] C. Durante [a]

[a] Department of Chemical Sciences, University of Padova, Via Marzolo1, 35131, Padova, Italy
[b] Institute of Materials for Electronics and Magnetism, Trento unit c/o Fondazione Bruno Kessler, Via alla Cascata 56/C, 38123 Trento, Italy
e-mail presenting author: mattia.parnigotto@phd.unipd.it

Water electrolysis is a leading and promising method in global decarbonization efforts, providing a sustainable and fossil fuel-independent approach for hydrogen production. In the pursuit of economically viable water electrolysis implementation, a fundamental requirement is the development of highly active and stable electrocatalysts that avoid the use of critical raw materials. In recent years, transition metal dichalcogenides (TMDs) have gained intensive attention due to their fascinating structure, catalytic properties, chemical stability, and low cost[1]. Today, the most studied TMD for the hydrogen evolution reaction is MoS_2, however, the literature still lacks promising catalysts in the alkaline electrolyte. Various synthesis routes have been developed to grow MoS_2 as a prominent HER catalyst that takes advantage of the use of different carbon-based supports such as graphene or carbon nanotube. Nevertheless, most of these methods need to be improved in order to reach a good industrial scalability for simple, reproducible, and low-cost production of new-generation MoS_2 electrodes. Ionized jet deposition (IJD) is emerging as a promising cost-efficient and flexible fabrication technique for growing MoS_2 thin films on silicon substrates, providing high processing efficiency and scalability [2]. Such a technique is based on the ablation process in a target induced by a pulsed electron beam, and, subsequently, the plasma plume of ejected molecular-sized species propagates toward the substrate (figure 1 a).

The aim of this study is to explore the versatility of IJD fabrication in synthesising MoS_2 directly on the surfaces of various carbon papers, both doped (with sulphur or nitrogen) and undoped. The aim is to investigate the synergistic enhancement of activities resulting from the presence or absence of heteroatoms within the carbonaceous supports. Furthermore, the research aims to analyse how variations in IJD growth parameters can control surface properties, defects, and crystallinity of MoS_2, thus influencing active sites for the hydrogen evolution reaction (HER). Finally, a comparison of these activities will be made with commercially available standard materials (figure 1 b).

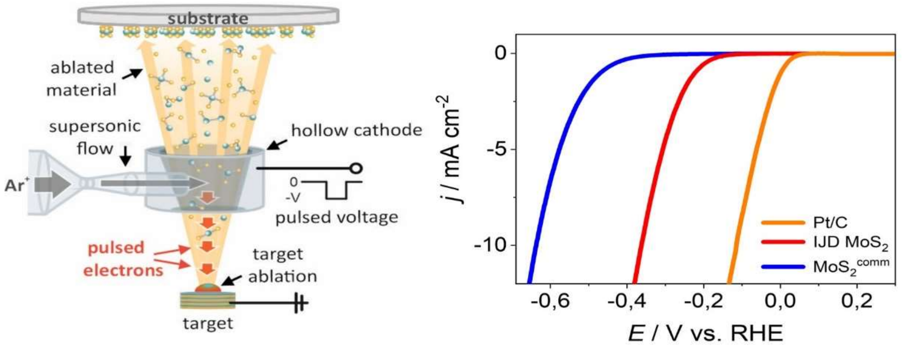

Figure 17: a) schematic sketch of the main IJD components and b) HER alkaline polarisation curves of commercial MoS_2, MoS_2 IJD-deposited and benchmark Pt/C.

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Electrochemistry as the control and operative tool for the design of an industrially relevant process for recycling post-consumer spent lithium-ion batteries

Mirko Magni[a], Giulia Cassardo[a], Giovanni Riva[a], Pegah Roustazadeh[a], Andrea Grassi[b], Edoardo Guerrini[b]

[a]Department of Environmental Science and Policy, Università degli Studi di Milano, 20133 Milano, Italy
[b]Engitec Technologies SpA, 20026, Milano, Italy

Electrochemical devices called Lithium-Ion Batteries (LIBs) are almost ubiquitous today, from portable electronics to electric vehicles. The tight dependence of this technology from some critical materials is forcing the scientific and industrial community to find out effective strategies to recover such materials from the constantly increasing spent LIBs, aiming at reducing the EU's socio-economic dependence on foreign Countries. To achieve the stringent recovery rate defined by EU for the coming years recyclers still need efficient hydrometallurgical recovery processes.

Despite the relatively simple working principle, specific features of LIB technologies (crafting process, plenty of cathode chemistries, shapes and dimensions) entails challenges for the recycling processes. Thus, the development of a robust multi-step process capable of working with shredded batteries, of any types, is up to date the most plausible solution. Besides mechanical and separation stages, the core of any hydrometallurgical recycling process employs the dissolution of metal oxides from positive electrode (i.e., leaching stage) and the recovery of the dissolved metals (i.e., precipitation, electrodeposition). In the scientific literature, some weak or missing points still exist resulting into a slow rate of transferring the know-how to the industrial level. They could be stated as follow: i) the type of studied materials are quite different from real industrially relevant samples; ii) a robust process monitoring system is still missing (unaffected by complex matrixes, heterogeneity and intense color); iii) processes assuring high selectivity in the separation of the multi-component leachate are not still so effective/competitive.

In the present applied research project, carried out through a joint collaboration with an engineering company part of the Consortium of the European Battery Innovation project (IPCEI Batterie 2), we are contributing to fill these experimental gaps. Using mainly electrochemistry as the investigation tool, we are:

i) testing the efficacy and behavior of many low cost and commonly available organic acids and complexing agents in the leaching of aliquots of kilograms-scale black mass batches from "industrial grade" grinded spent LIBs;
ii) developing *in operando* electrochemical protocols for the on-line monitoring of both the leaching and recovery stages;
iii) approaching to the separation of the complex leachate in different streams, each one enriched in only one metal species, through an electrodialysis cell of an intermediate scale between benchtop and pilot-scale one.

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An analysis on the evolution, potential and characteristics of redox flow batteries with a focus on the search for new electrolytes

Maria Viviana Scopelliti,[1] Lorenzo Guarneri,[2] Francesco Montorsi,[2] Egidio Monticelli,[2] Enrico Calzavacca,[2] Laura Borgese[1]

[1]*Department of Mechanical and Industrial Engineering, University of Brescia, 25123-Brescia, Italy*
[2] *AB Impianti s.r.l., Via Agnelli 9, 25034-Orizinuovi (BS), Italy*
m.scopelliti001@studenti.unibs.it

So far, the main sources of energy used have predominantly been non-renewable. In addition to being limited in supply, these sources cause serious environmental pollution. To address these challenges, technologies aimed at sustainable energy production have been developed. Currently, the most widely adopted energy sources are wind and solar energy, but they suffer from the limitation of intermittent generation. To overcome this limitation, energy storage systems have been developed to store the generated energy and release it to the grid when needed. Among various storage technologies, Redox Flow Batteries (RFBs) have gained significant interest in the scientific community for their ability to store energy on a large scale. RFBs distinguish themselves with an innovative design that utilizes active materials dissolved in liquid electrolytes contained in separate tanks. The electrochemical energy conversion takes place within the electrode cells. RFBs offer several advantages, including flexibility in adapting energy and power capacity, long battery life, and fast recharging times. Among the different redox couples studied for RFB development, Vanadium Redox Flow Batteries (VRFBs) have been the most extensively researched and commercialized. VRFBs are valued for their high efficiency, long lifespan, and fast response times, although their high-cost limits widespread adoption of this technology. For this reason, ongoing research focuses on refining these technologies, with particular attention to the development of new electrolytes capable of improving the performance, energy density, and overall efficiency of RFBs at lower costs(1). In particular, the use of titanium as a base for RFB electrolytes has received attention. Titanium(2), an abundant and cost-effective element in the Earth's crust, offers significant advantages due to its high solubility in acidic solutions, enabling the development of high-energy-density RFBs. The most promising redox couples for titanium-based RFBs are Ti/Mn, Ti/Fe, and Ti/Ce. The ultimate objective is to reduce production costs and improve the efficiency of RFBs by minimizing energy losses and increasing the lifespan of electrochemical cells, utilizing technologies already in the market and used for VRFBs.

