Società Chimica Italiana

Programma del XXVI Congresso Nazionale della Società Chimica Italiana

Centro Congressi Hotel Ariston
Paestum (SA), 10-14 settembre 2017

➢Divisione di Elettrochimica

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SOMMARIO

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Programma Scientifico

Divisione di Elettrochimica

Lunedì 11 Settembre 2017

Hotel Savoy Sala Verdi	
Sessione Elettrochimica I	
Chairperson: Musiani-Velardo	
9:00 - 9:15	*Saluto Presidente*
9:15 - 9:30	ELE OR01: La Mantia, Erinmwingbovo, Koster, Brogioli *Dynamic impedance spectroscopy of a Prussian blue derivative thin film*
9:30 - 9:45	ELE OR02: Brutti *The mixed olivine $Li(Co_{1/3}Fe_{1/3}Mn_{1/3})PO_4$ material as positive electrode for lithium batteries*
9:45 - 10:00	ELE OR03: Capobianco, Landi, Caruso, Peluso *Hole site energies and electronic couplings for hole transport in DNA inferred from electrochemistry and quantum chemical predictions*
10:00 - 10:15	ELE OR04: Valenti, Boni, Melchionna, Marcaccio, Rapino, Bonchio, Prato, Fornasiero, Paolucci *Co-axial nanostructures for energy conversion: synergic effects between carbon nanotubes and metal oxide*
10:15 - 10:30	ELE OR05: Gennaro, Lorandi, Fantin, Isse, Matyjaszewski *The use of rotating disk electrode to measure a complete set of kinetic and thermodynamic ATRP parameters*
10:30 - 11:00	Coffee Break
Hotel Savoy Sala Verdi	
Sessione Elettrochimica II	
Chairperson: Scialdone-Longoni	
11:00 - 11:15	ELE OR06: Di Noto, Negro, Vezzù, Nale, Bang, Bertasi, Pagot, Zlotorowicz, Pace *Graphene-based "core-shell" hierarchical nanostructured low-pt electrocatalysts for proton exchange membrane fuel cells*
11:15 - 11:30	ELE OR07: Passaponti, Rosi, Salvietti, Castello, Giaccherini, Innocenti *Microwave assisted pyrolysis of waste tires: evalutation by rotating ring-disk electrode technique of the catalytic efficiency in O.R.R.*
11:30 - 11:45	ELE OR08: Brandiele, Durante, Rizzi, Gennaro *New evidences of platinum-yttrium alloyed nanoparticles formation on carbon support and catalytic activity for oxygen reduction reaction*
11:45 - 12:00	ELE OR09: Dall'Asta, Buchholz, Ferrara, Changas, Quartarone, Tealdi, Passerini *$Na_{0.44}MnO_2$ - based cathodes for greener sodium-ion full cells: novel synthesis and electrode processing*
12:00 - 12:15	ELE OR10: Zaffora, Di Franco, Di Quarto, Valov, Habazaki, Santamaria *Fabrication of Hf-Nb anodic oxides and their use in resistive switching devices*
12:15 - 12:30	ELE OR11: Quartarone, Angioni, Millia, Mustarelli, Doria, Temporiti, Mannucci, Corana *Photosynthetic microbial fuel cell with polybenzimidazole-type membrane: highly efficient synergy between bacteria and microalgae for simultaneous wastewater removal and biorefinery*
12:30 - 12:45	ELE OR12: Lo Vecchio, D'Urso, Aricò, Baglio *Nanoclusters based on CoNC and FeNC for oxygen reduction reaction and their applications in direct methanol fuel cell*
12:45 - 13:00	ELE OR13: Navarra, Agostini, Lombardo, Matic, Panero *Gel polymer electrolytes for high-loading sulfur composite electrodes in Li-batteries*

13:00 - 14:00	Intervallo Pranzo

	Sala Paestum B
14:00 – 15:00	*Sessione Poster 1 (ELE PO01 – ELE PO24)*
	Hotel Savoy Sala Verdi
	Sessione Elettrochimica III
	Chairperson: Di Noto
15:00 - 15:15	ELE OR14: Dini, Bonomo, Scorretti, Di Carlo *Study of the influence of the electrolyte on the photoconversion properties of p-type dye-sensitized solar cells*
15:15 - 15:30	ELE OR15: Pagot, Bertasi, Vezzù, Nawn, Sun, Nale, Negro, Di Noto *EMImCl/(TiCl$_4$)$_{1.4}$/(δ-MgCl$_2$)$_x$ Ionic Liquid Electrolyte for Mg-ion Batteries*
15:30 - 15:45	ELE OR16: Tranchida, Pituccio, Di Franco, Di Quarto, Santamaria *Growth and characterization of atmospheric and anodic oxide films on weathering steels*
15:45 - 16:00	ELE OR17: Lo Faro, Trocino, Zignani, Aricò *Syngas production via co-electrolysis of H_2O and CO_2 fed to a Solid Oxide Cell*
16:00 - 16:15	ELE OR18: De Bon, Isse, Gennaro *Improvements of electrochemically mediated atom transfer radical polymerization of styrene with ionic liquids*
16:15 - 16:30	ELE OR19: Colo', Renault, Bella, Gerbaldi, Brandell *An electrolyte study on Na_2BDA anode for Na-based organic batteries*
16:30 - 17:00	Coffee Break
	Hotel Savoy Sala Verdi
	Sessione Premi
	Chairperson: Durante-Soldà
17:00 - 17:15	ELE PZ01: Longoni *Investigation of sodium-ion battery materials - Premio di Dottorato "Engitec Technologies"*
17:15 - 17:30	ELE PZ02: Zampardi *In situ analysis of surface and bulk phenomena in lithium-ion batteries by means of scanning electrochemical microscopy - Premio di Dottorato "Fondazione Oronzio e Niccolò De Nora"*
17:30 - 17:45	ELE PZ03: Fantin, Lorandi, De Bon, Pan, Matyjaszewski, Gennaro, Isse *Electrochemical methods for atom transfer radical polymerization of aqueous and metal free systems - Premio di Dottorato "Fondazione Oronzio e Niccolò De Nora"*
17:45 - 18:00	ELE PZ04: Pargoletti, Cappelletti, Vertova, Pifferi *Bare and titanium-doped manganese dioxide nanoparticles. Their pivotal role in energetic and sensoristic applications - Premio di Laurea "Bio-Logic SAS"*
18:00 - 18:15	ELE PZ05: La Monaca, De Giorgio, Focarete, Fabiani, Zaccaria, Arbizzani *Electrospun polymer separators based on PVdF-PEO blends for Li-ion batteries - Premio di Laurea "Photo Analytical s.r.l."*
18:15 - 18:30	ELE PZ06: Proietto, Galia, Scialdone *Electrochemical conversion of carbon dioxide to formic acid. Study of the effect of the operating parameters - Premio di Laurea "Ametek Scientific Instruments"*
	Sala Argiva
18:30 - 20:00	*Assemblea dei Soci della Divisione di Elettrochimica*

Lunedì 11 Settembre 2017

Sala Penelope
Sessione Congiunta: Chimica Analitica - Elettrochimica - Gruppo Sensori
Chairperson: Roda

11:00 - 11:20	ANA/ELE/GS KN01: Arduini, Cinti, Scordo, Massoud, Moscone, Palleschi *New sustainable and cost-effective paper-based electrochemical (bio)sensors*
11:20 -11:50	ANA/ELE/GS OR01: Scavetta, Mariani, Gualandi, Tonelli, Tessarolo, Fraboni *All PEDOT: PSS electrochemical transistors as a platform for sensing*
11:50 - 12:10	ANA/ELE/GS OR02: Soldà, Giorgio, Pelicci, Dale, Paolucci, Rapino *Development of enzyme-based microsensors for ex vivo analyses*
12:10 - 12:30	ANA/ELE/GS OR03: Abollino, Ruo Redda, Durbiano, Conca, Malandrino, Giacomino *Potential and limitations of voltammetric measurements for the characterization of electrode surface*
12:30 - 12:50	ANA/ELE/GS OR04: Fabiani, Volpe, Delibato, Pucci, Piermarini, Palleschi *Development of an electrochemical magneto-immunosensor for the detection of Campylobacter: a preliminary study*

13:00 - 14:00	Intervallo Pranzo

Sala Paestum A	
Sessione Congiunta: Chimica Analitica - Elettrochimica - Gruppo Sensori	
Chairperson: Daniele	
15:00 - 15:30	ANA/ELE/GS KN02: Lesch, Jovic, Costa Bassetto, Girault *Preparing nanoparticles on large electrodes using inkjet printing and flash light irradiation*
15:30 -15:50	ANA/ELE/GS OR05: Rapino, Trinei, Soldà, Giorgio, Bartolini, Iurlo, Marcaccio, Zerbetto, Pelicci, Paolucci *Rapid, low-cost and portable electrochemical assay for heart injury diagnosis*
15:50 - 16:10	ANAELE/GS OR06: Tomei, Neagu, Arduini, Moscone *Carbon black modified screen-printed electrodes to detect chlorine dioxide.*
16:10 - 16:30	ANA/ELE/GS OR07: Mazzaracchio, Neagu, Porchetta, Palleschi, Moscone, Pomponi, Faggioni, Lista, Arduini *Bacillus anthracis spore detection by using a label free impedimetric aptasensor*
16:30 - 17:00	Coffee Break

Martedì 12 Settembre 2017

Hotel Savoy Sala Vivaldi	
Sessione Congiunta: Chimica Fisica - Elettrochimica - Enerchem	
Chairperson: Minguzzi-Brutti	
9:00 - 9:30	ELE KN01: Ruffo *Negative electrode materials for sodium ion batteries*
9:30 - 9:45	FIS OR51: Lamberti, Litti, De Bastiani, Sorrentino, Gandini, Meneghetti, *Petrozza* *High-quality, ligands-free, mixed-halide perovskite nanocrystals ink for optoelectronic applications*
9:45 - 10:00	ELE OR20: Musiani, Verlato, Barison, Cimino, Lisi, Mancino, Paolucci *Electrochemical preparation of nanostructured CeO_2-Pt catalysts on Fe-Cr-Al alloy foams for the low-temperature combustion of methanol*
10:00 - 10:15	FIS OR52: Binetti, Le Donne, Acciarri, Marchionna *New earth-abundant thin film solar cells based on Cu_2MnSnS_4*
10:15 - 10:30	ELE OR21: Durante, Daniel, Mattiacci, Rizzi, Gennaro *Platinum free electrocatalyst based on Fe-Nx moieties supported on mesoporous carbon prepared from polysaccharides for oxygen reduction reaction*
10:30 - 11:00	Coffee Break
Hotel Savoy Sala Vivaldi	
Sessione Congiunta: Elettrochimica - Chimica Fisica - Enerchem	

	Chairperson: Binetti-Gerbaldi
11:00 - 11:15	FIS OR53: Mustarelli, Invernizzi, Patrini, Vezzù, Di Noto *Polyurethane-based Electrostrictive Nanocomposites as High Strain - Low Frequency Mechanical Energy Harvesters*
11:15 - 11:30	FIS OR54: Chiarello, Bernareggi, Pedroni, Magni, Pietralunga, Vassallo, Selli *A bilayer* WO_3 *n-n heterojunction photoanode prepared by RF diode sputtering for improved photoelectrocatalytic water splitting*
11:30 - 11:45	ELE OR22: Bella, Colò, Zolin, Pugliese, Stephan, Gerbaldi *Lignocellulosic materials for electrochemical energy storage and conversion*
11:45 - 12:00	FIS OR55: Brutti, Panero, Paolone, Reale *Hydrides as high capacity anodes in lithium cells: An Italian "Futuro in Ricerca di Base FIRB-2010" Project*
12:00 - 12:15	ELE OR23: Bertasi, Di Noto *Secondary magnesium batteries: an overview on ionic liquid -based electrolytes*
12:15 - 12:30	FIS OR56: La Gatta, Milano, Ragni, Agostiano, Farinola, Trotta *Bio-hybrid complexes in artificial photosynthesis*
12:30 - 12:45	ELE OR24: Minguzzi, Fracchia, Visibile, Naldoni, Malara, Locatelli, Vertova, Ghigna, Rondinini *Operando (photo)electrochemical X-ray absorption spectroscopy for water splitting*
12:45 - 13:00	FIS OR57: Beneduci, Capodilupo, Corrente, Fabiano, Maltese, Cospito, Ciccarella, Chidichimo, Gigli *Electronic coupling in H-shaped tetra-arylamine mixed-valence compounds*

13.00 - 14.00	Intervallo Pranzo

Mercoledì 13 Settembre 2017

	Hotel Savoy Sala Verdi
	Sessione Elettrochimica IV
	Chairperson: Mussini-Fantin.
15:00 - 15:15	ELE OR25: Di Quarto, Maniscalco, Di Franco, La Mantia, Santamaria *Synergistic use of impedance and photoelectrochemical measurements to study the electronic properties of anodic* TiO_2
15:15 - 15:30	ELE OR26: Battistel, Reynard, Dennison, Girault *Recovery of low grade heat by redox flow battery*
15:30 - 15:45	ELE OR27: Lorandi, Michieletto, Fantin, Chmielarz, Isse, Gennaro, Matyjaszewski *Boosting aqueous atom transfer radical polymerization of hydrophilic and hydrophobic monomers by means of electrochemistry*
15:45 - 16:00	ELE OR28: Chiarotto, Feroci, Pandolfi *Voltammetric analysis and chemical reactivity of ionic liquids (ILs) used as "green" reaction media and precursors of efficient catalysts*
16:00 - 16:15	ELE OR29: Scialdone, D'Angelo, Vicari, Galia *New processes to produce renewable energy: reverse electrodialysis and thermally regenerative ammonia battery*
16:15 - 16:30	ELE OR30: Comisso, Armelao, Cattarin, Guerriero, Mattarozzi, Musiani, Rancan, Vàzquez-Gòmez, Verlato *Preparation of porous oxide layers by oxygen bubble templated anodic deposition followed by galvanic displacement*
16:30 - 17:00	Coffee Break
	Hotel Savoy Sala Verdi
	Sessione Elettrochimica V
	Chairperson: Santamaria-Zampardi

17:00 - 17:15	ELE OR31: Mussini, Arnaboldi, Buzzi, Monaco, Sannicolò, Benincori, Apolloni, Penoni, Cirilli *Inherently chiral molecular materials with 2,2'- and 3,3'-bisindole atropoisomeric cores: interactions between equivalent redox sites, configurational stability and enantioselection ability*
17:15 - 17:30	ELE OR32: Macchia, Alberga, Manoli, Mangiatordi, Palazzo, Torsi *Organic bioelectronics probing conformational changes in surface confined proteins*
17:30 - 17:45	ELE OR33: Di Franco, Seyeux, Zanna, Maurice, Marcus *Physicochemical characterization and corrosion behaviour of surface oxide films on bright annealed ferritic stainless steel*
17:45 - 18:00	ELE OR34: Zignani, Reis, Saglietti, Oliveira, Trocino, Maisano, Ticianelli, Aricò, Lo Faro La_2NiO_4*@Ni core-shell based catalyst as pre-layer for a commercial Solid Oxide Fuel Cell fed with biofuels*

Premi

Premi di Dottorato

Premio "Engitec Technologies"

Gianluca Longoni, Università di Milan-Bicocca,

Premio "Fondazione Oronzio e Niccolò De Nora"

Marco Fantin, Università di Padova

Giorgia Zampardi, Ruhr-Universität Bochum

Premi di Laurea

Premio "Bio-Logic Sas"

Eleonora Pargoletti, Università degli Studi di Milano

Premio "Photo Analytical S.R.L."

Andrea La Monaca, Alma Mater Studiorum - Università di Bologna

Premio "Ametek Scientific Instruments"

Federica Proietto, Università degli Studi di Palermo

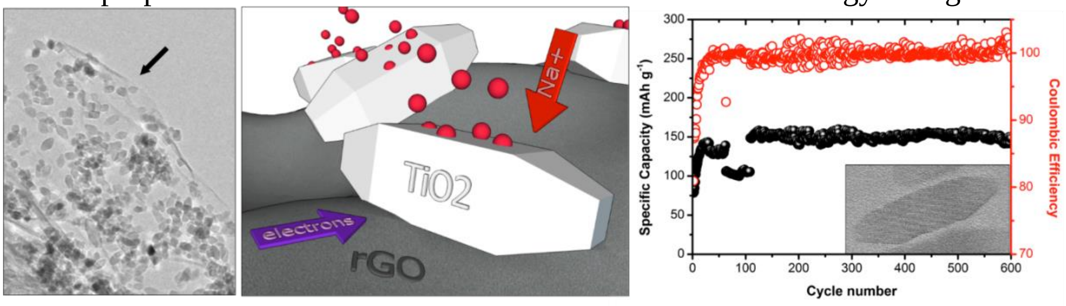
Premio di Dottorato "Engitec Technologies": Investigation of Sodium-Ion Battery Materials

Gianluca Longoni[a,b]

[a]Materials Science Department, University of Milan-Bicocca, via R. Cozzi 55, 20125, Milan, Italy,
[b]Nanochemistry Department, Istituto Italiano di Tecnologia, Via Morego 29, 16163 Genova, Italy

Na-ion battery technology has recently aroused great interest among all the scientific community as a valid and more environmentally friendly alternative to Li-ion batteries. The PhD research activity has been mostly devoted to the investigation of reliable active materials for sodium ion battery technology. All the investigated materials, either anode or cathode, have been investigated trying to highlight the major limits and difficulties connected to sodium intercalation and conversion reactions. Among these, some are: i) assessment of Na^+ diffusion in an intercalating host structure, ii)products and reversibility of transition metal oxides conversion reactions, iii) effects of materials crystalline properties on electrochemical performances and iv) features influencing the overall stability of a functional material. In order to keep the broadest view over the problem, it has been chosen to systematically start, for each species electrochemically investigated, from its synthesis and chemical-physical characterization. Rather than a pure electrochemical analysis, a continuous parallelism between morphological features, structural characteristics and performances was encouraged, eventually obtaining a detailed overlook of different classes of active materials for rechargeable (secondary) sodium-ion batteries.

The contribution will mainly focus on the most significant findings related to electrochemical mechanism-crystalline properties correlation of nanostructured anatase-TiO_2, investigated as anode material for sodium-ion batteries. A solvothermal surfactants-mediated synthesis was specifically tuned to achieve different crystalline facets expression on nano-sized TiO_2 mono crystals. An effective support on reduced graphene oxide sheets was adopted as well, in order to minimize agglomeration and crystal size biasing on sodium diffusion and electron transfer. Electrochemical properties and energy storage mechanism were thus investigated and experimental evidence of the macro-effect of crystalline facets expression on sodium uptake properly addressed. Following an intercalation pseudocapacitance-type of mechanism(1), TiO_2 crystals expressing {100} family facets predominance, ensured a relatively high cation exchange rate, accompanied with an outstanding stability over cycling, which eventually resulted in capacities above 150 mAh g^{-1} maintained for over 600 cycles(2). This work is meant to encourage the investigation of crystalline appearance-electrochemical properties correlation of nanostructured materials for energy storage.



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2. Longoni, G.; Pena Cabrera, R. L.; Polizzi, S.; D'Arienzo, M.; Mari, C. M.; Cui, Y.; Ruffo, R. Shape-Controlled TiO_2 Nanocrystals for Na-Ion Battery Electrodes: The Role of Different Exposed Crystal Facets on the Electrochemical Properties. *Nano Lett.* **2017**, acs.nanolett.6b04347.

Premio di Dottorato “Fondazione Oronzio e Niccolò De Nora”: In Situ Analysis of Surface and Bulk Phenomena in Lithium-ion Batteries by means of Scanning Electrochemical Microscopy

Giorgia Zampardi[a,b]

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The formation of the solid electrolyte interphase (SEI), which occurs through the irreversible decomposition of the electrolyte components, is of fundamental importance in lithium-ion batteries since it affects the specific irreversible charge loss, the long term stability and the safety of the battery system. Nonetheless, only few *in situ* techniques are available for analysing the SEI in its native environment (1), such as Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and differential electrochemical mass spectrometry (DEMS), and none of them allows a direct experimental observation of the SEI electronic character.

In this context, scanning electrochemical microscopy (SECM) in its feedback mode of operation has been recently proposed (2) as an *in situ* technique to visualise the conductive or insulating nature of the surface of a Li-ion battery electrode via the recycling of a free-diffusing redox couple present in solution (Fig.1).

After placing a SECM inside a glovebox (traces H_2O and O_2 < 2 ppm), the experiments were performed holding at a constant position and at a constant potential a Pt microelectrode in close proximity of a sample surface during its polarisation. Before the SEI formation, the electrode surface is electronically conductive and the current recorded at the micro-electrode in proximity of the sample surface (I_{Fb}) is higher than the one recorded in the bulk (I_{bulk}), thanks to the redox couple recycle (positive feedback). After the SEI is formed, the sample surface turns to be electronically insulating and the I_{Fb} is lower than the I_{bulk} (negative feedback). In this way, through the observation of the variation of feedback current recorded at the Pt microelectrode, it is possible to monitor the electronic character of the electrode surface under analysis, enabling the *in situ* and *in operando* determination of the SEI.

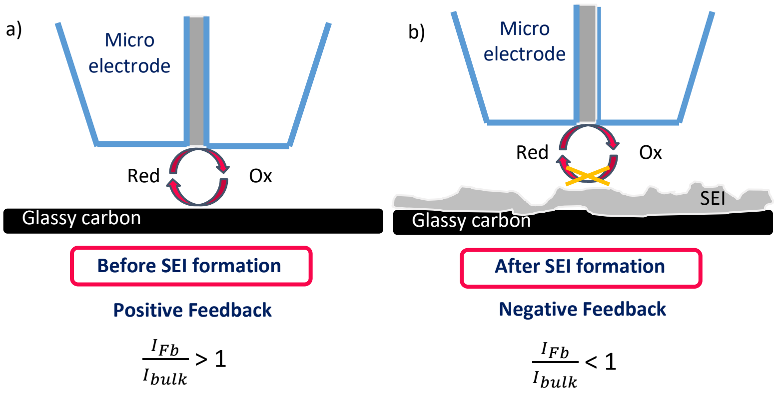

Fig.1 Schematic representation of the working principle of the feedback mode SECM applied to a Li-ion battery electrode. a) Positive feedback: no SEI on the sample surface, b) Negative feedback: SEI formed on the sample surface.

Here, an overview of the method is presented starting from its development up to the most important findings on different lithium-ion battery systems, such as: the formation of a SEI on titanium oxide based electrodes; the influence of the applied potential range on the SEI stability, the role of Li ions on the formation of an insulating layer, and the effect of commonly used additives as vinylene carbonate on the SEI formation on carbonaceous electrodes; and the nature of the surface layer formed on high operating voltage active materials for next generation Li-ion batteries.

References
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2. Zampardi G., Ventosa E., La Mantia F., Schuhmann W., Chem. Comm. 49 (2013), 9347

Premio di Dottorato "Fondazione Oronzio e Niccolò De Nora": Electrochemical Methods for Atom Transfer Radical Polymerization of Aqueous and Metal Free Systems

Marco Fantin,[a,b] *Francesca Lorandi,*[b] *Francesco De Bon,*[b] *Xiangchen Pan,*[a] *Krzysztof Matyjaszewski,*[a] *Armando Gennaro,*[b] *and Abdirisak A. Isse*[b]

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In occasion of the 2017 Ph.D. Prize "Fondazione Oronzio e Niccolò De Nora", I will present some contributions of electrochemistry to the field of atom transfer radical polymerization (ATRP).[1-9] ATRP is a controlled radical polymerization used worldwide to prepare macromolecules with complex but well-defined architectures.
ATRP is generally catalyzed by transition metal catalysts, which can be accurately investigated by electrochemical techniques. Electrochemical methods to understand the mechanism of ATRP will be discussed, together with strategies to reduce the environmental impact of the procedure. An electropolymerization approach will also be introduced.

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Premio di Laurea “Bio-Logic Sas”: Bare and Titanium-doped Manganese Dioxide Nanoparticles. Their Pivotal Role in Energetic and Sensoristic Applications

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The most prominent feature of metal-air batteries is the combination of a metal anode and an air electrode with open structure to draw cathode active materials from air (1). Oxygen reduction is the main cathodic process, but unfortunately it is affected by overpotential loss under operation conditions (1). Thus, an effective catalyst is required. Owing to their structural flexibility and versatility, manganese oxides have been widely applied in several research fields (2,3). Since MnO_2 possesses quite a lot polymorphic phases, its controlled synthesis is pivotal. Hence, this Thesis work was focused on *i*) the hydrothermal synthesis of bare and novel Ti-doped MnO_2 nanopowders, *ii*) their deep physico-chemical characterization and *iii*) their application as electrocatalysts for the Oxygen Reduction Reaction (ORR). In the synthetic route, the oxidizing agent was varied (*i.e.* $(NH_4)_2S_2O_8$ for samples labelled as MH_N and $KMnO_4$ for MH_K ones) to study the correlation between the physico-chemical properties and the electrochemical performances of the nanopowders. Indeed, it has been possible to observe that both the oxidants cations and Ti-dopant ions play a pivotal role in modifying the nanopowders structural, morphological and surface properties. For the electrochemical tests, Linear Sweep Voltammetries (LSVs) have been carried out in KOH (-1.0 – 0.0 V *vs* SCE). Gas Diffusion Electrodes (GDEs), prepared by adding the synthesized uncalcined MnO_2 to the air-cathode slurry, have performed explicitly better than GDEs made of only carbonaceous matrixes, proving synthesized MnO_2 to be good electrocatalysts for the ORR (4). Furthermore, GDE(MH_K) seems to have less diffusive limitations probably due to the much higher O_2 permeability, which is connected to the greater MH_K pore volume (confirmed by BET analyses). On the kinetic point of view (Tafel elaborations), high values of exchange current densities have been determined for GDEs with Ti-doped nanopowders. In particular, the presence of 5% Ti-doped MH_N has led to an increase of almost six orders of magnitude (4). Parallel to the above investigation, a preliminary forefront study about the use of MH_K sample (chosen for its highest BET surface area) for $CHCl_3$ detection was developed. Thus, Glassy Carbon Electrodes (GCEs) were modified by drop casting of a suspension of the adopted MnO_2 in DMF (20 µL, 0.5 g cm^{-3}). Contrary to the response obtained with only GCE (no peaks evidence), the presence of MnO_2 (at neutral pH) has caused the appearance of two peaks in the Cyclic Voltammetry (CV) anodic scan (ascribable to two characteristic reactions of MnO_2) and a further broad peak in the cathodic scan (at -0.5 V *vs* SCE) that can be due to the reduction of O_2 (5). The presence of chloroform has led to a linear decreasing of the specific CV peaks currents, because of the adsorption of the pollutant molecules onto the electrode surface (indirect detection method).

