Elettrochimica

ELE-KN-01 Lithium Batteries: a look into the future

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Li-ion batteries today exceed at least by a factor of 2.5 any competing technology thanks to the high value of energy density, i.e. 150 Whkg^{-1} and 650 Whl^{-1}. Due to their unique features, these batteries are the power sources of choice for the portable electronic market (including popular products such as cellular phones, lap-top computers, mp3s, etc) and are aggressively entering in the power tool equipment market and, in particular, in the emerging sustainable vehicle market. However, the present Li-ion batteries, although commercial realities, are not yet at such a technological level to meet the power requirements of efficient hybrid or electric vehicles. Reduction in cost, enhancement in safety and rate, and, especially improvement in energy density, are mandatory requirements. In this presentation, after a brief introduction on the basic characteristics of lithium-ion cells, the research currently in progress in our laboratory for upgrading their performance, are reviewed and discussed. It will be shown that the safety issue may be addressed by replacing the current, flammable liquid organic carbonate electrolyte solutions with more reliable polymer membranes, e.g., based on chemically stable polymer matrices and/or on not flammable ionic liquids. The cost of the battery may be reduced by moving from the common, expensive cathode and current collector materials to more affordable alternatives. The rate capability is strictly depending upon the morphology of the electrodes, as in fact demonstrated by few examples here illustrated. Finally, jumps in energy density may be achieved by totally renewing the battery chemistry. The most significant examples are provided by the lithium-sulfur and the lithium-air systems. Few preliminary results obtained on these "superbatteries" will be also presented.

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ELE-KN-02 Advanced Electrocatalysts for Intermediate Temperature PEM Fuel Cells

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Pt-alloy electrocatalysts have been investigated for operation in a polymer electrolyte membrane (PEM) fuel cell up to a temperature of 130 °C and at pressures up to 3 bar abs. [1, 2]. The aim was to evaluate their performance and resistance to degradation. Nanosized Pt and PtCo catalysts with crystallite size of about 3 nm were prepared by using a colloidal route. A suitable degree of alloying and a face-centered cubic (fcc) structure were obtained for the PtCo catalysts by using a carbothermal reduction. The surface properties were investigated by X-ray photoelectron spectroscopy (XPS) and low-energy ion scattering spectroscopy (LE-ISS, $3He^+$ at 1kV) [2]. The formation of a Pt skin layer on the surface of the alloy electro-catalyst was obtained by using a pre-leaching procedure. Furthermore, the amount of Pt-oxides on outermost atomic layers was much smaller in the PtCo than in the Pt catalyst. These characteristics appeared to influence catalysts' performance and degradation. Accelerated tests (electrochemical cycling) at 110 °C and low R.H. showed good stability for the PtCo alloy. Furthermore, better performance was obtained at intermediate temperatures for the pre-leached PtCo as compared to the Pt cathode catalyst.

Acknowledegement
The author acknowledge the financial support of the EU through the QuasiDry Project 256821. "The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2010-2013) under the call ENERGY-2010-10.2-1: Future Emerging Technologies for Energy Applications (FET)."

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ELE-KN-03 Dissociative Electron Transfer to Organic Halides: From Theory to Applications.

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The electrochemical reductive cleavage of carbon-halogen bonds in organic compounds has been the object of intense interest and investigation for many years, both from mechanistic and synthetic viewpoints. An important issue of the reduction process is whether the reductive cleavage occurs in a single step, breaking of the bond being concerted with the electron transfer, or in two steps with the transient formation of a radical anion.

The electroreduction of various organic halides, representative of both stepwise and concerted mechanisms, has been comparatively analysed at GC and at some potential electrocatalytic cathodes, namely Ag, Cu, Pd, Ag-Pd and Cu-Pd. All these materials are good electrocatalysts and, among them, Ag, either bulk or nanoparticles, is one of the best. So far, various factors such as the type of the halogen atom, the molecular structure of RX, the surface morphology of the electrode and adsorption/desorption behavior of the halide ions have been identified to play an important role in the electrocatalytic reduction. Furthermore, the existence of a strong linkage between catalysis and mechanism of dissociative ET has been shown for the reduction of a series of chlorides in aprotic solvents.

The reduction of organic halides and, in particular, the extraordinary catalytic properties of silver have been applied in several electrosynthetic processes. In particular, the electrosynthesis of fine chemicals and pharmaceutical products by electrocarboxylation of the corresponding chlorides at Ag has been successfully achieved and, in some cases, also a first scale up has been developed with very encouraging results.

More recently, the mechanism of catalytic reduction of activated alkyl halides has attracted much attention, in relation to atom transfer radical polymerization (ATRP), which is a powerful method of living radical polymerization (LRP) that can be applied to a wide range of monomers for the synthesis of polymeric materials with pre-determined molecular weights, low polydispersities and desired molecular architectures The mechanism of reductive cleavage of model alkyl halides used as initiators in LRP, has been investigated in acetonitrile using both experimental and computational methods. Both theoretical and experimental investigations have revealed that DET to these alkyl halides proceeds exclusively via concerted rather than stepwise manner, giving useful information on the mechanism of LRP and the possibility of optimizing the polymerization processes.

ELE-KN-04 Carbon Molecular Nanosystems Investigated by Electrochemical Tools

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Over the last two decades, we have assisted to the subsequent rise on the stage of the new molecular materials of the three different low dimensional carbon nanomaterials, from 0D fullerenes to 1D nanotubes and, more recently, 2D graphene. Their unique structural, optical and redox properties are showing an increasing potential for a wide range of applications, energy conversion devices, in-vivo and in-vitro biosensing and catalysis [1], and electrochemistry has always played a special role in the investigation of their electronic properties, as either individual entities [2] or functionally integrated in molecular or macroscopic devices [3].

Herein we shall report examples of our recent studies on the fundamental redox properties of pristine and chemically-modified carbon nanosystems, investigated by either bulk or scanning probe techniques and on their exploitation in electrochemical biosensing and energy conversion devices (Figure 1).

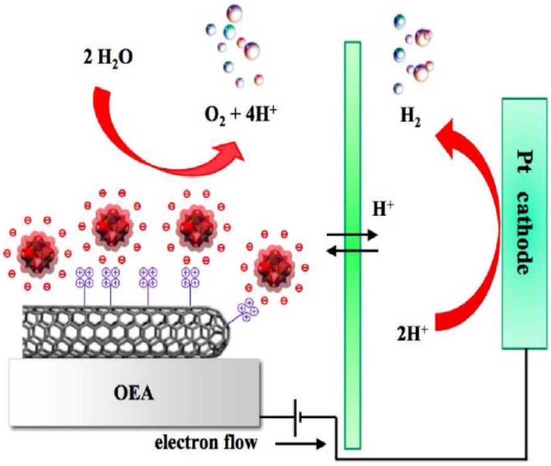

Figure 1

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ELE-KN-05 Electrochemistry in wastewater and soil remediation

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The progress of the research in electrocatalysis and electrode material science since the middle of last century, has led to a substantial decrease of the environmental impact in important fields of industrial electrochemistry like chlor alkali and aqueous electrometallurgy.

As far as anode materials are concerned, the introduction of oxide-modified titanium devices, originally proposed for chlorine production in the second half of the ‘60ies, found further important applications for oxygen-evolving anodes.

Research on this topic has led, in turn to processes related with pollution abatement in wastewaters. In fact, stable oxygen-evolving anodes are currently used in electrochemical processes of abatement of heavy metals by cathodic deposition, of consolidated commercial interest. More recently, specific types of anode materials have been tested for the so called electrochemical incineration of organic pollutants. This type of application, which would be of great interest for the abatement of bio-refractory substrates, and more, generally, for the minimization of chemical reactants involved in the decontamination process, has been the subject of a number of fundamental papers, although the level of commercially interesting technology has not been reached yet. In this communication, the main features, pros and cons, of different types of electrochemical incineration will be discussed, together with results of possible practical interest.

One more potential application of electrochemistry in environmental remediation is represented by soil decontamination. The so called electrokinetic soil remediation substantially consists of an electrochemically sustained solvent transport through a saturated soil matrix which causes transfer of neutral and charged contaminants through the soil. Together with solvent transport, also electromigration of ionic components of soil solution also takes place and may favor the yield of the overall decontamination. Electrokinetic soil remediation has been discussed first by R. Lagemann in late 80ies, and then in early 90ies by Y.B. Acar and A.N. Alshawabkeh. Much experimental results have been accumulated, essentially on model-polluted-soils, essentially caolinite and a few other clay components and data on real soil samples are rare. In this frame, inevitably, also the evidence for commercial installations is practically missing, even considering pilot-plant scale. Yet, the future of soil reclamation more and more imposes the *in.situ* or at least *on-site* technologies and this makes the electrokinetic approach a promising one, provided the level of knowledge on the performance under real conditions are mdae available.

On these aspects some basic elements of knowledge will be dealt with in the communication, together with some original experimental results.

ELE-OR-01 Electrodeposited iridium oxide as studied by tip/substrate steady state voltammetry

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Iridium oxide is well known for its wide field of applications that range from electrocatalysis to electroanalysis, from electrochromism to neural stimulation.
In this work, the properties of electrodeposited iridium oxide films (EIROFs) have been studied by scanning electrochemical microscopy (SECM) in the feedback mode by means of the so-called tip/substrate (T/S) voltammetry under steady state conditions.
This SECM mode was intensively used in the past for the study of conducting polymers, as in reference [1].
The main purpose is the study of the reversible solid state-redox transitions that occur over iridium oxide in the potential range around 0.4 -1.4 V (RHE) and that are at the basis of all its applications. The transitions are observed and studied by combining (i) the use of suitable reversible redox couples and (ii) the effect of selecting different solution pHs for "shifting" the potential of the redox transitions themselves. In fact, the latter are pH dependent as evident from the common equation:

$$IrO_x(OH)_y + \delta H^+_{(solution)} + \delta e^-_{(oxide)} = IrO_{x-\delta}(OH)_{y+\delta} \qquad (1)$$

Moreover, being EIROFs highly hydrated films, protons are free to move in the whole electrode mass. In particular conditions, the transition includes a conversion semiconductor/conductor (like in the Ir(III)/Ir(IV) transition), that has a remarkable effect on the feedback current. The possible individuation of electrogenerated iridium species of different valencies via their reaction with one form of the redox couple, by analogy with a recent publication [2] on oxidized Pt, is also discussed.

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Acknowledgements: The financial contributions of PRIN 2008 – "Pt-free electrocatalysts for direct alcohol fuel cells." 2008N7CYL5 and PUR-Università degli Studi di Milano (2009 – 2010) funds are gratefully acknowledged.

ELE-OR-02 Electroanalytical determination of benzidine by differential pulse voltammetry on different electrodes.

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Benzidine is a solid organic compound which evaporates slowly, especially from water and soil. It was used in the synthesis of azo-dyes widely employed in textile, printing, leather, paper making, drug and food companies around the world. However, in 1973 benzidine was identified as a carcinogenic agent for human urinary bladder because its oxidation by human enzymes can permit its binding with DNA. For these reasons, it belongs to the list of the Priority Pollutants [1-2]. Although benzidine production and use was forbidden in many countries since 1970s, benzidine based azo-dyes are still used in many research laboratories and industries, and its detection and determination is a primarily concern.

Various methods for detection of benzidine are proposed in the literature, such as colorimetric, spectroscopic, electrochemical [3] and chromatographic ones. In particular, liquid, high performance liquid and gas chromatography are the most used techniques, frequently associated with mass spectrometry.

Electroanalytical techniques and particularly those based on pulsed voltammetry, which are suitable for trace analysis, constitute an interesting alternative in terms of very high sensitivity, low response time, small dimensions and low costs.

In this presentation a new method for quantitative detection of benzidine based on differential pulse voltammetry on Glassy Carbon (GC) and Platinum wire bare electrodes is proposed. The use of carbon-based or platinum-based screen printed electrodes (SPE) is also investigated.

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ELE-OR-03 ELECTROKINETIC REMEDIATION OF SOILS CONTAMINATED BY MERCURY

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The electrokinetic approach, for the extraction of metal ions from dispersed solid matrixes, has received extensive description in the scientific literature of the last twenty years. The application of electric fields of suitable intensity, through saturated portions of soils, can determine the displacement of charged species. In principle, this effect has two components: one is the electromigration, the other is the component due to the electroosmotic drag of the spatial ionic charge facing the charged surface of soil particles.

In the case of electromigration, the electric field has essentially the role of "driving force" for the movement of ionic species through the water impregnating the dispersed solids and the soil in particular. The effect remains even if the solid matrix is finely divided.

The application of this technology, when aimed to the removal of mercury present in metallic form, requires its prior dissolution, which can be facilitated by adding appropriate chemicals. Designing an intervention requires a preliminary speciation of the contaminant in the soil, as well as the execution of electrochemical tests at a laboratory scale.

The analysis of soil with speciation of the pollutant was carried out following the approach proposed by Boszke et al. *"Mercury mobility and bioavailability in soil from contaminated area"*, Environmental Geology (2008) 55: 1075-1087. The soil analysis was repeated after the electrochemical laboratory test, for an assessment of the amount of removed Hg. In addition, results obtained with this method were compared with those acquired using the alternative EPA 3200 procedure for speciation.

The electrochemical laboratory test was performed on approximately 400 kg of soil, and for a period of about three months. After treatment, the soil analysis showed a significant reduction of total Hg (approximately 60% of the total).

Basing on these results, an intervention in the field is being planned: estimation of time required to achieve the objective of remediation has been based on the removal of mobile and mobilizable forms of Hg.