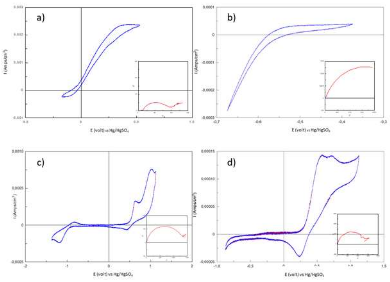

Figure 18:Cyclic voltammetry and Nyquist plots (insets) of glassy carbon electrode immersed in: a) FeSO4; b) TiOSO4; c) VCl3; d) VOSO4.

My industrial doctorate aims to develop expertise in the field of RFBs and compare the achievable performance using various electrolytes, comparing them with vanadium in laboratory-scale systems (Figure 18). Additionally, I will strive to enhance RFB performance by testing different electrodes and membranes that can be subsequently implemented on a larger production scale. In this contribution, I will present preliminary results of the comparison obtained through the study of redox couples in a classical three-electrode electrochemical system.

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Ternary alloys of Ni-Fe-P for alkaline electrolyzer

S. Carbone[a], R. L. Oliveri[a], B. Patella[a] R. Miceli[a], F. Pellitteri[a], A. O. Di Tommaso[a], G. Aiello[a], R. Inguanta[a]

[a]Department of Engineering, Università degli Studi di Palermo, Viale delle Scienze, 90128 Palermo, Italy

e-mail presenting author: sonia.carbone@unipa.it

Renewable energy resources (solar, wind, ect) could replace fossil fuels but have the disadvantage of being intermittent. From this perspective, the role of hydrogen is crucial. It could fill the role of fuel, storage medium and energy carrier [1]. Prominent among the various methods of hydrogen production is the water-splitting process. This process represents a clean, zero-emission way to produce hydrogen if the electricity comes from renewable sources. However, green hydrogen production by water electrolysis is not economically sustainable. Many researchers are focusing their work on developing low-cost electrode/electrocatalysts with high catalytic activity toward the water-splitting reaction. The main attention is focused on non-noble metal catalysts. In particular, transition metals-based electrocatalysts are considered one of the best options thanks to their stability in alkaline media and electrocatalytic activity [2]. Currently, the most investigated transition metal catalysts includes sulfide, phosphide, and nitride. In addition to the type of material, electrode morphology is another important aspect. Nanostructured shapes have a very high surface area improving the electrocatalytic performance of the electrodes. In this work, a ternary alloy of Ni-Fe-P with nanowires morphology was investigated.

The synergistic effect between the three elements ensures a very high electrocatalytic activity [3]. Electrodes were obtained by template electrosynthesis which is a simple, cheap and scalable method. Electrodes morphology was studied by scanning electrode microscopy (SEM). Energy dipersive spectroscopy (EDS) confirmed the presence of three elements. Electrodes were tested both as cathodes and anodes by Cyclic Voltammetry (CV), Quasi Steady State Polarization (QSSP) and Galvanostatic Test. All the tests were performed in 30% w/w KOH aqueous solution and at room temperature. The obtained results were compared with those obtained in our previous work relative to the behavior of binary alloy of Ni-Fe NWs [4]. Preliminary results show a better performance of the ternary alloy than binary ones.

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Non-enzymatic electrochemical sensor based on NiFe alloy for sugar detection

F. Mazzara[a], B. Patella[a], M. Russo[b], A. O'Riordan[c], G. Aiello[a], C. Torino[d], A. Vilasi[d], Rosalinda Inguanta[a]

[a] Laboratorio Chimica Fisica Applicata., Dipartimento di Ingegneria, Università degli Studi di Palermo, Viale delle Scienze, 90128 Palermo, Italy
[b] Dipietro Group, 96010, Siracusa, Italy
[c] Nanotechnology group, Tyndall National Institute, University College Cork, Dyke Prade, Cork, Ireland
[d] Istituto di Fisiologia Clinica (IFC)-Consiglio Nazionale delle Ricerche-Reggio Calabria-Italy

francesca.mazzara04@unipa.it

Sugars are essential organic compounds for humans, that play several fundamental roles in their life and development. They are naturally present in a wide range of food and directly produced in the human body [1]. Their detection is an important factor in the food as well as in the medical sector. Sugars can be naturally found in fruit, vegetables and honey or they may be added as additives during food processing, beverages and other preparations. While natural sugars are required by the body to satisfy energy needs, added sugars are harmful to human health. Therefore their quantification is very important to evaluate the quality of many foodstuffs. Sugar consumption has been indicated as a major cause of several chronic diseases such as obesity, heart disease, diabetes and dental caries. The World Health Organization suggests that free sugars should make up no more than 10% of our daily energy intake [2]. The European Commission has implemented a series of policies aimed to regulating sugar intake such as taxes on high-sugar foods. For sugars detection, electrochemical sensors have met great success, with respect to the other conventional technique, due to the simplicity of use, speed in response and high sensitivity and selectivity [3]. In particular, non-enzymatic sensors are very stable and sensitive with respect to enzymatic ones.

In this work, nanostructured electrodes based on nickel-iron (NiFe) alloys, obtained by template electrosynthesis method were employed for sugars detection. The electrodes consist of nanowire arrays with a Fe content of 78.95 at%, that have a very high surface area and thus a very high electrocatalytic activity [4]. All samples were characterized by XRD, SEM and EDS analysis in order to study morphology and evaluate the composition and crystalline phases of the alloy. The obtained electrodes were tested as sugar sensors in an aqueous solution by chronoamperometry technique. NiFe electrodes show good behavior in terms of sensitivity and stability. Sensors were also validated using real samples of foods. The achieved results were in good agreement with conventional techniques.

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Electrochemical sensors for worker safety in manufacturing industries

M. G. Bruno[1], B. Patella[1], C. Torino[2], A. Vilasi[2], C. Cipollina[3,4], S. Di Vincenzo[5], E. Pace[5], A. O'Riordan[6], R. Inguanta[1], G. Aiello[1]

[1]*Applied Physical Chemistry Laboratory, Department of Engineering, Università degli Studi di Palermo, Viale delle Scienze, 90128 Palermo, Italy*
[2]*Institute of Clinical Physiology, National Research Council, 89124 Reggio Calabria, Italy*
[3] *Institute of Biomedical Research and Innovation, National Research Council, 90146 Palermo, Italy*
[4]*Ri.MED Foundation, 90133 Palermo, Italy*
[5]*Institute of Translational Pharmacology, National Research Council, 90146 Palermo, Italy*
[6]*Nanotechnology Group, Tyndall National Institute, University College Cork, Cork, T12 R5CP, Ireland*
mariagiuseppina.bruno@unipa.it

The National Institute for Occupational Safety and Health has attributed most occupational diseases of industrial workers to excessive exposure to dangerous substances. In particular, occupational lung diseases are caused by the inhalation of harmful substances such as dust particles and gases [1].

The use of DPI and periodic health checks for industrial workers certainly reduces risks, but a more effective prevention strategy should include real-time monitoring of physiological parameters [2].

In this context, recent academic and industrial research has focused on the development of smart wearable systems for continuous health monitoring. This has been possible mainly due to significant progress in micro- and nanotechnology and the miniaturization of devices [3]. In such regard, electrochemical sensors represent a promising alternative due to their speed of response, simplicity of operation, and lower cost than traditional methods of diagnosis [4].

This research activity involves the development of a smart mask based on an electrochemical sensor for the non-invasive detection of hydrogen peroxide in exhaled breath. In particular, a higher concentration of this biomarker indicates the onset of oxidative stress, a pathological condition that can lead to more serious diseases, such as asthma and COPD (Chronic Obstructive Pulmonary Disease) [5].