In conclusion, the present Thesis work focused on the deep investigation of bare and Ti-doped MnO_2 electrocatalytic nanoparticles showing novel and promising results (3,4).

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Premio di Laurea "Photo Analytical SRL": Electrospun Polymer Separators Based on PVdF-PEO Blends for Li-Ion Batteries

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Li-ion batteries are one of the most mature and most wide spread energy storage systems on the market. Today Li-ion technology is approaching its limits of energy density (200–250 Wh/kg) (1) thanks to new and advanced high-voltage and high-capacity electrode materials. Hence, most electrochemical research seeks to improve cycle life and safety. However, in order to meet the new conditions required by high-voltage electrodes and to enhance the other aforementioned features, the development of so-called inactive materials is mandatory. A key inactive material is the separator. In the last years electrospun polymer separators (EPS) have gained great attention for applications in lithium batteries (2) thanks to their good mechanical properties, high porosity and safety improvements. Polyvinylidenedifluoride (PVdF) and its copolymers are probably the most widely studied (3). PVdF is characterized by excellent electrochemical stability, and its high dielectric constant ($\varepsilon = 8.4$) permits better dissolution of lithium salts and, thus, a larger amount of charge carriers. One PVdF drawback is a high melting point that does not execute the shutdown function (4). We submit a novel strategy to overcome this limitation by blending PVdF with a polymer of lower melting-point such as polyethyleneoxide (PEO), which can also coordinate and transport Li^+ through local relaxation and segmental motion of its chains. Two blends with the same composition (PVdF:PEO, 90:10 w/w) were prepared using PEO of different molecular weight (Mv 100,000 and 1,000,000). For the sake of comparison, an EPS of PVdF was also prepared. The PVdF-PEO based separators ensure increased conductivities, greater electrolyte uptake and higher porosities than commercial polyolefines, all factors that improve cell performance (5,6). They are also safer than PVdF separators thanks to lower shutdown temperature, even if their mechanical properties are not yet comparable with those of the latter. The two blends were soaked in 1M $LiPF_6$ – ethylene carbonate:dimethyl carbonate (1:1 w/w) and the electrochemical performance were tested in a Li/EPS/$LiFePO_4$ cell and discussed on the basis of their physical, mechanical, thermal and morphological properties.

Acknowledgments: Alma Mater Studiorum – Università di Bologna is acknowledged for RFO financial support

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Premio di Laurea "Ametek Scientific Instruments": Electrochemical Conversion of Carbon Dioxide to Formic Acid. Study of the Effect of the Operating Parameters.

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Electrochemical conversion of CO_2 is considered one of the more appealing approaches to introduce renewable energy in the chemical and energy chain and to mitigate the greenhouse gases effect. In this work, the reduction of carbon dioxide was performed in undivided electrochemical cell to produce formic acid, which is one of the highest value-added chemicals and economically feasible for large-scale applications (1). It is well known that the main hurdle of the reduction of CO_2 from water solution is the low CO_2 solubility in water. In order to overcome this obstacle, a specific investigation on the effect of the CO_2 pressure and other operating parameters at tin flat cathodes was carried out. It was shown that an increase of the pressure leads to a drastic enhancement of the formic acid concentration. Indeed, the utilization of moderately high CO_2 pressures (15–30 bar) allowed to obtain high concentrations of formic acid (up to 0.46 mol L^{-1}) at high current density (up to 90 mA cm^{-2}) employing cheap and simple undivided cell (2).

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Keynote e Conferenze su Invito

- ANA/ELE/GS KN01: Fabiana Arduini, Tor Vergata University, Rome
- ANA/ELE/GS KN02: Andreas Lesch, EPFL Valais Wallis, Laboratory of Physical and Analytical Electrochemistry, Sion
- ELE KN01: Riccardo Ruffo, Università di Milano Bicocca

New sustainable and cost-effective paper-based electrochemical (bio)sensors

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Electronic equipment generated 9 million tons of waste in 2005 in EU, and it is expected to grow to more than 12 million tons by 2020. To decrease the environmental pollution of electronics, the development of sustainable sensors, including paper-based electrochemical devices, are attracting growing interest thanks to their cost-effectiveness, suitability for in situ analysis, and environmentally friendly.

In this keynote, we reported the recent advancements on paper-based electrochemical (bio)sensors for environmental, biomedical, and agrifood sectors carried out by our group.

We described a novel reagentless paper-based electrochemical phosphate sensor, manufactured with a simple and inexpensive approach. By following three easy steps, consisting of wax patterning, paper chemical modification, and electrode screen-printing, the filter paper provides an effective electroanalytical platform to sense phosphate ions in standard solutions and in real samples (river water). This novel and highly sustainable configuration allows for the determination of phosphate ions with high reproducibility thanks to the use of heptamolybdate as reagent loaded on paper and carbon black as ink nanomodifier, achieving a detection limit of 4 mM. The filter paper has been also combined with the butyrylcholinesterase enzyme (BChE) for the detection of pesticides in rivers and wastewaters. The principle of this approach is based on dual electrochemical measurements, in parallel, of butyrylcholinesterase enzyme activity towards butyrylthiocholine, with and without exposure to contaminated samples. The sensitivity of this device is largely improved using a carbon black/Prussian Blue nanocomposite as a working electrode modifier. A strip of a nitrocellulose membrane, that contains the substrate, is integrated with a paper-based test area that holds a screen-printed electrode and BChE, allowing a reagent-free detection of Paraoxon down to 3 µg/L. Beside the filter paper, the office paper has also been exploited as substrate to print the electrode. An office-paper based sensor has been developed for monitoring Zn(II) in biological fluids. The printed sensor modified with bismuth film has been used to detect it by stripping analysis, with a detection limit of 25 ng/mL and a relative standard deviation of 8%. To highlight the feasibility, reliability, and easiness of the proposed electrochemical sensor, Zn(II) has been detected in serum and sweat at a physiological level (µg/mL). The sensor printed on office paper has been also combined with alcohol oxidase enzyme for the detection of ethanol in beer samples. After optimizing the analytical parameters, such as pH, enzyme, concentration, and working potential, the developed biosensor allowed a facile quantification of ethanol up to 10 mM, with a detection limit equal to 0.52 mM. Recently, we have also combined the sensor fabricated using wax printing and screen-printing technologies with a printed holder made by a 3-D printing technology. This device is able to measure the BChE activity in serum, with a linear range up to 12 UI/mL and a detection limit lower than 1 UI/mL.

Preparing Nanoparticles on Large Electrodes Using Inkjet Printing and Flash Light Irradiation

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Coating electrodes with catalytically active metal and alloyed metal nanoparticles (NPs) can improve significantly the performance of commercial electrocatalytic and (bio)analytical devices. Nevertheless, the price of many noble and scarce metals requires sustainable strategies to synthesize NPs and to prepare nanoparticle-decorated surfaces. In addition, the cost-effective and high-throughput optimization of the NP properties as a result of the NP size, shape, composition and synergistic effects with support materials is very attractive for academia as well as industry. This is especially true if process conditions are easily tunable, highly reproducible and fully up-scalable.

The fabrication of NP-coated electrode surfaces can be achieved in various ways, usually started with a NP synthesis, with or without support particles and dispersed in solution, before an ink or paste is formulated. Subsequently, this mixture is casted by dropping, dispensing or printing onto the sensing device structure. Afterwards, thermal post-processing results in the removal of solvents and stabilizers achieving electrodes with catalytically active and well-adhered NPs. Alternative strategies apply metal precursors that are electrochemically, (photo)chemically or thermally (thermal decomposition by equilibrium heating in a furnace) converted into the according NPs.

In this contribution, we demonstrate our novel approach where defined thin films of metal precursors, e.g. chloroplatinic acid, are first deposited onto various electrode surfaces by using inkjet printing and then irradiated with a high energy light pulse from a Xenon flash lamp to generate NPs within a fraction of a second (1). Due to the rapid absorption of the flash light by the precursor-coated electrodes temperatures of several hundred degrees Celsius are generated immediately inside the printed films. The result is a rapid thermal decomposition of the precursor into the pure metal or alloyed metal nanoparticles. As for the well-known thermal decomposition processes at equilibrium heating conditions, side products are simply gaseous (e.g. HCl, Cl_2 and H_2O) leaving pure metal on the electrode surface (2-3).

We use an integrated inkjet printing (with three printheads) and flash light irradiation platform to prepare the NP-decorated electrodes (e.g. Pt deposited on ITO, graphene or carbon nanotubes) of square centimeter size only within few minutes at ambient conditions (4). This allows a rapid optimization and up-scaling of the process outcome. The final electrodes were optically and electrochemically analyzed, the latter in particular with Soft-Probe Scanning ElectroChemical Microscopy (Soft-Probe-SECM) (5).

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Negative Electrode Materials for Sodium Ion Batteries

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The world annual consumption of energy is in the range of 100 TWh whose largest part of this energy is supplied by fossil fuels or nuclear plants. Both these technologies are nowadays considered as not sustainable, however the global energy demand is still increasing. In this dim picture, renewable energy supplied by sun, wind, earth crust heat, and sea represent a viable and environmental friendly alternative which is leading to the investigation, development, and commercialization of new technology such as solar cells, wind mills, heat pumps, etc. The full exploitation of the energy produced by these primary sources, which are intrinsically intermittent, represents another technological issue which is currently approached by the design of better energy distribution grids and the large use of energy storage devices. Moreover, an important part of the total energy consumption is related to the automotive field, where fossil fuels still play a predominant roles. Just in the last few years the automotive market is showing an exponential growing interest in electrical power units to feed hybrid or full electrical vehicles.

Electrochemical energy storage units are currently used in high or low tech portable devices. The most demanding high tech tools require the use of high energy density system, such as lithium ion batteries. Smart grid developers or automotive engineers are looking with growing interest at the development of better batteries with higher performances, however, the figure of merits depends on the specific applications. Few years ago, due to the large use of lithium, several investigators are questioning about its availability and possible material shortness. There are several answers to this issue: the design of better lithium based systems (lithium air, lithium sulfur), the lithium recycling, actually non convenient, or the development of lithium free battery technology.

Aim of the present contribution will be the description of the current researches performed at the Material Science Department of the University of Milano Bicocca on materials for sodium ion secondary battery, focusing in particular on the negative electrode. Usually, research efforts in this field are directed towards the production of optimized phases by a trial and error procedure focused on the electrochemical performances rather than a full understanding of the mechanism beyond the electrochemical reaction. In our case, however, the scope is to elucidate the structure properties correlations by combining SEM, TEM, XRPD, and Raman measurements with the electrochemical behaviour in half cells vs. metallic sodium. Several phases, representative of different reaction classes have been investigated: conversion oxides (Co_3O_4, Fe_2O_3), intercalation or pseudo-capacitive oxides (TiO_2), and carbons, which show different reaction mechanism depending on their properties. Specific morphologies were designed to optimize the sodium uptake/release from the electrolyte addressing preparation routes towards proper particle size and shape.

Comunicazioni Orali

Dynamic impedance spectroscopy of a Prussian blue derivative thin film

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Dynamic multi-frequency analysis (DMFA) has been proposed as a technique to measure non-stationary impedance spectra, in order to extract kinetic parameters of unstable systems under non-stationary conditions. This allows an in-depth understanding of reaction pathways as the evolvement of the kinetic parameters can be monitored. We have demonstrated that the data fitting can be performed with standard equivalent circuits (1). Herein we show the application of DMFA on the measurement of the kinetic parameters for the intercalation reaction of cations in Prussian blue derivatives. The working electrode consists of a 1 mm glassy carbon electrode coated with a layer of electrodeposited Nickel hexacyanoferrate (NiHCF), which is unstable under oxidation. The electrolyte is composed by 0.5 M A_2SO_4 [A=Na, K] in water. The DMFA is performed by using multi-sine perturbation, which covers the frequency range from 8 Hz to 100 kHz, and it is added to a quasi-triangular cyclic voltammetry with scan rate equal to 160 mV s^{-1}. The impedance of the system is obtained using a modified definition of the dynamic impedance, based on the inverse Fourier transform (iFT):

$$Z(\omega, t) = \frac{\mathrm{iFT}\left[\Delta U \cdot f(\omega, bw)\right](t)}{\mathrm{iFT}\left[I \cdot f(\omega, bw)\right](t)}$$

where f represents a filter function, ω and bw are the central frequency and the bandwidth of the filter, respectively, and t is time. The obtained impedance spectra were fitted using an algorithm based on the non-linear least squares minimization with an additional constraint on the smoothing of the fitting parameter. The impedance spectra were fitted using a modified porous electrode model, taking into account a single step mechanism for the intercalation of the ion in the host structure. The fitting had a standard deviation χ^2 lower than $9.0 \cdot 10^{-4}$. The dependence of the parameters such as interface capacitance (C_{dl}), charge transfer resistance (R_{ct}) and Warburg coefficient (σ) on the potential in the cathodic scan is shown in the figure. The evolution of the parameters with the polarization potential will be discussed in the frame of the model for intercalation.

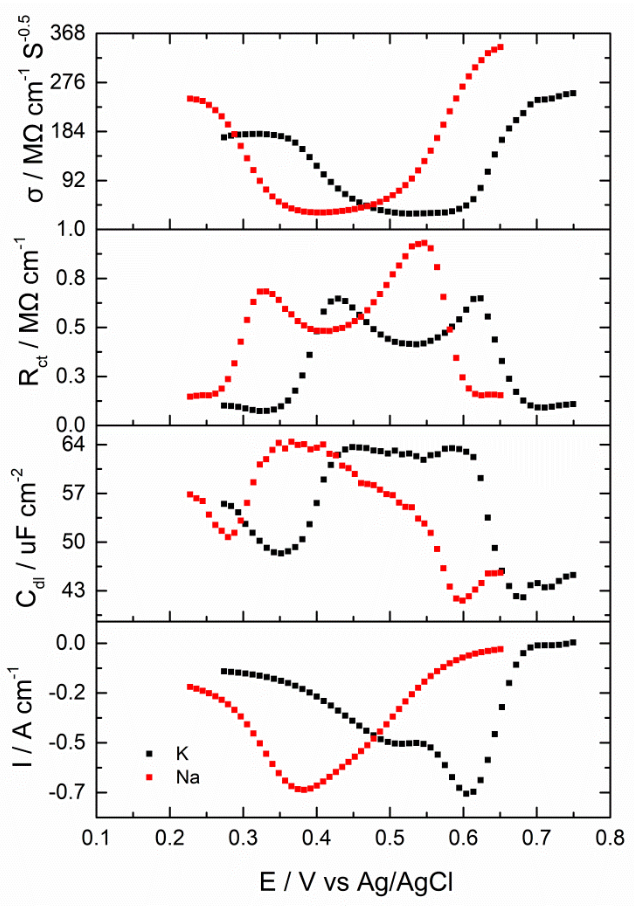

Figure: Dependence of kinetic parameters on the polarization potential in the cathodic scan.

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The mixed olivine Li($Co_{1/3}Fe_{1/3}Mn_{1/3}$)PO_4 material as positive electrode for lithium batteries

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Polyanion-type electrode materials are one of the great success in the field of electrochemistry: within this family, $LiFePO_4$ (LFP) is a now mature material exploited as cathode material in lithium-ion cells. Recently the attention of the scientific community is focusing the advantage of the substitution in the LFP olivine lattice of Fe with Mn, Co or Ni. In fact the Mn^{3+}/Mn^{2+} and Co^{3+}/Co^{2+} couples show increasing redox potentials, thus opening the door to improvements in the energy performances. The mixed $LiCo_{1/3}Fe_{1/3}Mn_{1/3}PO_4$ (LCFMP) stoichiometry is one of the most promising one. Compared to LFP in lithium cells (LIC) the LCFMP cathodes shows a similar practical specific capacity (120 $mAhg^{-1}$) and an higher working potential (4.2 V vs. Li to be compared to 3.5 V vs Li of LFP). In our laboratories developed an original synthetic route by exploiting a solvothermal treatment followed by an high temperature pyrolysis with sucrose. Our characterization suggests that the LCFMP material consisted in an single phase (see figure 1a for the X-ray diffraction pattern, XRD) crystallized in an olivine lattice similar to LFP (space group 62 Pnma with cell parameters a=10.332Å, b=6.014 Å, c=4.720Å) with an homogeneous round-shaped particle morphology of approximately 50-150 nm in diameter (see figure 1b). Moreover the LCFMP material is free from any contamination from pyrophosphates or Li_3PO_4 as highlighted by FTIR.

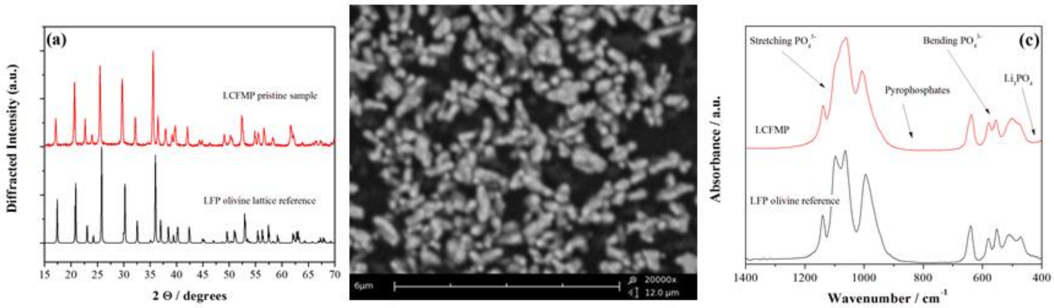

Figure 1. (a) XRD pattern of the LCFMP sample, (b) SEM micrograph and (c) FTIR spectra compared to the reference LFP phase.

The LCFMP electrodes are able to supply a specific capacity in galvanostatic tests on LICs that exceeds 165 $mAhg^{-1}$ in the first charge (corresponding to the full de-lithiation, being the maximum theoretical capacity 167 $mAhg^{-1}$) and 110 mAhg-1 in the first discharge (corresponding to 67% of reversible lithium incorporation). The capacity retention at cycle 20 is approximately >90% in discharge compared to cycle 1.

Hole site energies and electronic couplings for hole transport in DNA inferred from electrochemistry and quantum chemical predictions

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Singly ionized DNA exhibits long range hole transport (HT) covering distances up to 200 Å (1). Hole transport has great biochemical and technological relevance, as it controls the site distribution of the oxidative damage in DNA and makes DNA a potential conduit for nanoelectronics. Different mechanisms for the hole transport have been invoked so far: ion gated transport, thermal activated hopping, and superexchange among others. Independent of the kinetic mechanism, hole transfer in oxidized DNA is modulated by the complex mosaic of low-lying electronic states, whose accessibility depends on the effective in-situ hole energies of nucleobases and the electronic couplings between interacting nucleobases (2,3).

The hole energies for adenine (A) and guanine sites were quantified by using voltammetry, the influence of hydrogen bonds on the oxidation potential was also determined. Information for cytosine oxidation was inferred by spectroelectrochemistry experiments (4-6).

Herein we have used the above data to obtain a complete set of hole-site energies and electronic couplings covering all nucleobases, including pyrimidines, which are very difficult to oxidize in solution. The above quantities have been estimated by analyzing in terms of the two-state model the oxidation potentials inferred from differential pulse voltammetry and the ionization potentials predicted by quantum chemical computations carried out for oligonucleotides including the sugar-phosphate backbone and solvation

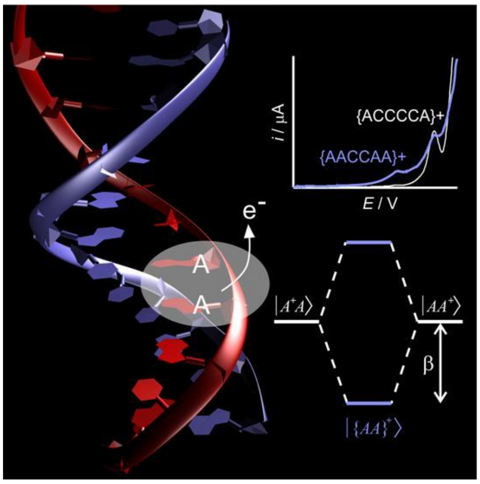

Figure 1: differential pulse voltammograms of adenine-rich single stranded oligonucleotides rationalized in terms of the two-state model.

Hole energies and electronic couplings were then used as parameters in a simple tight-binding model Hamiltonian, which allows for the prediction of reliable estimates of the oxidation potential of any DNA sequence. As an example, the lowering of the oxidation potential for single stranded oligonucleotides containing an increasing number of adjacent adenines is predicted to be ca 0.25-0.30 V for the AA step, in good agreement with voltammetric observations (0.27-0.31 eV). That result testifies that adenine tracts give rise to delocalized hole domains (Figure 1), greatly facilitating hole transport in DNA (7). Although stacking interactions are found to be less effective in stabilizing the positive charge on adjacent guanines inside a strand, our model confirms that consecutive guanines constitute a very efficient trap for the hole (8).

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Co-axial Nanostructures for energy conversion: synergic effects between carbon nanotubes and metal oxide

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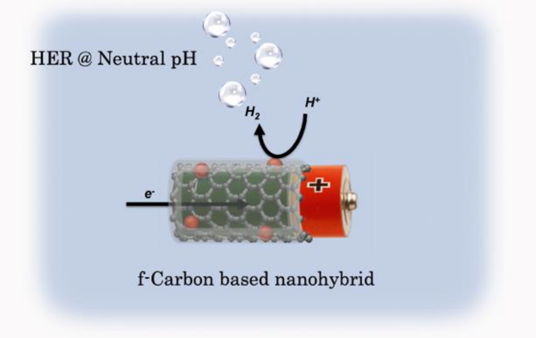
The growing need for energy on global scale and the realization that the so called oil-based economy cannot sustain our world anymore, prompted researchers to find new ways to "power" the planet.(1) In particular a lot of efforts have been done in the field of chemical energy conversion, that remains very challenging because of the requirement for higher efficiencies.(2) The splitting of water to high energy chemical fuels is one of the most attractive and pursued alternatives; among the major issues there is the need to find catalytic systems that are able to boost the overall reaction efficiently and durably.(3)

In this context our group recently focused the attention on the study of catalytic systems for the oxygen reaction (such as oxygen evolution (4) and oxygen reduction (5)). Our last efforts have been done in the development of new C-based nanocomposites that combine the unique properties of multiwall carbon nanotubes (MWCNTs), metal oxides (TiO_2 and CeO_2) and Pd nanoparticles (Pd NPs).(6) The nanocomposites MWNT@Pd/TiO_2 and MWNT@Pd/CeO_2 have been designed and evaluated as electrocatalyst for the reaction of hydrogen evolution (HER) and for the CO_2 reduction, respectively.

Both systems exhibit very good performances and efficiencies, showing physical and chemical properties that differ to those expected from the simple sum of the individual building blocks. Due to these synergic effects, we shed light on the role of the MWCNTs in terms of their influence on the electronic properties of the two semiconductors (e.g. presence of surface states and different doping levels), resulting in better electrocatalytic activities.



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The use of rotating disk electrode to measure a complete set of kinetic and thermodynamic ATRP parameters

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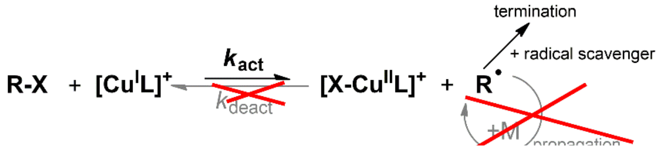
Electrochemical tools are extensively used to study mechanisms and kinetics of various processes. Atom Transfer Radical Polymerization (ATRP) is the foremost technique in the synthesis of macromolecules with predetermined molecular weights (MWs), narrow MW distribution and finely tunable architectures. A thermodynamic and kinetic understanding of this process is required for a wise selection of the proper setup and experimental conditions.



Scheme 1. ATRP mechanism for k_{act} determination.

In 2011, we firstly proposed the use of a rotating disk electrode (RDE) to measure the activation rate constant, k_{act}, of ATRP, with relative ease and precision compared to traditionally used techniques (UV-Vis, stop-flow) (1,2). The activation reaction is kinetically isolated by adding an excess of a radical scavenger that reacts with generated radicals (**Scheme 1**). k_{act} is measured by monitoring the decrease of limiting current of $[Cu^IL]^+$ oxidation, which is proportional to the amount of catalyst consumed by reaction with the initiator, RX.

Recently, we adapted this approach to measure the equilibrium constant, K_{ATRP}. Indeed, by simply omitting addition of the radical scavenger and allowing the system to equilibrate, K_{ATRP} can be determined by using a slightly modified version of an equation proposed by Fischer (3). Under particular conditions, K_{ATRP} can be determined only by using a huge excess of RX, otherwise Cu(I) is consumed by a side reaction known as Cu(I) catalyzed radical termination (CRT) (4). However, once K_{ATRP} is measured, k_{CRT} can be obtained with the same technique if $C_{Cu(I)} = C_{RX}$. Moreover, under the last cited conditions, an excess of radical scavenger can be added after few minutes, allowing the simultaneous determination of k_{act} and K_{ATRP} (**Fig. 1**). k_{deact} is then known as K_{ATRP}/k_{act}. Concluding, by means of RDE, the complete set of thermodynamic and kinetic parameters of ATRP can be quickly determined. The reproducibility of the data was also carefully verified.