ELE-OR-04 Electrochemical capabilities in both photoreduction and detection of toxic Cr(VI) pollutant

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Chromium is widely used in several industrial processes such as metal plating, leather tanning, paint making and others [1,2]. Due to its acute toxicity, carcinogenic action and high mobility in water, Cr(VI) is in the list of priority pollutants of most countries. In aquatic environments, chromium is present mostly as hexavalent Cr(VI) and trivalent Cr(III). Cr(III) is less noxious and usually immobile through precipitation or adsorption onto solid phase. Therefore, the rapid and accurate monitoring of both chromium species and the efficient reduction of Cr(VI) to Cr(III) in contaminated waters are highly desirable.

Specifically, Cr(VI) ions in water can be completely photoreduced to Cr(III) at the surface of UV-excited TiO_2 photocatalysts [3]. The transfer of photocatalytic results from slurry to immobilized particles on substrates is a general concern, primarily due to the elimination of filtration steps. Thus, the first part of this presentation is focused on the electrophoretic deposition (EPD) of TiO_2 as an alternative procedure to deposit the oxide in dense layers, avoiding slurry filtration steps [4]. The second part of the presentation will be devoted to the study of the photocatalytic performances of titania layers by comparing traditional polarographic techniques with a new environmentally friendly electroanalytical approach based on the use of bismuth screen printed electrodes [5].

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ELE-OR-05 Electrodeposition of metal nanoparticles on commercially available Digital Versatile Disk (DVD) for sensing and catalysis.

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The success and the spreading of a technology strongly relies on the possibility of employing economical and widely available row materials, and easy production methods. In this work, we have exploited the possibility to use the metallic surface of a commercial Digital Versatile Disc (DVD) as an electrodic support for the fabrication of optical and electrodic devices to be employed in sensing and in catalysis. Nowadays, with the advent of the new storing devises, DVDs represent nothing else than a technological waste. On the other hand, they are also a real silver/gold mine in the form of smooth reflecting films, usually prepared by sputtering over a polycarbonate nanostructured support. In fact, DVDs have a surface layer made of Ag or an Ag alloy, which in this work has been used as a support for the electrodeposition of nanoparticles (NPs) of Ag or Cu. The electrodeposition has been carried out in a galvanostatic or potential-controlled pulsed deposition mode, evaluating important parameters, such as current density, applied potential and the chemical environment, which influence the nucleation and the growth of the metal NPs. The modified substrates have been characterized by cyclic voltammetry in aqueous and organic electrolytes in order to evaluate the stability of the metal NPs. Furthermore, the electroreduction of molecular probes, such as benzyl chloride, has been investigated to check whether nanostructuring and surface morphology affect the electrocatalytic activities of these metals.

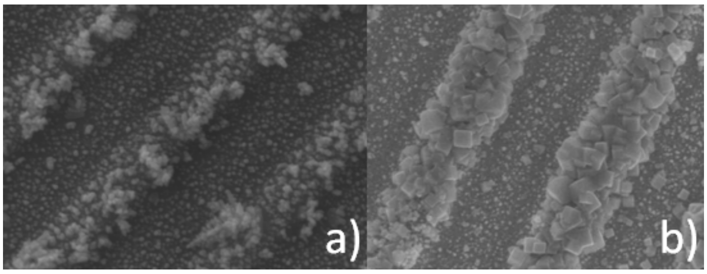

Figure 1.

AFM and SEM characterizations of the functionalized supports reveal that the deposited NPs preferentially pack over the groves of the DVD grating (Fig. 1 a and b). Furthermore, microRaman experiments have pointed out that DVD derived SERS substrates are very good candidates for the development of convenient and disposable sensing platforms [1]; in fact, the substrates show really interesting SERS properties and Enhancement Factors, which are clearly affected by the shape and distribution of the NPs.

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ELE-OR-06 Pyrrolidinium imide - based composite gel electrolytes for Li batteries

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Blends of PVdF and ionic liquids (ILs) are interesting for application as electrolytes in plastic Li batteries. They combine the advantages of the gel polymer electrolytes (GPEs) swollen by conventional organic liquid electrolytes with the nonflammability, and high thermal and electrochemical stability of ILs.

In this work we report on some PVdF-HFP composite membranes swollen with a solution of LiTFSI in ether-functionalized pyrrolidinium-imide ionic liquid ($PYRA_{12O1}TFSI$). The liquid electrolyte was tested both as pure system (Li-IL) and mixed with proper amounts of EC/DEC as co-solvents in order to find an optimal composition with an enhanced ionic conductivity and preserved thermal stability. The membranes were filled in with silica nanoparticles of different microstructures. The ionic conductivity and the electrochemical properties of the gel electrolytes were studied in terms of the nature of the filler.

Each membrane was thoroughly characterised from the physico-chemical and electrochemical points of view. Particular attention was devoted to the investigation of the Li/gel compatibility by taking into account several key-factors, like the filler morphology and IL amount in the liquid electrolyte.

Battery tests, performed at room temperature on the conventional solid state cell Li/composite gel polymer/$LiFePO_4$, are also presented.

ELE-OR-07 New electrocatalyst for Li/Air cathode batteries: MnO_2 *via* hydrothermal method

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Since the first announcement in 1996 by Abraham, Li/air batteries have attracted the attention because of their high specific capacity (up to $1800 \mathrm{mAh \cdot g^{-1}}$), thanks to the positive pole reaction based on the reduction of O_2, that can be directly provided by the air without the necessity to upload the chemical reagent in the battery. At the same time, secondary Li/air cells suffer serious limitations under recharging conditions, because the “combustion” products, Li_2O_2 and/or Li_2O, can clog the carbon-based cathode pores, thus reducing the performance and lifetime of the batteries. It is well accepted that their complete removal during the charge cycle is hard to accomplish without an appropriate catalyst. The use of electrolytic MnO_2 has been proved to be rather effective, but the overall performance of the modified cathode material is still inadequate to guarantee the expected long life cycles to the new Li/air batteries.

In this context we present a new composite material based on ordered mesoporous carbon cathode modified with MnO_2 electrocatalytic nanopowders prepared by an hydrothermal method, based on the oxidation of Mn^{2+} by ammonium peroxodisulphate. The syntheses were carried out for 24 h at different temperatures (60, 90, and 120 °C) also in the presence of dopant species. The results are discussed in term of cyclic voltammetry experiments performed by hosting the new composite powders in cavity microelectrodes, and in term of laboratory Li/Air battery life cycles.

The financial contributions of PRIN 2008 – *“Development of the Li/air cell for automotive applications.”* 2008PF9TWZ, CARIPLO 2010 – 2010-0506 and PUR-Università degli Studi di Milano (2009 – 2010) funds are gratefully acknowledged

ELE-OR-08 Electrochemical behavior of Na_xCoO_2 prepared by hydrothermal reaction

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The cheaper and much higher natural abundance of sodium than lithium have renewed interest in compounds of the former as electrode materials for rechargeable batteries in the last years.
In the present contribute we report about the electrochemical behavior of Na_xCoO_2. The material was obtained by, cheap and easy to scale up, two steps preparation route: a solvothermal reaction, to produce cobalt oxide with controlled and nanometric morphology, followed by a solid state reaction with Na precursors. In particular, the phase prepared using NaOH as precursor shows the X-ray spectrum corresponding to $Na_{0.71}CoO_2$, according to the 30-1182 JCPDS card. SEM and TEM images point out a sub-micrometric morphology with well defined crystalline particles.
Electrodes were fabricated by standard battery technique on 304 stainless steel foils. Preliminary electrochemical characterizations were carried out in a three electrode flooded cell using 1.0 M Na_2SO_4 aqueous solution and a large $Na_{0.44}MnO_2$ intercalation compound counterelectrode. The CV trace (Figure 1) shows two electrochemical process taking place at potential ranges of 0.2-0.4 and 0.65-0.75 V vs. SCE, respectively. The electrode was cycled in the potential range 0.20-0.78 V vs. SCE at very low current density (2 μA/cm^2). The discharge specific capacity was about 26 mAh/g at the first cycle decreasing to 20 mAh/g after 20 cycles. The electrochemical properties will be also measured in organic electrolyte, in order to explore larger potential windows, and presented.

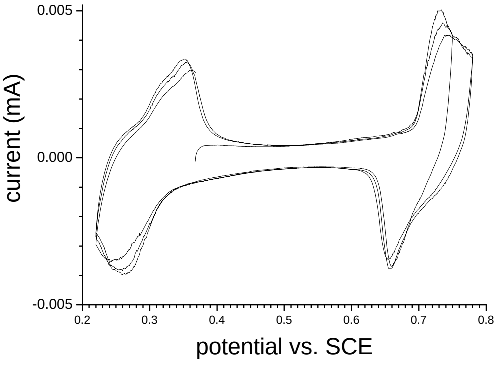

Figure 1. CV profile of Na_xCoO_2 in Na_2SO_4 water solution (scan rate 0.05 mV/s).

ELE-OR-09 New technologic Substrates for Energy devices by Electrodeposition

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The global environmental concerns and the escalating demand for energy, coupled with a steady progress in renewable energy technologies, are opening up new opportunities for the utilization of renewable energy resources. Electrodeposition is extensively used to deposit metals and metallic alloys at the industrial level, with a wide range of applications from large area surface treatments to most advanced electronic industries. Electrodeposition of semiconducting materials represents a new challenge, not only from the academic but also from the economic point of view, since this method presents interesting characteristics for large area, low cost and generally low temperature and soft processing of materials. The Electrochemical Atomic Layer Epitaxy (ECALE) method was used to obtain binary compound semiconductors such as Cu_xS and Sn_xS_y on Ag(111). The amount of the elements deposited in the first layers of the compound was determined by the oxidative stripping of cations, followed by the reductive stripping of anions. This study reviews the state of art of the literature on the knowledge about these binary and pseudo ternary system, and it sets up perspectives for photovoltaic applications. Chalcogenide based materials are of considerable interest as promising semiconductor for electro-optic devices, thermoelectric devices and optical recording media.

Selective Electrodesorption Based Atomic Layer Deposition (SEBALD) was used to prepare new bimetallic electrodes for fuel cells. This new method of Electrodeposition, recently pointed out in Florence on the base of ECALE method, allows to deposit under morphological and compositional control those metals that cannot be deposited at underpotential.

ELE-OR-10 Dye sensitised solar cells with nickel oxide photocathodes prepared via microwave plasma sintering

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NiO electrodes for cathodic dye-sensitised solar cells (DSSCs) can be obtained by sintering the spray deposited NiO nanoparticulate layers through a newly developed treatment that involves microwave plasma technique (PAMW).[1] This technique proved to be versatile in controlling the morphology of NiO coatings and the adhesion of these to the electrically conductive transparent substrates. NiO coatings have been tested in cathodic DSSCs with Erythrosin B,[2] P1[3] and Fast Green[4] sensitisers. The largest overall efficiencies of the DSSCs with a single photoactive NiO cathode were obtained with P1-sensitised samples. The incident photon-to-current conversion efficiency (IPCE) reached values as high as 30% for NiO electrodes with a highly mesoporous morphology. The photogenerated charge carriers in the PAMW-NiO DSSCs displayed relatively long lifetimes (in the order of 1 s) under open circuit conditions. The transport times of the charge carriers in the DSSCs were independent on the incident light intensity under short-circuit conditions.

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ELE-OR-11 Electrochemical Deposition of Cu and Ni Nanowires Directly on Electrode Surface

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Electrochemical deposition is a popular method for the preparation of conductive nanowires or nanotubes in suitable templates, like alumina and polymeric track etched membranes. The procedure normally includes coating of one side of the membrane with a noble metal or alloy to provide the conductive substrate. We propose an alternative approach based on a specific cell assembly: the membrane, laid over a commercial sponge soaked with electrolyte, is pressed against the disk working electrode, placed face down, by raising the cell containing the counter electrode (two-electrode operation). In this way, a deposit of metal nanowires may be directly obtained on the electrode substrate of identical or different material.

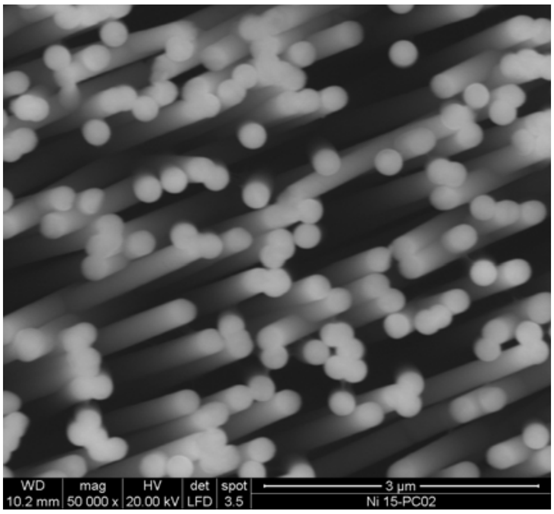

Figure 1. SEM image of Ni nanowires deposited in a Whatman membrane with pores of 200 nm nominal diameter.

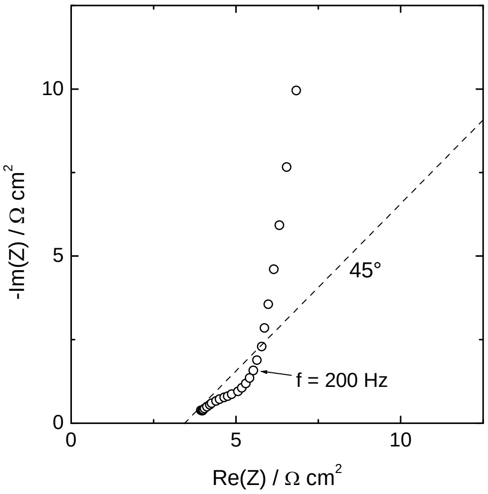

Figure 2. Impedance plot of a Ni disk with Ni nanowires of 200 nm diameter (0.1 M NaOH, E = 0.1 V vs Hg/HgO).