This sensor was fabricated through a sustainable production process, from the CDs at the end of life because their silver layer can be used for its good electrochemical properties. In particular, this layer was peeled off the CD and a three electrodes configuration was given using a laser cutter.

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p-40

Fabrication of Ni-alloy nanostructured elecrodes for alkaline electrolizers.

Salvatore Geraci[1], Sonia Carbone[1], Roberto Luigi Oliveri[1], Bernardo Patella[1], Rosario Miceli[1], Filippo Pellitteri[1], Massimo Caruso[1], Giuseppe Aiello[1], Rosalinda Inguanta[1]

[1] *Department of Engineering, Università degli Studi di Palermo, Palermo, Italy*
e-mail presenting author: salvatore.geraci01@unipa.it

In last years, renewable energy sources are becoming more and more important owing to the progressive decarbonization of energy processes to reduce CO_2 emissions [1,2]. In this view, governments and authorities all around the world are encouraging the use of renewable energies by promoting laws and initiatives for the most sustainable energy transition [3,4]. One of the main drawbacks of renewable sources is their unpredictability, consequently, interest in hydrogen has drastically increased. One way to produce green hydrogen is by water electrolysis using only electricity from renewable sources. It is a viable strategy to take advantage of the surplus electricity. The most relevant part of the cost of electrochemical hydrogen comes from the electricity cost and catalysts. For this reason, research is focused on improving the performance of the electrolyzer, using more efficient and less expensive materials, such as transition metal alloys like Nickel-based alloy [5]. One of the possible ways to improve the performance of electrolyzers is based on the development and fabrication of nanostructured electrodes with a low cost and high electrocatalytic activity.

In previous works, Ni nanowires were fabricated by template electrosynthesis, featuring by very high surface area. Starting from the best-performing nickel-iron alloy previously studied [6], this work focuses on the fabrication of nickel-iron-sulfur electrodes. In an aqueous solution containing nickel and iron, a third element was added in different concentrations in order to obtain electrodes with different compositions. The chemical and morphological features of these nanostructured electrodes were studied through scanning electrode microscopy (SEM) and energy diffraction spectroscopy (EDS) analyses, and those results will be presented and discussed. Electrochemical and electrocatalytic tests (Cyclic Voltammetry (CV), Quasi Steady State Polarization (QSSP) and Galvanostatic Step) were carried out to establish the best alloy composition for both hydrogen and oxygen evolution reactions. Long-term tests performed at a constant current density in an aqueous solution of potassium hydroxide (30% w/w) will be also reported.

Acknowledgments

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Nickel alloy electrodes for the evolution reaction of hydrogen and oxygen in a water-alkaline electrolyser

R.L Oliveri, S.Carbone, B.Patella, S. Geraci, G. Aiello, F. Pellitteri, A. O. Di Tommaso, R Miceli, R. Inguanta

Dipartimento di Ingegneria, Università degli Studi di Palermo, 90128 Palermo, Italy

Hydrogen as an energy carrier is a promising solution to the problems associated with the current fuel-based energy system [1]. It provides a sustainable fuel for a wide range of applications, from transport to small electronic devices or stationary applications. Among various methods, water electrolysis is one way, if not the only way, to produce green H2. This is possible if the electrical input is provided by a renewable energy (RE) source. Alkaline electrolysis has recently gained considerable attention as a viable method for producing green hydrogen from renewable sources, as its technology is cheaper than that based on acid solutions, since it requires precious metals as electrocatalysts [8-9]. Researchers currently focus on improving electrolyzers, such as increasing their dynamics and efficiency.

This work investigates the fabrication and characterization of nanostructured Ni alloy and Ni foam electrodes with the aim of reducing the overpotential losses associated with driving the anode oxygen evolution reaction (OER) and the cathode hydrogen evolution reaction (HER) in alkaline environments. Ni alloy nanowires with very high surface area and high electrocatalytic activity were prepared by template electrosynthesis [4-7]. It has been found that alkaline electrolysers with Ni nanowire electrodes coated with different electrocatalysts have good performance and are stable even at room temperature [8-11]. For comparison, Ni foam (NF) and Ni foil (NS), differently functionalised with the same electrocatalysts, were tested. The electrodes were characterized by SEM and EDS. Quasi-steady-state polarization (QSSP), galvanostatic step (GS) and galvanostatic tests were then performed on each electrode. The electrodes were tested individually and compared. The best performing electrodes in terms of OER and HER were identified. Each test was carried out in an alkaline electrolyte (aqueous potassium hydroxide solution, 30% by weight).

The electrodes were then tested in an alkaline electrolyser for a period of 6 hours at a constant current density in order to evaluate their performance. The cell consists of two vessels separated by a polystyrene membrane to ensure electrical continuity and prevent gas mixing (one for the anode and one for the cathode). Following individual tests of the nanostructured Ni alloy electrodes and Ni foam with nickel alloy as anode and cathode, the performance of the foam and nanostructured electrodes used as electrolysers was evaluated. Quasi steady-state polarizations were performed by scanning the cell potential at a rate of 0.1667 mVs-1 from 1.48 V, which is the thermodynamic cell potential, E°, to 4.5 V. The tests were stopped when a current density of 0.5 Acm-2 was reached. The results are very encouraging, as the high ratio of real surface area to geometric surface area was immediately beneficial.

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Electrochemical immunosensor based on nanostrurtured gold foam micro disk multiplexed electrodes for sensitive cortisol detection

N. Moukri,[1] V. B. Juska,[2] B. Patella,[1] C. Cipollina,[3] A. O'Riordan,[2] R. Inguanta.[1]

1 Dipartimento di Ingegneria, Università degli Studi di Palermo, 90128-Palermo, Italy
2 Tyndall National Institute, University College Cork, T12 R5CP-Cork, Ireland
3 Fondazione Ri.MED, 90128-Palermo, Italy
e-mail presenting author: nadia.moukri@unipa.it

We have developed an advance electrochemical immunosensing platform based on nanostructured gold foam micro disk electrodes whose applicability is shown with cortisol detection. The micrometer scale size of the electroactive area is advantageous for electrochemical sensor measurements due to its high signal-to-noise ratio, lower detection limit. Furthermore such devices can be transform to wearable and portable devices. Our device has three sensing electrode areas, disk shaped, with 100 µm diameter. This device is microfabricated on Si substrate using electronics-standard lithography, deposition and etching techniques, more details can be found in our previous works [1], [2]. The electrodes were first modified with gold foam via hydrogen bubble template based electrochemical deposition in order to increase the active surface area [2] [3]. After that, an antifouling layer based on chitosan, graphene oxide (GO), and bovine serum albumin (BSA) was deposited on the gold foam. Since chitosan and BSA have abundant functional groups, such surface provide flexibility for bioconjugation such as carbodimide or glutaraldehyde chemistry for biomolecules immobilisation. We have shown the steps involved for the immunosensor construction in Figure 1. The differential pulse voltammetry (DPV) was used to detect cortisol, evaluating the decrease in peak current of $Fe(CN)_6^{3-/4-}$ after cortisol incubation with concentrations ranging from 0.01 to 5 pg mL^{-1}.

The resulting sensor showed high sensitivity and very low limit of detection. It was then evaluated whether the sensor also performed in complex matrices such as fetal bovine serum and artificial saliva. The sensor showed excellent selectivity, supporting the antifouling coating successful performances. These promising results motivate additional investigations since these three-electrode device could provide a solid platform for the development of a multiplex sensor that simultaneously detect cortisol and other biomarkes.