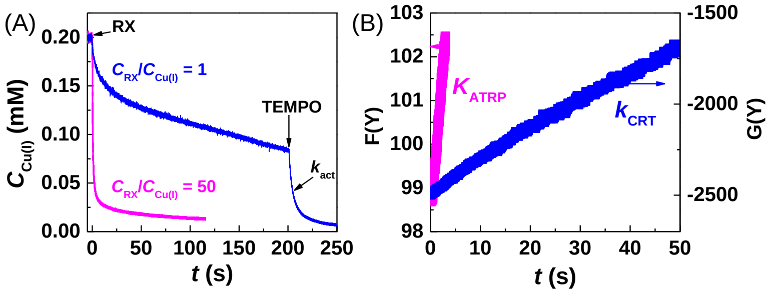


Figure 1. Disappearance of Cu(I) vs. time (A) and fitting of elaborated data (B) for the reaction of 10^{-3} M $[Cu(I)Me_6TREN]^+$ with methyl 2-bromoproprionate in MeCN, T = 40 °C. F(Y) and G(Y) are functions of $C_{Cu(I)}$.

Acknowledgment: The author FL wants to thanks Fondazione Gini for the financial support.

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Graphene-Based "Core-Shell" Hierarchical Nanostructured Low-Pt Electrocatalysts for Proton Exchange Membrane Fuel Cells

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The operation of proton exchange fuel cells (PEMFCs) is bottlenecked by the sluggishness of the oxygen reduction reaction (ORR) (1). Accordingly, the development of advanced electrocatalysts (ECs) capable to promote the ORR kinetics is one of the main goals of the research. It is further highlighted that, as of today, the only ORR ECs capable to provide PEMFCs with a performance level compatible with applications require a high loading of strategic elements such as platinum-group metals (PGMs), raising critical issues associated with supply shortages and high costs (1).

This work addresses the above points by the development of innovative ECs characterized by the following features: (i) a low loading of PGMs; (ii) an improved ORR activity in comparison with conventional state-of-the-art ECs (2); (iii) a *"core-shell"* morphology. In the proposed ECs the *"core"* support exhibits a hierarchical structure including the following constituents: (i) graphene flakes, to exploit the benefits associated with the large specific surface area and high electron mobility of graphene (3-6); (ii) carbon black nanoparticles, to further promote the mass and charge transfer processes of the ECs; and (iii) copper nanoparticles, which are introduced as a sacrificial component modulating the EC morphology and the chemical composition of ORR active sites. The hierarchical *"core"* support is covered by a carbon nitride *"shell"*, providing *"coordination nests"* that embed the ORR active sites (7). The latter are based on a very low loading of Pt (*ca.* 3 wt% of the EC) and also include Ni and Cu as *"co-catalysts"*. The proposed L-PGM ECs are obtained customizing the synthetic protocol devised in our research group (7). In this work, the final ECs are obtained after a post-synthesis activation process carried out by electrochemical cycling, that plays a crucial role to modulate the physicochemical properties and the morphology. Preliminary results indicate that the proposed approach is promising, as the proposed L-PGM ECs exhibit an improved specific and mass activity in comparison with the state of the art.

The assay of the metals in the L-PGM ECs is evaluated by inductively-coupled plasma atomic emission spectroscopy (ICP-AES). Vibrational spectroscopies (e.g., confocal micro-Raman) and wide-angle X-ray diffraction (WAXD) are adopted to probe the structure. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM), both conventional and at high resolution, are used to study the morphology. Cyclic voltammetry with the rotating ring-disk electrode method (CV-TF-RRDE) investigates the electrochemical performance and ORR reaction mechanism. Finally, the fuel cell performance in operating conditions is tested on PEMFC prototypes including the proposed L-PGM ECs at the cathode.

Acknowledgements: This work was funded by the Strategic Project of the University of Padova "From Materials for Membrane-Electrode Assemblies to Energy Conversion and Storage Devices – MAESTRA". The research leading to these results has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n°696656.

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Microwave Assisted Pyrolysis of Waste Tires: Evaluation by Rotating Ring-Disk Electrode technique of the catalytic efficiency in O.R.R

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In recent years the fossil sources dependence of our society for both fuels and essential raw materials and the global warming have led to an increasing use of renewable sources and waste valorization processes. Nowadays the outstanding increase in the number of vehicles worldwide is among the most environmental problem because of the emission of harmful pollutants and the solid wastes disposal, in particular the removal of the used tires (1). There are several technologies for tires recycling. Thermal treatments may be used such as pyrolysis: a thermal decomposition process performed at higher temperature in an inert atmosphere which allows the transformation of complex substances in simple molecules. Pyrolysis transforms starting materials into three potentially useful classes of products: char, liquid and gas. These products can be easily stored, transported and used as a source of chemicals and energy. Among several heating technologies and apparatus used in pyrolysis process, microwave assisted pyrolysis (MAP) attracted attention, in recent years, due to the considerable advantages of this technology over conventional pyrolysis process (2,3,4). The use of microwaves requires the presence of material: water, carbon, metals or materials able to absorb microwaves and releasing energy. Recently Undri et.al (5) reported the correlation between experimental conditions of pyrolysis (MAP) and some of the characteristics of char. Interesting ICP-MS analysis showed the presence of several metal. It was observed that char obtained from microwave assisted pyrolysis of waste tires showed an interesting electrocatalytic activity in the Oxygen Reduction Reaction (ORR) in alkaline medium. ORR is regarded as one of the most important electrocatalytic reactions in electrochemical energy conversion system such as fuel cells and several industrials process. In order to speed up the ORR kinetics to reach a practically usable level in fuel cell, a cathode ORR catalyst is needed. Platinum-based materials are the most practical catalyst. Nevertheless, owing to the limited reserve in nature of Platinum-group metals, and their high cost, extensive research has focused on developing alternative catalyst. To remove and replace platinum with less expensive materials it was proposed to exploit a synergic mechanism with one metal able to break the O-O bond of molecular oxygen and second metal capable in reducing the adsorbed oxygen so formed. The basic idea of this work comes from the consideration that the presence of specific metals in addition to an appropriate rate together with a high carbon content are mandatory requirements for catalysts for ORR (6).

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New evidences of platinum-yttrium alloyed nanoparticles formation on carbon support and catalytic activity for oxygen reduction reaction

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Recently, the preparation of Pt bimetallic systems has attracted considerable attention because the amount of Pt could be reduced while the catalytic activity and stability may be maintained or even improved, due to the so called "*geometric effect*" and "*ligand effect*". From theoretical calculations Pt_3Y exhibits the second highest ORR activity ever measured on a polycrystalline electrode, surpassed only by single crystal Pt_3Ni (111) and, above all, it has a catalytic activity greater than pure platinum (1,2).

In this work Pt_xY NPs, where Y atoms are in part alloyed with the Pt, were synthesized via a solid state method involving the chemical reduction of $Pt(acac)_2$ and $Y(NO_3)_3 \cdot 6H_2O$ salt precursors by H_2/N_2 flow at high temperature on different carbon supports.(3)

The influence of the Pt_xY formation, NPs shape and dimension, and ORR activity, in terms of mass activity (MA) and specific activity (SA), were investigated with different commercial and homemade carbon support, which possess different surface area, porous distribution, conductivity and surface functional groups. XPS and XRD analysis confirmed the Pt_xY alloy formation. The best syntheses afforded small spherical Pt_xY NPs (2.71 nm) on a commercial Carbon Black (Pt_xY@MC7) and on MWCNT (Pt_xY@MC5), which showed a higher current densities than the Tanaka catalyst but containing a lower amount of Pt. The mass activity determined at 0.9 V vs RHE were 606 mA/mg$_{Pt}$ and 453 mA/mg$_{Pt,}$ respectively. The catalytic activity towards ORR was compared with the commercial Tanaka taken as standard reference (205 mA/mg$_{Pt}$), confirming the increased activity of the Pt_xY alloy.

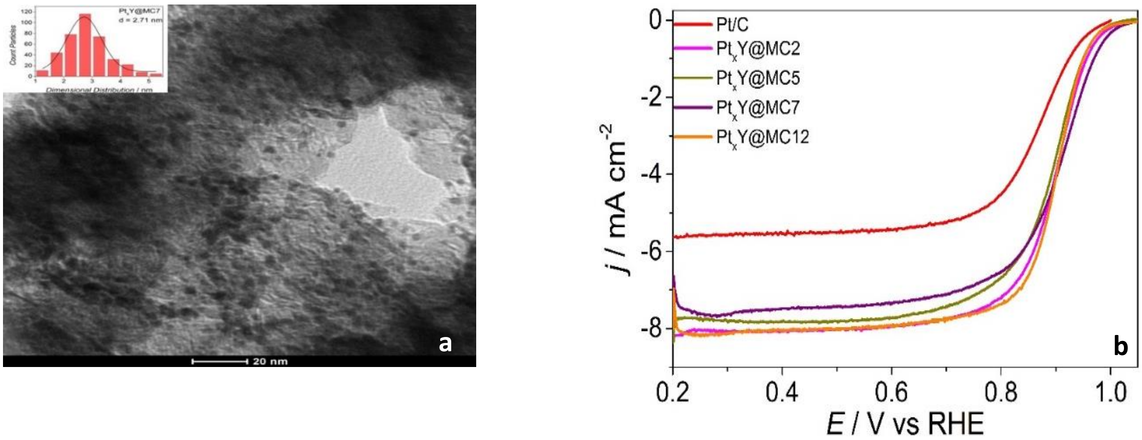

Figure 1 (a) TEM image for the best Pt-Y/C catalysts and particle size distribution; (b) LSV on several prepared catalysts and Tanaka Pt/C 50% in O_2 saturated 0.1 M $HClO_4$ recorded at RDE, v = 20 mVs^{-1}, rotation rate 1600 rpm.

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Na$_{0.44}$MnO$_2$ - based cathodes for greener sodium-ion full cells: novel synthesis and electrode processing

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Due to lithium shortage and its high costs, the current research regarding energy storage/conversion devices is trying to shift from the conventional lithium technology to newer ones. In particular, sodium-ion cells are now being studied not only to improve their electrochemical performances like capacity retention and durability but also to decrease their environmental impact, using non-harmful chemicals. Here, we present a Na$_{0.44}$MnO$_2$ (NMO) - based cathode that has been casted employing CarboxyMethylCellulose (CMC) as binder, thus allowing us to substitute the toxic N-methyl-2-pyrrolidone with water to carry out the electrode processing. The electrode was tested with various electrolyte compositions to find out the optimized combination of the two cell components that could decrease the counter-electrode polarization, and at the same time improve the capacity retention thanks to a synergistic effect, to reach the ultimate goal of preparing a CMC – based full cell. Then, to furtherly take into account the environmental problems, we have focused on the synthetic strategy to prepare the NMO powder. We developed a cheaper alternative to the solid-state synthesis (SS), reported by Sauvage et al(1), (that we were employing during the over-mentioned studies): the "urea based - combustion synthesis (CS)". This method was definitely faster and less expensive than the conventional one: it employed lower temperatures, shorter annealing times and an eco-friendly chemical like urea. Furthermore, the CS-NMO powder being composed by micro-slabs smaller than the ones composing SS-NMO (see figure 1-a), guarantees better electrochemical performances particularly at high C rates (see figure 1-b).

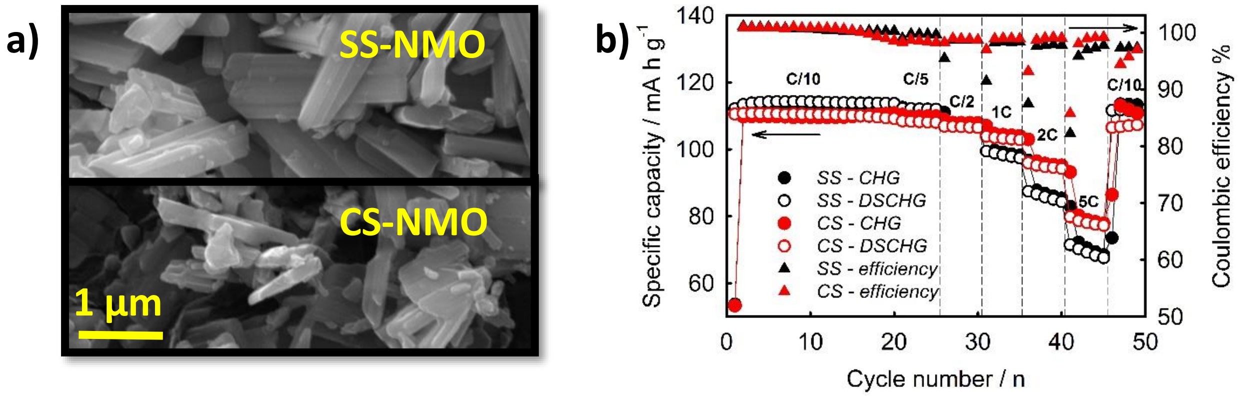

Figure 1 | a) SEM micrographs of the SS-NMO and CS-NMO powders acquired at a SEM Mag. of 50.0 kx. b) Galvanostatic cycling at various C rate of SS-NMO and CS-NMO electrodes employing the same electrolyte composition (NaPF$_6$ 1M in PC).

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Fabrication of Hf-Nb Anodic Oxides and Their Use in Resistive Switching Devices

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In last decades scientists efforts have been devoted to find new materials to replace SiO_2 as dielectric in micro and nanoelectronics devices. Among transitional metal oxides, HfO_2 is nowadays one of the most suitable materials due to their peculiar features, such as large band gap (5.1-6.1 eV), high dielectric constant (20-25), low leakage current and thermal stability with Si (1). For electronics applications, such as ReRAMs (Redox-based resistive switching memories), uniform, flaw-free and smooth oxides are necessary, joined with a detailed understanding of chemical and physical properties as a function of the fabrication conditions. Despite the oxide films have macroscopic dielectric (high-*k*) properties, deposited as nanoscale thin films they behave as solid electrolytes (2). Anodizing is a low-cost electrochemical technique which allows to grow barrier-type oxides on valve metals (Hf, Nb, Ta, Ti etc.) surface whose structure, morphology, composition and thickness can be easily tailored by controlling the process parameters. Recently it was also reported that alloying low amounts of Nb to Hf substrate leads to anodic films with higher dielectric constant with respect to that of pure HfO_2 (3). In order to properly change anodizing conditions to obtain suitable oxides features, a study about growth kinetics of Hf-Nb mixed anodic films is needed, since amorphous-crystalline transition during the oxide growth was reported in literature for similar anodic films, with consequent detrimental effects on oxides properties (4).

This work is aimed to study the changes of oxides features during anodic films growth of sputtering-deposited Hf-Nb alloys. Mixed oxides were prepared by anodizing alloys with different Nb content (from 4at.% to 76at.% of Nb) in neutral electrolyte with different growth rates and up to different formation voltages. Morphological and structural features were analyzed by *ex-situ* X-Ray Diffraction, Glow Discharge Optical Emission Spectroscopy, Transmission and Scanning Electron Microscopy, X-Ray Photoelectron Spectroscopy. Photoelectrochemical measurements, differential capacitance and impedance measurements were carried out in order to study oxides solid state properties and to estimate their dielectric constant. Finally we fabricated ReRAM-type devices by depositing Pt top electrodes on the anodic films surfaces. Electrical characterization was performed to check, first of all, whether these devices exhibit resistive switching and, in addition, they are suitable for the use in redox-based memories.

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Photosynthetic microbial fuel cell with polybenzimidazole-type membrane: highly efficient synergy between bacteria and microalgae for simultaneous wastewater removal and biorefinery

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There is growing interest towards simultaneous production of bioenergy and valuable materials by PMFCs. We showed very efficient systems based on polybenzimidazole as separator. Two cells were investigated, Pt-electrocatalysed and Pt-free, operated as microbial carbon capture devices, by using wastewater as anolyte and *Scenedesmus acutus* strain in the catholyte. The Pt-cell generated higher power density over 100 days, resulting in improved wastewater treatment efficiency.

The CO_2 fixation of PMFC grown microalgae leaded to high production of valuable compounds. Significant quantity of lutein was obtained, as well as relevant amount of other carotenoids. Lipids were excellently accumulated (49%$_{dw}$) in the C_{16-18} range, particularly indicated for the biofuel production.

We demonstrate the implemented sustainability of such PMFCs as technology for simultaneous wastewater treatment and biorefinery. The use of PBI is very promising for energy performances and sustainability. It is also autoclavable, so allowing a re-use of the separator with beneficial cost effects.

Nanoclusters based on CoNC and FeNC for oxygen reduction reactions and their application at the cathode of a direct methanol fuel cell

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Polymer electrolyte fuel cells (PEFCs) are attracting remarkable interest as an alternative power source with low environmental impact. Direct methanol fuel cells (DMFCs) are a subcategory of PEFCs well suited for portable applications. Nowadays, the widespread commercialization of a DMFC is hindered by the cost of the components. This cost is, in part, due to the precious metals, in particular Pt, used as the catalysts of the fuel cell. To solve this problem, the attention of many researchers is focused on the replacement of the expensive Pt catalyst with more abundant non precious metals. Here, in-house CoNC and FeNC have been prepared by, first, chelating the metals with ethylene diamine tetra acetic acid, known as EDTA (nitrogen precursor). UV-Visible (UV-Vis) spectrometry has been used to ensure the chelated metal formation. In the next step, the chelated metals have been deposited on a high surface area oxidized carbon support to increase the electrical conductivity. The latter composite material has been thermally treated at 800°C (CoNC8 and FeNC8) or 1000°C (CoNC10 and FeNC10) in nitrogen atmosphere in order to create the catalytic sites that will be able to perform the oxygen reduction reaction (ORR) in the acid medium. Electrochemical tests have been carried out to investigate the activity of the electro-catalysts for the ORR and the performance and durability in DMFCs. Moreover, some portions of the most performing electro-catalysts have been treated in HNO_3 to leach out the unalloyed ions and, then, thermally treated a second time. Informations about the crystalline structure, size and morphologies have been obtained by X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques, whereas the elementary percentage composition has been studied with CHNS analyser and energy dispersive X-ray spectroscopy. Finally, the nature and the oxidation states of the nanoclusters have been related to the electrochemical results by using X-ray photoelectron spectroscopy (XPS).

Gel polymer electrolytes for high-loading sulfur composite electrodes in Li-batteries

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Important safety hazards are related to the use of liquid electrolytes in lithium batteries, due to the volatility of organic molecular solvents, the limited temperature range for safe ion conduction and fear of leakage of the solution.

Various attempts have been made to overcome these problems. An approach, which reduces flammability, is the replacement or the hybridization of volatile solvents with ionic liquids (ILs). Moreover, the idea of using IL-Li salt solutions or their mixture with molecular solvents to form gel-type polymer electrolytes (GPE) has been successfully demonstrated, achieving improved safety and stability (1,2,3).

In this work, optimized liquid electrolytes, composed by ether-based solvents with and without an ionic liquid additive, were used to swell selected polymer matrices. The proposed GPEs reveal advanced performance in Li-S batteries, by addressing the issue of sulfide anions dissolution from high-loading sulfur cathodes.

Two different approaches, suited for polymer matrices based on polyethylene oxide (PEO) and polyvinylidene fluoride (PVdF), will be discussed. In both cases, a pristine membrane is first prepared and then activated by the liquid electrolyte, according to a well addressed swelling procedure.

Acknowledgements:
The results of this work have been obtained in the framework of the Projects AnaLiS (Advanced, nanostructured, lithium sulfur batteries with high storage capability), funded by Sapienza University of Rome (DR n. 88569, 16/12/2016), and LISSEN (Lithium Sulfur Superbattery Exploiting Nanotechnology), funded by the European Community (Seventh Framework Program, project number 314282).

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Study of the influence of the electrolyte on the photoconversion properties of *p*-type dye-sensitized solar cells

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In the framework of the research on dye-sensitized solar cells of *p*-type (*p*-DSCs) the definition and optimization of the electrolyte have been the most crucial aspects for the reach of the recent records of photo-conversion for this type of photoelectrochemical devices (1-3). At the basis of this progress there was the replacement of the redox shuttle of reference I_3^-/I^- (4) with opportune redox mediators which deliver higher photocurrents and produce larger open circuit photovoltages with respect to I_3^-/I^-. In the present study we intend to optimize the chemical composition of the liquid electrolyte for *p*-DSCs employing different couples of redox mediator, various additives for the stabilization of the photocathode surface (made of NiO), and variable concentrations of redox shuttle, supporting electrolyte and surface stabilizers. Beside the general conditioning of the overall performance, the analysis of the influence of *p*-DSC electrolytes has concerned the aspects of the extent of optical self-absorption of the electrolyte, of the chemical aggressiveness of the redox species and of the control of the phenomena of electronic back-donation by the photoreduction product. Non obvious correlations have been found between the four main cell parameters (overall efficiency, short-circuit photocurrent density, open circuit photovoltage, fill factor) and the conductivity of the electrolyte. Another relevant aspect of the investigations here reported has concerned the influence of the electrochemical stability of the electrolyte on the general performance of the *p*-DSC.

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EMImCl/$(TiCl_4)_{1.4}$/$(\delta\text{-}MgCl_2)_x$ Ionic Liquid Electrolyte for Mg-ion Batteries

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The rapid advance in the fields of portable electronics, load leveling and peak shaving for the power grid and zero-emission automotive applications require the development of new and improved electrical energy storage systems (1). Since the 90's major improvements have been achieved in magnesium battery technology (2-4). In comparison to Li, Mg offers the following advantages: (i) a higher volumetric capacity (3832 vs. 2062 $mAh\cdot cm^{-3}$); (ii) far greater abundance in the Earth's crust, lowering the costs; (iii) a safer operation and a better compatibility with the environment; and (iv) an acceptable standard reduction potential (-2.36 vs. -3.04 V) (5-7). The main roadblock for these devices is the development of an efficient and stable electrolyte that is able to reversibly deposit and strip magnesium. Although Grignard and other organo-magnesium compounds exhibit good electrochemical performances (7), they do not exhibit an optimal stability due to their high vapor pressure and flammability. Ionic liquids dissolving a Mg salt with a high crystalline disorder were proposed as promising alternative electrolytes to organo-Mg systems owing to their good electrochemical performance and lack of flammability and thermal stability issues (8,9).

In the present work a new family of electrolytes is proposed, based on 1-ethyl-3-methylimidazolium chloride (EMImCl), titanium(IV) chloride ($TiCl_4$) and increasing amounts of $\delta\text{-}MgCl_2$. Specifically, four EMImCl/$(TiCl_4)_{1.4}$/$(\delta\text{-}MgCl_2)_x$ electrolytes, with $0.00 \leq x \leq 0.23$ are prepared and extensively characterized. The chemical composition was determined by Inductively-Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The thermal stability was gauged using High-Resolution Thermo Gravimetric Analysis (HR-TGA) and the phase transitions are highlighted with Modulated Differential Scanning Calorimetry (MDSC). Chemical interactions were studied through Fourier-Transform spectroscopy in the medium and far infrared (FT-MIR and FT-FIR) regions and confocal micro-Raman spectroscopy. The electrochemical performance was studied with: (i) Cyclic Voltammetry (CV), to probe Mg deposition and stripping; (ii) Linear Sweep Voltammetry (LSV), to evaluate the electrochemical stability window; (iii) Chronopotentiometry (CP) experiments coupled with ICP-AES, to confirm and quantify the Mg deposition; and (iv) Broadband Electrical Spectroscopy (BES), to elucidate the long-range charge migration mechanisms of the electrolytes. High level density functional theory (DFT) based electronic structure calculations were undertaken to elucidate structures and vibrational frequency assignments.

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Growth and Characterization of Atmospheric and Anodic Oxide Films on Weathering Steels

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Nowadays Weathering Steels are considered a good compromise between Carbon Steel, in terms of their corrosion resistance, and Stainless Steels due to their much lower price (1). They contain less than 3% of elements such as Cr, Ni, Cu and P, providing much higher atmospheric corrosion resistance due to the formation of thick (up to tens μm) passive films. Thanks to their properties COR-TEN (CORrosion resistance and TENsile strength) weathering steels can be widely use in coastal atmospheres for the construction of bridges, transmission tower, buildings, guardrails, lighting poles, ornamental sculptures, facades and roofs, and there has been an increase in the use of this material in recent years as part of the image of contemporary cities (2).

It is known that after a long term exposure in aggressive and corrosive ambient it is formed in WS surface an adherent rust layer with oxides/oxi-hydroxides mainly constituted by magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), lepidocrocite (γ-FeOOH), akaganeite (β-FeOOH), goethite (α-FeOOH). Several papers tried to highlight the role of alligants in influencing the composition, structure and, consequently, corrosion resistance of passive films on WS (1,3). According to the authors these films show a multilayer structure with an inner compact and adherent layer constituted mainly by Cr, Cu or P enriched α-FeOOH, and an outer porous layer working as a barrier toward diffusion of aggressive species toward the metal (1,3,4). Formation of α-FeOOH is crucial to provide good corrosion resistance to WS, so it is necessary to understand how corrosion conditions can lead to the formation of a more or less protective compact rust layer.

In this work we studied the corrosion resistance of WS after long term atmospheric corrosion in quasi neutral aqueous solution without and with the addition of chloride ions. For comparison we also prepared anodic films on WS by potentiostatic polarization below and above the transpassive potential. Polarization curves were recorded to estimate the corrosion potential, the corrosion current density, as well as the pitting potential in presence of Cl- ions. Electrochemical impedance spectroscopy (EIS) was employed to estimate the polarization resistance. In order to get information on the electronic properties of the passive films, we also performed a photoelectrochemical investigation to estimate their band gap and conductivity type. We also studied the dependence of the measured capacitance as a function of the potential to highlight the formation of a compact thin barrier layer and a porous thick outer layer. All the experimental findings were finally used to get more insight the passivation mechanism of WS during exposure to atmospheric conditions.