Figure 1 shows the morphology of Ni wires and Figure 2 the impedance data of the electrode, from which we could estimate a roughness factor f_r = 23±2. Electron backscatter diffraction (EBSD) shows that the head of wires with diameter of 200 nm or lower is almost always monocrystalline for Cu and frequently also for Ni.

Acknowledgments. Financial support of the Regione Veneto to the 12 months stay of A. Gambirasi at IENI-CNR (Asse “Capitale Umano”, DGR 2215/2009) is gratefully acknowledged.

ELE-OR-12 Microstructure and transport properties of thin film electrolytes for Solid Oxide Fuel Cells

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Alternative energy production is one of the major problems for future sustainable development. Solid oxide fuel cells (SOFCs) are a promising technology for this aim, but their mass development is hindered by high costs and stability issues related to their high operation temperature (1000°C). Significant research efforts are thus being devoted to decreasing the SOFC operation temperature in the intermediate range (below 700°C, IT).

Aim of our research is to push the limit of SOFC operation temperature to the lowest possible value, developing highly performing nanostructured materials and innovative device architectures to eventually fabricate miniaturized SOCFs operating at 450-700°C.

Proton and anion conducting electrolytes, characterized by high conductivity at IT, were developed in thin film form to reduce their ohmic resistance.

One of the main factors impairing the electrolyte conductivity is the presence of blocking grain boundaries. The strategies adopted in our laboratory to solve this problem are the fabrication of monocrystalline or highly textured [1] films using pulsed laser deposition (PLD) and the modification of the grain boundary nature using nanostructured materials prepared by wet-chemistry methods to control the sintering procedures.

Pulsed laser deposition (PLD) is particularly promising amongst the different film deposition techniques because of its ability in reproducing complex target compositions onto the film.

Highly-textured, epitaxially oriented $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_3$ (LSGM) and $BaZr_{0.8}Y_{0.2}O_3$ (BZY) films were grown by pulsed laser deposition on different substrate (e.g. MgO, NGO, LAO). The study of the microstructure/transport properties correlation was the main aim of the present work. In both cases films with good crystalline quality were obtained.

BZY films grown on (100)-oriented MgO substrates showed the largest proton conductivity ever reported for BZY samples (0.11 S/cm at 500°C).The excellent crystalline quality of BZY films allowed for the first time the experimental measurement of the large BZY bulk conductivity above 300°C, expected in the absence of blocking grain boundaries.[2]

Our results demonstrated that optimizing the control of the crystallographic quality by reducing the mismatch between the substrate and the deposited film is a key issue to achieve electrolyte thin films with optimized electrical performances.

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ELE-OR-13 Preparation and characterization of Pt/IrO_2 electrocatalysts for unitized regenerative fuel cell (URFC) applications

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Hydrogen energy storage systems coupled to renewable power sources are being proposed as a means to increase energy independence, improve domestic economies, and reduce greenhouse gas emissions from stationary and mobile fossil-fueled sources. New technologies for production and utilization of hydrogen as energy carrier are electrolysers and fuel cells, respectively. Both processes may alternatively occur in the same device based on a proton exchange membrane (PEM). This device is called unitized regenerative fuel cell (URFC). Compared with conventional secondary batteries, URFCs advantages rely on high energy density, long-term energy storage, durability and environmental protection. Whereas in comparison to the separate fuel cell and electrolyzer based systems, URFCs are significantly more compact and they allow considerable system simplification. Moreover, URFC devices are characterized by rapid start up, they can operate efficiently at low temperature without the need of cumbersome power consuming auxiliaries and can provide stable operation even in the presence of a large number of start up/ shut down cycles. However, URFC electrodes are not the simple linear combination of electrodes used in fuel cells with those used in electrolysis cells. One of the main technical breakthroughs for URFCs is the development of efficient bi-functional electrocatalysts for the oxygen reaction.

In this work, nanosized Pt/IrO_2 electrocatalysts are synthesized by decorating Pt nanoparticles onto the surface of a nanophase IrO_2 support using an ultrasonic polyol method. The synthesis procedure allows deposition of metallic Pt nanoparticles on Ir-oxide without causing any occurrence of metallic Ir which is significantly less active for oxygen evolution than the corresponding oxide. The nanosized Pt/IrO_2 (50:50 wt.%) is sprayed onto a Nafion 115 membrane and used as bi-functional oxygen electrode, whereas 30 wt.% Pt/C is used as bi-functional hydrogen electrode in the URFC. Electrochemical activity of the membrane-electrode assembly (MEA) is investigated in a single cell at room temperature and atmospheric pressure both under electrolysis and fuel cell mode to assess the perspectives of the URFC to operate as energy storage device in conjunction with renewable power sources.

ELE-OR-14 Nafion influence on Oxygen Reduction Reaction catalyzed by Pt-free materials.

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Fuel cells for low temperature applications are the subject of intensive research because they may offer a reduction of primary fossil fuel consumption and greenhouse gas emission. However, one most problematic aspect arises from the kinetic slowness of the oxygen reaction. For this reason, electrode materials are, at present, based on platinum nano-dispersed onto carbon. Nevertheless, the natural scarcity and cost of platinum justify the search for alternate, non-precious materials, even though less catalytically performing. Their utilization may introduce unexpected or unpredictable electrocatalytic behaviour, because of the unknown interactions between these new materials and Nafion. In fact, in fuel cells Nafion is used as both the electrode separator and as an ion-conducting binder of the catalyst layer affecting platinum activity and fuel cell performance [1]. Catalytic sites of platinum and platinum-free catalysts obviously have different nature, thus implying possibly different interaction mechanisms with the Nafion binder, to affect catalytic activity.

In this work, we present some results about the oxygen reaction reduction (ORR) on a Pt/C commercial catalyst and on lab-synthesized platinum-free catalysts in acid, that were obtained by varying the electrode preparation method and the added Nafion quantity. In a first method a Nafion suspension was deposited onto a catalytic layer previously dried onto the Rotating Disk Electrode (RDE) graphitic tip, in a second one Nafion was directly added to catalyst suspensions, before the RDE tip deposition.

Voltammetric results show that the catalytic layer thickness and the relative Nafion quantity affect the experimental I/E curve morphology and the presence of a well defined limiting current regime. Optimized experimental conditions (relative quantity of Nafion to carbon quantity) to obtain good results were determined differing for Pt/C and Pt-free catalysts.

[1] M. Watanabe, H. Igarashi, and K. Yosioka *Electrochimica Acta*, *40*, **1995**, 329.

ELE-OR-15 Fuel flexibility: a key challenge for SOFC technology

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A major worldwide challenge is the development of cleaner and sustainable sources of energy aimed at reducing the environmental threat of global warming and overcoming the finite nature of fossil fuel reserves. Promising energy conversion and storage technologies, including fuel cells and lithium batteries, are being developed to solve these problems. The performance of such energy systems depends crucially on the properties of their component materials; therefore, it is primarily through the development of innovative materials with improved functional properties and more affordable costs that the pressing need for environmentally-friendly technologies could find a solution. The choice of Solid Oxide Fuel Cells (SOFCs) compared to other fuel cell technologies has the great potential of the fuel flexibility especially those widely available and/or characterized by low cost [1]. Like most fuel cells, SOFCs will operate better on hydrogen than on conventional fuels whereas the direct feed of coal-based fuels directly in a SOFC in the presence of a state-of-the-art anode would result in carbon deposition and rapid as well as irreversible cell degradation [2]. Typically, air or steam have to be introduced with fuel into the anode with systematic control to prevent coking [3]; therefore, the introduction of an anode materials resistant towards coke formation under non humidified conditions would improve the commercialization path for applications ranging from small and medium distributed generation systems (0.5 - 50 kWel) to uninterrupted power supply (UPS), auxiliary power units for vehicles and mobile generators for civilian as well as military applications.

This paper concerned the investigation of an innovative electrocatalyst as anode material for the direct oxidation of various kinds of fuel in SOFCs and the main purpose of this work was the investigation of the effect of the use of hydrogen, syngas, methanol, ethanol, glycerol, and propane on the cell performance.

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ELE-OR-16 Preparation and Characterization of Electrocatalysts by Spontaneous Deposition of Noble Metals (Pd, Pt) on Ni Foam

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Pd and Pt were deposited by metal displacement reactions, using a commercial Ni foam as a supporting frame. The modified foam samples were characterized by electrochemical techniques and SEM-EDX, to assess the noble metals loading, their distribution on the Ni foam and their electrochemically active surface areas.

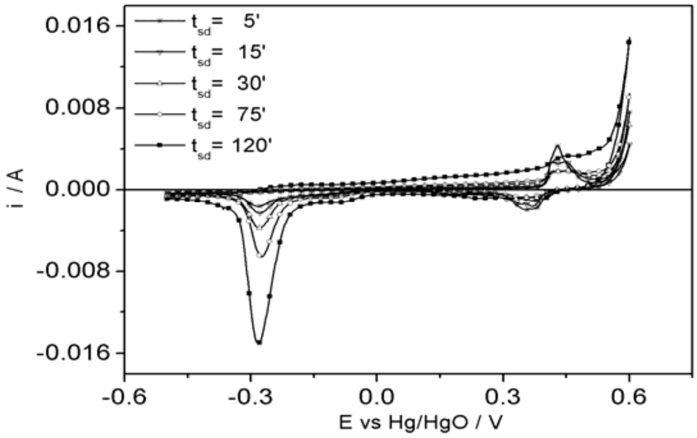

Figure 1.

Cyclic voltammograms recorded with Pd-modified Ni foam electrodes (volume 0.0425 cm^3) in 1 M KOH for different spontaneous depositions times. The reduction peak at ca.-0.28 V, ascribed to the reduction of Pd oxides, was used to quantify the Pd surface area.

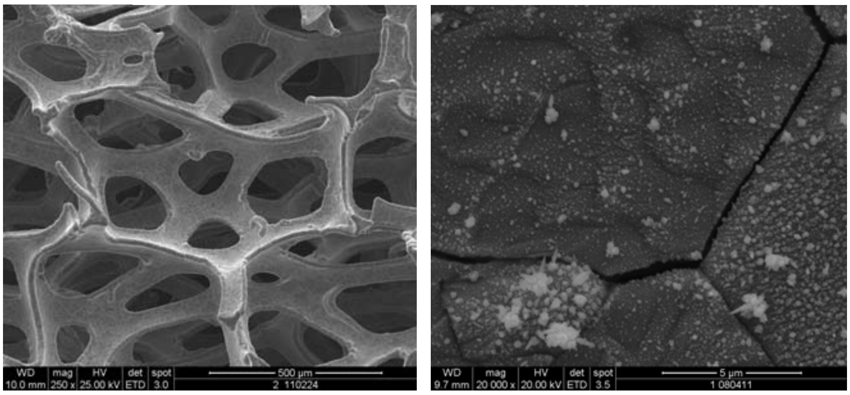

Figure 2.

SEM images of the commercial Ni foam (left) cell and of Pd deposits obtained by immersion of the foam in 0.005 M PdCl$_2$, for 60 min (right).

Different morphologies, from nano- to micro-scale clusters were obtained by varying deposition parameters (concentration of PdCl$_2$ solution and deposition duration). The Pd-modified electrodes were tested in the oxidation of alcohols. In the case of methanol, the peak current per unit Pd mass exceeded 600 A g^{-1}.

Acknowledgments. The authors acknowledge the financial support of the Italian Ministry for Economic Development (MSE) – MSE-CNR Agreement on National Electrical System.

ELE-OR-17 Oxidation of Methanol, Ethanol, Ethylene Glycol and Glycerol at Pd-modified Ni Foam Electrodes

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Electrodes prepared by spontaneous deposition of Pd onto Ni foams were investigated as anodes for the oxidation of various alcohols and polyols (methanol, ethanol, ethylene glycol and glycerol) in alkaline media. Figure 1 shows the voltammograms obtained in 1 M KOH + 0.5 M alcohol solutions, with electrodes with a 2.4 mg cm^{-3} Pd loading per unit foam volume, corresponding to a 8 to 9 μg cm^{-2} Pd loading per unit true surface area of the Ni foam. The current, expressed in A g^{-1}, is normalized with respect to the Pd mass.

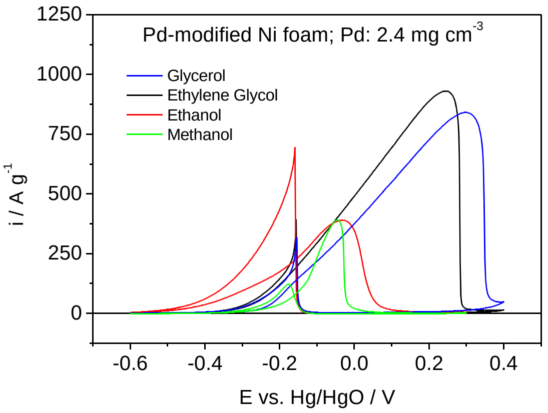

Figure 1
Cyclic voltammograms recorded with Pd-modified Ni foam electrodes in 1.0 M KOH + 0.50 M alcohol.