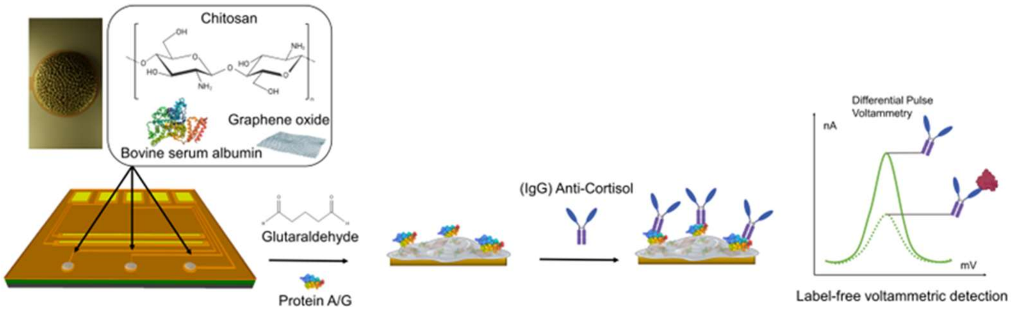

Figure 1: Schematic image of the immunosensor construction on the multiplexed device.

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Self-Discharge behavior of Pseudocapacitive Manganese Oxide in different electrolyte atmospheres

P. Zaccagnini,[1,2] M. Reina,[1,2] M. Sperti,[1] M. Serrapede,[1,2] L. Baudino,[1] A. Pedico,[1] S. Bianco,[1] A. Lamberti[1,2]

[1] *Department of Applied Sciences and Technologies, Polytechnic of Turin, Corso Duca degli Abruzzi 24, 10129-Turin, Italy*
[2] *Centre for Sustainable and Future Technologies, Italian Institute of Technology, Via Livorno 60, 10144-Turin, Italy*
e-mail presenting author: pietro.zaccagnini@polito.it

The phenomenon of self-discharge, which significantly affects the performance of supercapacitors (SCs), has not received extensive research attention in the field of electrochemical energy storage devices. Conway's theories have been extensively studied in the literature, exploring various parasitic mechanisms that impact the charge retention capability of SCs [1,2,3]. These investigations have also encompassed pseudocapacitive materials, including manganese oxide [4].

This study focuses on optimizing electrodes and electrolytes for the application of micro-supercapacitors (µSCs), utilizing laser-induced graphene (LIG) electrodes as current collectors [5]. Specifically, we investigate the influence of O_2 impurities on the open circuit voltage properties of the assembled devices. The preliminary results in Figure 1 reveal significant observations: in panel (a), variations in the oxidation peak can be observed under different electrolyte gas atmospheres, while in panel (b), it is evident that the leakage current at a floating voltage of 1.05 V vs Ag/AgCl is reduced when employing the outgassed electrolyte. Such observations open the possibility to define a refined protocol for the proper charge-balancing procedure, especially for aqueous electrolyte-based devices, accounting for the effects of gas impurities.

This result is part of a project that has received funding from the European Research Council (ERC) under the European Union's ERC Starting Grant Grant agreement No. 949916

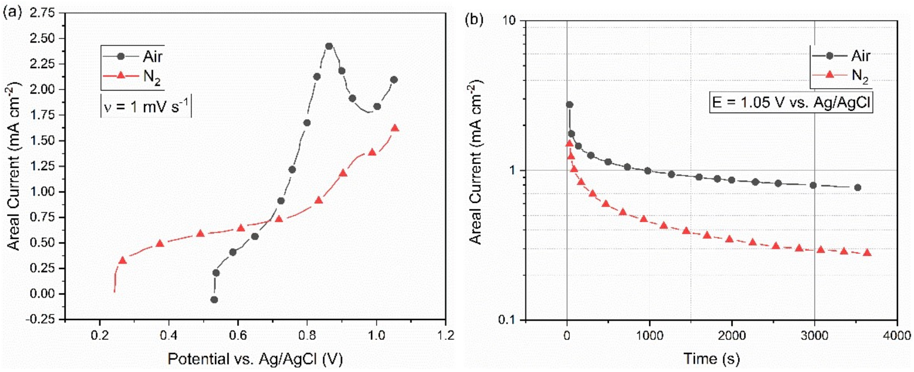

Figure 1: In panel (a), the LSV profile recorded at 1 mV s-1 in 1M Na2SO4 in different atmospheric conditions. In panel (b), the measured leakage currents at the floating potential of 1.05 V vs. Ag/AgCl.

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Formulating PEO-polycarbonate blends as solid polymer electrolytes by solvent-free extrusion

M. Gastaldi,[a,b] F. Gambino,[a,b] G. Meligrana,[a,b] G. A. Elia,[a,b] C. Gerbaldi [a,b]

[a] *GAME Lab, Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi, 24, 10129, Torino, Italy*
[b] *National Reference Center for Electrochemical Energy Storage (GISEL) - INSTM, Via G. Giusti 9, Firenze 50121, Italy*
E-mail: matteo.gastaldi@polito.it

Lithium-ion batteries (LIBs) are the power source of choice in portable electronics, thanks to the elevated gravimetric and volumetric energy densities compared to other rechargeable systems, and more recently widely used in electric vehicles and grid energy storage. The high energy density is granted by an operating voltage of ~4 V obtained by employing organic aprotic electrolytes. However, safety issues such as leakage, combustion, and explosion deriving from flammable liquid electrolytes are still amongst the major bottlenecks of the technology. Solid polymer electrolytes (SPEs), composed of a lithium salt dissolved in a polar polymer matrix, have been regarded as promising candidates for replacing liquid electrolytes in LIBs. SPE suffer from low ion mobility at room temperature, which restricts their use. Polyethylene oxide (PEO) is a well-known material that can reach, in formulation with lithium salts, high conductivity values at room temperature, and its low glass transition temperature (T_g) makes it a good candidate for SPE. Although all these advantages, PEO presents some drawbacks, like the strong dipolar interaction and complexation of Li^+ that prevent the migration of lithium ions and segmental mobility in crystalline phase. Moreover, the reduced electrochemical stability window (~4.0 V vs. Li^+/Li) hampered the use of the high-voltage cathode materials [1–3].

Polycarbonates (PC), instead, show excellent lithium salt solubility and a moderate interaction between carbonate groups and Li^+ that ensure ions and segmental mobility. PCs show higher t_{Li+} values and wider electrochemical stability windows than PEO, but as a principal drawback, they have high T_g values, which makes these materials semicrystalline at low to moderate temperatures and restrict ion transport [4]. In this work, we selected three PCs, characterized by an increasing chain length, to blend with PEO in different proportions. By means of a design of experiment (DoE), we aim to compare the chemical, mechanical and electrochemical properties of polymeric electrolytes composed of PEO blended with a polycarbonate at fixed LiTFSI salt concentration. The study helps identifying the best PC and the ideal ratio at which the ionic conductivity, the electrochemical window and the elastic modulus are optimal, thus ensuring their practical application in all-solid-state lithium-based batteries. In addition, all the formulations were prepared exploiting a mini-extrusor. This instrument enabled us to avoid the use of toxic or flammable organic solvents. The presence of an inert gas line in the mini-extrusor also garanted an inert atmosphere during the blending of the polymers.

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Single-ion conducting polymer electrolytes enabling advanced Li-metal solid-state batteries

F. Gambino[1,2], M. Gastaldi[1,2], G. Lingua[1,2], P. Vlasov[3], A. S. Shaplov[4], E. Lozinskaya[5], G.A. Elia[1,2], C. Gerbaldi[1,2]

[1] Group for Applied Materials and Electrochemistry (GAME Lab), Department of Applied Science and Technology (DISAT), Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129-Turin, Italy
[2] National Interuniversity Consortium of Materials Science and Technology (INSTM), Via G. Giusti 9, 50121-Florence, Italy
[3] Department of Macromolecular Chemistry, Saint-Petersburg State University, Saint Petersburg 198504, Russia
[4] Luxembourg Institute of Science and Technology (LIST),5 Avenue des Hauts-Fourneaux, L-4362, Esch-sur-Alzette, Luxembourg
[5] A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences (INEOS RAS), Vavilov str. 28, GSP-1, Moscow 119991, Russia
matteo.gastaldi@polito.it

The pressing demand for long-lasting, high-power portable electronics and the emerging large-scale diffusion of electric vehicles (EVs) and energy storage from renewable sources require batteries improved energy density at reduced cost, along with enhanced cycle life and safety. Considering their intrinsic properties, polymer electrolytes are considered one of the most promising solutions among several solid-state electrolyte possibilities.[1,2,3].