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Syngas production via co-electrolysis of H_2O and CO_2 fed to a Solid Oxide Cell

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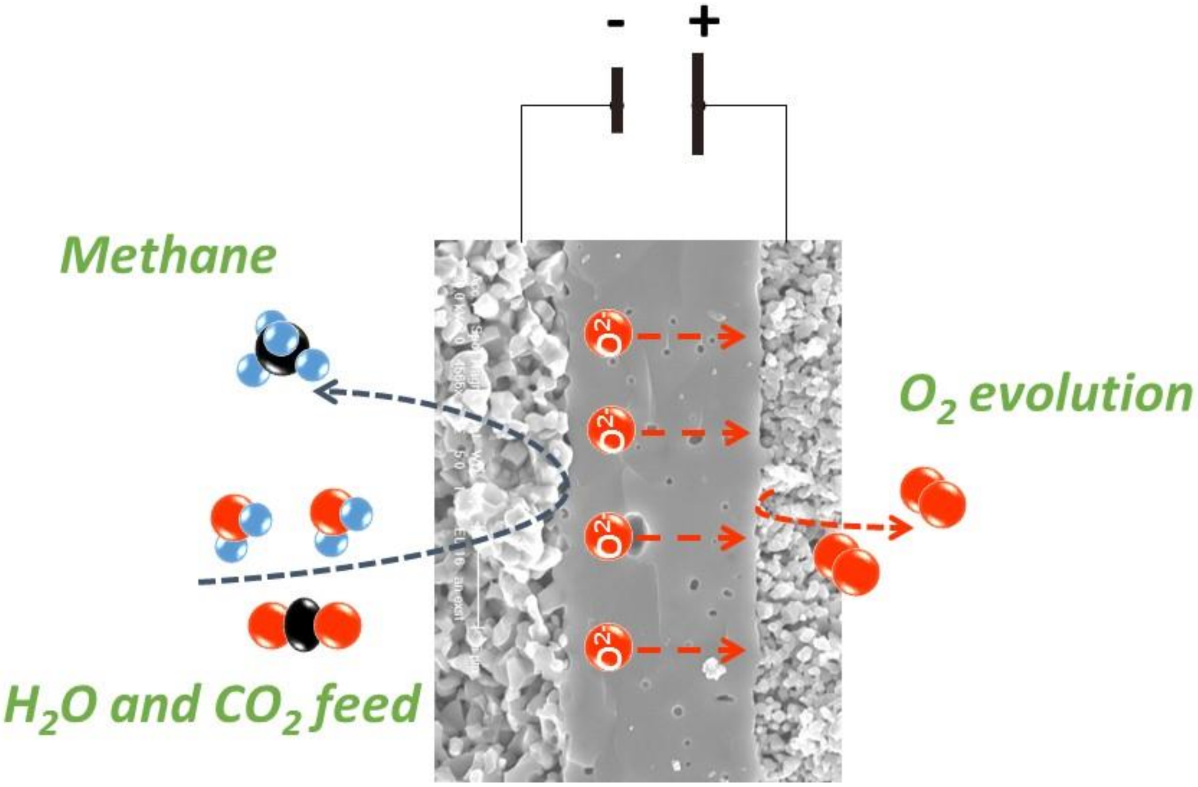
An investigation of syngas production using solid oxide electrolysis was carried out. A conventional solid oxide cell based on Ni supporting cathode, thin yttria-stabilized zirconia electrolyte, yttria-doped ceria interlayer, and strontium-doped lanthanum cobaltite and ferrite-based perovskite anode (Ni-YSZ/YSZ/YDC/LSFC) was used for the reduction of CO_2 and water to syngas. This process was assisted by H_2 added to the reactant in various amounts to maintain the Ni sites in a metallic state. This is necessary to favour CO_2 reaction and to avoid any ohmic constraint that may derive from the occurrence of Ni re-oxidation as consequence of the presence of oxidising species like CO_2 and water. The outlet gas was analysed by gas chromatography. The presence of CO and CH_4 beside CO_2 and H_2 was detected in the outlet stream. Analysis of outlet gas composition revealed that CO was produced by both electrochemical and catalytic mechanisms. Suitable conversions were achieved with dry gases.



SEM image of a planar SOEC operating in co-electrolysis mode

Improvements of electrochemically mediated Atom Transfer Radical Polymerization of Styrene with ionic liquids

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Atom Transfer Radical Polymerization (ATRP) is a powerful and versatile polymerization technique for the synthesis of polymers and copolymers of precise architecture. Polymerization is mainly catalyzed by Cu complexes with amine ligands and a reversible exchange of a halogen atom between a dormant species P_n-X and $[Cu^IL]^+$, which produces the propagating radical $P_n^\bullet$ and $[XCu^{II}L]^+$, is at the heart of the process. The equilibrium is strongly shifted toward the dormant state ($K_{ATRP} << 1$), thus the concentration of $P_n^\bullet$ is very low and terminations are negligible (1). Electrochemically mediated ATRP (*e*ATRP) is an advanced ATRP technique allowing fast (re)generation of Cu^I from Cu^{II}, easy control of the distribution of Cu(I) and Cu(II) species and the possibility of switching the process from active to dormant state and vice versa (2,3). Room Temperature Ionic liquids (RTILs) are green salts, which are gaining relevance in many applications for their non-volatility, non-flammability and versatility. They solvate a wide range of compounds in a wide range of conditions. In electrochemistry, they act as both solvents and background electrolytes, allowing elimination of additional supporting electrolytes. ATRP of styrene has several drawbacks including long reaction time due to propagation rate, high temperatures (>100 °C), limited conversion and limited solubility of polystyrene in polar solvents. 1-butyl-3-methylimidazolium trifluoromethanesulfonate, [BMIm][OTf] has been used for the first time in *e*ATRP of styrene. The results show that polymerizations performed in this ionic liquid are significantly faster than those in common organic solvents. However, the limited solubility of polystyrene in [BMIm][OTf] caused precipitation and poor control of the reaction. It was found that running the polymerization in ethyl acetate, a green solvent, using the ionic liquid as supporting electrolyte (less than 0.5 M) strongly enhance polymerization rate with narrow dispersity and higher conversion, compared to pure ethyl acetate. The polymerization of styrene was studied also in polar solvents such as dimethylformamide, dimethylsulfoxide and acetonitrile, where longer reaction times, higher dispersity and lower conversions were observed. In conclusion, *e*ATRP of styrene in ethyl acetate using [BMIm][OTf] as supporting electrolyte performs well and provides good results in a system greener than conventional ATRP. Thanks to the use of electricity, no by-products are produced since no chemical reducing agents are involved; moreover, the system requires a low catalyst load that does not contaminate the polymer.

Acknowledgments – With the contribution of Fondazione Cariplo, grant no. 2011-1851 and Università di Padova (CPDA150001). FDB thanks Fondazione Cariparo for a PhD fellowship.

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An Electrolyte Study on Na_2BDA Anode for Na-Based Organic Batteries

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Energy production and storage plays a key role in the development of portable devices, hybrid and electric vehicles and in the energy storage system for renewable energy, such as wind and solar resources. Lithium ion batteries (LIBs) dominate the global market on these, but the geographically constrained resources and the difficult extraction of metallic lithium lead to prices increment, removing the idea of low-cost technologies.

An alternative on lithium technology is sodium, very abundant, cheap and with suitable electrochemical properties, close to those of lithium. A lot of work on sodium technology has to be done in order to catch up with lithium (1).

Electrode materials research is the first step which must be done for meet the high energy storage demand. At the moment the most common chemistries used in batteries are based on inorganic compounds (e. g. $LiCoO_2$, $LiMn_2O_4$, $Li_4Ti_5O_{12}$, etc…), that are expensive and synthesized from high temperature reactions, and also the end-of-life treatment is difficult and energy greedy. One possible approach as alternative is switching to the organic based materials, in which a lot of synthesis routes can be chosen and a lots of compounds can be synthesized. Furthermore, the possibility to prepare materials from recyclable organic materials (e. g. biomass) is really appealing (2).

However, organic compounds are often associated with drawbacks such as poor conductivity, low energy density and high solubility in liquid electrolytes. Especially for the last point an accurate study on the electrolytes involved in the batteries is mandatory, because is well known how the ion-transport media affect the performances of the batteries system.

In this work we present an overview on our recent results on using disodium benzenediacrylate (Na_2BDA) as electrode material for Na-based organic batteries (3,4), in different electrolyte media. In particular, the galvanostatic cycling behaviors in Na|electrolyte|Na_2BDA pouch-cell configuration are shown.

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Electrochemical preparation of nanostructured CeO_2-Pt catalysts on Fe-Cr-Al alloy foams for the low-temperature combustion of methanol

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Methanol is a valuable energy feedstock for the future beyond oil and gas, due to its easy storage as a liquid at room temperature, and an excellent fuel for catalytic combustion, a process that is stable in a wide methanol/air operating range, and produces ultra-low NO_x, CO and VOC emissions. Lightweight catalytic burners are often realized using metal foams, due to their outstanding properties in terms of heat and mass transfer coupled with low pressure-drops and thermal resistance. Among the foam materials, Fe-Cr-Al alloy (Fecralloy) have outstanding resistance to high temperatures.

The procedures for depositing firmly anchored, homogeneous catalytic layers onto the foam substrates are often cumbersome and involve many steps. Therefore, there is interest for innovative preparation methods which take advantage of the metallic nature of the foam support, such as electrodeposition and spontaneous deposition through galvanic displacement. Both approaches are capable to form well-dispersed, homogeneously distributed noble metal nano-particles strongly adhering to the substrate (1, 2).

As a part of an ongoing research project, our groups have recently prepared Pt-based structured catalysts for the low-temperature combustion of methanol by electrochemical methods (3). These catalysts consisted of Pt nanoparticles, deposited onto Fecralloy foam supports by pulsed electrodeposition from H_2PtCl_6 aqueous solution, and CeO_2 thin films electrodeposited from a nitrate baths. Reduction of nitrates induced a local pH increase at the foam/electrolyte interface and caused the precipitation of mixtures of $Ce(OH)_3$ and CeO_2, which were converted to CeO_2 by heating in air. The Pt loading in the catalysts was measured by ICP-MS, while the noble metal surface area was determined by cyclic voltammetry, through the H desorption charge. Although the presence of a CeO_2 film decreased the Pt surface area accessible to electrolyte it enhanced the performance of the catalysts towards methanol combustion, without affecting the activation energy of the process. The enhanced catalytic performance of the CeO_2-Pt-Feclalloy catalysts as compared to Pt-Fecralloy was ascribed to the formation of additional active sites along the interface of CeO_2-coated Pt nanoparticles.

Acknowledgements. The authors acknowledge the financial support of the Italian Ministry for Economic Development (MiSE) and MiSE-CNR Agreement on National Electrical System.

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Platinum free Electrocatalyst based on Fe-Nx moieties supported on Mesoporous Carbon prepared from polysaccharides for Oxygen Reduction Reaction

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The physical amount of platinum existing on the Earth is barely enough to cover the world demand in the next forty years for fuel cell vehicles. Furthermore, the high cost and the low durability of platinum-based catalysts are serious obstacles to the large-scale commercialization of PEMFCs. Nitrogen doped mesoporous carbons are emerging as a new class of Pt free materials for ORR (1,2) In particular, it was observed that doped carbons containing small amount of transition metals, such as Fe or Co, can catalyze the O_2 reduction to H_2O at overpotentials comparable to that of the most active Pt catalyst (3).

In this paper, nitrogen doped mesoporous carbons containing Fe (Fe@N-MC) were prepared from agarose gel embedding an iron ($FeCl_2$, $FeSO_4$, etc.) and nitrogen (1,10-phenanthroline) precursors. The formation of a hydrogel embedding an iron metalorganic complex, assures an optimal Fe dispersion before pyrolysis. Several types of porogen agents (silica, carbamate, carbonate, etc.) were inserted to induce a hierarchy pore structure in the final pyrolyzed material. After the freeze-drying of the gel, aimed at removing the gelling solvent, the material is subjected to a first thermal treatment at 500 °C, obtaining a crude product, which is further activated at high temperature 900 °C under hydrogen flow. XPS analysis reveals the presence of various forms of iron oxides and a distinct peak due to the Fe−Nx bond at 708.6 eV (Fig. 1a). Beside Fe-Nx not visible from TEM analysis, iron is present as core shell NPs with iron oxide core and carbon shell. The catalytic performances of catalyst ink prepared from Fe@N-MC were investigated by cyclic voltammetry and by rotating ring-disk electrode in 0.1 M $HClO_4$ attesting that O_2 is reduced following an almost $4e^-$ pathway at very positive potentials (0.8 V vs RHE) (Fig. 1b).

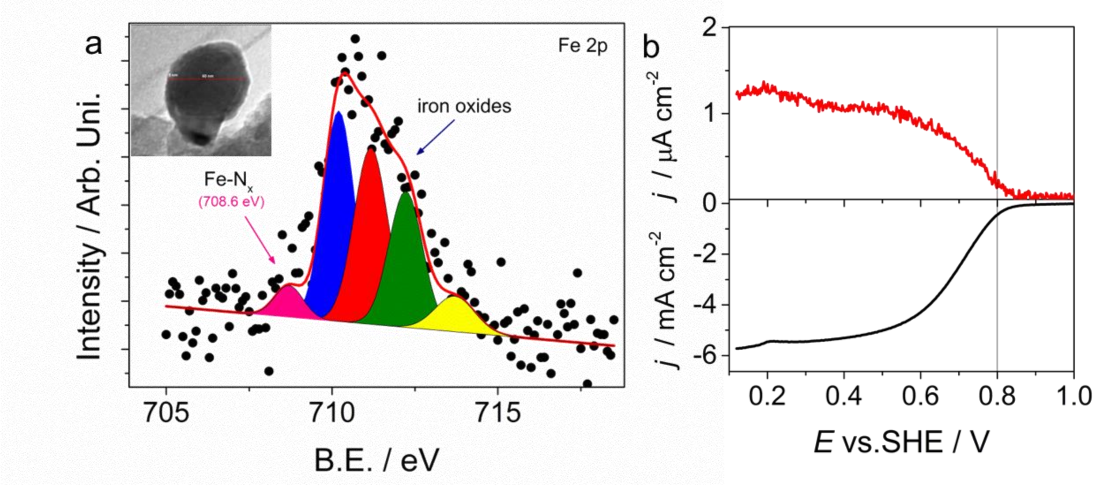

Figure 1. (a) Fe 2p XPS detailed study and deconvolution signals, and Fe NP TEM image. (b) Example of RRDE measurement on Fe@N-MC in 0.1 M $HClO_4$ at 1600 rpm and υ = 5 mV/s.

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Lignocellulosic Materials for Electrochemical Energy Storage and Conversion

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In the last 20 years, the Li-ion battery market has rapidly grown thanks to the extensive diffusion of mobile electronics devices. In order to lower the cost and reduce the environmental impact of batteries, efforts must be devoted to reduce the amount of inactive components in the cell, to substitute synthetic polymer binders/separators and organic solvents with low-cost and biosourced materials and to develop new eco-friendly processes for the manufacture of cell components (both electrodes and electrolyte). Natural nanoscale-microfibrillated cellulose (NMFC) fibers are readily available; they show stiffness, impressive mechanical robustness, low weight and, furthermore, their preparation process is easy and does not involve chemical reactions.
Here we review the use of paper-making technique for manufacturing:

- Bio-inspired all-paper Li-ion polymer cells, constituted by NMFC-binded paper-electrodes, and NMFC reinforced polymer electrolytes (1). The use of NMFC as filler/binder leads to produce high performing, safe and extremely flexible electrolytes for LiBs. No organic solvents or synthetic polymer binders are used during the entire electrode/electrolyte/cell preparation process.
- Cellulosic membranes as separators/electrolytes for post-lithium technologies, such as Na-ion and Li-S (2,3), thus demonstrating the possibility of obtaining “truly green” energy storage devices in the near future.
- Paper-based flexible electrodes and electrolytes for third generation solar cells (4), useful to lower oil-derived components and typical temperatures used to electrodes processing.

This materials platform is promising not only for the sustainable manufacture of energy devices components, but also for their processability at the end of life. For example, the all-paper lithium cell can be easily re-dispersed in water by simple mechanical stirring, as well as common paper handsheets and battery materials can be recovered using well-known water-based recycling process.

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Secondary Magnesium Batteries: an Overview on Ionic Liquid -based Electrolytes

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A critical roadblock toward the development of post-lithium-ion batteries is the lack of electrolytes that are safe and electrochemically stable whilst demonstrating good compatibility with the electrode materials (1).

It was recently shown that haloaluminate ionic liquids (ILs) can provide a viable alternative to conventional electrolytes due to their low volatility, negligible flammability and good electrochemical performance (2,3,4).

Following this, an overview on recent advancements on electrolytes for secondary Magnesium batteries is presented with particular reference to imidazolium and pyrrolidinium -based ionic liquids. Insights on the interplay between structure and conductivity of BF_4^-, $Cl^-/AlCl_3$ and I^-/AlI_3 -based systems are given, thus providing an in-depth understanding of the relation between Mg-ion speciation, long-range charge transfer mechanism and electrochemical performance of this very promising class of materials.

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Operando (photo)electrochemical X-ray absorption spectroscopy for water splitting

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Electrochemical in-situ and operando X-ray absorption spectroscopy (XAS) represents one of the most powerful available tools to study the fine structure and the behavior of electrode materials. This serves to better elucidate important reaction mechanisms and to better define structure/activity relations.

This becomes particularly crucial in electrocatalysis, for studying the oxidation state transitions and during the catalytic cycle, in photoelectrochemistry, for highlighting the local structure and the kinetics of charge recombination/transfer at surface defects and/or to study charge transfer among different layers in composite photoelectrodes.

In our recent work, we developed new methods and techniques to carry out operando XAS on electrodes and photoelectrodes with the aim of highlighting: (i) the kinetics of charge transfer across interfaces (1,2), (ii) the role of the (photo)electrode material during the reaction process (3), (iii) the role of the overlayer in composite photoelectrodes (4).

In particular, we developed FEXRAV (5), that consists in recording the absorption coefficient at a fixed energy while varying at will the electrode potential and allows to quickly map the variation of the oxidation states of the element under consideration in a desired potential window.

More recently, we carried out the first experiment on pump&probe operando XAS on a photoelectrode (6). In addition, we extended the use of energy dispersive XAS to Ir-based electrocatalysts (7) and improved the use of operando XAS for the steady-state study of photoelectrodes by recording parallel dark/light spectra adopting an innovative procedure (4).

This presentation is devoted to review some of our most significant studies, with a particular emphasis on both photoanode, (α-Fe_2O_3 /IrO_x, α-Fe_2O_3/NiO(OH)) and photocathode (Cu_xO) systems.

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Synergistic use of Impedance and Photoelectrochemical Measurements to study the electronic properties of anodic TiO_2

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Anodic titanium oxide has attracted much attention due to its potential widespread applications, including capacitors, photocatalysis and solar energy conversion. For capacitor applications in the microelectronics industry, a dense and flaw-free barrier oxide must be formed as a dielectric layer. In contrast to anodic aluminium oxide ($\varepsilon_{ox} = 10$) and tantalum oxide ($\varepsilon_{ox} = 27$), which are currently used in commercial electrolytic capacitors, anodic oxide films on Ti develop with a high population density of flaws on high purity titanium in aqueous electrolytes. Thus, anodic titanium oxide-based capacitors have not been realized practically despite the large permittivity of the oxide. Effective suppression of crystallisation has been demonstrated by incorporation of silicon species from the metal substrate, i.e., anodizing of a Ti–6at.% Si alloy (1). Another investigated strategy to hinder TiO_2 crystallization is to induce incorporation of foreign species from the electrolyte. Their concentration and distribution influence the electronic properties of the anodic oxides and, consequently, the onset of crystallization. In the present work we want to show the effect of anodizing condition on the structure on anodic oxide on Ti.

The anodic films were prepared according to two different procedures: 1) a patented procedure, consisting of a pickling step carried out in a 5% HF/40% HNO_3 mixture followed by an anodizing step (potensiostatic polarization at 3.9 V for 30 min) in HCl (18.5%v/v) (Pedeferri's treatment); 2) a pickling step carried out in a 5% HF/40% HNO_3 mixture followed by a potenziostatic anodization at 5 V vs. Ag/AgCl for 30 min in 0.1 M sodium biborate aqueous solution (pH = 8.5). Photoelectrochemical measurements were performed in order to estimate band gap, flat band potential and conductivity type of the anodic films as a function of growing conditions, while information of the dielectric constant of the oxides were obtained by impedance measurements. The differential capacitance curves recorded at several frequency of the a.c. signal are interpreted in the frame of amorphous semiconductor Schottky barrier, since the usually employed Mott and Schottky model results to be not suitable to explain the dependence of the measured capacitance as a function of potential. The experimental findings were used to sketch the density of states distribution for amorphous TiO_2 as a function of the anodizing conditions.

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Recovery of Low Grade Heat by Redox Flow Battery

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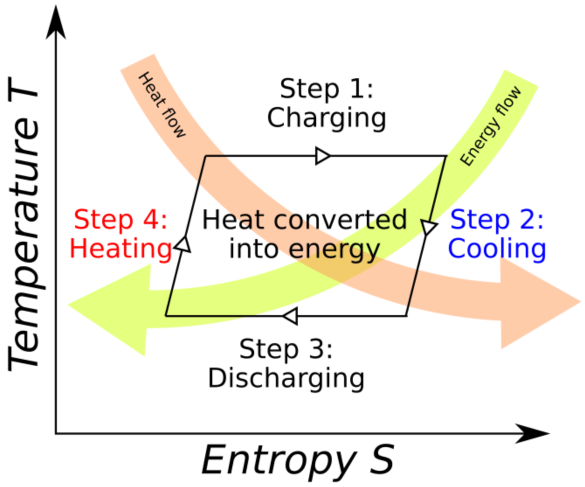
Low grade heat, heat available at temperature lower than 250 °C and even below 100 °C, is everywhere. It is available from solar concentrator and geothermal sources or from domestic and industrial heat waste. It is speculated that only in USA it is possible to recover 8000 TWh of heat per year (1).

However, it is difficult to recover such heat because of the low thermal difference. Recently, an American group introduced the thermal regenerative electrochemical cycle (TREC) as new strategy to recover low temperature heat (2). In the TREC a battery is charged and discharged at two different temperatures as shown in the figure and the variation in cell voltage is used to recover energy. The figure shows the example of a battery charging at higher temperature and discharging at lower temperature. Because of different thermal coefficients in the anodic and cathodic reaction, voltage is larger during discharge than during charge which results in a net conversion of thermal energy into electrical energy.



Thermodynamic cycle for a TREC with heat and energy flow directions.

In this work, we demonstrate the use of a redox flow battery to recover low grade heat. All-vanadium redox flow batteries are a promising technology for large scale energy storage. Unlike conventional batteries, the charge is stored in the liquid phase and not in the electrodes. Two acidic electrolytes, one containing V^{V}/V^{IV} redox couple and the other containing V^{III}/V^{II} redox couple, circulate between the tanks reservoirs and the electrode compartment. This kind of battery has the advantage that the reservoirs and the tube connections can be used directly as heat exchangers. In thermal regenerative operations, the battery, as exemplified in figure, absorbs heat during charge storing it as electrical energy in the electrolytes and release it upon discharge rejecting the heat into the environment.

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Boosting aqueous Atom Transfer Radical Polymerization of hydrophilic and hydrophobic monomers by means of electrochemistry

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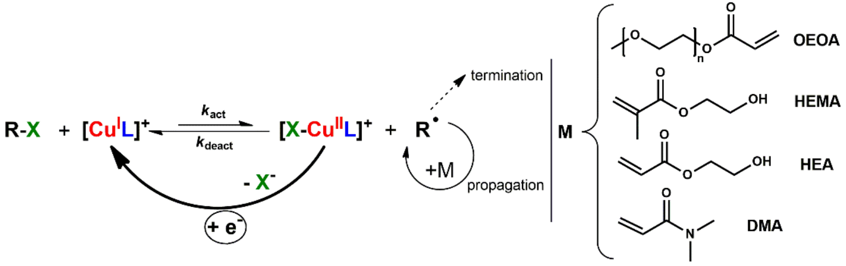
Water is a green, inexpensive, and non-toxic medium, widely used to run controlled radical polymerizations of hydrophilic monomers. Moreover, increasing interest is devoted to the aqueous polymerization of hydrophobic monomers, because water ensures good heat transfer and low viscosity.

Atom Transfer Radical Polymerization (ATRP) is the most used technique to produce polymers with predetermined molecular weights (MWs) and complex architectures. Electrochemistry allows to tune the control over the process, in the so-called Electrochemically mediated ATRP (*e*ATRP). Despite the challenges of aqueous *e*ATRP, oligo (ethylene glycol) methyl ether methacrylate (OEOMA) was successfully polymerized by *e*ATRP, identifying the best conditions over several parameters: monomer loading, pH, nature and amount of halide ions, and applied potential (1,2).

Herein, the *e*ATRP of other hydrophilic monomers is reported (**Scheme 1**). Favorable conditions for OEOMA were adapted to its acrylate equivalent, OEOA, and hydroxyl ethyl (meth)acrylate (HEA and HEMA). Linear kinetics, experimental MWs matching theoretical values and narrow MW distribution confirmed the controlled process. *e*ATRP was successfully applied to another family of hydrophilic monomers, acrylamides, after preliminary electrochemical investigation of the properties of ATRP catalysts in these media.