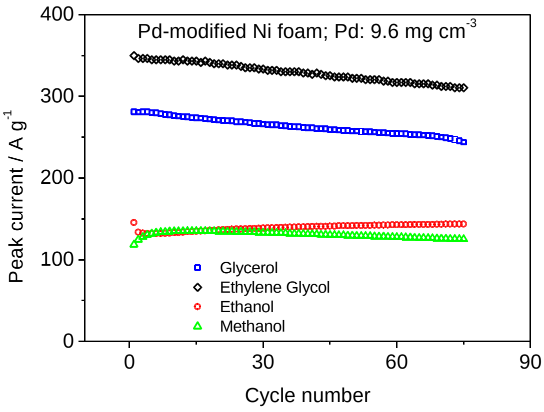

Figure 2
Stability test of Pd-modified Ni foam electrodes.

The Pd-modified Ni foam electrodes are very active in the oxidation of all alcohols and polyols. The peak current per unit Pd mass increases upon decreasing Pd loading. For ethylene glycol, oxidation currents higher than 2000 A g^{-1} are obtained with Pd loading lower that 1 mg cm^{-3}. Figure 2 shows that the performance of Pd-modified Ni foam electrodes is stable upon repetitive cycling.

Acknowledgments. The authors acknowledge the financial support of the Italian Ministry for Economic Development (MSE) – MSE-CNR Agreement on National Electrical System.

ELE-OR-18 Tuning of the optical and dielectric properties of anodic film on sputtered deposited Ta-Nb alloys.

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Anodic oxides on tantalum and niobium have been studied in the last decades for their possible application in electrolytic capacitors industry owing to their large values of dielectric permittivity (ε_{Nb2O5} = 53 - 57 and ε_{Ta2O5} = 27 - 31). More recently, Ta_2O_5 or mixed tantalum oxides (containing d-metal cation, for instance Ti or Nb), have been proposed as possible candidates to be used as gate dielectric in integrated circuits. Mixed tantalum-niobium oxides appear very promising dielectrics for electrolytic capacitors or integrated circuit, owing to the expected higher values of dielectric permittivity with respect to pure Ta_2O_5, provided that an improving in thermal stability and leakage current with respect to niobium oxide are obtained.

In this frame we have started an extensive investigation on the characterization of anodic oxides grown on magnetron sputtered Ta-Nb alloys covering all the range of composition. More specifically, in this work we want to discuss the influence of the anodizing bath composition on the solid state properties of anodic films grown on these alloys. Thus, anodic layers were grown at several formation voltages in electrolytes with different composition in order to study the effect of possible incorporation into the oxide of species coming from the solution.

The grown films were characterized by photocurrent spectroscopy in order to derive information on their optical band gap as well as on the zero photocurrent potential of the mixed oxide/electrolyte interfaces. Differential admittance and electrochemical impedance measurements were also carried out for some selected composition (including pure Ta_2O_5 and Nb_2O_5) to get information on their electronic properties.

ELE-OR-19 Electrocatalytic Activation of Alkyl Halides at Copper Electrodes

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The electrochemical activation of carbon-halogen bonds is a widely investigated subject because of its importance in synthetic and environmental applications, especially the abatement of polychlorinated volatile organic compounds (VOCs). Reduction of alkyl halides suffers from a very high activation free energy owing to the concerted nature of bond rupture and electron transfer. The process requires electrocatalysis and a few metals such as Ag, Cu, Pd and their alloys [1] are known to possess good electrocatalytic properties, which in some cases have been exploited in different applications [2].

Although, from an economic point of view, Cu is more appealing than Ag or Pd, its use as a cathode for RX reduction has been less examined. Herein we report the results of a study on the feasibility of preparative-scale electrolyses of alkyl halides at Cu cathodes. As model compounds we selected some VOCs of environmental interest, namely CCl_4, $CHCl_3$, CH_3CHCl_2 and CH_3CCl_3.

The process was investigated in DMF + 0.1 M $(C_3H_7)_4NBF_4$, both in the absence and presence of proton donors. All electrolyses resulted in a complete dehalogenation of the starting substrate as well as its intermediates. No electrode fouling was observed during electrolysis, but both the charge consumption and product distribution were found to be strongly dependent on the proton availability of the reaction medium (Fig. 1).

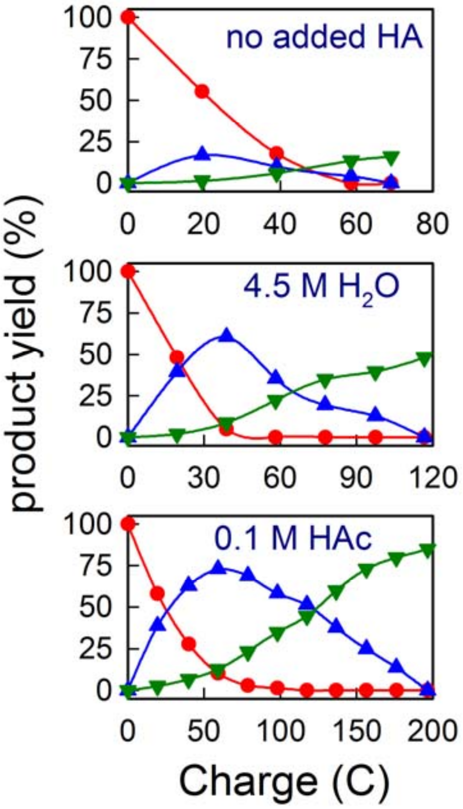

Fig. 1. Electrolysis of 0.01 M $CHCl_3$ (●) in DMF at Cu; products: CH_2Cl_2 (▲),CH_4 (▼).

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ELE-OR-20 Mechanism and Kinetics of Activation of Alkyl Halides by Cu(I) Complexes Used as Catalysts in Atom Transfer Radical Polymerization

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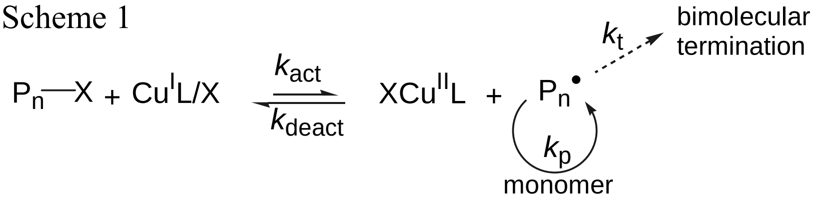
Atom transfer radical polymerization (ATRP) is one of the most used methods of controlled/living radical polymerization for the synthesis of a vast range of well-defined, low-polydispersity polymeric materials [1]. The process is initiated by a reversible reaction between a transition metal complex (mainly Cu(I) with an amine ligand, Cu^IL^+) and an activated alkyl halide to produce the propagating radical (Scheme 1).

Scheme 1



The initiation reaction is considered to involve a transfer of a halogen atom from the alkyl halide to the metal center. A fundamental question which, however, has not been adequately addressed is on the nature of the active Cu(I) species, since the metal ion exists under ATRP conditions as a multiplicity of species [2]. A second important issue on the activation reaction regards determination of the activation rate constants. Several methods, mainly limited to the study of slow reactions, have previously been proposed to measure k_{act} [3].

Herein, we first examine the mechanism of the activation reaction with the aim of unambiguously identifying the active Cu(I) species. We investigated the kinetics of activation of RX by Cu^IL^+ (L = Me_6TREN) in CH_3CN both in the absence and presence of X^-. It is found that although the system $Cu^I/L/X^-$ is mainly composed of Cu^IL^+, XCu^IL and $Cu^IX_2^-$, only Cu^IL^+ is an active catalyst reacting with RX. Next, we describe electrochemical methods for the determination of k_{act} both for slow and fast reactions and apply them for the measurement of k_{act} for a variety of activated alkyl halides and Cu(I) complexes.

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ELE-OR-21 Enhanced structural order of Self-Assembled Monolayers of aromatic thiols in contact with aqueous solution.

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Owing to their ease of preparation and their versatility, Self-Assembled Monolayers (SAMs) are still today the most popular way to finely tailor the surface of noble and coinage metal to every need [1]. Even if they are essentially stable and highly ordered systems, their employment is still conditioned by their limited durability and by the presence of defects in the layer. For several years SAMs have been studied as corrosion inhibitors for copper and its alloys. The direct relationship between the layer thickness and its protective properties [2] drove the investigation, until now, toward long-chain alkylic thiols, whereas very few studies were carried out on the aromatic thiols [3]. In the present work we used different techniques to study the adsorption on polycrystalline copper of one aromatic thiols, Benzenethiol (BT), and one alkylic thiol, 1-Undecanethiol (1-UT), comparing their protective properties and their stability up to a week in an aggressive environment such as H_2SO_4 0.5 M. Both Electrochemical Impedance Spectroscopy (EIS) and linear polarization highlighted different trends for aged 1-UT and BT. In fact, although freshly prepared 1-UT showed the best performance, as expected from its thickness, it degraded very rapidly. On the contrary BT SAMs showed a noticeable increase of the protective properties during the first hours of exposure to the electrolyte; this led to a superior performance of BT over any 1-UT sample. Raman spectroscopy suggested that this behaviour is related to an enhancement of the structural order of the aromatic layer, whereas XP spectroscopy allowed us to reveal that the bond with the substrate is very much stabler for BT than 1-UT. Finally Dynamic Contact Angle (DCA) experiments showed a surprisingly increase in the BT hydrophilic character, leading us to suppose a direct role of the water molecules in the BT structural reorganization. This hypothesis was supported observing that the same thiols adsorbed on a polycrystalline gold surface and aged in ultrapure water showed a very similar behaviour, as verified by EIS and Cyclic Voltammetry in the presence of a reversible redox couple such $[Fe(CN)_6]^{3-/4-}$. The pinholes analysis carried out by the EIS data revealed for BT an increase in the average distance between the defects, which is coherent with a reduction of the number of collapsed sites and thus with an improvement of the three-dimensional structural order.

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ELE-OR-22 “Genetically modified” spider-like oligothiophenes: electron properties and electropolymerization

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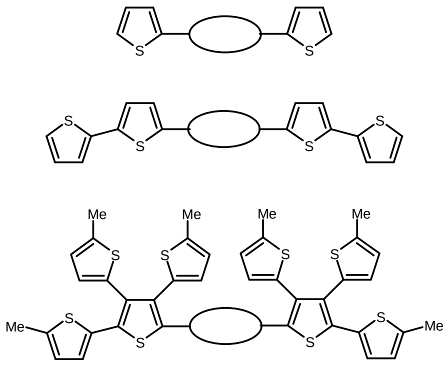
Multithiophene-based semiconductors are a virtually boundless class of molecular functional materials with very promising potential applications in a variety of fields, like electronics, energetics, sensoristics. Starting from our previous exhaustive work on “spider-like” branched oligothiophenes, affording a reliable rationalization of the relationships between structure and electronic properties[1,2], we have recently developed many structure modifications with respect to the original all-thiophene systems, aiming to achieve finer and wider modulation of both the HOMO and LUMO levels. In particular, the “core” of our oligothiophene systems has been modified by inserting appropriate building blocks of different electron richness, asymmetrically affecting both the LUMO and HOMO energy levels and localization along the main conjugated backbone, thus achieving one more freedom degree in tuning the electron properties of the molecule.



A wide series of “genetically-modified” spider-like oligothiophenes and their electrodeposited conducting polymers have been investigated by CV and EIS, focusing on the effect of core modification at constant thiophene side chains, and on the effect of increasing length and/or branching in the thiophene side chains at constant modified core. The core modification appears to be much more effective on the HOMO and LUMO energy levels and positions, while effective conjugation in the thiophene side chains is more determining on the oligomerization ability. The exhaustiveness of our investigation affords interpretative and predictive criteria which could usefully exploited in target-oriented molecular design.

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ELE-OR-23 Self-limited growth of Ag nano-rods into AAO nanopores

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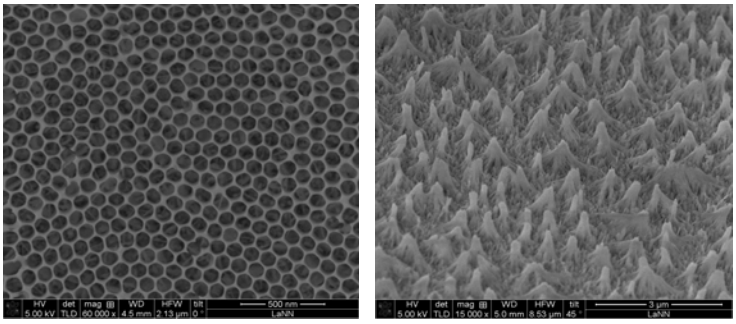
The anodization process of aluminum to give Anodic Alumina Oxide (AAO) described by Fukuda[1] is an effective way to prepare a regular and reproducible nano-patterned substrate on large areas. An extraordinarily large number of papers has been published on this subject and many of them focus on the growth of metal nano-rods inside the AAO pores. The formation of ordered arrays of metals nano-rods (e.g. Au, Ag or Cu) can find application in many fields, from (electro)-catalysis to Surface Enhanced Raman Scattering (SERS). Despite the relatively easy way in which AAO is prepared, there is a serious drawback in the use of DC electrodeposition for the filling of the pores because of the barrier layer which forms at the base of the AAO pores and at the interface with the Al metal substrate. In this contribution we describe an optimized preparation of the AAO substrates (see SEM on Fig. below, left), and we exploit an alternative approach to deposit the nano-rods by AC electrodeposition. The characterization of the final samples has been carried out by Angle Resolved X-ray Photoelectron Spectroscopy (ARXPS) and Scanning Electron Microscopy (SEM) measurements. It was possible to observe by ARXPS a somehow unexpected "shadowing" effect due to the incomplete filling of the pores by the metal nano-rods. It was observed that the metal nano-rods growth is self-limited and not-depending on the amount of current which flows in the electrochemical cell, producing an unfilled gap at the top of the pores whose average depth is measured simply by varying the detection angle with respect to the sample surface. A simple etching procedure in NaOH solutions allows to partially dissolve the AAO matrix so that the upper part of the Ag nano-rods protrudes outside the AAO matrix and its XPS signature start to loose the angle-dependence. Bunches of nano-rods eventually form (see Fig. below, right), with their tips in contact.