In this work, we focus on the development of a specific family of solid-state polymer electrolytes namely polyanions. Because of their single-ion nature, the lithium transport number values approach unity; this accounts for remarkable benefits to the electrochemical performance, because Li$^+$ ions are predominantly engaged in the redox reaction while anions remain relatively inactive.

Different single-ion conducting polymer electrolytes (SICPEs) were prepared, also in the framework of the PSIONIC HORIZON EU project, which demonstrated greatly enhanced performance towards the state of the art of solid-state systems in terms of mechanical properties and electrode compatibility. Several polymerization techniques, including also controlled polymer chain growth (RAFT polymerization), were explored for the synthesis of different families of SICPEs. The novel solid-state polymer electrolytes were thoroughly characterized in terms of physico-chemical and electrochemical properties. Interestingly, the architecture, as well as the nature of the backbone chain, of the block copolymers drastically affect the properties and the electrochemical performance of the SICPEs, allowing great compatibility with high-voltage cathode (NMC) and improved mechanical properties. Indeed, phase separation coming from partial incompatibility between blocks have been deeply investigated as well.

Summarising, we demonstrated that by the effective design and optimization of block-copolymers structure it is possible to achieve several advantages from mechanical/morphological point of view: phase separation, truly solid-state, enhanced mechanical properties; and from the electrochemical one: single ion conducting features, high lithium ion transport, high electrochemical stability towards anodic potential, effective prevention of dendrite growth.

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Structure-activity relationship in NIR photosensitizers for transparent Dye-Sensitized Solar Cells

S. Galliano,[i] A.Y. Segura Zarate,[i] M. Bokan,[i] N. Barbero,[i,ii] M. Bonomo,[i] D. Pasculli,[i] R. Borrelli,[iii] W. Naim,[iv] F. Grifoni,[iv] P. Chotard,[v] S. Ceurstemont, [v] F. Barath,[v] F. Sauvage,[iv] C. Barolo [i,ii,vi]

[i] *Dept. of Chemistry, NIS Interdept. and INSTM Reference Centre, Università degli Studi di Torino, Via Quarello 15/A, 10125-Torino, Italy*
[ii] *Institute of Science, Technology and Sustainability for Ceramics (ISSMC-CNR), Via Granarolo 64, 48018-Faenza (RA), Italy*
[iii] *Dept. of Agricultural, Forest and Food Sciences, Università degli Studi di Torino, Largo Braccini 2, 10095-Grugliasco (TO), Italy*
[iv] *CNRS, Laboratoire de réactivité et Chimie du Solide, Université Picardie Jules Verne, UMR 7314, Amiens, France*
[v] *G-LYTE SAS, Amiens, France*
[vi] *ICxT Interdept. Centre, Università degli Studi di Torino, Lungo Dora Siena 100, 10153-Torino, Italy*

e-mail presenting author: simone.galliano@unito.it

Dye-Sensitized Solar Cells (DSSCs) offer an interesting and sustainable choice for the development of transparent, and even colorless, photovoltaic devices, thanks to their ability to exploit diffuse and low-intensity light as well as their wide versatility in dyes, electrolytes and redox couples. Among them, the photosensitizer plays a crucial role in obtaining transparent wavelength-selective NIR-DSSC system [1]. Until now, different families of NIR chromophores have been investigated with relatively low success in terms of transparency to visible light and power conversion efficiency.

In this work, thanks to the joint efforts of different research groups within the European IMPRESSIVE project (https://impressive-h2020.eu/), we proposed fully transparent DSSCs based on organic polymethine dyes (e.g. squaraine and cyanine) that can display intense absorption in NIR region close to 900 nm, while negligible in visible region (Figure 1). Power conversion efficiency up to 3% and average visible transmittance (AVT) up to 76%, while reaching a color rendering index (CRI) of 92 [2]. Starting from these results and their structure-activity relationship, innovative strategies on synthesis approach and device optimization should be applied to outperform the obtained values and to design stable and low-cost materials for the implementation in real devices [3].

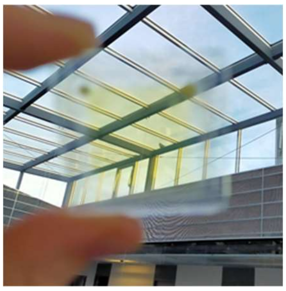

Figure 1: Transparent DSSC with NIR dye.

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Multitechnique investigation of polyol-based Deep Eutectic Solvents as innovative and sustainable electrolytes in electrochemical energy storage devices

M. Bonomo,[i,j] D. Motta,[i] G.A. Elia,[j,z] A. Damin,[i] G. Lingua,[j,z] S. Nejrotti,[i] S. Galliano,[i] C. Barolo,[i,j] C. Gerbaldi,[j,z]

[i] *Department of Chemistry and NIS Interdepartmental Centre, University of Turin, Via Pietro Giuria 7, Torino, 10125, Italy*
[j] *National Reference Center for Electrochemical Energy Storage (GISEL) - INSTM, Firenze 50121, Italy*
[z] *GAME Lab, Department of Applied Science and Technology (DISAT), Politecnico di Torino, Torino 10129, Italy*
e-mail presenting author: matteo.bonomo@unito.it

Concerns related to the energy crisis lead the scientific community to move towards electrical energy production methods more sustainable than those based on fossil fuels, among which solar and wind power play a major role [1]. However, these sources are intermittent and somehow unpredictable. Therefore, it is mandatory to integrate photovoltaic and wind energy systems with efficient electrochemical energy storage systems (EESS), such as batteries and supercapacitors, to store the possible excess of energy produced and supply additional power in case of insufficient electricity supply [2]. One of the main concerns for EESS is the use of thermally unstable electrolytes and critical raw materials enriched electrodes; thus, the scientific community is focusing on the design, characterisation and application of more sustainable electrodes and electrolytes [3,4].

In this contribution, we present a detailed spectroscopic and electrochemical investigation of sodium and zinc-based Deep Eutectic Solvent (DES) electrolytes. DES are an emerging class of low-cost and sustainable systems that are based on a halide salt (organic or inorganic), which acts as a hydrogen bond acceptor (HBA), and an alcohol/organic acid, which acts as a hydrogen bond donor (HBD). They demonstrate promising ionic conductivity, low vapour pressure and good inertness to air and humidity. However, these values are still lower compared to the ones reached with conventional electrolytes based on organic solvents or Ionic Liquids, which generally reflects in less appealing electrochemical performance [5,6]. Aiming to reach wider and more effective exploitation of DES as electrolytes, a thoughtful design of a new combination of HBA and HBD is necessary. In this work, we formulated eutectic mixtures based on $ZnCl_2$ or NaCl as HBA, and glycerol or ethylene glycol as HBD. A multi-technique characterisation (based on thermal analysis, Raman spectroscopy and electrochemistry) is conducted to discern the eutectic composition from not eutectic ones and to clarify the nature and the role of the intermolecular interaction established in DES. These latter will play a paradigmatic role in tuning the properties of the mixtures (i.e. conductivity, viscosity and electrochemical stability window) and the electrochemical behaviour of the electrolytes operating in real lab-scale devices (batteries and supercapacitors). The most promising systems are evaluated with cyclic voltammetry and galvanostatic cycling as a further step toward practical application.