Moreover, *n*-butyl acrylate which is a hydrophobic monomer, was polymerized in water with good yield and very narrow MW distribution, in a miniemulsion environment (3). To achieve these results a hydrophilic catalyst was combined to an anionic surfactant, forming ion-pairs able to enter the hydrophobic monomer droplets and catalyze the process. This novel catalytic concept was deeply studied by means of Cyclic Voltammetry, determining the amount of complex bound to the surfactant. Overall, *e*ATRP was confirmed as a versatile and robust technique for the aqueous polymerization of both hydrophilic and hydrophobic monomers.



Scheme 2. Mechanism of eATRP and hydrophilic monomers emploid in the present work.

Acknowledgment: This work was supported by the University of Padova (CPDA150001). FL wishes to thank Fondazione Aldo Gini for a financial support.

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Voltammetric analysis and chemical reactivity of ionic liquids (ILs) used as “green” reaction media and precursors of efficient catalysts

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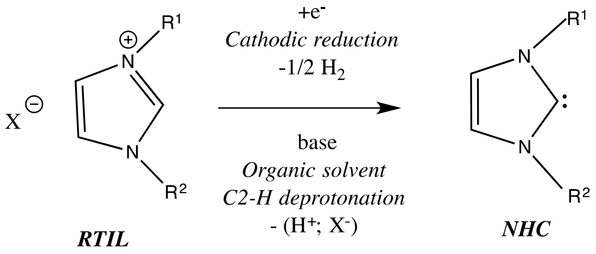
Room temperature ionic liquids (RTILs), owing to their specific properties (chemical and thermal stability, etc.) have been frequently used as “green” reaction media in clean organic syntheses as substitutes for conventional, toxic and volatile organic solvents (VOCs). Considering that an organic synthesis often involves the generation of a significant amount of wastes, the scientific community is strongly interested in alternative methodologies according to the current pressing demand of a sustainable chemistry. Therefore, the discovery of “greener” and efficient catalysts and mild conditions for their generation in the reaction mixture are regarded as significant targets in modern organic synthesis. In the past few decades, N-heterocyclic carbenes (NHCs) have emerged not only as powerful ligands for transition metals (1) but also as organocatalysts (2) for various molecular reactions and as catalysts in metal-free polymer synthesis.(3) Owing to the acidity of the C2-H group of imidazolium salts, NHCs could be prepared by deprotonation of these structures with suitable bases. Also the electrochemical methodology allows obtaining NHCs by cathodic reduction of azolium salts, thus avoiding the utilization of bases.(4) Nevertheless, some NHC-catalysed reactions, or anyhow requiring the presence of NHC, were carried out using imidazolium based acetate or chloride salts in the absence of any base or reducing agent purposely added to the reaction mixture.



Due to its excellent sensitivity, voltammetric measurement can highlight the presence of NHC. The voltammetric analysis will be directed to realize the role of the anion part of the salt as regards the possible presence of free NHC in neat ionic liquids. The electrochemical behaviour of different salts systems will be presented in order to clarify whether the catalytic activity is due to the anion, the NHC or both. Further information can be obtained by evaluating the influence of cation and anion of different salts using them as bases in two classical and important base-catalysed reactions: the Knoevenagel condensation and the transesterification reaction.

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New processes to produce renewable energy: reverse electrodialysis and thermally regenerative ammonia battery

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In the last years, research activities increasingly focused on renewable energy sources characterized by no emission of environmental unwanted substances, no thermal pollution and without net emission of greenhouse gases. In this frame, various processes were studied in the last years including microbial fuel cells, reverse electrodialysis, microbial reverse electrodialysis and thermally regenerative ammonia battery. Reverse electrodialysis (RED) appears as one of the more promising process for direct electricity production from salinity gradients, based on the use of many pairs of anion and cation exchange membranes situated between two electrodes (1). It is worth mentioning that salinity gradients can be regenerated using waste heat. An alternative approach to convert waste heat to electricity, called a thermally regenerative battery (TRB) based on using ammonia (TRAB), was recently shown (2). TRBs operate using chemical potentials obtained by adding ligands into a metal salt solution. In a TRAB, copper ammine complexes are produced when ammonia is used as the ligand only in the anolyte, necessary to charge the battery. Aside from this difference, anolyte and catholyte contain the same electrolytes: copper nitrate and ammonium nitrate, in the same concentrations. The performances of these processes to generate renewable energy are discussed. In the case of RED, the process is evaluated in both lab and pilot-plant scale for the generation of energy and the treatment of wastewater. For TRAB, the main advantages and disadvantage of the methods will be assessed by a series of experiments performed in lab cells.

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Preparation of Porous Oxide Layers by Oxygen Bubble Templated Anodic Deposition Followed by Galvanic Displacement

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In recent years, there has been considerable interest in the hydrogen bubble–templated electrodeposition of porous metals (1). In this process, an electrolysis performed at high cathodic current density causes simultaneous metal ion reduction and hydrogen evolution, leading to the formation of highly porous metal films on the cathode, normally consisting of nanocrystals. Our group has recently shown that a symmetric anodic process can be used for producing porous layers of PbO_2 which, due to their enhanced surface area, exchange much larger charges than compact layers, when cycled in H_2SO_4 solutions (2,3).

The oxygen bubble templated anodic deposition of porous oxides cannot be extended to compounds which electrical resistivity, significantly higher than that of PbO_2, prevents the use of large current density. Some of these oxides may be obtained in a two-step process, by combining oxygen bubble templated anodic deposition and galvanic displacement. In the latter, a porous PbO_2 layer reacts with a low-valent cation M^{n+} in solution to yield its higher-valence oxide and Pb^{2+}, according to:

$$PbO_2 + M^{n+} \rightarrow MO_x + Pb^{2+}$$

We have preliminarily reported on this two-step preparation route for $M^{n+} = Mn^{2+}$ (4), and we have recently extended the process to $M^{n+} = Co^{2+}$.

The main steps of the work were the following.

- Porous PbO_2 layers were deposited from either methanesulfonic acid or perchloric acid media. Their porosity was controlled through the deposition current density.
- Galvanic displacement reactions were carried out by immersing porous PbO_2 layers in either Mn^{2+} or Co^{2+} solutions at open circuit. Acetate solutions, where Pb^{2+} is soluble, were used, in the temperature range 25-75°C.
- XPS analyses were used to establish that the compounds formed by galvanic displacement were MnO_2 and Co_3O_4. Due to their amorphous nature, XRD analyses did not provide additional information.
- SEM was used to assess the morphology of Mn-modified and Co-modified PbO_2 layers, and showed that porosity was maintained. Inspection of cross-sectional images allowed the determination of the thickness of the MnO_2 and Co_3O_4 layers as a function of reaction time.
- Recognizing that galvanic displacement is a peculiar corrosion process, methods that are current in corrosion studies were used to determine the deposition rate. Thus, quasi-steady-state curves for PbO_2 reduction and Mn^{2+} or Co^{2+} oxidation were compared using Evans' diagrams. Deposition rates were calculated from the current values at which the partial reactions had identical and opposite rates.
- The effects of Mn^{2+} concentration and reaction temperature on the deposition rate were elucidated.

Hence, the proposed method allows the preparation of low conductivity oxides of controlled porosity, not attainable by direct electrodeposition.

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Inherently chiral molecular materials with 2,2'- and 3,3'-bisindole atropoisomeric cores: interactions between equivalent redox sites, configurational stability and enantioselection ability

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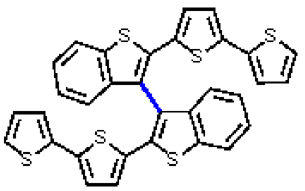
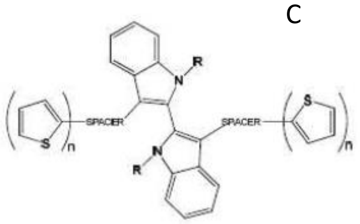
The peculiarity of inherently chiral molecular materials is that the same element endows the molecule with both its key functional property and with chirality, coinciding with the main molecular backbone featuring a tailored torsion; this results in outstanding chirality manifestations. Recently we have presented "inherently chiral" enantiopure electrodes resulting in large potential differences for the enantiomers of chiral probes in voltammetry experiments; they were prepared by electrooligomerization of monomers having atropoisomeric bibenzothiophene (A) or bithiophene cores. (1-5). Concurrently, we have also developed a large family of inherently chiral monomers having 2,2'- or 3,3'-bisindole atropoisomeric cores (B, C).

A



B



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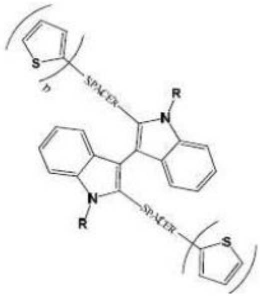

Since indole is electron richer than thiophene, the first two oxidations are shifted at significantly less positive potentials, and localized on the two interacting moieties of the bisindole core rather than on the terminal thiophene wings, and therefore are chemically reversible (oligomerization can be achieved cycling around the third oxidation peak). Moreover, indoles can be N-alkylated, affording modulation of important properties such as solubility and therefore processability.

We will present a detailed electrochemical study on the monomer redox properties and oligomerization ability as a function of the molecular structure in this compound family. A quite original and attractive feature concerns the interaction between the two equivalent redox centers in the biindole cores, (which can be estimated from the potential difference between the corresponding oxidation peaks), since it can be shown to account for the atropoisomeric energy barrier (depending on the 2,2' or 3,3' connectivity and on the N-alkyl substituents), and to be also nicely modulated by temperature and solvent polarity. Thus electrochemistry can provide information on the torsional energy barrier and on the enantiomer stability, confirmed by other approaches.

Finally, enantioselectivity tests on films obtained by electrooligomerization of the more configurationally stable 2,2'-oligomers yield large potential differences for the antipodes of very different chiral probes, also of pharmaceutical interest.

The support of Fondazione Cariplo/Regione Lombardia "Avviso congiunto per l'incremento dell'attrattività del sistema di ricerca lombardo e della competitività dei ricercatori candidati su strumenti ERC - edizione 2016" (Project 2016-0923) is gratefully acknowledged.

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Organic bioelectronics probing conformational changes in surface confined proteins

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The study of proteins confined on a surface has attracted a great deal of attention due to its relevance in the development of bio-systems for laboratory and clinical settings. In this respect, organic bio-electronic platforms can be used as tools to achieve a deeper understanding of the processes involving protein interfaces, since the energetic and electrostatic contributions play the main role in shaping the device response.(1, 2) Biotin-binding proteins such as avidin, streptavidin and neutravidin have been integrated in an organic thin-film transistor (TFT) to investigate the changes occurring in the protein-ligand complex morphology and dipole moment.(3) To this end, functional bio-interlayer and the newly introduced pre-formed complex TFTs have been proposed to separately address these two features. This has been achieved by decoupling the output current change upon binding, taken as the transducing signal, into its component figures of merit. In particular, the threshold voltage is related to the protein dipole moment, while the field-effect mobility is associated with conformational changes occurring in the proteins of the layer upon ligand binding, directly impacting on the transport properties of the organic semiconductor. The probing of a protein bio-layer by means of assessed approaches is not capable to provide information on both the electrostatic and the conformational changes. Molecular Dynamics simulations on the whole avidin tetramer in presence and absence of ligands were carried out, to evaluate how the tight interactions with the ligand affect the protein dipole moment and the conformation of the loops surrounding the binding pocket. These simulations allow assembling a rather complete picture of the studied interaction processes and support the interpretation of the experimental results.

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Physicochemical characterization and corrosion behaviour of surface oxide films on bright annealed ferritic stainless steel

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The corrosion resistance of stainless steels is determined by the thickness, structure, composition and electronic properties of the oxide layers grown on their surface and isolating the metallic substrate from the environment. Surface analytical techniques such as X-Ray Photoelectron Spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) have been and still are widely applied to characterize thickness, chemical structure and composition of thin and ultrathin surface oxide films. PhotoCurrent Spectroscopy (PCS) is a technique applied to obtain direct information on the electronic properties of thin photoconducting surface films on metals and alloys. In the present work, XPS and ToF-SIMS have been combined to PCS in order to perform an integrated physico-chemical characterization of surface oxide films grown on bright annealed ferritic stainless steel in different conditions. Ferritic stainless steels are a nickel-free (i.e. cheaper) alternative to austenitic stainless steels. They are process-annealed to high temperature (~ 1000 °C) in order to reduce hardness and achieve the ductility required for mechanical machining. Bright annealing, is performed under inert gas atmosphere (a mixture of hydrogen and nitrogen) in order to minimize the reaction with oxygen and to avoid the growth of oxide scales and preserve a bright appearance. Our results show that on as-received bright annealed samples the surface oxide film is ~ 2.0 nm thick and has a bilayer structure with an inner layer close to pure Cr(III) oxide and an outer layer of mixed Fe(III) and Cr(III) oxide as shown by XPS and ToF-SIMS. By PCS electronic band gaps of the inner and outer layers are measured close to 3.4 eV and 2.8 eV, respectively, and the oxide films behave as an insulator with an inversion potential of ~ - 0.7 V vs. Ag/AgCl at $\lambda = 309$ nm and at pH ~ 9.5. After thermal treatment in air between 350°C and 550 °C, the surface oxide films thickens and the outer layer is enriched in Fe(III) as shown by XPS and ToF-SIMS. PCS confirms iron enrichment of the outer layer with a band gap reduced to 2.0 eV; photocurrent intensity increases according to thickening and iron enrichment. Polarization curves and electrochemical impedance spectra evidence a decrease of the polarization resistance and a cathodic shift of the corrosion potential after thermal treatment. The knowledge of the structure, composition and electronic properties of these surface films will be discussed to rationalise their corrosion behaviour.

La_2NiO_4@Ni core-shell based catalyst as pre-layer for a commercial Solid Oxide Fuel Cell fed with biofuels

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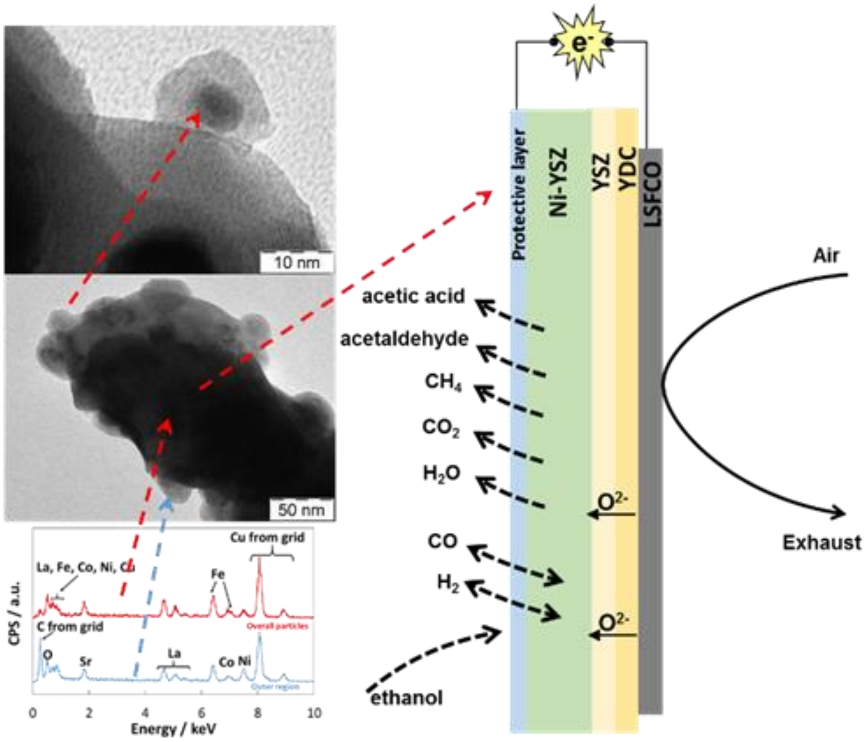
Solid oxide fuel cells (SOFCs) based on conventional nickel-yttria stabilized zirconia (Ni-YSZ) anodes can not be fed directly with organic fuels because of the associated formation of carbon deposits. This work explores a simple approach to solve such relevant limiting factor that affects the utilization of dry biofuels such as ethanol and glycerol directly fed in SOFCs. The approach consists in depositing a composite multifunctional electrocatalyst layer on the SOFC anode to work as an internal integrated fuel processor. A protective layer based on a composite made of Ni-modified perovskite and gadolinia-doped ceria is coated on a conventional SOFC anode based on Ni-YSZ. Beside the oxygen storage properties of ceria, the composite electrocatalyst is characterized by the presence of La_2NiO_4@Ni core-shell nanoparticles in the outer layers and surface basicity properties. Efficient dehydrogenation mechanism, carbon deposition-free cracking reactions and internal reforming assisted by a H_2/H_2O "shuttle mechanism" appear as the key steps involved in the direct oxidation of the biofuels at the modified SOFC anode.



Protective layer and scheme of the "shuttle mechanism" suggested in the present paper

All PEDOT:PSS electrochemical transistors as a platform for sensing

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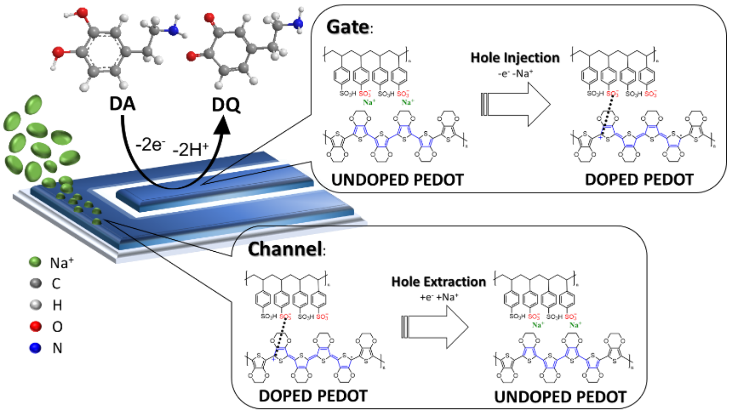
Organic electrochemical transistors (OECTs) are devices which find growing interest in the field of biological and chemical sensing. Although the OECT transduction is based on electrochemical reactions, the transistor architecture offers several advantages respect to amperometric sensors such as signal amplification, the use of an easy and cheap readout electronics, low supply voltage (usually < 1 V), low power operation (< 100 μW), bio-compatibly, and, moreover, they can be easily miniaturized and adapted to non-flat, flexible and even textile devices [1]. This contribution want to report the potentiality of such devices by describing an OECT based only on PEDOT:PSS as conductive material, that can be exploited to obtain low cost sensors [2, 3] with very high performance.

The sensor was optimized by studying the response to different redox compounds of biological interest such as ascorbic acid, dopamine, adrenaline and uric acid. The bio-molecules react with PEDOT:PSS by extracting charge carriers from the transistor channel, and consequently an increase of analyte concentration leads to a decrease of the absolute value of the drain current.



The main drawback of such devices is the lack of selectivity which hinders its wide use in real applications. To address this issue we use a dual approach: on one side we have implemented a potentiodynamic approach that exploits the variation of the operating gate bias voltage in order to obtain a trans-conductance curve wherein the waves due to different redox compounds are separated. On the other side the physical and chemical modification of the PEDOT lactice of the gate electrode offers great opportunities for the implementation of a selective sensor.

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Development of enzyme-based microsensors for *ex vivo* analyses

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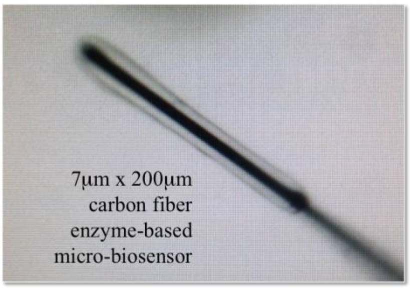
Nowadays real-time quantitative measurements of many proteins, metabolites and cancer biomarkers, are feasible by the use of biosensors for *in vitro* and *in/ex vivo* studies (1). Although, strategies on biosensor design are rapidly increasing, enzymatic biosensors remain a large and important field of study. Enzymes achieve molecular recognition of the substrate based on structural complementarity and exploit an analyte-dependent step to convert an electrochemically inert substrate to an active product, often revealing high selectivity, sensitivity, time scale and information content. Even if, amperometric biosensors have been around since the early 1960s (2-3), it is the production of very tiny micro-electrode biosensors that offers great utility for studying chemical signalling for *in vitro* (at single cell level) and *in/ex vivo* studies. These microelectrode biosensors have the advantage of offering a better spatial and temporal resolution and they are considerably less invasive than other electrode (i.e. microdialysis electrodes) (4). The miniaturization of biosensors is challenging, as they need to be both extremely small and highly sensitive. In fact, smaller is the sensor, smaller is the electrode surface area, and consequently the recorded amperometric signal diminishes (1). The requirement in miniaturizing biosensors is to maintain a signal to noise ratio that enables effective and sensitive detection of the analyte. The tiny sensing surface of the sensor has to be coated with a high density of enzymes in their native active conformation. Furthermore, for *ex vivo* analyses, it is mandatory to control the selectivity of the signal and the mechanical strength of the sensor itself, which has to enter in tissues without damaging.

In this work, we present the development of small, robust and highly active micro-electrode enzymatic biosensors for detecting metabolites, such as glucose, lactate and ATP from single living cells to tissues analysis.



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Potential and limitations of voltammetric measurements for the characterization of electrode surface

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In this work we tested the possibility to use voltammetry for the evaluation of the area of solid electrodes. In the first step of the research study we adopted two voltammetric techniques, well known in the literature: i) cyclic voltammetry (CV) at different scan rates, followed by processing of the peak height with the Randles-Sevcik equation; ii) linear sweep voltammetry (LSV) at different electrode rotation rates, followed by data treatment with Levich equation (1,2).

The ferrocene/ferrocenium redox system was chosen as a probe for its well-known reversible process of diffusion-controlled single electron transfer. Acetonitrile and tetrabutylammonium esafluorophosphate were used as solvent and supporting electrolyte respectively. Initially attention was focused on a solid gold electrode (SGE). The evaluation of its area was made both on the electrode as received, without applying any treatment, and after a drastic surface treatment, to compare the effect of mechanical polishing on the measured area. The results obtained showed that such a treatment gave rise to a significant decrease of the standard deviation of the results and a decrease of the value measured for the area.

Method i) was then applied to a glassy carbon electrode (GCE) in three different conditions: unmodified and modified with an Au-film (AuF-GCE) and with an Au-nanoparticle layer (AuNP-GCE), to investigate the influence of the “roughness” of the electrode surface on the value measured for the area. According to the literature, the above-mentioned electrochemical techniques should respond to the electrode projected areas (2,3): however, we found that the measured areas differ for each modification, suggesting that the morphology of the active surface influences the results of the calculation. Subsequently, method i) was applied to home-made carbon paste electrodes (CPE) of different sizes, to test the relationship between the diameter of the electrode body and the measured area. The calculated areas were compared with those obtained by recording electrode images by scanning electron microscopy (SEM) and processing the data with Wolfram Mathematica software.

In the second step of the study, the actual active surfaces of the SGE and of the two Au-modified GCEs were estimated by CV in H_2SO_4, from the areas of the cathodic peak obtained in each voltammogram, through the theoretical charge associated with the reduction of the oxide layer per unit surface area of gold (4).

In conclusion, voltammetry provide information on the area of solid electrodes, but, despite the notoriety of the equations considered in this study, there are some doubts about the kind of “area” actually involved in the measurement process; further studies are required to correctly interpret experimental results.

Finally, the evolution of the SGE surface during an extended period of usage was checked by periodically recording cyclic voltammograms in H_2SO_4. Clear differences were observed in the CV curves over time and a relationship between the shapes of the voltammograms and the performance of the electrode was found: therefore CV can be a used to monitor the state of the SGE surface and identify the need for a mechanical polishing or even a substitution of the electrode.

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Development of an electrochemical magneto-immunosensor for the detection of *Campylobacter*: a preliminary study

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Campylobacter is an important pathogen genus that cause acute bacterial diseases in humans worldwide. Most infections (about 90%) are caused by *C. jejuni* species, less frequent are those caused by *C. coli*, while sporadic cases are caused by *C. lari* species and *C. upsaliensis*. Outbreaks of Campylobacteriosis have traditionally been linked to the consumption of food products of animal origin (e.g. meat and eggs) but, more recently, an increasing number of outbreaks have been associated to contaminated fruits and vegetables, especially raw leafy green vegetables (1). Conventional bacterial testing methods rely on specific microbiological media to isolate and enumerate viable bacterial cells in food. These traditional methods are very sensitive and inexpensive, but require several days to generate results because they rely on the ability of microorganisms to multiply to produce visible colonies. Therefore, rapid, sensitive and specific methods to detect pathogens are needed. In this work a sandwich ELIME (Enzyme-Linked Immuno Magnetic Electrochemical) assay to detect *Campylobacter* is reported. The proposed system is similar to that already developed by our research group for *Salmonella enterica* (2,3). Magnetic beads (MBs), coupled to a strip of eight-magnetized screen-printed electrodes, effectively supported a sandwich immunological chain. Enzymatic by-product is quickly measured by differential pulse voltammetry, using a portable instrument. Different antibodies, blocking agents and treatments for bacterial cultures were tested. The final system employs: MBs tosyl-activated blocked with dry milk and coated with a capture polyclonal antibody anti-*Campylobacter*, whole *Campylobacter* cells (inactivated with NaN_3) and a detection antibody conjugates with ALP enzyme. For a simple and rapid assay the coating and blocking steps were performed in a preliminary phase, while the two sequential incubations for the immuno-recognition events were merged in a single step of 1 h. The final proposed conditions are those that ensured the best analytical performance for *C. coli*, while, to date, there are still difficulties to detect *C. jejuni*. The future work will focus on improving the response towards *C. jejuni* and the next application of the assay in contaminated matrices, such as irrigation water and vegetables, object of various community alerts in the last few years.