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ELE-OR-24 Electronic Properties of Corannulene Species and their Electrochemically Generated Graphene-like Structures.

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Corannulene is a bowl-shaped aromatic hydrocarbon recalling the fullerene surface and it is particularly intriguing to develop new materials, for its unique redox and luminescent properties. It is known to undergo several reduction processes and an oxidation which has been scarsely investigated, so far, being a completely irreversible process that brings about the rapid fouling and passivation of the electrode surface [1]. As for the reduction processes only the anion and dianion of corannulene have been electrochemically reported, while its tetraanion cluster was prepared with alkali-metal in THF [2].

We have reinvestigated the redox properties of this species over a large range of experimental conditions, by using "*traditional*" solvents for electrochemistry or "*unconventional*" ones (i.e., liquid NH_3 and liquid SO_2). This allowed us to observe, for the first time, the reversible electrochemical generation of up to the triply reduced corannulene [3]. On the oxidation side, the adoption of suitable ultra-dry solvents and electrolytes with very high oxidation resistance and low nucleophilicity allowed to explore the reactivity of the electrogenerated corannulene carbocations.

In this communication the interesting redox, spectroelectrochemical and luminescence properties of a class of corannulene species, together with the structure of their electrochemically generated films, will be discussed. Also the highly efficient blue electrochemiluminescence (ECL) of corannulene [4] compounds and the obtained polymeric films will be reported.

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ELE-OR-25 Thiophene/Ferrocene Systems as Possible Catalyst in the Cathodic Oxygen Reduction Reaction.

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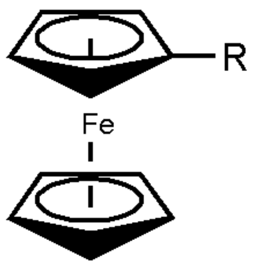
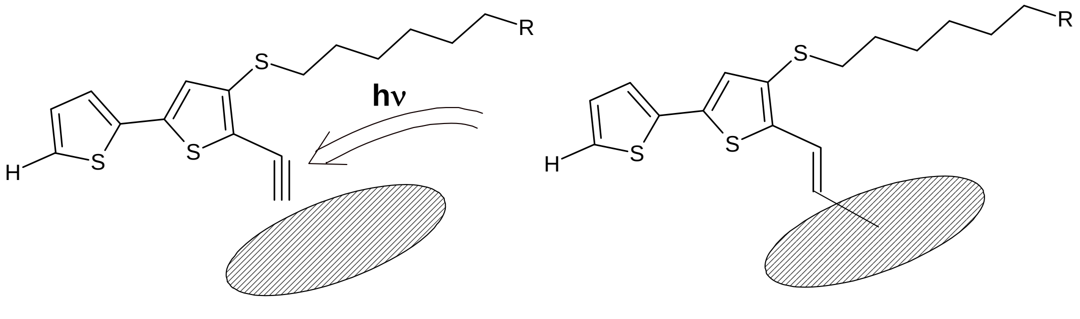
Various experimental strategies are exploited to graft Glassy Carbon and Si(111) surfaces. The Ferrocene redox couple on the Si(111) surface: photochemical grafting, surface chemical reaction using a Pt catalyst, post functionalization Si(111) surface previously modified with undecanoic acid. In figure 1 consider the substituent as being R = –H (FC), $-CH_2-OH$ (MFC), $-CH=CH_2$ (VFC). Cyclic voltammetry and electrochemical impedance spectroscopy are used to characterize the grafting process and the surface state. In particular, the dynamics of the electron transfer is assessed as a function of different Si(111) - molecular spacer - ferrocene systems. In addition bithiophene compounds are synthesized bearing suitable groups, which allow the grafting on the electrode surface. As shown in figure 2. In this case the chemisorption is achieved by UV triggered grafting of an alkyne moiety *via* a double bond formation (*figure 2*).





R = CH_3, CN

Fig. 2: The BT grafted to the silica surface

The organic film was characterized with various techniques, such as Cyclic Voltammetry, MALDI-TOF, XPS. The presence of the double bond allows to extend the conjugation (and thus the conductivity) of the OT chain to the electrode (transducer). The possibility to functionalize the thiophenes (at present the substitution of ferrocenes on the beta position is pursued) with different moieties the lateral chain makes these system very versatile and easily customizable.

ELE-OR-26 Electrochemical and theoretical studies for a better insight of the features of doped TiO_2 nanoparticles

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Doping titania by both metals[1] and non-metals[2] has attracted considerable attention due to a red-shift of the light absorption edge. A lively debate on the causes that provoke the shift of the absorption onset has arisen and grown. The main point of discussion concerns the eventual narrowing of the semiconductor band gap as a consequence of the doping or the creation of intra gap states. Also, the chemical nature and the location in the solid of the guest species responsible for visible light activity is still controversial.[3]

In this work, we report on TiO_2 samples obtained by a sol-gel synthesis using different dopant species.

From the electrochemical point of view the shift of the flat-band potentials (E_{fb}) of semiconductors plays an important role deciding photocatalytic as well as photoelectrochemical properties of thin oxide films and powders in general.

In particular, impedance spectroscopy has been applied to determine the value of the flat-band potential[4] of TiO_2 thin film electrodes prepared on conducting glass substrates and photovoltage measurements[3] in slurry to assess the Quasi Fermi level.

Theoretical ab initio Density Functional Theory (DFT) calculations[3] were performed to evaluate the Fermi Energy location at the band-gap and the presence of intra-gap states for doped samples. By the conjunction of the theoretical DOS calculations and the electrochemical measurements a deeper insight of the properties of doped titania semiconductors was achieved.

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ELE-OR-27 Development of new PBI membranes for high-temperature polymer fuel cells

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The current research on polymer electrolytes for fuel cells is focused on the optimization of a membrane working at about 120°C and low humidity levels (<30%), which are the real operative conditions in case of automotive applications [1]. Among the wide variety of tested polymer systems, PBI-based membranes, doped with phosphoric acid, are considered to be the best alternative to Nafion, due to their high conductivity even with no or low humidification and other promising electrochemical performances.

After a brief introduction on the problems of the membranes for HT-PEMFCs, I will report on the experimental strategies followed in our laboratory in order to design better systems. First of all, new polymeric architectures, based on polybenzimida-zole, have been synthesized with an increased number of basic sites, differently interspaced along the polymer backbone [2]. Subsequently, composite membranes were prepared by dispersing in the previously prepared matrices micro- and nanosized fillers, which differ for morphology, microstructure and chemical nature [3, 4].

Finally, new monomers including oxygen and other chemical moieties have been synthesized, and the consequent polymer have been prepared and tested [5]. In all cases, in situ-electrochemical tests and impedance spectroscopy were performed to evaluate the MEA performances.

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ELE-OR-28 Exhaustive depletion of recalcitrant chromium fraction by electrocoagulation in a continuous flow pilot plant.

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Nowadays there is a great concern about the increasing release of heavy metals into environment, since these substances can have harmful effects on many form of life. In this frame, Cr release represents a menace to natural life and public health for its mutagenic and carcinogenic properties. Wastewaters containing Cr are discharged into the aquatic environment from various industries like those of metal finishing, electroplating, pigments, tannery and chemical manufacturing. In particular, the leather industry which uses Cr for the tanning of animal skins and hides, produces a large amount of wastewater containing Cr concentrations much higher than those allowed for the more stringent environment requirements.

Conventional treatments generally assure quite satisfactory Cr removal; the rising problems are the requirements of expensive equipments and monitoring systems, the use of additional chemicals that cause a secondary pollution, high energy consumption and large production of toxic sludge which require disposal. Electrochemical processes have been proved to be competitive methods allowing high removal efficiency without requiring supplementary addition of chemicals and reduced volume of sludge produced. Electrocoagulation and electroprecipitation, in particular, seem to be promising technologies when wastewater with high Cr concentrations are considered. The limit for these processes is represented by the presence, in wastewater, of stable Cr complexes with the organic substances. Recent studies [1] have shown that recalcitrant Cr abatement may be improved by using an ozonization pre-treatment followed by an electrocoagulation with Fe electrodes.

In order to evaluate the possibility to develop this process on industrial scale, electrocoagulation treatment was investigated using a specifically designed pilot plant. Working conditions were first defined by experiments done on laboratory apparatus. Then tests were carried out in the pilot plant which operates in batch recirculation mode until selected working conditions are reached and then as a continuous flow system, in steady-state conditions. Mathematical models to represent the behaviour of the whole system in the different operating mode were developed. Comparison of experimental data against simulation results of the whole system operating in batch recirculation mode validated the proposed model.

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ELE-OR-29 Template electrosynthesis of nanostructures for water electrolysis

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About 95% of the hydrogen used today comes from natural gas or light hydrocarbons reforming and coal gasification, the remainder being high-purity hydrogen produced by water electrolysis. In order to realize benefits of a hydrogen economy, this must be produced cleanly, efficiently and affordably from renewable resources, preferentially available close to the end-users. The goal is a sustainable cycle of hydrogen production and use: in the first stage of the cycle, hydrogen is produced from renewable sources then used to power a fuel cell [1]. This cycle produces no pollution and no greenhouse gases.

In this context, development of low size electrolysers producing high-purity hydrogen with high efficiency and low cost is of great importance. Electrode materials play a fundamental role in influencing electrolyser performances; consequently, in the last years considerable efforts have been put for obtaining highly efficient and inexpensive catalysts. To reach both goals, we have developed nanostructured electrodes, with very large active area, constituted by PdCo alloys (cathode) and RuO_2 (anode) [2], to be potentially used in PEMEL electrolyzers. In fact, PdCo alloy is a valid alternative to Pt for hydrogen evolution, whilst ruthenium oxide is one of the most active catalysts for oxygen evolution. In this work, both these materials were electrodeposited using two different types of support: carbon paper, in order to fabricate a porous nanostructured film, and anodic alumina membrane, in order to obtain regular arrays of nanostructures.

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ELE-OR-30 Electrochemical treatment of organic pollutants in macro and micro reactors

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Electrochemical processes are considered among the more promising for the treatment of waste waters contaminated by bio-refractory or toxic organic pollutants. These methods are environmental friendly, involve very mild operative conditions (ambient temperature and atmospheric pressure), limited operative costs and can oxidize toxic organic compounds effectively. However, electrochemical processes present some important disadvantages when performed in conventional reactors such as: 1) To achieve reasonable cell voltages when the medium has not an adequate conductivity, one needs adding to the system a supporting electrolyte. 2) Low current efficiencies are usually achieved in direct oxidation processes when a high abatement of the organic pollutants is required, mostly due to the fact that mass transfer rates towards electrodes are extremely reduced at low pollutant concentrations.

It has been recently shown that the utilization of microfluidic electrochemical reactors (e.g. cells with a distance between the cathode and the anode of tens or hundreds of micrometers) can contribute to minimize these problems. Thus, very small distances between electrodes lead from one side to a drastic reduction of the ohmic resistances, thus allowing electrochemical incineration of organic pollutants without supporting electrolyte, and on the other side to the intensification of mass transport of the pollutants towards electrodes surfaces. Furthermore micro devices may simplify the scale-up procedure, since this only requires a simple parallelization of many small units and allow a fast screening of the effect of operative parameters. We have recently studied the electrochemical abatement of some organic pollutants such as 1,1,2,2-tetrachloroethane and Acid Orange 7 in both conventional and micro reactors. A critical evaluation of the effect of the micro reactor on the performances of the process has been, in particular, carried out.

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ELE-OR-31 Carbon dioxide as C_1 source in ionic liquids: role of electrogenerated $O_2^{\cdot -}$ as activating agent.

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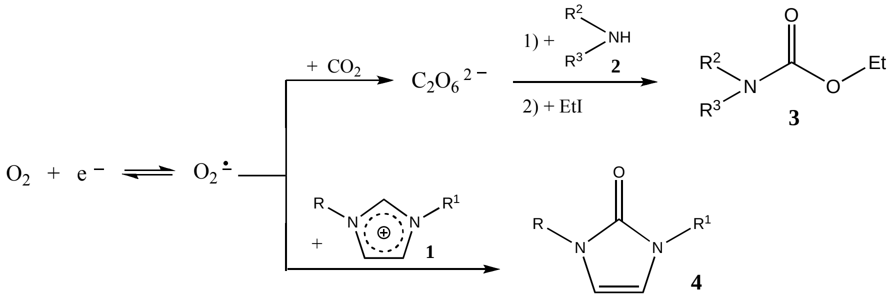
The set up of ecofriendly methodologies of synthesis (a significant target in modern organic chemistry) requires, *inter alia*, the removal of any toxic and/or hazardous reagent and solvent. Many authors have suggested the utilization of room temperature ionic liquids (RTILs) as green solvents (due to their negligible vapour pressure, chemical and thermal stability, etc.) [1] and of CO_2 as harmless and cheap renewable carbon source [2], in particular in the synthesis of carbamates, in place of toxic and harmful classic reactives (phosgene and its derivatives) [3].