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Ligand Effect on Electrochemical Properties of Superatomic Di-NHC/PPh3-Stabilized Molecular Gold Nanoclusters

Mattia Reato, Matteo Bevilacqua, Andrea Biffis, Flavio Maran, Sabrina Antonello

Department of Chemistry, University of Padova, Via Francesco Marzolo 1, 35131, Padova, Italy
mattia.reato@phd.unipd.it

Nowadays, molecular gold nanoclusters (AuNCs) are considered one of the most promising systems in nanoscience. This is because, unlike gold nanoparticles, AuNCs are true molecular species that exhibit distinctive correlations between the structure and the chemical nature of both the core and the stabilizing ligands [1-3]. The most extensively studied AuNCs are those protected by alkanethiolate ligands where the metal core is surrounded by "staples", consisting in [Au(I)n(R)m] motifs (where R = alkanethiolate), thus stabilizing the cluster core. However, the peculiar staples structure in AuNCs presents some crucial drawbacks for catalytic processes, making communication with the external environment more difficult. For this reason, the modification of the organic-protecting monolayer with alternative ligand systems is becoming increasingly intriguing. Among many options, the combination of phosphines and N-heterocyclic carbenes complex (NHCs) as ligands is gaining more and more interest in recent years [4]. The physical properties of these nanosystems are far from being exhaustively described and, among these, the electrochemical investigations are rather limited and often affected by significant imprecision. In this work, the electrochemical properties of novel AuNCs species (core ranging from 11 to 13 Au atoms) protected by phosphines (PR3) and di-NHCs will be illustrated. We addressed two main issues regarding the electron transfer properties of these NCs. Firstly, the definition of the HOMO-LUMO gap and its correlation with the cluster dimension and/or ligand properties. Secondly, the understanding of how the carbene ligands could affect the redox properties in terms of reduction and oxidation potentials, stability, and additivity factors. The preliminary conclusions of these experiments will be presented

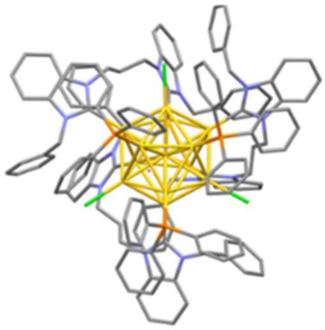

Figure 1: X-ray structure of an AuNC (core composed of 13 Au atoms) protected by di-NHCs and phosphine ligands [5].

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Chemical conversion coatings on AZ31 Magnesium alloys for Biodegradable Implants

G. Tranchida,[i] V. Verro,[i] F. Di Franco,[i] M. Santamaria[i]

[e]*Engineering Dept., University of Palermo, Viale delle Scienze, Building 6, 90128-Palermo, Italy*
e-mail presenting author: giada.tranchida@unipa.it

Nowadays biomedical materials are widely studied to be used as implants in human body to replace damaged hard and soft tissues. Among them, metallic materials (i.e. Ti-Al-V alloys, stainless steel, Mg alloys, etc.) are the most widely employed in clinical applications for permanent and biodegradable implants, since they exhibit excellent properties in terms of high mechanical strength, fatigue resistance and easy processing. Biodegradable implants can be implanted for an appropriate period to fix and then disappear avoiding surgical interventions. Mg alloys have attracted increasing attention over the last two decades as suitable candidate for biodegradable biomedical devices due to their good mechanical properties, biocompatibility, strength-to-weight ratio and similar to human bone properties (Young's modulus and specific density) [1,2]. However, the potential clinical applications of these alloys have been hindered by their poor corrosion resistance in chloride containing environments (as human body fluids or blood plasma). Moreover, the high degradation rate of Mg alloys is so high that the mechanical integrity is not always maintained until the diseased or damaged bone tissue healed. Finally, the concomitant hydrogen evolution reaction can delay healing process due to the formation of gas pockets around the implant or even cause alkaline poisoning in the vicinity of the corroding surface with deleterious effects for the surrounding biological environment. Therefore, different surface modification strategies must be encountered for the degradation of Mg alloys. A survey of the published literature reveals that there are many coating technologies which can be used to coat the magnesium substrate, such as physical vapor deposition, laser surface treatment, electrodeposition and electrophoresis (EPD), anodic oxidation and chemical conversion coating [3-5]. This work aims the development of a chemical/electrochemical multi-step process for the production of protective coatings on AZ31 alloys (2.89 wt.% Al, 0.92 wt.% Zn, 0.05 wt.% Mn, 0.01 wt.% Si, 0.004 wt.% Fe, 0.002 wt.% Cu, 0.001 wt.% Ni, Mg balance) for biomedical application. In particular, conversion layers were grown in alkaline stannate solution (9.95 gL^{-1} NaOH, 49.87 gL^{-1} $K_2SnO_3 \cdot 3H_2O$, 9.95 gL^{-1} $NaC_2H_3O_2 \cdot 3H_2O$, 49.87 gL^{-1} $Na_4P_2O_7$, pH = 11.5–12.0) at 82°C as a function of immersion time. Further, post conversion treatments were employed such as EPD for the co-deposition of biopolymers and hydroxyapatite (HA) in order to improve the biocompatibility and osteointegration of the resulting coatings and electrodeposition of metals as antibacterial agents. X-ray Diffraction and Raman Spectroscopy were carried out in order to get more insight about the composition of the multifunctional coatings, while their morphology was studied by Scanning Electron Microscopy (SEM). Their corrosion resistance was characterized by open circuit potential (OCP) measurements, electrochemical impedance spectroscopy (EIS) and by recording polarization curves in Simulated Body Fluid (SBF) at 37 °C. The amount of hydrogen evolved from corrosion of AZ31 was evaluated through GC-TCD during long-term immersion tests.

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Nickel-Iron-Oxide Catalysts for Anion-Exchange Membrane Electrolyzers

V. Baglio, A. Caprì, I. Gatto, C. Lo Vecchio

Istituto di Tecnologie Avanzate per l'Energia "Nicola Giordano" (ITAE-CNR)
Salita S. Lucia sopra Contesse 5, 98126 Messina, Italy
e-mail presenting author: vincenzo.baglio@itae.cnr.it

The efficiency of electrolysis systems depends on the kinetics associated with the oxygen evolution reaction (OER) at the anode. OER is a kinetically slow reaction (with high overpotentials) that requires efficient electrocatalysts to accelerate the reaction. The best non-PGM materials employed to date have been based on mixed transition metal oxides (Ni, Co, Fe, Mn, with spinel or perovskite structures). Nickel-iron-oxide-based materials have shown good catalytic activity towards OER.

In this work, a Ni-Fe-oxide catalyst has been synthesised by a liquid-phase method, at atmospheric pressure, via the so-called *oxalate* route. The brown precipitate obtained was then filtered under vacuum and dried in an oven at 80°C overnight. The obtained sample was subjected to different thermal treatments, at 350°C, 450°C, and 550°C for 2h, in a furnace with a heating rate of 10°C/min. The objective was to determine the effect of the calcination temperature on the structure, composition, particle size, and catalytic activity of the obtained species.

Morphological analyses were performed by Transmission Electron Microscopy (TEM). The structure and the surface composition were evaluated by X-ray diffraction analysis (XRD) and X-ray photoelectron spectroscopy (XPS), respectively. The electrochemical characterization was first performed by the Rotating Disc Electrode (RDE). Then, the catalysts were deposited by spray coating technique onto a Fumasep® FAA3-50 anion-exchange membrane to realize a catalyst-coated membrane (CCM) and tested in a 5 cm^2 single cell setup (zero-gap approach) supplying a 1 M KOH solution to the anode side [1].

The obtained results were finally compared in order to identify the optimal thermal treatment for the synthesis process. The behaviour of the catalysts was then compared with the performance shown by commercial catalysts (NiO and IrO_2) tested under the same conditions.