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Rapid, Low-cost and Portable Electrochemical Assay for Heart Injury Diagnosis

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Early and fast diagnosis and prognosis of heart injury are of paramount importance for a successful treatment of the diseases. Furthermore, heart related pathologies, also caused by anticancer treatment, are determinant in cancer patient survival. Several molecular markers of heart damage are emerging and electrochemically-driven trapping and signal transduction of biomarkers have proven to be effectively employed in the development of sensing devices and assays.

For instance, cytochrome c (cyt c), an inner mitochondrial membrane (IMM) protein, which plays an important role in oxidative phosphorylation, can be detected as heart failure marker. This protein is not detectable in healthy patients' blood but it has been demonstrated that during some diseases, which also involves the cellular apoptosis, cyt c is released [1]. In particular, cyt c is released from cellular membrane as a consequence of the treatment of infarction. [2] A fast monitoring of cyt c concentration can help to control the progression and extension of the heart injury guiding the therapeutic actions.

In this view, there is an urgent need to develop biochips/sensors/devices for the rapid detection of markers, such as cyt c, in very early stages of the diseases to evaluate the real state of the injury and to operate with fast bedside therapies.

Herein, we show some strategies based on optimized chemical affinity for the trapping and the detection of heart injury markers and for signal amplification.

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Carbon black modified screen-printed electrodes to detect chlorine dioxide

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Chlorine compounds have always been the most used chemical agents for water disinfection. However, alternative disinfectants have been investigated to avoid harmful by-products generated by the reaction between free chlorine and organic substances present in water. Among the different compounds used for the treatment of water, chlorine dioxide can be considered a good alternative to chlorine. Chlorine dioxide is employed in several industrial fields, including food, textile, and paper industries. Furthermore, chlorine dioxide is used to produce disinfected water with satisfactory characteristics in terms of odor and taste. (1,2)

Chlorine dioxide is often used because of its excellent oxidizing and disinfecting properties against bacteria, viruses and algae, combined with the absence of harmful by-products, such as trialomethanes. Moreover, it is active in a wide range of pH, unlike free chlorine. (3)

Actually, the maximum residual disinfectant level using chlorine dioxide in water is 0.8 ppm, accordingly to the United States Environmental Protection Agency (EPA), thus analytical tools are required to control the disinfectant level. (4)

Due to the industrial needs in the control of disinfectant level in different processes, the development of cost-effective and easy to use sensors is highly requested.

The goal of the Tecnosens Spin-off is to fabricate miniaturized and sustainable electrochemical sensors for the monitoring of disinfectant compounds.

Herein, we report a novel and cost-effective probe for the *in-situ* determination of chlorine dioxide in swimming pool water.

This sensor was fabricated using screen-printed electrodes modified with carbon black (CB), a cost effective and raw nanomaterial with excellent electrocatalytic properties as demonstrated by our research group and corroborated by also other groups, like Compton's group. (5,6)

The working electrode was modified by drop casting with 2 µl of a carbon black dispersion (1 mg/ml) prepared in a mixture of N,N-Dimethylformamide/H_2O 1:1 (v/v). Under optimized conditions (potential of + 0.1 V vs Ag/AgCl and Britton-Robinson buffer 0.02 M + KCl 0.02 M, pH =2 as working solution), the sensor showed a linear response up to 10 ppm (R=0.989), sensitivity and LOD equal to 13.4 nA/ppm and 0.03 ppm, respectively.

The interfering species including NO_3^-, SO_4^{2-}, CO_3^{2-}, HCO_3^- and Cl^- were evaluated, demonstrating the selectivity of this device.

The study of matrix effect and the accuracy of the sensor was estimated in swimming pool water, obtaining a satisfactory recovery value (78 ± 8)%.

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Bacillus anthracis spores detection by using a label free impedimetric aptasensor

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Since 1930, biological weapons have been developed and used in different countries; they include microorganisms like virus and bacteria which can be used in terroristic attacks, affecting the human health. For instance, *Salmonella typhimurium* was spread in food samples by a religious sect in the western USA; *Bacillus anthracis* spores were used in 2001 to contaminate letters in the Washington area (1).

For the safety of citizens at worldwide level, there has been a continuous interest in the development of robust and reliable analytical tools for the detection of these agents, to provide an early alarm in case of terroristic attacks. The detection of these agents is usually carried out using laboratory-set techniques like real-time PCR, which are not suitable for in field applications and fast early warning, due to the lack of portability, power requirements, long response time and expensive procedures. In this context, electrochemical biosensors offer advantages in terms of high sensitivity, miniaturization, integration, low cost, and power requirements. For the development of biosensors able to detect these agents, antibodies are mainly used as biocomponents, but their production requires the use of animals; in addition, their stability is often affected by environmental conditions. To overcome these drawbacks, synthetic DNA aptamer sequences were recently employed to develop aptasensors (2).

Herein we describe the development of an impedimetric label free biosensor for the detection of *B. anthracis* spores, using the BAS-6R aptamer as biocomponent. This aptamer sequence has been selected among a library of 92 DNA aptamers by Bruno et al., demonstrating a good selectivity for *Bacillus* spores when tested in fluorescence, using a fluorophore and a quencher as labels (3). We developed a miniaturized label free aptasensor for *B. anthracis* spores using this aptamer as biocomponent and the electrochemical impedance spectroscopy as technique. The aptamer BAS-6R was immobilised on gold screen-printed electrodes by exploiting the affinity between the gold working electrode area and the thiol chain at the 5′ position of BAS-6R, while the spores presence has been detected by evaluating the increase of the charge transfer resistance (R_{ct}). To optimise the aptasensor, different working conditions, including the amount of aptamer and blocking agent, the time of aptamer incubation, the type of working buffer have been studied. This aptasensor was then tested against *B. anthracis* spore simulants, namely *Bacillus Cereus 14579*, *Bacillus Subtilis*, *Bacillus Cereus* 11778, observing a significant R_{ct} variation in the presence of *B. Cereus 14579* (10^5 CFU/mL), thus demonstrating the binding between the aptamer and this *Bacillus*. This aptasensor has showed the capability to detect *B. anthracis* spores simulant in the range comprised between 0.5 x 10^5 CFU/mL and 7 x 10^5 CFU/mL, it has also demonstrated its suitability for a rapid analysis.

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High-Quality, Ligands-Free, Mixed-Halide Perovskite nanocrystals Ink for Optoelectronic applications

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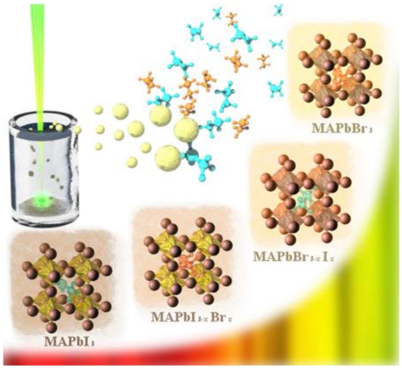
It is now well established that the primary optoelectronic properties of perovskite-halides – such as their tunable direct bandgap, high absorption coefficient, low exciton binding energy, and balanced ambipolar carrier transport – meet many of the requirements for a high-efficiency solar energy conversion technology(1). But in spite of the huge research effort, yet they are far from the market.
Given the simple processability of perovskite-halides, typically from solutions at relatively low temperatures, a non-negligible level of unintentional structural and chemical defects at temperatures relevant for device operation are currently limiting the devices efficiencies and causing instability - i.e. hysteretic behaviours (2) and formation of metastable phases upon photoexcitation which hampers the band-gap tunability (3) - and low reproducibility, especially in view of large area deposition.
In more established semiconductors, such as Si for example, the understanding and control of defects has been a cornerstone of their successful development in devices. Defects thus remain one of the interesting material characteristics in solution processable perovskites that underpin limitations in device operation and influence further progress towards reaching the highest possible power conversion efficiencies. So far, high quality colloidal nanocrystal of perovskites (not necessarily quantum confined) have been demonstrated. However, they all need bulky and insulating organic ligands to remain in suspension, thus hampering the fabrication of conductive thin films.



We demonstrate, for the first time, the synthesis of ligand free metal-halide pervskite nano-crystal inks by Laser Ablation Synthesis in Solution (LASiS).[4] This methodology, simple and easy to use for large scale materials production, allows to produce nano-crystals solutions to print conductive thin films electrically and photo-stable. In fact, we show that such films do not present any hysteretic behavior under polarization, typical in presence of ion migration and permit monotonic tunability of the band gap across the visible spectrum, in absorption and emission, without the formation of sub-band gap emissive phases upon photo-excitation.

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New Earth-abundant thin film solar cells based on Cu_2MnSnS_4

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As it is well known, in the last decade much attention has been focused on I_2-II-IV-VI_4 thin films as an attractive possibility for the synthesis of In and Ga free chalcogenides which may allow terawatt range photovoltaic (PV) applications. A new alternative to copper zinc tin sulfide/selenide belonging to this class of materials is copper manganese tin sulfide (CMTS), a p-type semiconductor fully based on Earth-abundant and low-cost elements which shows an important advantage with respect to copper zinc tin sulfide/selenide. As a matter of fact, not only the abundance in the Earth's crust of Mn is two order of magnitude higher than that of Zn (1100 ppm vs 79 ppm), but the amount of Zn produced in 2015 was 4'600'000 tons lower than that of Mn (13'400'000 Zn tons vs 18'000'000 Mn tons). Therefore, since Mn is definitely cheaper than Zn, optimized CMTS could potentially provide Wp cost definitely lower than copper zinc tin sulfide/selenide, which is crucial for thin film PV applications. CMTS, which crystallizes into a stannite structure (space group: I-42m), shows high absorption coefficient (α=10^4 cm^{-1}) and direct band gap suitable for PV applications. So far, CMTS was mainly studied as bulk magnetic semiconductor, while, only in the last two years, the present authors (1) and Chen et al. (2) reported on CMTS thin films for PV applications. The latter reported on CMTS layers prepared by direct liquid coating followed by annealing in nitrogen atmosphere and/or post-sulfurization in sulfur vapors, which provided solar cells with 0.49% maximum efficiency. Our work deals instead with CMTS thin films grown by a two-step vacuum process. The metal precursors deposited on Mo-coated soda lime glass (SLG) by thermal evaporation are annealed in sulfur vapors for 1h at 585°C with an initial 1h step at 115°C to enhance the metal intermixing. Of the many possible stoichiometries, Cu-poor/Mn-rich CMTS films with Mn/Sn ratio around 1 were chosen in order to prevent the development of both highly conductive (e.g. $Cu_{2-x}S$) and insulating (e.g. MnS) secondary phases. Several techniques, including Scanning Electron Microscopy, Energy Dispersive Spectroscopy (EDS) , Raman spectroscopy and Photoluminescence have been used to test the quality of CMTS thin films, while CMTS/CdS/iZnO+AZO solar cells were inspected both by External Quantum Efficiency and current density-voltage (J-V) measurements under 1 sun illumination. The beneficial effects of low temperature post-deposition annealing either in air or inert atmosphere between 200 and 275°C on CMTS solar cells were investigated, both in terms of electrical performance and modification of the material properties. In particular, a 40 min 225°C annealing in air lead to the best overall performance: efficiency 0.83%, open-circuit voltage 354 mV, short-circuit current density 5.8 mA/cm2, fill factor 40%.

The reasons behind these beneficial modifications of the device parameters were investigated by Raman and PL spectroscopies. Results showed that post-deposition thermal treatments in air between 200 and 275°C generally reduce generally reduces the density of the bulk defect, thus reducing recombination losses and increase the of CdS crystalline quality, while red-shifting its absorption edge.

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Polyurethane-based Electrostrictive Nanocomposites as High Strain - Low Frequency Mechanical Energy Harvesters

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Energy harvesting of wasted energy is increasingly important for powering wearable electronics in Internet-of-Things world [1]. Here, we reported on innovative nanocomposites made of electrostrictive polymer (thermoplastic polyurethane, TPU), and high-k ceramic filler ($CaCu_3Ti_4O_{12}$, CCTO), which offered outstanding results in recovering energy by human gait. The excellent mechanical properties of TPU allowed up to 50 vol% of filler into the composite without loosing film elasticity even for high strains (~30%). CCTO was able to increase of more than one order of magnitude the resistance of the film harvesters with respect to pure TPU, without lowering the dielectric constant and the breakdown voltage. The combined effect of high dielectric strength, high resistance and allowable strain make these composites very promising as energy harvesting actuators.

By means of careful broadband electric spectroscopy coupled with microstructure analysis, we were able to address the mechanisms underlying energy recovery. In particular, long-range charge migration phenomena mainly occurred along conductivity pathways, which are formed at the extended interfaces between the polymer strands and the filler. Our model allowed optimal tailoring of electrostrictive nano-composite actuators.

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A Bilayer WO_3 n-n Heterojunction Photoanode prepared by RF Diode Sputtering for Improved Photoelectrocatalytic Water Splitting

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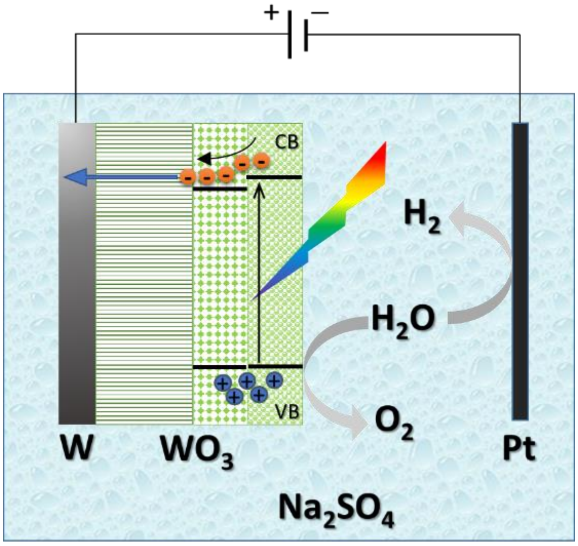
A bilayer WO_3 photoelectrode was prepared by radio frequency (RF) plasma sputtering in reactive 40%O_2/Ar atmosphere by depositing on a tungsten foil two successive WO_3 coatings at two different total gas pressures (3 Pa and 1.7 Pa, respectively), followed by calcination at 600 °C (1). Its photoelectrocatalytic (PEC) activity was evaluated by both Incident Photon-to-Current Efficiency (IPCE) measurements and separate evolution of H_2 and O_2 by water splitting in a two-compartment PEC cell (2), and compared with those of the corresponding single layer grown at constant pressure (1.7 Pa or 3 Pa). FESEM analysis revealed that the photoanodes have a nanostructured porous double layer surmounting a columnar basement (Staffa-like morphology, after the name of the Scottish island). Tauc plot of the single layer revealed that the sample prepared at lower pressure possesses a 0.1 V wider bandgap (2.94 eV) than that prepared at higher pressure (2.82 eV). Both Mott-Schottky analysis and XPS valence band spectra showed that this difference was essentially due to a shift of the conduction flat band (CB) potential. Thus, this work demonstrates that the total pressure during WO_3 deposition by RF diode sputtering affects the position of the CB energy very likely due to the different extent of crystal structure distortion induced by oxygen vacancies (3), in agreement with the crystal field theory (CFT). Lowering the pressure increases the oxygen vacancies, and produces a shift of the CB towards higher energy. The equivalent n-n heterojunction at the interface of the double-layer (see Figure) creates a built-in electric field that facilitates the photopromoted electron transfer toward the lower laying conduction band material, while the columnar innermost layer introduces percolation paths for efficient electron transport toward the conductive tungsten foil. Both phenomena contribute to decrease the interfacial charge transfer resistance (R_{ct}) as measured by impedance spectroscopy and lead to a *ca.* 30% increase in the PEC performance compared to the monolayer and to a 93% faradaic efficiency, which is among the highest reported so far for WO_3 photoanodes. Upon methanol addition an outstanding 4-fold photocurrent density increase up to 6.3 mA cm^{-2} was attained over the bilayer WO_3 photoanode, much larger than the usually observed current doubling effect.



Acknowledgment
This work received financial support from the Regione Lombardia and Cariplo Foundation co-funded "SmartMatLab Centre" project (Grant No. 2013-1766)

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Hydrides as High Capacity Anodes in Lithium Cells: An Italian “Futuro in Ricerca di Base FIRB-2010” Project

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Automotive and stationary energy storage are among the most recently-proposed and still unfulfilled applications for lithium ion devices. Higher energy, power and superior safety standards, well beyond the present state of the art, are actually required to extend the Li-ion battery market to these challenging fields, but such a goal can only be achieved by the development of new materials with improved performances. Focusing on the negative electrode materials, alloying and conversion chemistries have been widely explored in the last decade to circumvent the main weakness of the intercalation processes: the limitation in capacity to one or at most two lithium atoms per host formula unit. Among all of the many proposed conversion chemistries, hydrides have been proposed and investigated since 2008. In lithium cells, these materials undergo a conversion reaction that gives metallic nanoparticles surrounded by an amorphous matrix of LiH. Among all of the reported conversion materials, hydrides have outstanding theoretical properties and have been only marginally explored, thus making this class of materials an interesting playground for both fundamental and applied research. In this communication, we illustrate the most relevant results achieved in the frame of the Italian National Research Project FIRB 2010 Futuro in Ricerca “Hydrides as high capacity anodes in lithium cells” and possible future perspectives of research for this class of materials in electrochemical energy storage devices.

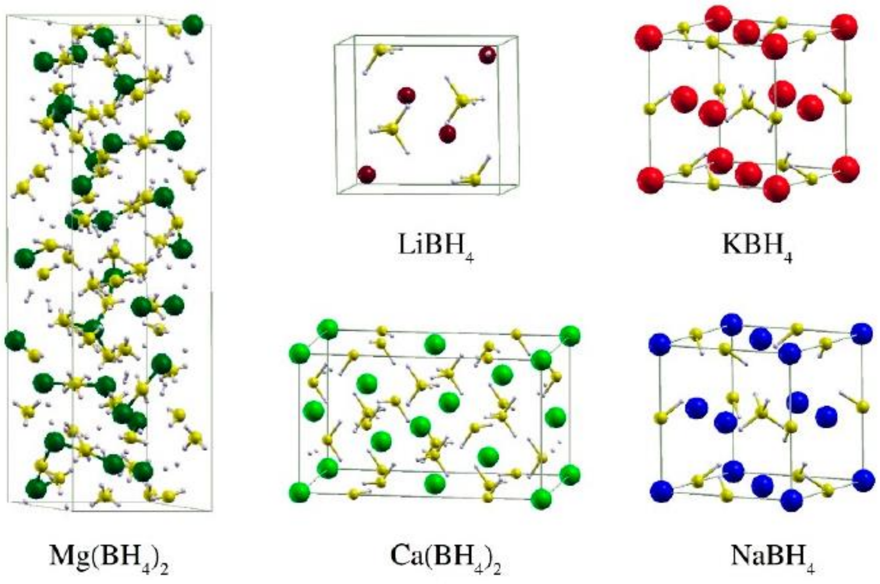

Figure 1. Crystal structures of the borohydrides phases.

Bio-Hybrid Complexes In Artificial Photosynthesis

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The sun was born five billion years ago and it is estimated that it will continue to irradiate the same amount of energy for another five billion years. Sun is a renewable energy source, inexhaustible within the humankind life, and, every year, Earth receives an amount of solar energy ten thousand times greater than that the entire planet population uses (1). The ability to convert solar light into chemical energy is the fundamental feature of photosynthetic systems. Photosynthesis is the most important biological process, supplying Earth's biosphere with oxygen and energy for living organisms' metabolism (2). All life on Earth depends on photosynthesis directly or indirectly, and has been deeply investigated by scientists with the aim of reproducing it in the laboratory, mimicking the Nature, and, consequently, producing green energy efficiently, following the artificial photosynthesis way (3). The complexity of the natural photosynthetic systems is difficult to reproduce *in vitro*; however, it is largely related to their living character and can be reduced in a biomimetic environment. In this regard, ideal biomimetic systems must efficiently harvest the sunlight, with the help of suitable antennas, and convert the energy in a stable charge-separated state with a lifetime long enough to allow ancillary chemistry to take place. In the purple, no sulphur photosynthetic bacterium *Rhodobacter sphaeroides R26*, energy from sunlight is harvested by antennas and transferred to reaction center (RC), a most efficient photoconverting transmembrane protein. During the electron transfer process, the RC, upon photon absorption, promotes one electron sitting on the bacteriochlorophylls dimer (D), the electron donor, in its excited state and then it shuttles to the electron acceptors the ubiquinone-10 Q, generating the charge separated state D^+Q^-. In the presence of external electron donors, the oxidized D^+ is reduced again and a second photon impinges a second electron so that the quinone Q, now doubly reduced, is doubly protonated and it is released as quinol. Cytochrome c_2 is the physiological electron donor to the oxidized dimer. Our idea is to build a supramolecular architecture made up of the photosynthetic bacterial reaction center, an artificial light-harvesting antenna, synthesized *ad hoc*, belonging to the class of heptamethine cyanines, with the task of increasing the RC absorption cross section in the visible range, and an electron donor redox protein, the cytochrome c_2. These three components were connected to each other by covalent bonds obtaining a stable bio-hybrid supramolecular complex, easily interfaceable to a semi-conductive surface, with the aim of assembling a sustainable sunlight-to-energy converting device based on proteins.

Insert references in brackets as follows: (1) (1,2,3) and add reference list at the bottom of the abstract using justified Times New Roman 10, with line-spacing 1. As indicated below:

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Electronic coupling in H-shaped tetra-arylamine mixed-valence compounds

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Organic mixed-valence compounds (MVs) are donor-acceptor compounds that possess an open shell ground state (1). Amongst the MVs particularly interesting are those with arylamines connected through a conjugated bridge. The nature of the bridge as well as that of the substituents on the arylamine moieties, determines the electrooptical properties of such compounds. Specifically, the intervalence charge transfer transition (IVCT) in the near infrared region (NIR), occurring upon photoexcitation of the oxidized monocation species, is heavily affected by the above structural parameters. These compounds can be designed to work as electrochromic materials in smart devices for controlling the solar thermal radiation, as well as for the generation of high charged radical species for high spin magnetic materials (2,3). Here we present organic MVs with an innovative H-shape design, where four redox centres are bridged "vertically" via a dibenzofulvene backbone and "horizontally" via a bis-(dibenzofulvene)-thiophene bridge. They are oxidized to stable high charged radical species, showing IVCT in the NIR, in contrast to the linear systems lacking one dibenzofulvene-bisamine moiety at one end of the thiophene bridge, where band bleaching occurs upon dication formation. Electrochemical, spectroelectrochemical and TD-DFT results, show that the IVCT in high oxidation states of the H-shape MVs is due to the activation of both vertical and horizontal electron transfer pathways (4). The innovative H-shape design may improve the potential electrooptical applications of MVs, highlighting the importance of the coupling between multiple redox centres and paving the way for the development of three-dimensional multicentre mixed valence compounds.

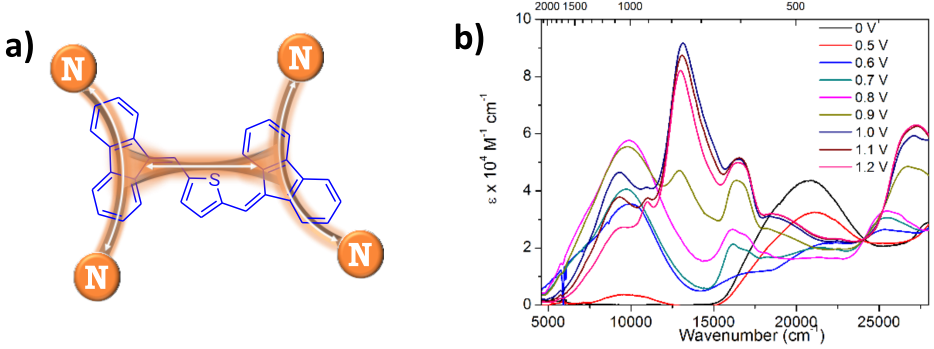

Figure 1. H-shape MVs based on the bis(dibenzofulvene)tiophene bridge a); example of the electrochromic response of an H-shape compound in the Vis-NIR region b).

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Comunicazioni Poster

A Solid-Liquid Soggy-Sand Electrolyte for Dye-Sensitized Solar Cells

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The electrolyte is one of the crucial components in dye sensitized solar cells (DSSCs), allowing for fast diffusion of charge carriers between the electrodes and directly affecting photocurrent density (J_{SC}), photovoltage (V_{OC}), and fill factor (FF). Quasi-solid state DSSC electrolytes typically ensure mechanical properties of a solid and diffusive property of a liquid, circumventing practical problems such as solvent volatility, leakage, photodegradation and corrosion of counter electrode (1). In this study, a polyethylene glycol dimethyl ether (PEGDME, M_w = 150 g mol^{-1}) based I^-/I_3^- electrolyte containing mesoporous SiO_2 particles (MSU-H, 15 nm pores) is investigated in terms of ionic conduction and DSSC performance. Similarly as in "soggy sand" electrolytes, preferential adsorption of anions is observed by Zeta potential measurements and ionic conductivity of the liquid electrolyte can be enhanced (2). High values of photovoltaic parameters at 1 sun irradiation (J_{SC} = 11.5 mA cm^{-2}, V_{OC} = 0.69 V, FF = 0.47, 6.3% efficiency) at 2.8 vol% SiO_2 suggests an improved regeneration kinetics of the dye molecules. Transient photocurrent experiments confirmed favorable mass transport. A remarkably high 11.2% efficiency was measured under 0.2 sun irradiation.

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Metal-Support Interaction in Pt nanoparticle supported on Nitrogen Functionalized Mesoporous Carbon: a combined DFT and Experimental Approach

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Proton exchange membrane fuel cell (PEMFC) wide spreading is still hindered by the bottleneck of the oxygen reduction reaction (ORR). Actually, large amounts of precious Pt metal are required to promote the sluggish kinetics, causing the PEMFCs to be economically uncompetitive with conventional technologies. One way to reduce the metal loading, while increasing the metal nanoparticles (NPs) catalytic activity, is to support them on activated surface able at triggering their activity by increasing the number of active sites or by electronic interaction (1). Pt NPs on nitrogen functionalized mesoporous carbon (NMC) have proved to be interesting materials for ORR (1).