In the past, the electrochemical activation of CO_2 for the syntheses of carbamates from amines has been carried out by us via: a) direct cathodic reduction of carbon dioxide in CO_2-saturated CH_3CN solutions or CO_2-saturated RTILs solutions of amines; b) selective cathodic reduction of O_2 to superoxide ion $O_2^{\cdot -}$ in O_2/CO_2-saturated CH_3CN solutions of amines. Recently, we have studied the possibility to extend this last methodology to O_2/CO_2-saturated ionic liquids **1** solutions containing amines **2** (Scheme) [4]. The activation of CO_2 has been carried out at -1.4 V (*vs* Ag), less negative than the reduction potential of CO_2 (-2.4 V, *vs* Ag) and in the absence of volatile and toxic organic solvents, supporting electrolytes and any catalyst (according to the growing demand of ecofriendly methodologies). The complex reactivity of $O_2^{\cdot -}$ has been analyzed: its reaction with CO_2 (yielding the carboxylating agent $C_2O_6^{2-}$) instead of RTIL (yielding 2-imidazolones **4**) is selective enough and carbamates **3** have been isolated in valuable current yields.



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ELE-OR-32 The microbiocidal electrolyzed activated solution (EAS) protects plants against pathogens and stimulates plant defenses.

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The fight against plant pathogens is of primary importance in agriculture, to ensure that quail/quantitative features of fruits and vegetables fit the market requirements. Synthetic products like pesticides and agrochemicals can protect plants against pathogens but they can be toxic or environmental unfriendly; therefore, the use of less toxic and less persistent products is highly encouraged.

It is known that the electrolysis of water enriched in salts can produce highly reactive oxidative species, which are characterized by a short life span and a potent antimicrobial activity, even at low doses.

In the last few years, our group has developed the system for the production of an electrolytically activated solution (EAS) and has been studying the beneficial microbiocidal effect of EAS on plants affected by different pathogens.

Investigations have been also focused on the effects of EAS on plant cells at the molecular level, to ascertain possible prompting of plant defences against pathogens. Through a RealTime PCR approach, we found that this solution is able to stimulate endogenous defences by a rapid and strong activation of several pathogen-related genes, when sprayed on tobacco and apple plants.

Repeated treatments with EAS amplify the gene induction pattern without showing phytotoxicity or stress effects. In addition, dedicated GC-MS analyses have shown that salicylic acid, one of the plant hormones involved in pathogen-resistance, is only partially involved in this phenomenon. These results show for the first time that EAS can be easily produced and used for the protection of crops against pathogens, with little impact on the environment and low costs. This solution is not simply microbiocidal but it also acts as signal molecule for the plant cells to synthesize defense proteins.

ELE-OR-33 Electroreduction of benzyl chloride on silver-based electrode materials in acetonitrile media: the role of water and of Ag surface

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The remarkable electrocatalytic activity of silver is well documented in the literature [1] and recently, the combination of electrochemical, spectroscopic and theoretical studies [2], using benzyl chloride (BzCl) as model organic compound, has demonstrated that the reduction pathway implies the formation sequence of silver-substrate/product adducts, starting from a weakly adsorbed benzyl chloride-Ag specie, followed by the strongly adsorbed benzyl radical-Ag and benzyl anion-Ag species. The last ultimately desorbing to give the final reaction products.

In this context the present contribution discusses the effect on the voltammetric signal of the presence of small amounts of water in the acetonitrile used as solvent. The source of proton from water may affect the normal reaction pathway and change the electrode activity. This provokes significant variations in electrode currents and potentials even at very low water content, thus providing an internal diagnostic signal for the quality of the solvent. This has immediate application to the comparison between electrode materials (e.g., massive silver, silver nanocubes and Ag-nanocubes supported on carbon) prepared by different procedures, and allows to evidence the effects of the morphology and size of silver particles on their electroactivity.

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[2] Yi-Fan Huang, De-Yin Wu, An Wang, Bin Ren, Sandra Rondinini, Zhong-Qun Tian, and Christian Amatore "Bridging the Gap between Electrochemical and Organometallic Activation: Benzyl Chloride Reduction at Silver Cathodes", J. Amer. Chem. Soc. 2010, *132*, 17199-17210; DOI: 10.1021/ja106049c

ELE-OR-34 Synthesis and characterization of materials for electrochemistry

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In this thesis work, materials that can find application in lithium ion batteries have been explored. In particular, cathode materials and electrolytes have been studied.
Concerning cathode materials, the interest have been focused on the highly studied, both in academic research and in commercial industry, $LiFePO_4$ compound, but also on NASICON type materials such as $LiTi_2(PO_4)_3$ and $Li_3V_2(PO_4)_3$. An extensive study has been carried out on $LiFePO_4$ in order to optimise its properties in view of its final application in cells. Therefore, an accurate investigation on different synthesis procedures has been carried out over the entire doctoral period. The development of a hydrothermal synthesis has allowed to obtain samples with a high level of purity and therefore suitable for the use in lithium ion batteries. Then, studies on the relationships between transport properties and microstructure of the synthesised olivine have been carried out. Our findings contribute to shed further light on the complex relationships among chemistry, morphology and electrochemical properties of the technologically relevant $LiFePO_4$ compound [1].
Many efforts were also devoted during the doctoral period to the study of electrolytes. In particular ionic liquids, being a very promising ionic transport media for liquid electrolytes, have received much attention in this thesis work. New pyrrolidinium-based and piperidinium-based ionic liquids with ether functionalities have been deeply characterized. Encouraging results have driven the work to the use of these ionic liquids in the preparation of gel polymer electrolytes and films based on the PVdF-HFP copolymer, on the thermoplastic polyurethane TPU and on PEO. The use of silica fillers in the case of PVdF-HFP and TPU based GPEs has allowed to obtain membrane with good mechanical properties and also good electrochemical features. In particular the PVdF-HFP membranes showed very good cycling performances [2].

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ELE-OR-35 Glucose electrooxidation

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The electrooxidation of glucose has attracted a lot of interest due to its application in blood glucose sensors and biological fuel cells. Glucose sensors optimization is highly necessary to improve the treatment of Diabetes Mellitus while biological fuel cells have been studied in order to explore new, renewable energy sources alternative to fossil fuels. During my PhD I worked on both *abiotical* and *microbial* electro-catalyzed glucose electrooxidation; the former (at gold electrodes) applied to glucose sensing and glucose-gluconate fuel cells, the latter for the development of microbial fuel cells (MFCs).

The complex oxidation of glucose at the surface of gold electrodes was studied in detail by cyclic voltammetry. An oxidative current peak occurs during the cathodic sweep showing a highly linear dependence on glucose concentration. Its application in blood glucose sensing has been hindered by the presence of inhibitors: chlorides are the most problematic because of their high concentration in the blood and the difficulty inherent in trying to separate them from glucose. In order to overcome this problem, on the basis of mechanistic studies, a four-step, three electrode (silver gauze, gold pin and platinum counter electrode) technique was exploited.

After optimizing fuel composition and operating conditions in order to selectively oxidize glucose to gluconate we developed a new anode material for glucose-gluconate direct oxidation fuel cells by electrodepositing gold nanoparticles on a “conductive textile” realized by conformally coating polyester textile substrates with single walled carbon nanotubes. The electrochemical characterization showed higher current densities with respect to the previously reported materials.

MFCs are devices that convert chemical energy into electrical energy by the catalytic activity of microorganisms. A novel carbon nanotube-cotton composite material with high conductivity and high porosity was proposed to be used as anode. The randomly intertwined CNT-cotton fibers create a 3D active space for biofilm growth while the incompact macroporous structure allows efficient mass transfer for microbial metabolism inside the anode. Compared to commercial carbon cloth anode, the CNT-cotton achieves 64% higher power density and 75% higher energy recovery efficiency in MFCs.

ELE-OR-36 Development and characterization of catalysts for electrolytic hydrogen production and chlor – alkali electrolysis cells

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The industrial production of chlorine is today essentially achieved through sodium chloride electrolysis, with only a minor quantity coming from hydrochloric acid electrolysis. The main problem of all these processes is the high electric energy consumption which usually represents a substantial part of the total production cost.

This activity was addressed to the investigation of the oxygen reduction at gas-diffusion electrodes as well as to the surface and morphology analysis of the electrocatalysts. Specific attention was focused on deactivation phenomena involving this type of GDE configuration. The catalysts used in this study were based on a mixture of micronized silver particles and PTFE binder. In this study, fresh gas diffusion electrodes were compared with electrodes tested at different times in a chlor-alkali cell. Electrode stability was investigated by life-time tests. The surface of the gas diffusion electrodes was analyzed for both fresh and used cathodes by scanning electron microscopy and X-ray photoelectron spectroscopy. The bulk of gas diffusion electrodes was investigated by X-ray diffraction and thermogravimetric analysis.

Water electrolysis is one of the few processes where hydrogen can be produced from renewable energy sources such as photovoltaic or wind energy without evolution of CO_2. In particular, an SPE electrolyser is considered as a promising methodology for producing hydrogen as an alternative to the conventional alkaline water electrolysis. This work was mainly addressed to a) the synthesis and characterisation of IrO_2 and RuO_2 anodes; b) conducting Ti-suboxides support based on a high surface area.

a) Nanosized IrO_2 and RuO_2 catalysts were prepared by using a colloidal process at 100°C; the resulting hydroxides were then calcined at various temperatures. The attention was focused on the effect of thermal treatments on the crystallographic structure and particle size of these catalysts and how these properties may influence the performance of oxygen evolution electrode. Electrochemical characterizations were carried out by polarization curves, impedance spectroscopy and chrono-amperometric measurements.

b) A novel chemical route for the preparation of titanium suboxides (Ti_nO_{2n-1}) with Magneli phase was developed. The relevant characteristics of the materials were evaluated under operating conditions, in a solid polymer electrolyte (SPE) electrolyser, and compared to those of the commercial Ebonex®. The same IrO_2 active phase was used in both systems as electrocatalyst.

ELE-OR-37 Electrodeposition of Metal-Oxide-Metal nanowire heterostructures for ReRAM applications

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As larger capacity is required to modern semiconductor non-volatile memories, technical and physical limits arise, which the conventional scaling down of the photolithographic technology will hardly overcome. One of the most promising approaches for future high-density mass storage is represented by the Resistive switching Random Access non-volatile Memories (ReRAM). The functioning of such memories is based on the switching between high and low conductive states under applied electrical pulses. In particular, nanoscaled Metal/Oxide/Metal (MOM) heterostructures are currently investigated as possible building blocks for memory devices beyond the 16 nm technology node [1]. Whereas the resistive switching behavior of MOM thin films has been widley investigated, a better characterization and understanding of switching phenomena at the nanoscale is still required.

In the present study, the electrochemical synthesis and resistive switching characterization of MOM heterojunctions nanowires (NWs) are addressed. MOM NW array were fabricated by electrodeposition of either Ni or Au/Ni/Au multilayers into Anodic Aluminum Oxide (AAO) templates (pore diameter og 60 nm), followed by mechanical polishing of the AAO template and thermal oxidation.

The electrodeposition of Ni and Au was carried out from sulphate-based and cyanide-based electrolytes, respectively. Mechanical polishing of the resulting AAO templates was performed in order to expose the NWs from the AAO template surface, favoring thermal oxidation and allowing the electrical characterization of the NW array. Thermal treatment were carried out at 400 °C in oxygen atmosphere for times ranging from 3 to 30 minutes. Structure and morphology of the heterojunction NWs embedded into the AAO matrix were characterized by Scanning Electron Microscopy (SEM), High Resolution Transmission Electron Microscopy (HR-TEM), X-Ray Diffraction (XRD) and Atomic Force Microscopy (AFM). The resistive switching properties of the MOM heterojunction nanowires arrays were studied by current-voltage measurements.

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ELE-OR-38 The PVD approach for the preparation of Ir-Sn dioxide thin films*

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The request for electrodes exhibiting satisfactory catalytic activity and high stability, under particular conditions of potential and current density, has stimulated the synthesis of new materials with improved performances. Among them, devices based on RuO_2 and IrO_2 found wide application in the field of DSAs (dimensionally stable anodes) for their ability to associate a good electrocatalytic activity to a high resistance to corrosion. Often, a greater stability leads to a decrease of catalytic activity, but it is possible to find a compromise by using mixtures of oxides. Besides the conductive and electroactive oxide (typically noble metal oxides, such as IrO_2, RuO_2, PtO_x and RhO_x), other oxides are added to the mixture (these are oxides of so-called "valve" metals, like TiO_2, SnO_2, Ta_2O_5, Nb_2O_5 and ZrO_2), which have the dual purpose of increasing the corrosion resistance of the electrode, and to dilute the primary oxide as to minimize the device production costs.

For the preparation of film electrodes, a physical vapor deposition (PVD) technique has been used: in particular, the attention was focused on the reactive sputtering. This method ensures a better homogeneity of the film, in terms of thickness and roughness, compared to conventional pyrolytic techniques used for electrodes preparation.

The synthesis of thin-film-electrodes was carried out at room temperature, and their characterization was attained through electrochemical as well as surface tests; then, further information was obtained studying the catalytic properties of films towards the chlorine evolution reaction.

** Premio di Laurea 2011 "Photoanalytical".*

ELE-OR-39 Electrochemical Immunosensors and Peptide Self-Assembled Monolayers for Cancer Biomarker Protein Detection

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This Thesis concerns the development of a very efficient immunosensor electrochemical device for detecting cancer biomarker proteins, and possible ways to improve its efficiency by modifying parts of the system that are relevant to improve stability and electron transfer through the modified electrode surface (see Figure 1). [1]

We focused our attention on Nanog detection. Nanog is a protein that may be involved in carcinogenesis of cervix and progression of cervical carcinoma. Nowadays, the researchers still do not know the detection limit of this biomarker and the difference of concentration between healthy individuals and patients with cancer. Therefore, we aimed at making an electrochemical sensor capable of displaying very high-sensitivity immunoarrays and low detection limit. Sensors were prepared and, particularly, several conditions to make Nanog-based electrodes were essayed. Eventually, we could optimize the conditions and obtain a nice calibration plot. Most of the initial work was carried out using the sample handling technology, but then we integrated the system into a microfluidic device, the goal being to automate the method as much as possible.