Acknowledgements
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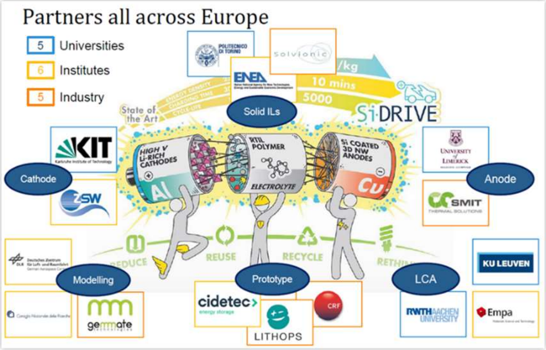
Crosslinked polymer and composite membranes as electrolytes for li-based batteries in the framework of the Si-Drive project

M. Falco[1,2], S. Saffirio[1,3], F. Smeacetto[3], G.B. Appetecchi[4], G. Meligrana[1,2], G.A. Elia[1,2], C. Gerbaldi[1,2]
[1] GAME Lab, Dept. Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi, 24, 10129, Torino, Italy and [2] National Reference Center for Electrochemical Energy Storage (GISEL) - INSTM, Via G. Giusti 9, Firenze 50121, Italy
[3] GLANCE Group, Dept. Applied Science and Technology - DISAT, Politecnico di Torino, Italy
[4] ENEA, Materials and Physicochemical Processes Technical Unit (SSPT-PROMAS-MATPRO), Roma, Italy
marisa.falco@polito.it; claudio.gerbaldi@polito.it

Currently the main application of Li-ion batteries is in portable electronics, but new emerging applications such as EVs require low cost, improved energy density, cycle life and safety [1]. The ambition of Si-DRIVE EU project is proposing next-generation batteries for EVs built in Europe, designed to ensure recycling above 50%. Si-Drive battery will contain a high specific capacity Si-based anode and a Co-free high-V cathode to reduce cost and improve sustainability.



On the electrolyte side, the 1st generation of electrolytes for Si-Drive includes selected ionic liquids with high ionic conductivity and wide electrochemical stability. The 2nd generation of electrolytes combines the ionic liquids and the precursors of the polymer matrix to obtain crosslinked self-standing flexible films. The addition of ceramic super Li ion conductors to obtain composite polymer electrolytes is also envisaged to improve the electrochemical stability window of the electrolyte [3]. Here we present the different polymer electrolytes and semi interpenetrating polymer networks encompassing ionic liquids and ceramic materials having ionic conductivity > 10 mS/cm at 20 °C, which can be in situ-deposited and crosslinked on top of the electrodes, and combined to form bi-layered electrolyte membranes to tune the compatibility with the electrode materials. The cycling performance with different positive and negative electrodes at ambient temperature is also demonstrated [4].

Acknowledgments

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Old and New Materials for the Electrooxidation of Glycerol

Nicola Comisso, Luca Mattarozzi, Lourdes Vázquez-Gómez, Enrico Verlato

ICMATE CNR, 4 Corso Stati Uniti, 35127 Padova, Italy
e-mail presenting author: nicola.comisso@cnr.it

In the frame of PNRR old and new materials has been tested for the electrooxidation of glycerol in basic media. Together with the well know palladium [1] we have tested rodium [2,3] and an alloy between these two metals [4]. A known catalyst in heterogeneous system [5], composed by two non-noble metals, prepared by electrodeposition was tested as electrocatalyst for the same reaction.

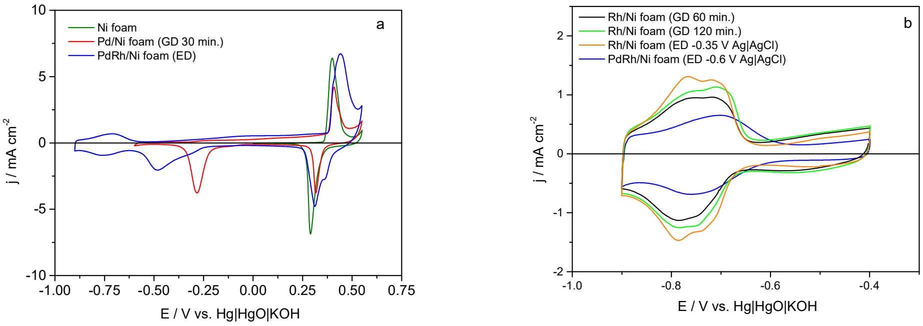

Figure 1: Voltammetric test in KOH 2 M at 25 °C under nitrogen; (a) full range; (b) limited range.

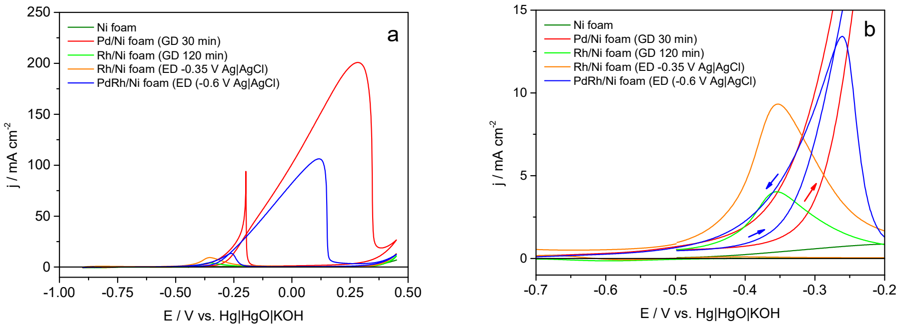

Figure 2: Voltammetric test in KOH 2 M and Glycerol 1 M at 25 °C under nitrogen, the fifth cycle: (a) full potential range, with complete oxidation peaks; (b) detail about the peaks onset.

The results obtained are interesting with some curiosity emerged during the tests.

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In-situ forming redox-mediated solid electrolyte interphase for high energy and reversible anode-less seawater batteries

Y. Kim[i,ii], G. Di Donato[iii], A. Varzi[i,ii], A. Tsusumaki[iii], M. A. Navarra[iii], S. Passerini[i, ii, iii]

[i] Helmholtz Institute Ulm (HIU), Helmholtzstrasse 11, 89081 Ulm, Germany
[ii] Karlsruhe Institute of Technology (KIT), P.O. Box 3640, 76021 Karlsruhe, Germany
[iii] Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy
mariassunta.navarra@uniroma1.it

Sodium-based batteries attract increasing research interests due to the abundance of the resources employed. A promising Na-based battery, especially for on/offshore tidal power and wind power applications, is the Seawater Battery (SWB), which employs an eco-friendly, safe, natural and widely available renewable resource, i.e., seawater. In SWBs, seawater acts as a highly abundant sodium-containing cathode material leading to a rechargeable system that can be considered as a hybrid between batteries and fuel cells [1]. Despite its high theoretical capacity (1165 mAh g^{-1}) and a very low redox potential (−2.71 vs. SHE), Na metal anodes show high reactivity towards the commonly used electrolytes, which results in the evolution of gaseous decomposition products and the risk of dendritic sodium deposition among others. Sodium biphenyl (Na-BP) is well known as presodiation agent for sodium-based batteries [2,3]. Because of its high reversibility and low redox potential (vs Na/Na^+), BP can act as redox mediator, suppressing the electrolyte decomposition at the sodium metal anode. As such, the BP anolyte contributes to the reversible sodium cation storage via the formation of Na-BP and enables the homogeneous, low-overpotential sodium metal deposition [4]. As a result, the introduction of low-cost biphenyl allows for suppressing the continuous electrolyte decomposition and mitigates sodium dendrite growth. Herein, the addition of Tin(II) chloride ($SnCl_2$) as additive in biphenyl anolyte is investigated. $SnCl_2$ enables in-situ formation of Na-Sn alloy layer. The synergistic effect of biphenyl and $SnCl_2$ improve the reversibility enebling areal capacity of 5 and 10 mAh cm^{-2} helping to harvest larger amount of Na metal.

Acknowledgements
Part of this work has been developed within the framework of the project SBAM “Stoccaggio di energia con Batterie ad Acqua di Mare” funded by MiTE (Ministero per la Transizione Ecologica), in collaboration with CSEA (Cassa per i Servizi Energetici e Ambientali), CUP: B87H21012170003. YK, AV and SP acknowledge the basic funding of the Helmholtz Association.