In this paper we employed a new synthetic route for the simultaneous Pt NPs deposition and carbon support doping by using a platinum precursor bearing a nitrogen containing ligand such as 1,10-phenantroline or 2,2'-bipyridine. Metal NPs (average size 3 nm) were successfully synthesized by thermal solid state reduction on a commercial carbon. XPS analysis confirmed that during the treatment the ligand degrades and the nitrogen is embedded in the mesoporous carbon structure obtaining a surface modification of the carbon support, preserving the bulk conductivity and thermal stability (2).

Electrochemical characterization revealed superior mass catalytic activity towards ORR in those catalysts showing higher Pt-N interaction expresses as B.E. shift of nitrogen components (Fig.1a). Pyridinic, pyrrolic and graphitic functional groups were considered in a DFT computational investigation for discriminating the interaction with a single Pt atom and nitrogen defects. DFT analysis confirmed that the interaction between Pt and nitrogen depends on the number and different types of nitrogen functional groups, so that the most stable structure is observed when Pt interacts closely with 4 pyridinic groups (Fig.1b).

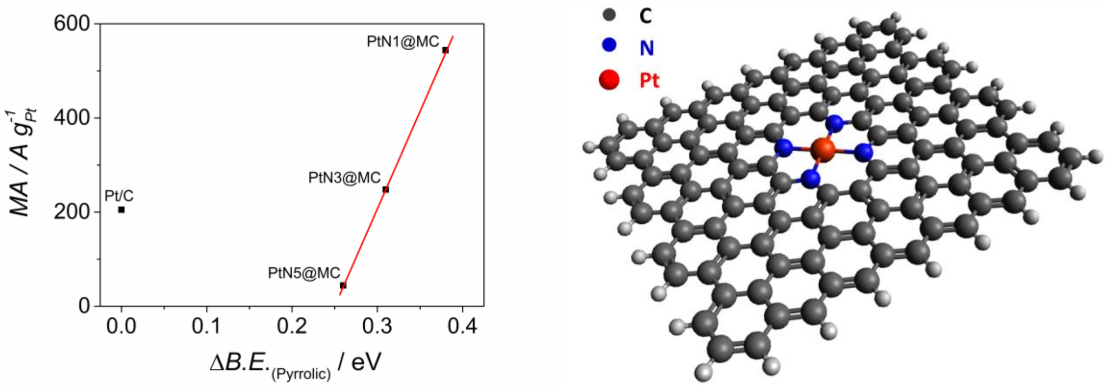

Figure 1. a) correlation between pyrrolic B.E: shift and mass activity towards ORR, b) DFT optimized structure of Pt atom on NMC.

Funding from University of Padova (PRAT CPDA139814/13) is acknowledged.

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Nitrogen and sulfur doped mesoporous carbon, prepared form templating silica gel, as interesting materials for supercapacitors

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Highly accessible surface area and heteroatom-doping are desired properties for carbon electrode materials to be used in electrochemical supercapacitors (1).
In this paper, nitrogen and sulfur doped carbon materials with wide mesopores (13-14 nm) were synthetized according to a hard template approach by pyrolysis of sucrose, 1,10-phenantholine or dibenzothiophene as carbon, nitrogen- or sulfur-carbon precursors, respectively. The morphology and dimension of mesopores were induced by sacrificial SiO_2 nanoparticles (10-20 nm), which after removal by an etching solution reveals a network of hemispherical pores (2,3). The interconnected pore structure was confirmed by scanning electron microscopy and transmission electron microscopy. X-ray photoemission spectroscopy and elemental analysis confirmed the presence of nitrogen and sulfur functional groups. The prepared materials were fully characterized by cyclic voltammetery, chronopotentiometry and electrochemical impedance spectroscopy in 0.5 M H_2SO_4. Notwithstanding the small surface (200 m_2/g) determined by BET method, the nitrogen doped mesoporous carbon showed high specific gravimetric (~170 F g^{-1}) and surface (~835 mF m^{-2}) capacitances, comparable with material showing surface area 5 to 10 times higher.

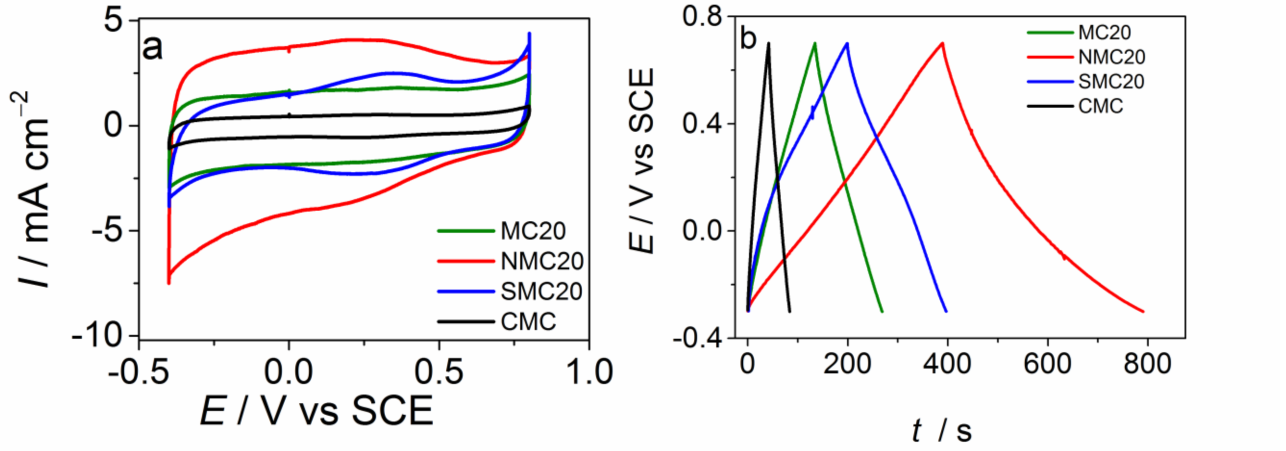

Fig1. Electrochemical data in 0.5 M H_2SO_4. (a) CVs of MCs electrodes at 5 mV s^{-1}. (b) Galvanostatic charge/discharge curves of MCs at $I = 0.26$ mA cm^{-2}.

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Electrochemistry of inherently chiral macrocyclic *vs* open-chain oligomers: reciprocal interactions between bibenzothiophene atropoisomeric cores?

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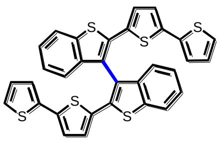
We have recently introduced "inherently chiral" enantiopure electrode surfaces of outstanding chirality manifestations, including large potential differences for the enantiomers of chiral probes in voltammetry experiments. (1-5) They can be prepared by electrooligomerization from monomer 1, having an atropoisomeric dibenzothiophene core, and consist of a mixture of macrocyclic and open-chain oligomers as those represented in the Figure, which we have electrochemically investigated one by one in detail. The results will be presented and discussed. Especially the macrocycles provide a quite attractive casebook of interactions between equivalent redox centers, possibly also requiring to take into account interactions between facing chains, especially in the case of the smaller ringlet.



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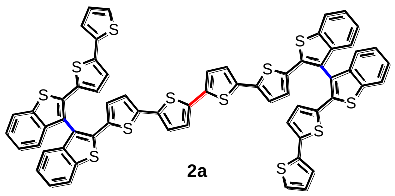

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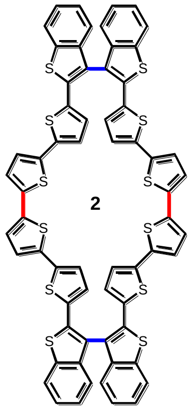

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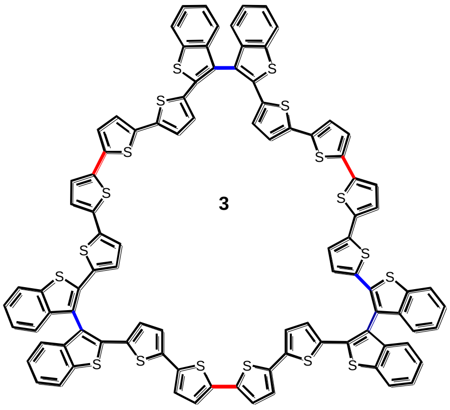

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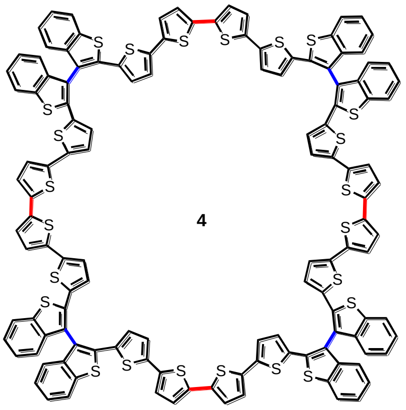

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The support of Fondazione Cariplo/Regione Lombardia "Avviso congiunto per l'incremento dell'attrattività del sistema di ricerca lombardo e della competitività dei ricercatori candidati su strumenti ERC - edizione 2016" (Project 2016-0923) is gratefully acknowledged.

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Mitigation of the side reactivity upon cycling of a LTO-LFP Li-ion battery

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Novel and safer Li-ion cells configurations have found commercialization in recent years in substitution to the usual C-NCA standard formulation. In particular the coupling of lithium titanate (LTO) negative electrodes with lithium iron phosphate (LFP) positive electrodes is in theory suitable for a full Li-ion configuration able: (1) to work in a potential range within the thermodynamic stability window of all the typical standard carbonate-based electrolytes; (2) to suffer only a limited performance decrease due to the use of a negative electrode material with a practical specific capacity 50% smaller compared to graphite; and (3) to disclose outstanding improvements in the power performances due to the excellent lithium ion mobility in both the positive and the negative electrode materials obtained by a fine tuning of the morphology, composition and structure.

Here we illustrate our recent studies about the unexpected complex reactivity upon cycling of a LTO-LFP full Li-ion cell. Our aim is to draw a fundamental description of the parasitic side chemistry that takes plane in a LTO-LFP Li-ion cell upon cycling in galvanostatic conditions. In this view coin cells as well as pouch cells have been assembled using commercial materials (Custom cells Gmbh and Solvionic) and electrodes recuperates for post mortem analysis by SEM, FTIR and Raman spectroscopy. Moreover the release of gaseous components upon cycling has been monitored by continuous in operando monitoring of the internal pressure in a LTO-LFP cell assembly and ex situ gas chromatography.

Our results support the occurrence of an unexpected complex parasitic chemistry with remarkable differences in the degradation processes depending on the galvanostatic cycling conditions of the cells.

This detrimental parasitic chemistry has been mitigated by the incorporation of a selective metallic getter able to sequestrate gaseous components released upon cycling. Evidences of the mitigation of the release of gas byproducts due to the side parasitic chemistry are here illustrated.

Electrochemically mediated Atom Transfer Radical Polymerization in ionic liquid/water mixtures

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Atom transfer radical polymerization (ATRP) is one of the most advanced techniques to produce polymers with precise and complex architectures, predetermined molecular weights, and high chain-end fidelity (1). Usually, ATRP is catalyzed by a copper−amine complex through a reversible equilibrium (K_{ATRP}) involving the activator and deactivator complexes, $[\mathrm{Cu^{I}L}]^{+}$ and $[\mathrm{X\text{-}Cu^{II}L}]^{+}$ (X = Cl, Br), respectively. $K_{\mathrm{ATRP}} << 1$ guarantees that the vast majority of the propagating chains is in the dormant state (P_n-X), while the concentration of active radicals (P_n•) is low to minimize the occurrence of radical termination reactions and promote concurrent growth of all polymer chains (2). In electrochemically mediated ATRP (*e*ATRP), one of the most recent and potent developments of ATRP, $\mathrm{Cu^{I}}$ is (re)generated by reduction of $\mathrm{Cu^{II}}$ at the working electrode. This allows to precisely control the $\mathrm{Cu^{I}/Cu^{II}}$ ratio, enhancing the overall polymerization control (3). Room Temperature Ionic liquids are gaining increasing relevance in many applications, especially for their non-volatility, non-flammability and versatility. Water is inexpensive, abundant and non-toxic, but its use in ATRP is limited to few water-soluble monomers. In this study, we explored the possibility of adding water into the polymerization medium to reduce process cost and increase the rate of polymerization (R_{p}) and cleanness of the system. Mixtures of a model ionic liquid, 1-butyl-3-methylimidazolium trifluoromethanesulfonate, [BMIm][OTf], and water have been used for the first time in *e*ATRP of hydrophobic acrylates and methacrylates. In [BMIm][OTf] containing 20 vol% H_2O, polymerizations proceeded faster than in the pure ionic liquid and yielded well-defined polymers. The increase of R_{p} correlates with the amount of H_2O and is consistent with enhanced activation rate of the dormant P_n-X. Indeed, the rate of activation of the C-X bond is usually much higher in water than in ionic liquids or organic solvents (4). *e*ATRPs were performed also in aqueous media (60 vol% H_2O) using [BMIm][OTf] as co-solvent to help dissolve both monomer and polymer, with excellent results (high conversion and low dispersity) for both hydrophobic and hydrophilic monomers. The prepared polymers were easily isolated by precipitation either with an excess of H_2O or by cooling. The ionic liquid and catalyst were recycled, with high yields, by evaporating water and unreacted monomer from the exhaust mixture. Reactions performed with fresh and recycled ionic liquid provided very similar results. In conclusion, *e*ATRP in [BMIm][OTf]/H_2O truly offers a powerful, fast and clean approach for the synthesis of tailor-made polymers.

Acknowledgments – With the contribution of Fondazione Cariplo, grant no. 2011-1851 and Università di Padova (CPDA150001). FDB thanks Fondazione Cariparo for a PhD fellowship.

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Electrochemical Conversion of Carbon Dioxide: effect of the cell and of operating parameters on the performances of the process

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Recycling technologies of CO_2 allow to introduce renewable energy in the chemical and energy chain, storing a renewable energy in the chemical form. In this context, electrochemical conversion of CO_2 is considered one of the more interesting approaches, using excess electric energy from intermittent renewable sources. (1) Furthermore, products can be selectively controlled by changing the operating conditions of electrolysis. In particular, in the last years, an increasing attention has been devoted to the electrochemical conversion of CO_2 to formic acid or formate in water. (2,3,4) The main hurdle of the reduction of CO_2 from water solution is the low CO_2 solubility in water. In this work, a systematic study on the effect of the CO_2 pressure and of other operating parameters on the conversion of CO_2 at tin flat cathodes to formic acid was performed to overcome this obstacle.

The reduction of CO_2 was first studied in a glass undivided cell at atmospheric pressure to evaluate the effect of various operating parameters, including the nature of the anode and of the supporting electrolyte, the mixing rate, the current density and cathode to anode area ratio. Subsequently, in order to improve the performance of the process, a series of electrolysis was performed in a batch stainless steel undivided cell in a wide range of pressure of CO_2 and current density. It was shown that an increase of the pressure leads to a drastic enhancement of the final formic acid concentration. Indeed, the utilization of relatively high CO_2 pressures (15–30 bar) allowed to achieve high concentrations of formic acid (up to 0.46 mol L^{-1}) at high current density (up to 90 mA cm^{-2}) and with cheap and simple undivided cell. (5)

Several researchers have discussed the economic feasibility for large-scale design of the CO_2 mitigation electrochemistry system, by suggesting that could be operationally profitable. Therefore, in the last stage, the process was performed in a pressurized filter-press cell, suitable for scale-up on applicative scale. The goal of this research is to provide an electrochemical process sustainable at applicative point of view characterized by a high yield and selectivity of the product. Long-term stability has also to be acquired in order to obtain an interesting alternative at commercial level for the conversion of carbon dioxide.

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Connections at the Interface: Shuttling the Electrochemical Stimulus from Electrode to Monomer Droplets in Dispersed Polymerization

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Electropolymerization under heterogeneous conditions is challenging because in dispersed media electrode and reactants are separated: the electrode is in contact with the continuous aqueous phase, while polymerization reactants (monomer, initiator, and radicals) are dispersed in the organic phase. Therefore, to trigger polymerization the electrochemical stimulus must first reach the aqueous phase (crossing the first electrode | liquid interface) and then shuttle to the dispersed phase (crossing the second liquid | liquid interface). Moreover, controlled radical polymerization (such as atom trasnfer radical polymerization, ATRP) poses an additional challenge in comparison to most organic reactions, because radicals must be continuously activated/deactivated after the electrochemical stimulus has reached the organic phase droplets. We used two strategies to establish efficient electro-chemical communication between electrode and droplets in order to obtain ATRP in a miniemulsion. First, we created a dual catalytic system, composed of two distinct copper catalysts (one hydrophilic and one hydrophobic). The two mediators created an unbroken connection from the electrode surface, via the aqueous continuous phase, to the monomer droplets. This enabled controlled polymerization and resulted in the production of well-defined polymeric latexes.(1)
The second—more refined—approach involved the *in situ* generation of hydrophobic ion pairs between anionic surfactants and ATRP cationic complexes. The ion pairs shuttled the active copper catalyst and the electrochemical stimulus to the monomer droplets, enabling controlled polymerization. This catalytic mechanism opens a new avenue for controlled radical polymerization in *ab-initio* emulsion (whereby both small micelles and large monomer droplets are present).(2)
Fast and well controlled polymerization of acrylic and methacrylic monomers in aqueous dispersed media was achieved with as low as 50 ppm of copper. Moreover, catalyst removal (by technique such as electrodeposition) was simple because during purification the hydrophilic cationic copper complexes easily left the hydrophobic polymer particles.

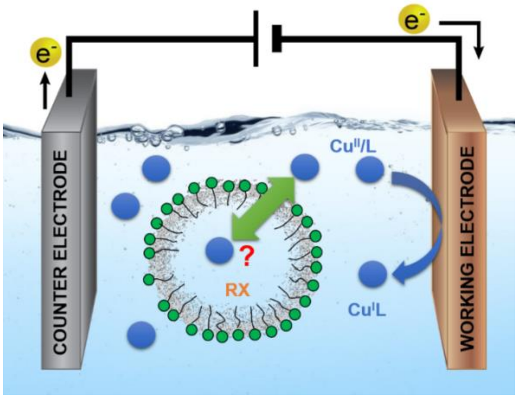

Figure 1. Scheme of electrochemically mediated ATRP in dispersed media (L = amine ligand)

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Artificial Inherently Chiral Electroactive Membranes

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Low-cost, continuous, high-efficiency resolution technology is clearly needed for commercial-scale preparation of enantiomerically pure substances. Membrane technology, fortunately, fulfils this need very well because of its high efficiency, low energy usage, simplicity, convenience for up- and/or down-scaling, and continuous operability. Membrane-based chiral resolution can be achieved using either enantioselective or non-enantioselective membranes. The enantioselective membranes themselves can carry out chiral separation of enantiomers because they contain chiral recognition sites (1). Considering the outstanding enantioselection ability achieved with our inherently chiral surfaces (2) we have decided to synthesize by electrooligomerization inherently chiral membranes. These membranes were electrodeposited on FTO electrodes from the enanantiopure monomers of our inherently chiral forefather (BT_2T_4) dissolved in acetonitrile + tetrabutylammonium hexafluorophosphate 0.1 M as supporting electrolyte. The chiral membrane detachment is then obtained by dipping the FTO in deionized water. Preliminary tests have shown that they are electroactive with a perfectly specular CD spectra. We have also performed experiments by inserting the enantiopure membrane in a support normally used for ISE electrodes.

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Electrochemical Impedance Spectroscopy Meets Arduino: Can We Make an Open-source Impedance Analyzer?

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Commercial potentiostats which offer modules to perform electrochemical impedance spectroscopy (EIS) have very high specifications like broad frequency range (> 6 orders of magnitude), high accuracy, and low distortions. However, they are much more expensive than standard instruments. Moreover, the instrument is a black box where often the scientist has little or no knowledge of the real operations, such automatic phase corrections or current range selection, or because of software usability some fine features are hidden, like for example the choice of an arbitrary integration time or inspection of harmonic distortions. Although the high quality of the hardware, these limitations hinder more sophisticated or particular applications or simply make troubleshooting more complicated.

On the other hand, the advent of chip, easy-to-program microcontrollers equipped with analog to digital (ADC) and digital to analog converters (DAC) give the possibility to build up a rather inexpensive impedance spectrometer with full control over any feature. Arduino paved the way of an electronic revolution, where almost everybody can be able to interface a computer to an instrument. Some relevant specifications of Arduino and Arduino-compatible microcontrollers are reported in the table.

Summary table for some microcontrollers.

	Arduino Due (1)	Teensy 3.6 (2)
Price	~35 €	~35 €
CPU clock frequency	84 MHz	180-240 MHz
Memory (flash+SRAM)	608 kB	1280 kB
Number of ADC	12	25
Number of DAC	2	2
ADC resolution	12 bits	>12 bits
DAC resolution	12 bits	12 bits

Several open-source projects already showed how to build up and program computer base oscilloscopes (reference (3) for example). Moreover, the high computational power and rather large memory allows to perform fast Fourier transforms on the chip or to buffer the data during streaming to the computer for more involved analysis giving large flexibility in the usage.

In this work we report the results achieved with some Teensy (Arduino-compatible) microcontrollers connected to standard potentiostats in performing EIS. The details of the analog front end, program, and signal processing, following the open-source spirit, are also shown and discussed.

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Thin films of MoS_2 on Ag(111)

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The transition metal dichalcogenides (TMDC) are materials of interest in the fields of the material chemists, physicists and engineers.

TMDC monolayer s are 2-dimensional (2D) material, as graphene, have the general formula MX_2, where M is a transition metal (as Ta, Nb, Mo or W) and X is chalcogen (as S, Se or Te) (1). Each layer of MX_2 is a trilayer, made up of a sandwich of two chalcogen layers on either side of a transition metal center layer.

The Electrochemical Atomic Layer Deposition (E-ALD) is one of these techniques that allows us to produce thin films of semiconductor. Exploiting Surface Limited Reactions (SLR), it enables the deposition of highly ordered ultra-thin films from diluted aqueous solutions and at room temperature and pressure.

Underpotential deposition (UPD) is a type of electrochemical SLR, where an atomic layer of a first element is deposited on a second, at a potential prior to (under) that needed to deposit the first element on itself, so that the resulting deposit is generally limited to an atomic layer.

It occurs when the depositing element is able to somehow interact with the substrate, so that the deposition of the layer in direct contact with the substrate occurs at a potential preceding bulk deposition, that is, the deposition of the element on itself.

In the study presented here, E-ALD was used to grow molybdenum disulfide MoS_2 on crystalline Ag[111] elecrtode. UPD anodic electrodeposition of Na_2S on crystalline Ag[111] electrode are well-known (2). The research move to discover the optimal conditions to deposit Mo on Ag/S from a solution of MoO_4^{2-} in alkaline buffer. This study has been carried by means of voltammetric techniques, and AFM characterizations of the deposit.

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Influence of Different Porosity Carbon Supports in the RRDE Analysis

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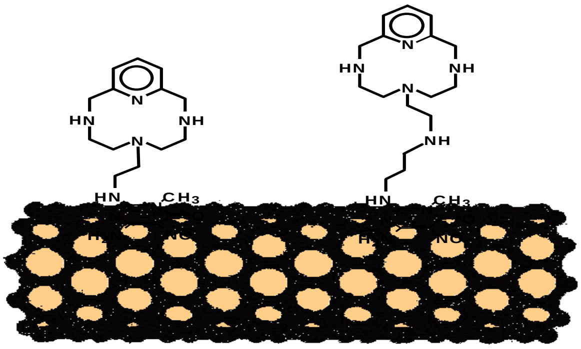
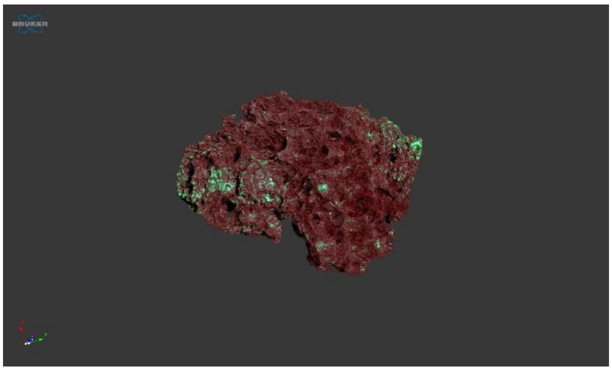
RRDE is an electrochemical technique furnishing information about the mechanism of the Oxygen Reduction Reaction (ORR) and its kinetic parameters (1). One of the most appealing applications of ORR consists in the study of reactions occurring at the cathode in energy converting systems such as fuel cells. In order to speed up the ORR kinetics to reach a practically usable level in fuel cell, a cathode ORR catalyst is needed. Platinum-based materials are the most practical catalysts. Nevertheless, owing to the limited reserve in nature of Platinum-group metals, and to their prohibitive cost, extensive research has focused on developing alternative catalysts. It was observed that the activity of an electrocatalyst increases hand to hand with the reaction surface area. The use of carbon supports is the right compromise to minimize the use of metallic catalysts. The high surface area of carbon supports is due by their high porosity (2). In this work we evaluated, by means of Rotating Ring-Disk Electrode (RRDE), the electrocatalytic properties of different porosity of carbon supports. Measurements were performed by using RRDE from Pine Instruments Co. All cyclic voltammograms (CV) and RRDE were carried out at scan rate of 5 mV/s in the potential range from -1,1 to +0,2 V vs Ag/AgCl/sat. KCl. The number of electrons transferred for O_2 molecule for each catalyst were calculate by Koutecky-Levich (K.L.) equation applied to the ORR curves obtained at different rotation rates (rpm) and from RRDE technique. The results were compared with data relating to the Glassy Carbon electrode and Pt-electrode. These results showed a different values on number of electrons between K.L. and RRDE. In fact, a high porosity of carbon supports showed a greater difference between the two techniques of analysis.