To improve the efficiency, we are about to further optimize the immunosensor by changing some elements of the transducer, particularly by using a SAM formed by peptides allowing very fast ET and by increasing the active superficial area thanks to nanostructured gold electrodes as an alternative to a bed of gold nanoparticles.

We carried out an investigation of related issues by using SAMs formed with thiolated α–aminoisobutyric acid (Aib) peptides of different lengths. The effect of the orientation of the peptide dipole moment was studied by attaching the thiolated moiety to either the nitrogen or carbon terminus.

The stability and conformational properties of such SAMs were assessed by an extensive IRRAS investigation, in comparison with the IR absorption spectroscopy of the free peptides. This study showed that, in these SAMs, most of the Aib peptides form 3_{10}-helices, and pack tightly, the surface coverage depending on both the peptide length and orientation.

The results nicely supported what recently found concerning the chemical and electrochemical stability of these SAMs as well as the efficiency of ET through them. Main outcome of this study is that we now know which peptides should provide the best transducer substrate supporting the actual Nanog-sensor architecture.

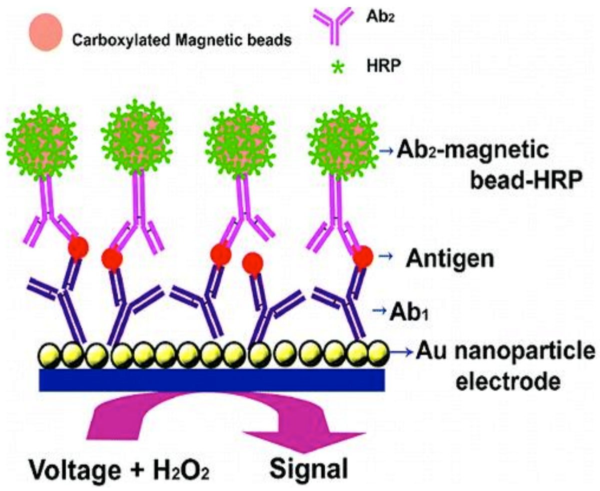

Figure 1. Scheme of the gold nanoparticles immunosensor.

The detection step involves immersing the sensor into buffer containing mediator, applying voltage, and injecting H_2O_2.

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ELE-PO-01 The electrocatalytic cleavage of carbon-halide bonds on Ag and Au in protic solvents

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In the last years we have showed in detail how the electrocatalytic cleavage of carbon-halide bonds is modulated by (a) the stepwise or concerted nature of the DET mechanism, (as a function of the electrode surface, of the nature of the halogen atom, and of the molecular structure of RX) and (b) the double layer structure (as a function of the nature and bulkiness of the supporting electrolyte ions). To both complete and support our interpretative scheme we are now concentrating on the solvent role.

Comparing aprotic with protic organic solvents after appropriate intersolvental normalization, interesting peculiarities emerge concerning protic media. Solvent proticity deeply affects both the reaction mechanism (on both non-catalytic and catalytic electrode surfaces) and the extent of the catalytic effects. We will discuss these items on the basis of a complete investigation carried out with a carefully controlled experimental protocol on two chloride and bromide couples, one aromatic and one aliphatic (representative of stepwise and concerted mechanism, respectively), in eight solvents, four of them aprotic and four protic, on the non-catalytic GC electrode and the catalytic Ag and Au ones. The results will be also discussed in the frame of our recently developed interpretative scheme of the carbon-halide cleavage mechanism.

ELE-PO-02 Controlled Aqueous Atom Transfer Radical Polymerization Under Electrochemical Generation of the Active Catalyst

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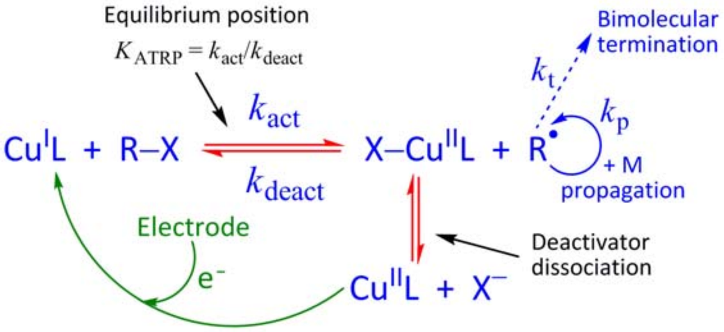
Controlled Radical Polymerizations (CRPs) in aqueous medium are very attractive from an economic and environmental point of view; besides the production of water soluble polymers, aqueous media are largely employed in the polymerization of non polar monomers through emulsion or miniemulsion techniques [1,2]. Moreover, the effectiveness of CRPs in aqueous saline buffers is a pre-requisite for the preparation of polymer-biomolecule conjugates under biological conditions [3]. Atom Transfer Radical Polymerization (ATRP) is nowadays the most used method in the field of the CRPs; despite its importance, well controlled aqueous ATRP remains a challenge, achieving only a limited success in the literature. The main drawbacks stem from a relatively high equilibrium constant K_{ATRP} and the instability of $X{-}Cu^{II}L$, resulting in a fast and uncontrolled polymerization. Recently, the first example of electrochemically mediated ATRP has been introduced as a technique allowing an unprecedented modulation of the rate of polymerization through the variation of the external applied potential, E_{app} [4]. In this communication, we report the successful controlled polymerization of poly(ethylene glycol) methyl ether methacrylate (PEOMA) in water under electrochemical reduction of the catalyst precursor $Cu^{II}L$ (L = TPMA, tris 2-pyridylmethylamine). Herein, we demonstrate that the magnitude of E_{app} not only acts as an electrochemical switch of the polymerization, but also as a tuner of the degree of control obtained in the final polymer.



Mechanism of electrochemical aqueous ATRP

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ELE-PO-03 BETA ALUMINA SOLID ELECTROLYTE FOR ZEBRA BATTERY

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Recently, there has been growing interest in sodium beta alumina battery technology as electrochemical energy storage systems for renewable storage. This technology is based on a solid Na^+-conducting electrolyte that separates a liquid sodium anode and a cathode containing sulphur (sodium/sulphur batteries) or metal chloride (ZEBRA batteries). The issues that hamper a widespread commercialization of this type of technology are related to the materials and manufacturing methods that affect cost, safety and performance. Beta alumina solid electrolyte (BASE) is the most widely used electrolyte in these systems because of its high Na^+ ionic conduction. β"-Al_2O_3 is the preferred phase for these applications since it exhibits a high sodium ionic conductivity (usually 0.2-0.4 S cm^{-1} at 300°C) [1]. It has been reported that the synthesis of this material by solid state reaction method starting from α-Al_2O_3 precursor yielded both β'- and β"-Al_2O_3 phases [1]. In order to identify the precursor composition suitable to achieve the highest β"-phase content, in this work the synthesis of Mg^{2+}- and Li^+-doped BASE ($Na_{1.67}Mg_{0.67}Al_{10.33}O_{17}$ and $Na_{1.67}Li_{0.33}Al_{10.67}O_{17}$ respectively) was carried out starting from different Al_2O_3 precursors such as α-Al_2O_3, γ-Al_2O_3, Boehmite (AlOOH) and Bayerite ($Al(OH)_3$) with Na_2CO_3; $MgCO_3$ or $LiCO_3$ were added as dopant. The effect of the experimental conditions on phase purity and microstructure of sintered specimens was inspected by XRD and SEM analyses. The sintering of Mg^{2+}- and Li^+-doped BASE samples were carried out by conventional heating technique. Moreover, a microwave-assisted heating process was investigated to obtain high heating rates, short holding time and attainment of the desired phase with improved homogeneity and microstructure at a significantly reduced cost. In light of the promising preliminary results, further studies with a single mode applicator are in progress, in order to evaluate the microwave absorption of these electrolyte materials and to improve the heating homogeneity, with the final aim of scaling up the process for the device development.

[1] Journal of Power Sources 195 (2010) 2431–2442

ELE-PO-04 Substrates for Energy devices

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The global environmental concerns and the escalating demand for energy, coupled with a steady progress in renewable energy technologies, are opening up new opportunities for the utilization of renewable energy resources. In this context Direct Alcohol Fuel Cells (DAFCs) represent a promising energy conversion device for mobile and stationary applications. Among the key issues to be addressed for their technological exploitation, the alcohol cross-over represents a limiting factor since the alcohol can be directly oxidized on the cathode and short-circuit the cell. In parallel, the recent improvement of anion membranes makes the development of alkaline DAFCs competitive with the acid ones.

In this work we present the preparation (electrodeposition and sol-gel) and characterization of Pt free metal and metal oxides as possible cathode and anode materials in alkaline DAFCs.

More specifically, the electrodeposition protocols include the Selective Electrodesorption Based Atomic Layer Deposition (SEBALD) used to prepare new bimetallic electrodes for fuel cells. This new method of Electrodeposition, recently pointed out in Florence on the basis of ECALE method, allows to deposit under morphological and compositional control those metals that cannot be deposited at underpotential. In parallel, low-temperature sol-gel synthetic process are adopted to produce tailored nanostructured mixed oxide disperse phase electrocatalysts, to be used as cathode material in membrane-electrode-assemblies (MEA).

Acknowledgements: The financial contributions of PRIN 2008 – "*Pt-free electrocatalysts for direct alcohol fuel cells.*" 2008N7CYL5 .

ELE-PO-05 Dissociative Electron transfer to Activated Alkyl Halide Initiators Relevant to Living Radical Polymerization.

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The mechanism of reductive cleavage of model alkyl halides (methyl 2-bromoisobutyrate, methyl 2-bromopropionate and 1-bromo-1-chloroethane), used as initiators in living radical polymerization (LRP), has been investigated in acetonitrile using both experimental and computational methods. Both theoretical and experimental investigations have revealed that dissociative electron transfer to these alkyl halides proceeds exclusively via concerted rather than stepwise manner. The reductive cleavage of all three alkyl halides requires a substantial activation barrier stemming mainly from the breaking C-X bond.

The activation step during single electron transfer LRP (SET-LRP) was originally proposed to proceed via formation and decomposition of $RX^{\bullet-}$ through an outer sphere electron transfer (OSET) process. These radical anion intermediates were proposed to decompose via heterolytic rather than homolytic C–X bond dissociation.

Here it is clearly shown that injection of one electron into RX produces only a weakly associated charge induced donor acceptor type radical anion complex without any significant covalent σ type bond character between carbon-centered radical and associated anion leaving group. Therefore, neither homolytic nor heterolytic bond dissociation applies to the reductive cleavage of C-X in these alkyl halides inasmuch as a true radical anion does not form in the process. In addition, the whole mechanism of SET-LRP has to be revisited.

The comparison of the experimental activation free energies with theoretically computed values shows a close agreement between theory and experiment. The agreement with experimental data, which fit very well the sticky model, is a relevant support for the appropriateness of this simplified model, which considers only the ion-dipole interactions.

ELE-PO-06 Pt free metal and metal oxides electrocatalysts for the Oxygen Reduction Reaction in alkaline DAFC

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Direct alcohol fuel cells (DAFCs) represent a promising energy conversion device for mobile and stationary applications. In comparison with H_2-based fuel cells, the alcohol cross-over may represent a limiting factor for their technological success since the alcohol can permeate the polymeric electrolyte and be directly oxidized at the cathode. This short-circuit implies not only an energy loss but may also result in the poisoning of the ORR electrocatalyst by CO and other products of alcohol oxidation.

In parallel the recent improvement of anion membranes, that allow for alkaline operating conditions with predictable advantages in terms of energy yield, makes the development of alkaline DAFCs competitive with the acid ones.

In this work we studied metal (Ag/C) synthetized by the wet method and metal oxides synthetized by the sol-gel technique (IrO_2-SnO_2), as possible cathode materials in alkaline DAFCs. The investigation is carried out using potentiodynamic techniques and the Rotating Ring Disk Electrode (RRDE) as support. The electrocatalytic powders are glued to the support with thin layer of Tokuyama anion exchange membrane. The influence of alcohol cross-over on the oxygen reduction reaction (ORR) kinetics was also considered.

The use of RRDE allow to obtain important information about the reaction mechanism since it is possible quantify *inter alia* the amount of hydrogen peroxide produced in a broad range of potentials.

A comparison study of different electrode materials in term of kinetic current, amount of hydrogen peroxide produced and the potential of the beginning the ORR was carried out. A interesting dependence of morphology and size of the Ag nanoparticles and of the iridium content (15-100%mol) on the ORR activity is observed.

The influence of the alcohol cross-over on the oxygen reduction reaction (ORR) kinetic is also presented and discussed.

Acknowledgements: The financial contributions of PRIN 2008 – *“Pt-free electrocatalysts for direct alcohol fuel cells.”* 2008N7CYL5 and PUR-Università degli Studi di Milano (2009 – 2010) funds are gratefully acknowledged.

ELE-PO-07 Spontaneous Deposition of Palladium onto Fecralloy®. Characterization of Pd-modified Fecralloy® Foam Electrodes

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Fecralloy® is a ternary alloy that typically contains 65-70 At% Fe, ca. 20 At% Cr and 10-15 At% Al. Owing to its very high stability at high temperature it is often used as supporting material for hydrocarbon oxidation catalysts, both in devices for low-temperature catalytic combustion and for pollutants abatement.