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Phenol abatement in a microfluidic reactor

S. Randazzo[a], A. Geagea[a,b], F. Proietto[a], A. Galia[a], O. Scialdone[a]

[a] Dipartimento di Ingegneria, Università di Palermo – Viale delle Scienze ed.6, 90128 Palermo, Italy
[b] Department of Chemical and petrochemical engineering, Université Saint Joseph de Beirut - Mar Roukoz, 0000, Beirut, Lebanon
e-mail presenting author: serena.randazzo@unipa.it

Microsystems technology, coming from information technology and miniaturization of data-processing devices, has entered many fields in daily life. In the context of chemical reactions, important potential benefits of microfluidic devices utilization, characterized by very low inter-electrode distances (in the range of tens or hundreds of micrometers), come from enhanced heat and/or mass transfer that allow better thermal control of unit operations, and from the ability to directly scale down, scale up or modularize the processes [1]. The achievement of higher product yield, selectivity and purity, improved safety and the access to new products have been claimed by researchers in the last years. Moreover, it was reported in the last few years that microfluidic reactors (MFR) can significantly improve the performances of some electrochemical processes for the synthesis of fine chemicals and the treatment of wastewater. Microreactors offer many advantages over conventional reactors; their small size and high interfacial surface areas give rise to short diffusion and conduction paths for laminar flow and enhanced mass transfer [2].

Large interest was devoted in the field of the wastewater treatment. Indeed, main advantages of the reduced inter-electrode distance in comparison with macro-devices are related to the operation with low concentrations of supporting electrolytes at low cell voltages and higher current efficiencies for the direct oxidation processes. Some preliminary works of some co-authors have shown the better performances obatiend by using microdevices [3].

However, up to now very few studies were devoted to the utilization of microreactors and no data on their utilization for wastewaters with high salinity are available.

In this work, a commercial undivided filter press flow cell equipped with one or more polytetrafluoroethylene (PTFE) spacers of micrometric thickness was used in order to evaluate the performances of this device for the degradation of phenol by anodic oxidation in the presence of chlorides. The variation of several parameters was explored also evaluating the effect on the by-products production.

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Composite Anion-Exchange Membranes for For High Performance Water Elecrolysis

N. Carboni(1), L. Mazzapioda(1), A. Caprì(2), I. Gatto(2), V. Baglio(2), M. A. Navarra (1,3)

(4) Dipartimento di Chimica, Università di Roma La Sapienza,
P.le Aldo Moro 5, 00185 Rome, Italy
(5) Istituto di Tecnologie Avanzate per l'Energia "Nicola Giordano" (ITAE-CNR),
Salita S. Lucia sopra Contesse 5, 98126 Messina, Italy
(6) Centro di Ricerca Hydro-Eco, Università di Roma La Sapienza,
Via Antonio Scarpa 16, 00161 Rome, Italy

nicholas.carboni@uniroma1.it

Alkaline technology is one of the two principal low temperature (from room temperature up to 80°C) operation techniques that is both lab-scale and commercially available, along with proton exchange membranes (PEM) electrolysis. Conventional alkaline technology is not an attractive option for renewable electricity storage because it performs poorly and is incompatible with intermittent operations when integrated with renewable energy systems due to the large inter-electrode distance and lack of a membrane separator. Alkaline water electrolyzers (AWEs) are outperformed by proton exchange membrane water electrolyzers (PEMWEs), but the latter have poor durability and are more expensive because PEMs like Nafion and Platinum Group Metal (PGM)-based catalysts are used[1]. The polymer-based Anion Exchange Membrane Water Electrolyzer (AEMWE), which has the advantage of containing non-precious metal catalysts (NPMC) and less expensive membranes, is a promising alternative for both PEMWEs and AWEs. It should combine the resilience of AWEs with the performance of PEMWEs in less corrosive environments. The poor hydroxide ion (OH^-) conductivity compared to protons (H^+), as well as the thermal and chemical stability, are the two key challenges facing the development of anion exchange membranes (AEM)[2]. To overcome those problems, in this work, various amounts of different fillers were incorporated into the Fumion® FAA-3 ionomer (10% w/w in NMP). The solvent casting technique was utilized to develop AEMs using these solutions. Cerium oxide (CeO_2) and graphene oxide (GO), the additives utilized, can theoretically improve the hydroxide conductivity and the stability of the membranes[3,4]. While graphene oxide was synthesized using a modified Hummers method[6], cerium oxide was obtained using a hydrothermal method[5]. The electrochemical investigations were conducted in a 5 cm^2 single electrolysis cell along with the morphological and structural characterizations utilizing various techniques.

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Corrosion enhanced by bacteria and archaea differently enriched on copper and copper alloys

Elena Maria Cazzulani,[i] G, Ghiara,[j]G. Chiarello,[i] P. Cristiani [z]

[i] *Università degli Studi di Milano, Department of Chemistry, Milano v. Golgi 19, 20133 Milano (Italy)*
[j]*Università degli Studi di Milano, Department SEPA, Milano v. Celoria 2, 20133 Milano (Italy)*
[i] *Ricerca sul Sistema Energetico – RSE, v. Rubattino, 54, 20134 Milano (Italy)*
e-mail presenting author: elena.cazzulani@unimi.it

The microbiological corrosion induced by methanogens is mainly studied on steel alloys, these being widely used in the Oil&Gas sector, where the most significant phenomena have been found. Most studies show that the effect of CO2-rich environments, pH and flow conditions could modify the interaction of methanogens with the substrate as for the use of hydrogenase and the catalyzation of protective corrosion products, such as Siderite or Vivianite [1]. In this work, the enrichment of a different pool of hydrogenotrophic methanogens and bacteria on the surface of two copper alloys (pure Cu and 60:40 brass) was documented, starting from the same microbial pool. The corrosion induced by methanogens enriched media, in comparison with sterilized media, were documented during replicated two-week tests. Electrochemical impedance spectroscopy (EIS) documented a different corrosion behaviour of the two materials, both affected by the biotic condition. This was confirmed by other electrochemical measurements and chemical characterizations of the corrosion products. Post-experiment observations performed by SEM and micro-Raman spectroscopy (µRS) underlined that microorganisms strongly affect the nature of corrosion products. Molecular analysis by next generation sequencing (NGS) of 16S RNA performed by swabbing the surface of the material and identifying the microorganisms constituting the microbial communities for each case evidenced a different enrichment of microorganisms depending on the material.

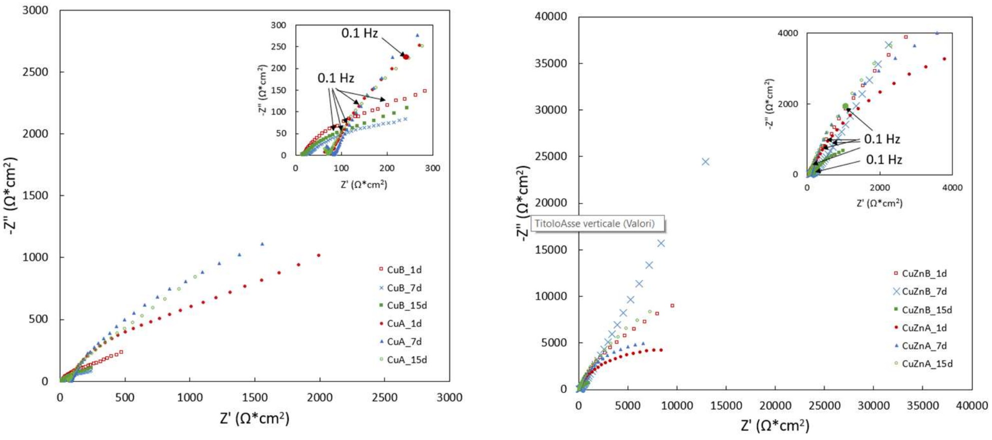

Figure 1: Nyquist plots for Cu (left) and CuZn (right) operated in biotic and abiotic conditions.

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