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Electrodeposition of Bismuth Thin Films

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The electrodeposition technique is an interesting approach for the production of materials with application in electronics devices and photovoltaics components, since needs simple conditions and has low costs (1). The EALD (Electrochemical Atomic Layer Deposition) method allows a high control on the deposit by the single-layers surface limited electrodeposition (2). With an automatized system for the repetition of different mono-layers deposition cycles we are able to control the thickness and composition of the entire final material, which is an important requested task in nanoscience.

In this study, we present the electrodeposition of bismuth-based materials, which is a relatively unexplored new field of research that is expected to show many desirable thermoelectric, optoelectronic and electronic properties for technologically innovative devices besides bismuth is a component of nanostructure topological insulators.

Thin films of both bismuth alone and semiconductors compounds have been explored with EALD using a silver (111) mono-crystal as substrate (3). Our goals were to grow a “massive” layer (up to hundreds of nanometers) of crystalline nanostructured bismuth, deposit a multi-layer crystalline structure of bismuth selenide investigating the optimal conditions to obtain these materials in addition to the understanding of the deposition mechanisms.

The synthesized thin films have been characterized electrochemically with cyclic and stripping voltammetry to obtain composition information followed by a morphological and microanalytical SEM-EDX investigation and structural characterization.

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Effect of Pressure on the Electrochemical Conversion of CO2 to CO

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To minimize the negative effect of carbon dioxide as a greenhouse gas and introduce renewable energy in the chemical and energy chain, an interesting approach is the Carbon Capture and Conversion. In this context, one of more appealing conversion strategies is the electrochemical reduction of CO_2, which could combines the utilization of excess electric energy from intermittent renewable sources with CO_2. (1) Furthermore, CO_2 can be selectively converted into various useful chemicals by changing the operating conditions of electrolysis. In particular, an increasing attention has been devoted to the electrochemical conversion of carbon dioxide to carbon monoxide. (2,3) The main obstacle of that conversion from water solution is the low CO_2 solubility in water. In this work, a methodical study on the effect of the CO_2 pressure and of other operating parameters on the conversion of CO_2 at flat cathodes to carbon monoxide was performed. In detail, the reduction of CO_2 was studied in different kind of electrochemical cells to evaluate the effect of various operating parameters, including the nature of the supporting electrolyte and the nature of cathode (Ag and Au), the current density, the pH and the pressure of CO_2. It was shown that an increase of the pressure leads to an improvement the stability of the electrode.

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Operative parameters and bacterial community effect on single chamber membraneless microbial fuel cell

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Municipal, domestic, animal and food processing wastewaters have a theoretical carbon content sufficient to globally sustain the whole water infrastructure. However, it is a common practice to use additional energy to remove it instead of trying to convert it (1). It is possible, indeed, to directly convert this organic content into electricity thanks to microbial fuel cells (MFCs), bio-electrochemical devices in which particular bacterial strains oxidize the organic matter using electrodes as final electron acceptor (2). What has been mainly adopted in this work, is usually reported as Single Chamber Membraneless (SCML) MFC. SCML-MFC were developed without any physical delimitation between the anodic and cathodic environments. With regards to a conventional MFC, SCML have reduced cost, both investment and exercise, avoiding the usage of membranes (3). In some SCML-MFC work, an horizontal cathode is used, lying at the interface between the liquid and the gas phase (4), circumstance that inspired our work (5). Other authors have changed electrode distance in order to asses this parameter influence (6), deducing that a closer distance could increase aeration of the anodic biofilm, lowering the performance. Thus, researchers concern designing SCML-MFC is to limit as much as possible anode oxygenation (8).In the present work, this very same path was followed, exploring the effect of cathode positioning, hydrodynamic regimen and evaluating the possibilities given by the usage of bio-cathodes with both pure *Shewanella putrefaciens* culture and mixed communities.

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Towards High Energy Density Aging Resistant Li-ion Polymer Batteries

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A wide interest is mounting towards polymer electrolytes, due to their application in energy efficient rechargeable batteries, photo-electrochemical cells, electrochromics, and supercapacitors. Polymer electrolytes exhibit unique advantages such as mechanical integrity, wide variety of fabrication methods in desirable size and shape, possibility to fabricate an intimate electrode/electrolyte interface and adapt to a lightweight, leak-proof construction, and economic packaging structure.

In this communication, we offer a summary of our results regarding the synthesis, physico-chemical and electrochemical characterization of solid polymer electrolytes (SPEs) based on different monomers/oligomers (methacrylic and/or ethylene oxide based) with specific amounts of lithium salt, plasticizers and/or fillers (1,2). Profoundly ion conducting ($\sigma > 10^{-4}$ S cm^{-1} at 20 °C), electrochemically stable (> 5 V vs. Li), self-standing, robust and tack-free SPEs are successfully prepared via a rapid and easily up-scalable process including a light and/or thermally induced polymerization step. The resulting crosslinking allows the incorporation of high amounts of plasticisers (e.g., RTILs) and lithium salt (based on TFSI^{-} anion), leading to a material with remarkable morphological characteristics in terms of homogeneity and mechanical abusability under highly stressful conditions.

Lab-scale Li-polymer cells assembled show stable charge/discharge characteristics without any capacity fading at C/5 current regime (> 130 mAh g^{-1} in $LiFePO_4$/Li configuration and > 150 mAh g^{-1} in TiO_2/Li configuration even @ 20 °C). The overall performance of the SPEs postulates the possibility of effective implementation in the next generation of safe, durable and high energy density secondary all-solid Li-ion polymer batteries working at ambient and/or sub-ambient temperatures.

Acknowledgements:
MARS-EV project has received funding from the European Union Seventh Framework Program (FP7/2007-2013) under grant agreement n° 609201.

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Novel Lithium Battery Single-Ion Block Copolymer Electrolytes based on Poly(Ethylene Oxide) and Methacrylic Sulfonamide

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Polymer electrolytes have been proposed as a replacement for conventional liquid electrolytes in next-generation lithium-based batteries, mainly because of their intrinsic enhanced safety and peculiar chemical structure that can be tailored as desired to display unique properties such as lithium-ion transference number (t^+) approaching unity. This new class of materials, namely Single-Ion Conductors, has attracted increasing interest in recent years. Nevertheless, practical application of polymer electrolytes is still limited mainly by low ionic conductivity (σ), which is far below 10^{-5} S cm^{-1} at 25 °C.

Herein, the preparation and characterization of new families of single-ion conducting copolymers based on the specifically designed lithium 1-[3-(methacryloyloxy)propylsulfonyl]-1-(trifluoromethylsulfonyl)imide (LiMTFSI) anionic monomer is described (1,2). RAFT polymerization was employed to prepare well-defined anionic di- and tri-block copolymers comprising poly(LiMTFSI) and poly(ethylene oxide) blocks (1). The effect of the macromolecular architecture and molecular weight on thermal and ionic conduction properties is thoroughly discussed. Block copolymers were semi crystalline, with a single glass transition temperature (T_g) due to the miscibility of the amorphous regions of both the blocks. T_g, ranging from –55 to 7 ºC, as well as degree of crystallinity (X_c, ranging from 51 to 0%) were both composition dependent. Block copolymers showed very high σ as compared to previous examples (up to ≈ 10^{-4} S cm^{-1} at 70 ºC) combined with and impressive $t^+ \approx 0.91$, and wide 4.5 V electrochemical stability. In addition to these promising features, solid polymer electrolytes were successfully tested in $LiFePO_4$/Li cell prototypes at different temperatures providing long lifetime up to 300 cycles, and outstanding rate performance up to C/2 (≈100 mAh g^{-1}).

Acknowledgements
This work was supported by grant of the President of Russian Federation ‘‘For Young Outstanding Professors” (MD-2371.2017.3).

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Solid-state lithium batteries adopting sulfide-based solid electrolytes

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All-solid-state lithium secondary batteries with inorganic solid electrolytes (SEs) attract much attention in terms of safety and reliability. Bulk-type solid-state cells composed of electrode and electrolyte powders have an advantage of achieving large energy density. Key materials to realize bulk-type lithium batteries are SEs with high Liþ ion conductivity and active materials with high capacities which are suitable for all-solid- state lithium batteries. Sulfide based SEs have been studied because of their remarkably high lithium-ion conductivities at room temperature (1).

This work was aimed to select optimized components for a solid-state lithium battery. We studied Li3PS4 (SE1) and LiI-Li3PS4 (SE2) (Samsung R&D Institute Japan) as glass-type electrolytes. Li3PS4 and LiI-Li3PS4 were characterized in terms of transport properties (Impedance spectroscopy) studying the temperature dependence of the ionic conductivity and structure (Raman Spectroscopy and X-ray diffraction). We studied these electrolyte in an all-solid-state-cell in combination with different kind of anodes.

Acknowledgments:
The results of this work were obtained in the framework of the "Solid-State batteries using composite anodes" Project, funded by Samsung R&D Institute Japan (contract n. 7/2016 of the Chemistry Department, Sapienza University of Rome).

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Design of bis(fluorosulfonyl)imide-based ionic liquids for lithium ion batteries

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The great demand for batteries with high power and energy densities promotes the need for an advanced lithium-ion battery technology. The electrolyte is a critical component involved in balancing energy and safety specifications. The electrolyte solutions that normally contain organic solvents have been replaced with highly stable ionic liquids (ILs) to combat the flammability. ILs are entirely composed of ions and having negligible vapor pressure. We have been designed novel ILs which are suitable for the battery applications. Heteroatom-modification of simple ILs can cause unexpected change in thermal- and electrochemical-stability. However, we recently revealed that the modification of cation in ILs with an ethoxyethylether chain improves liquid properties of ILs, i.e. suppresses crystallization at sub-zero temperature, without detracting from the stabilities (1). In this case, bis(trifluoromethanesulfonyl)imide ([TFSI]) anion was combined with the designed cation, because TFSI is one of the most common species and suitable to compare fundamental properties in the battery applications. Here we selected bis(fluorosulfonyl)imide ([FSI]) as a counter anion because of its small molecular weight and excellent ion transportation property. Physical and electrochemical properties in terms of density, thermal stability, ionic conductivity, and electrochemical stability will be shown in the presentation. The properties will be compared before and after the addition of lithium salts. The performance of the lithium metal half-cell and the lithium ion full cell will also be evaluated and compared.

Acknowledgement
A.T. acknowledge the project "Avvio alla Ricerca 2016" from Sapienza University of Rome for financial support.

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Electrode Protection by Polymer Deposition in Lithium Batteries

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Recently, a great interest has been focused on electrolytic media with salt concentration higher than 1 molar that is the one commonly used. Electrolytic systems with equimolar ratio between salt and solvent are extremely interesting especially for their thermal and electrochemical stability. In some cases they can be described as solvate ionic liquids (SILs), i.e. salts in which the cation or the anion is strongly coordinated to a third molecule, thus forming a complex ion. The strategy to use SIL for lithium batteries has already been pursued, particularly to ameliorate Li interface stability [1-4].

The ability of SILs in forming good solid electrolyte interphase (SEI) on lithium or on graphite anodes is of utmost importance for the stability of lithium metal and lithium ion batteries. Furthermore, the compatibility with the cathode and with the species that are here produced is mandatory in presence of the high-potential cathodes of lithium-ion batteries, of the cathodes where the reduction of molecular oxygen takes place in lithium/air batteries, or in presence of sulphur-based cathodes and soluble polysulfides in lithium/sulphur batteries [5-8].

In this contribution, we investigate the effect of highly concentrated solutions based on lithium bis (trifluoromethanesulfonyl) imide (LiTFSI), lithium triflate (LiTf) and 1,3-dioxolane (DOL) both on Li and on sulphur-based electrodes. Particularly, DOL polymerization from 5m LiTFSI-DOL and 5m LiTFSI-DOL:dimetoxyethane (1:1) solutions at voltage higher than 4 V [9, 10] is exploited to produce a protective polymer layer in-situ on the sulphur-based cathode, also in presence of a suitable (commercial or electrospun) separator, and the results are reported and discussed.

Acknowledgements: The authors thank for financial support MSE-ENEA Electrical System Research 2015-2017 "Energy storage for electric system" Project, MIUR-DAAD Joint Mobility Program "Interface properties of electrode materials".

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Mixed oxided electrodes containing manganese on pretreated titanium support for environmental applications

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Mixed oxide electrodes have been extensively studied for their electrocatalytic activity. In particular manganese oxide-based (MnOx) films combine low cost with a reduced electrogeneration of chlorinated by-products in the presence of chlorides and low cost.

In previous works (1), we have presented the performance of MnOx films grown on both untreated and microstructured titanium substrates and we have verified that the morphological and electrochemical properties are improved by a surface texturization. The method involves the oxide deposition on substrates modified at a nano-scale with an enhancement of electrocatalytic properties with significant increase in the life time of the electrode.

The present work investigates the electrochemical behavior of new manganese-based electrodes obtained by co-deposition of the manganese oxide in combination with other metals. In particular, different types of anodes have been obtained by co-deposition of Ru (Ruthenium) Mn (Manganese) and Cu (Copper) oxides with different ratio. These thin films have been prepared by thermal decomposition on titanium substrate from alcoholic solutions. The titanium substrates were pretreated by HF etching.

The obtained electrodes have been characterized in terms of chemical and morphological properties by scanning electron microscopy (SEM) and Energy Dispersive X-ray Analysis EDX. Moreover, their electrochemical behaviour was evaluated by potentiodynamic polarization curves and cyclic voltammetry tests. We also tested and compared their oxidizing ability in the degradation of aqueous solutions containing a model compound and small amount of chloride. Galvanostatic experiments were conducted in a membrane-free reactor. The treatment extent was assessed by detection of color and TOC decay. The electrogeneration of active chlorine, chlorate and perchlorate was also monitored. The preliminary results show that ternary oxides coated electrodes exhibit enhanced electrocatalytic activity with negligible formation of undesired chlorinated by-products.

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Scalable Fabrication of Graphene-based Textile Supercapacitors by Mimicking an Industrial Process

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Graphene-based electronic textiles have drawn significant research interest as the potential components for low-cost multifunctional flexible and wearable electronics for sportswear, military and health care applications (1). One of the key challenges to integrate these electronic devices to textiles is the requirement of being lightweight, flexible, and high performance power supply unit (2). Flexible supercapacitors are promising energy storage device that can meet these requirements while maintaining the same electrochemical properties such as high power density, longer life cycles, and quick charge/discharge (3). Recently, graphene (G) has been focus of much investigation for energy storage applications due to its extremely high specific surface area, excellent mechanical properties, and high thermal and electrical conductivity (4).

However, majority of the textile supercapacitors reported are based on reduced graphene oxide (rGO) and could only be produced at laboratory scale. Here, we report a simple, scalable, and cost-effective padding method for fabricating e-textile electrodes for flexible supercapacitors application. To our best knowledge, we report for the first time the use of electrochemically exfoliated G for textile supercapacitors.

Electrochemically exfoliated Graphene (G) was ultrasonically dispersed in Isopropanol/water 50/50 V.% solution. Then, Polyester-Cotton (PC), Cotton (C), and Nylon (N) fabrics were padded using G dispersion and dried in oven at 150°C for 15 minutes. The quality of both G was assessed by XPS and Raman spectroscopies. As prepared samples were characterized by SEM and Raman to evaluate the dispersion of active materials in the fabric. Fabrics were dip-coated into a gel electrolyte. Three gels were tested: PVA-LiCl, PVA-H_3PO_4, and PVA-KOH. Electrochemical characterizations were performed afterwards to evaluate the performance of the coated fabrics.

XPS and Raman confirmed the exfoliation and the quality of the G. SEM images of the padded fabrics (PC, C, and N) show a homogeneous dispersion after the padding procedure. Complete electrochemical characterizations demonstrate significant results for textile supercapacitors applications.

For the first time, a padding procedure mimicking an industrial process allows to obtain textile with suitable power sources for e-textile applications. Moreover, this procedure uses directly G as active material while previous research in this field was focused on rGO.

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Galvanostatic reduction of cinchona alkaloid-derived ammonium salts: a simple, highly efficient strategy for chiral modification of metal surfaces

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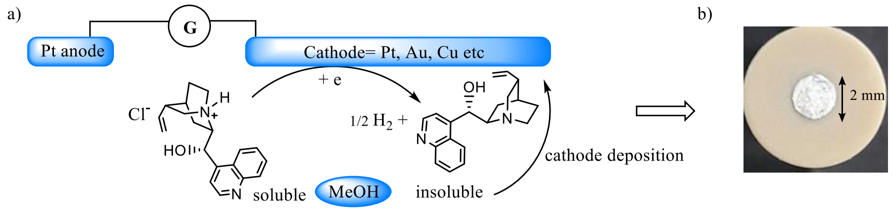
In the field of the asymmetric synthesis, the development of heterogeneous chiral catalysts attracts for a long time intense research efforts. With respect to the homogeneous ones, heterogeneous chiral catalysts offer several advantages for practical applications such as the easy separation from the reaction mixture, high stability and potential reusing for multiple times. In parallel, the flourishing of the “organocatalysis” as a powerful, low-cost and eco-friendly method to induce enantioselective reactions, has led to the development of a related research area which focus on the immobilization of the organocatalysts on different solid supports in order to combine the advantage of this kind of bioinspired chiral inductors with the beneficial to use them in heterogeneous manner. Indeed, several different strategies have been applied to manufacture chirally-modified surfaces, including covalent attachment, “ship-in-a-bottle” entrapment, chemical or electrochemical adsorption (1).

Among the most investigated modified surfaces with adsorbed organic molecules as chirality inductors, metal-cinchona alkaloid systems receive so far widely attention in view of their proven effectiveness, especially in enantioselective hydrogenation processes (2,3).

In this work we demonstrate that an effective deposition of cinchonine (CN) on various different metal surfaces can be easily achieved by cathodic reduction of cinchonine hydrochloride (CN·HCl) methanolic solution (scheme 1). Indeed, as depicted in scheme 1, the electrolysis, under galvanostatic conditions, induces H_2 evolution reaction which results in the absorption of insoluble CN at the cathode surface.



Scheme 1. A) Schematic depiction of the cell and chemical cathodic process. b) CN-modified Pt-electrode. Deposition time 600 *s*; *j*= 32 mA/cm^2

In order to determine coverage and apparent surface area and test the stability of the obtained CN layers, all the chirally modified metal surfaces will be investigated by electrochemical methods (4). In parallel, the catalytic abilities as well as the catalyst leaching of these materials will be tested in the asymmetric addition of aniline to chalcone as model reaction (5).

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Reliable first principles prediction of oxidation potentials: an important tool to design organic molecules for opto-electronic applications

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Charge separation and charge recombination processes are ubiquitous in modern opto-electronic devices and their kinetics can greatly affect device performances. An effective design of new organic molecules for opto-electronic devices cannot neglect kinetics considerations, which in turns requires highly reliable estimates of the redox potentials of the involved molecular units. Modern computational tools can be of great help in this task. DFT methods offer several advantages for computing oxidation free energy, providing sufficiently reliable results at reasonable computational costs.

Herein we present a benchmark study on the ability of different DFT approaches to predict oxidation potentials for a series of organic molecules, which are commonly used in opto-electronic applications. The comparison between predicted and experimental oxidation potentials, the latter ones obtained by cyclic voltammetry in organic solvents, with suitable supporting electrolytes, shows that standard hybrid functionals are capable of accurate predictions only for molecules with moderate push-pull character, whereas high-exchange meta functionals such as M05-2X and M06-2X provide better results for strong push-pull molecular systems. Noteworthy, by properly choosing the functional, the oxidation potential can be predicted with an accuracy of about 50 mV.

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Cospito Sante	FIS OR57
Costa Bassetto Victor	ANA/ELE/GS KN02
Dale Nicholas	ANA/ELE/GS OR02
Dall'Asta Valentina*	ELE OR09
D'Angelo Adriana	ELE OR29
Daniel Giorgia	ELE OR21
De Bastiani Michele	FIS OR51
De Bon Francesco*	ELE PO06
	ELE OR18

Iurlo Matteo	ANA/ELE/GS OR05
Jovic Milica	ANA/ELE/GS KN02
Karim Mohammad Nazmul	ELE PO22
Koster Dominique	ELE OR01
la Gatta Simona*	FIS OR56
La Mantia Fabio*	ELE OR01
La Mantia Fabio	ELE OR25
La Monaca Andrea*	ELE PO20 ELE PZ05
Lamberti Francesco*	FIS OR51
Landi Alessandro	ELE OR03
Lavacchi Alessandro	ELE PO13
Le Donne Alessia	FIS OR52
Lesch Andreas*	ANA/ELE/GS KN02
Lin Rongying	ELE PO16
Lisi Luciana	ELE OR20
Lista Florigio	ANA/ELE/GS OR7
Litti Lucio	FIS OR51
Lo Faro Massimiliano *	ELE OR17
Lo Faro Massimiliano	ELE OR34
Lo Vecchio Carmelo*	ELE OR12
Locatelli Cristina	ELE OR24
Lombardo Lucia	ELE OR13
Longoni Gianluca*	ELE PZ01
Lorandi Francesca*	ELE OR27
Lorandi Francesca	ELE PO08 ELE OR05 ELE PZ03
Macchia Eleonora*	ELE OR32
Magni Mirko	FIS OR54
Maier Joachim	ELE PO01
Maisano Susanna	ELE OR34
Malandrino Mery	ANA/ELE/GS OR03
Malara Francesco	ELE OR24
Maltese Vito	FIS OR57
Mancino Gabriella	ELE OR20
Mangiatordi Giuseppe F.	ELE OR32
Maniscalco Anna	ELE OR25
Mannucci Barbara	ELE OR11
Manoli Kyriaki	ELE OR32
Marcaccio Massimo	ELE OR04 ANA/ELE/GS OR05
Marchionna Stefano	FIS OR52
Marcus Philippe	ELE OR33
Maresca Giovanna*	ELE PO18
Maresca Giovanna	ELE PO19
Mariani Federica	ANA/ELE/GS OR01
Martinazzo Rocco	ELE PO04
Massoud Renato	ANA/ELE/GS KN01
Matic Aleksandar	ELE OR13

Mattarozzi Luca	ELE OR30
Mattiacci Giorgio	ELE OR21
Matyjaszewski Krzysztof	ELE PO08 ELE OR05 ELE PZ03 ELE OR27
Maurice Vincent	ELE OR33
Mazzaracchio Vincenzo	ANA/ELE/GS OR7
Mecerreyes David	ELE PO17
Melchionna Michele	ELE OR04
Meligrana Giuseppina	ELE PO16
Meneghetti Moreno	FIS OR51
Michieletto Alessandro	ELE OR27
Milano Francesco	FIS OR56
Millia Luca	ELE OR11
Minguzzi Alessandro*	ELE OR24
Monaco Rossella	ELE OR31
Montanaro Daniele	ELE PO21
Moreno Margherita	ELE PO16
Moscone Daniela	ANA/ELE/GS OR7
Moscone Danila	ANA/ELE/GS KN01 ANA/ELE/GS OR06
Musiani Marco*	ELE OR20
Musiani Marco	ELE OR30
Mussini Patrizia Romana*	ELE PO04 ELE OR31
Mussini Patrizia Romana	ELE PO09
Mustarelli Piercarlo*	FIS OR53
Mustarelli Piercarlo	ELE OR11
Nair Jijeesh R.	ELE PO16 ELE PO17
Naldoni Alberto	ELE OR24
Nale Angeloclaudio	ELE OR06 ELE OR15
Navarra Maria Assunta*	ELE OR13
Navarra Maria Assunta	ELE PO18 ELE PO19
Nawn Graeme	ELE OR15
Neagu Daniela	ANA/ELE/GS OR06 ANA/ELE/GS OR7
Negro Enrico	ELE OR06 ELE OR15
Oliveira Vanessa	ELE OR34
Orsini Monica	ELE PO21
Pace Giuseppe	ELE OR06
Pagot Gioele	ELE OR06
Pagot Gioele*	ELE OR15
Palazzo Gerardo	ELE OR32
Palleschi Giuseppe	ANA/ELE/GS OR04 ANA/ELE/GS OR7
Palombi Laura	ELE PO23
Pan Xiangchen	ELE PZ03
Pandolfi Fabiana	ELE OR28

Tomei Maria Rita	ANA/ELE/GS OR06
Tonelli Domenica	ANA/ELE/GS OR01
Torsi Luisa	ELE OR32
Tranchida Giada*	ELE OR16
Trinei Mirella	ANA/ELE/GS OR05
Trocino Stefano	ELE OR17
	ELE OR34
Trotta Massimo	FIS OR56
Tsurumaki Akiko*	ELE PO19
Tsurumaki Akiko	ELE PO18
Valenti Giovanni*	ELE OR04
Valov Ilia	ELE OR10
Vassallo Espedito	FIS OR54
Vàzquez-Gòmez Lourdes	ELE OR30
Velardo Amalia*	ELE PO24
Verlato Enrico	ELE OR30
	ELE OR20
Vertova Alberto	ELE PZ04
	ELE OR24
Vezzù Keti	ELE OR06

	ELE OR15
	FIS OR53
Vicari Fabrizio	ELE OR29
	ELE PO15
Visibile Alberto	ELE OR24
Vizza Martina	ELE PO11
Volpe Giulia	ANA/ELE/GS OR04
Wang Yi	ELE PO08
Yeates Stephen	ELE PO22
Zaccaria Marco	ELE PZ05
Zaffora Andrea*	ELE OR10
Zampardi Giorgia*	ELE PZ02
Zanna Sandrine	ELE OR33
Zerbetto Francesco	ANA/ELE/GS OR05
Zerbetto Mirko	ELE PO02
Zignani Sabrina*	ELE OR34
Zignani Sabrina	ELE OR17
Zilio Stefano	ELE PO05
Zlotorowicz Agnieszka	ELE OR06
Zolin Lorenzo	ELE OR22