We report on the spontaneous deposition of Pd on either Fecralloy® sheets or Fecralloy® foams with variable grade, defined by the number of pores per linear inch (ppi), by simple immersion of the Fecralloy® samples in acid $PdCl_2$ solutions, and on the characterization of the resulting materials by electrochemical and microscopic techniques. Although the final aim of this work is the preparation of catalysts for the gas-phase oxidation of biofuels, the Pd-modified Fecralloy® foam electrodes were preliminarily tested as anodes for the anodic oxidation of alcohols in alkaline media. Figure 1 shows cyclic voltammograms recorded with Pd-modified Fecralloy® foam electrodes in KOH and KOH+methanol solutions, for 3 different foam grades corresponding to different electrochemically active areas per unit foam volume.

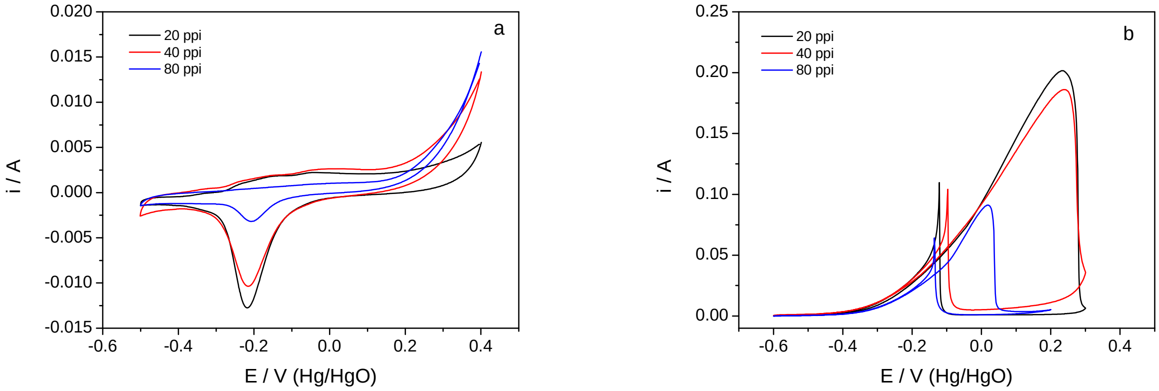

Figure 1. Voltammetric responses of Pd-modified Fecralloy® foam electrodes in 1 M KOH (a) and 1 M KOH + 0.5 M methanol (b). Electrode volume: 0.3 cm^3.

Acknowledgments. The authors acknowledge the financial support of the Italian Ministry for Economic Development (MSE) – MSE-CNR Agreement on National Electrical System.

ELE-PO-08 Synthesis of $LiFePO_4/C$ cathode materials for Li secondary battery

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Recently, $LiFePO_4$ has received a lot of attention, owing to its potential use as a cathode material in the next-generation lithium-ion batteries [1]. It features several interesting properties, such high specific capacity (170 $mAhg^{-1}$), high thermal stability and excellent electrochemical performance, and is low cost and not toxic. However the compound is an electric insulator at r.t. (10^{-9} Scm^{-1}) and it shows low Li^+ ionic mobility. In order to improve the physical properties of the material many studies have been focused on finding means to reduce these mentioned drawbacks. Several methods of synthesis of $LiFePO_4$ are known in the literature the most used ones being the solid state reaction and carbon-thermal reduction. The latter favors the formation of $LiFePO_4/C$ composite, which shows a measurable electrical conductivity. Here we report on an original synthetic route to prepare $LiFePO_4/C$ composites [2,3]. The idea behind it was to provide a precursor source containing iron, phosphorus and carbon, and, for this purpose, an appropriate hybrid organic-inorganic iron(II)-phenyl phosphonate, $[Fe(C_6H_5PO_3)(H_2O)]$ has been chosen. This compound is stable to the air and, when mixed with Li_2CO_3, under heat treatment provides sub-micrometric carbon coated $LiFePO_4/C$ composites. The thermal decomposition was carried out in a furnace by varying the experimental conditions, *i.e.* different heating temperatures, calcination times and inert gases in order to investigate the influence of the latter on the final product. The samples were characterized by elemental analysis, TG/DTA, X-ray powder diffraction analysis (XRPD), FT-IR spectroscopy. The morphology of the final products was investigated by means of scanning electron microscopy (SEM). The dependence of particle size and the role of impurities on the electrochemical behavior of the cathode material will be presented and discussed.

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ELE-PO-09 Novel acidic hydrogel electrolytes based on PVA and PVA blends

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Polymeric gels are attracting growing attention as “intelligent materials” because of their peculiar performances. They are materials with a network structure and can swell considerably in aqueous medium without dissolution [1].

In recent years, use of solid or gel electrolyte in batteries and other electrochemical devices has been considered especially for improving reliability, safety, flexibility and processability [2].

Research for materials with high ionic conductivity, large transport number, good electrochemical stability and mechanical strength is a very important part of the effort for synthesizing new solid polymeric electrolytes (SPEs) for different applications.

Due to its unique structure, chemical properties of polyvinyl alcohol (PVA) can be tailored either adjusting the hydrolysis degree or blending PVA with other polymers. PVA is a biocompatible and nontoxic polymer and exhibits minimal cell adhesion and protein absorption; in addition it has good chemical stability and can be easily gelled by a crosslinking agent.

We synthesized an acidic polymer hydrogel electrolyte using a methan sulfonic acid aqueous solution, PVA and glutaraldehyde solutions.

The polymer hydrogel viscosity was controlled adjusting the glutaraldehyde concentration, used as crosslinking agent: the relationship between its concentration and hydrogel viscosity was determined. For the use as gelled electrolyte in nanostructured electrochemical cells, the best compromise between viscosity and electrical conductivity was found, leading to performances close to those of the methan sulfonic acid solution.

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ELE-PO-10 Effect of Different Carbon Electrode Materials on the Specific Capacity of Non-aqueous Li-O_2 Cells in Various Electrolytes.

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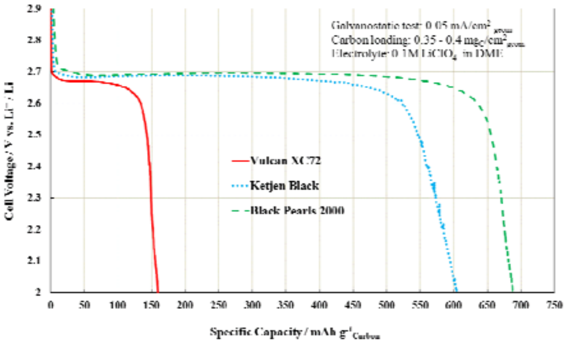
The demand for higher energy density power sources for future sustainable transportation has triggered the development of new Li-battery chemistry concepts. Since for current Li-ion batteries the positive electrode limits the specific energy of the battery, its improvement in capacity can lead to a remarkable increase of energy density in the whole battery, even more than improving its working voltage to ≈5 V vs. Li pursued in high-voltage cathode concepts [1]. Mankind use of the Oxygen Reduction Reaction (ORR) at the positive electrode in the so-called Li-Air battery could lead to a three-fold increase in specific energy for fully packaged batteries compared to state-of-the-art Li-ion batteries [2].

Some crucial factors for the optimization of the positive electrode are the specific surface area of the carbon material, affecting specific capacity and rate capability, and the binder/carbon ratio, which affects electrode porosity, oxygen diffusivity, and resistivity. On the other hand, the stability of the electrolyte in presence of the ORR intermediates like the superoxide ion-radical [3] and the stabilization of such intermediates with the solvent [4] are other very important factors to be taken into account.

In this contribution we examine the effect of different carbons as positive electrode materials on the specific capacity and cyclability of the test cells (Figure 1) in various organic solvents as electrolyte media.



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ELE-PO-11 Environmentally friendly corrosion inhibitor of the copper in 0.5 M sulphuric acid solution.

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Copper corrosion inhibition by gramine [3-(dimethylaminomethyl)indole] in the 0.5 M sulphuric acid solutions was studied in the temperature range 25-55 °C using electrochemical impedance spectroscopy techniques (EIS).

Gramine was dissolved at various concentrations (from $5\cdot10^{-4}$ to $7.5\cdot10^{-3}$) in 0.5 M sulphuric acid. The surface preparation of the specimens was carried out using silicon carbide paper up to grade 1200.

EIS measurements were performed after dipping the working electrode into the 0.5 M sulphuric acid solutions with or without inhibitor at E_{corr} with an a.c. voltage amplitude of 5mV. The frequency range was swept between 100 kHz and 10 mHz with 10 point for hertz decade.

The presence of gramine led to changes of the impedance plots in both shape and size. The plots of Nyquist exhibited that some impedance spectra consisted of one capacitive loop at the higher frequencies which was attributed to a faradaic process involving a charge transfer resistance in parallel with double-layer capacitance element [1]. The size of the capacitive arc increased by increasing the concentration of gramine. This indicated that gramine increased the charge transfer resistance and then it had an inhibiting effect on copper corrosion in 0.5 M sulphuric acid solutions. Inhibition efficiencies results showed that the gramine inhibited the copper corrosion in the temperature range 25-55 °C reaching the maximum value of 86% at 55 °C.

Impedance spectra also showed a depression of Nyquist-plot semicircles that can be related to the surface heterogeneity due the microscopic roughness of the electrode surface and inhibitor adsorption [2]. Moreover at the lower frequencies in both the uninhibited solutions and inhibited ones by lower inhibitor concentrations, the Warburg impedance appeared. In the copper corrosion in oxygenated sulphuric acid solutions at E_{corr} the anodic reaction is copper dissolution and cathodic reaction is oxygen reduction being the hydrogen discharge current density negligible as compared to oxygen reduction current density. Then the Warburg impedance could be attributed to oxygen transport from the bulk solution to the copper surface [3].

The adsorption behaviour of gramine followed Temkin's isotherm. The values of the standard free energy of adsorption of the gramine at 25 °C, 35 °C, 45 °C and 55°C were calculed.

A structural model of the interface copper/0.5 M H_2SO_4 was proposed.

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ELE-PO-12 Modulating Interfacial Interaction in the Electron Transfer Process of an Immobilized Cupredoxin

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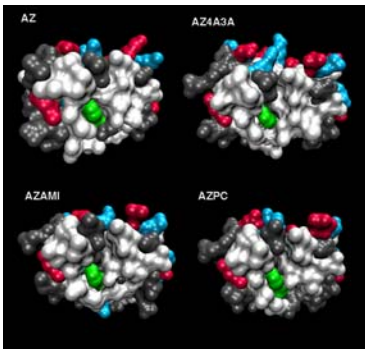
The hydrophobic patch involved in the electron transfer (ET) reaction of *Pseudomonas aeruginosa* azurin (AZ) was modified by mutating the C-terminal copper-binding loop. These proteins were non-covalently adsorbed onto gold electrodes modified with alkanethiol self-assembled monolayers (SAMs). In this way, a series of constructs were obtained which feature protein-SAM interactions of variable strength due to alterations in the area of azurin's hydrophobic patch. The distance-dependence of the ET kinetics for these adsorbed chimeric cupredoxins, measured through cyclic voltammetry using alkanethiols SAMs of variable chain length, indicate that the activation barrier for short range ET is dominated by the dynamics of molecular rearrangements accompanying ET at the protein-SAM interface. Contributions from internal protein dynamics and solvent molecules, but not protein reorientation, appear to be involved. This work provides direct experimental evidence for this mechanism which was proposed previously for azurin and also for electrostatically and covalently immobilized cytochrome *c*. This mechanism may therefore be utilized for short-distance ET irrespective of the type of metal center, the surface electrostatic potential and the nature of the protein-SAM interaction. The high electric field generated at the SAM-solution interface under these conditions would mimic those at the membrane-solution interfaces, where most ET proteins operate, therefore this mechanism is of relevance for physiological redox chains.



ELE-PO-13 RECLAMATION OF SOILS CONTAMINATED BY CHLORINATED ORGANICS: RESULTS FROM ELECTROOXIDATION TESTS

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The *in situ chemical oxidation* (ISCO) is a technology that requires injecting an oxidant into the ground, in order to treat organic pollutants (present in the soil matrix, or possibly in the groundwater).

A specific oxidant is chosen evaluating laboratory tests where the reactivity between the organic pollutants (targets) and the oxidant is assessed; concerning the area to be remediated, pre-treatment investigations are generally limited to the determination of pollutants distribution into the site, the characterization of the latter being realized through geological, topographical and hydrodynamic studies. Both an appropriate distribution of the oxidant in the subsurface, which must cover the entire impacted area, and the total amount of oxidant to be used are essential factors, deciding of the effectiveness of the approach to the field. In the traditional application scheme, the recourse to ISCO is usually limited to soils having medium to high permeability, and where the chemical oxidant demand is limited. Typically, the ISCO technology is applied to fields of prevalently sandy or gravelly character; however, if the matrix is characterized by a chemical oxidant demand much greater than that of polluting targets, the ISCO remediation does not appear to be feasible. The possibility of assisting the ISCO technology using an electrokinetic treatment, aiming at mobilizing the oxidant in soils with low permeability, through phenomena such as electromigration and electroosmotic flow, will be discussed. Besides, laboratory tests have shown that the application of an electric field can lead to a reduction of the aforementioned chemical oxidation demand of the soil, as well as of the concentration of halogenated pollutants (a phenomenon merely mentioned in the literature, and to whom the name of "*in situ electro oxidation*", ISEO, was given).

To deal with soils having a high chemical oxidation demand, a preliminary ISEO treatment may then allow the subsequent application of ISCO.

ELE-PO-14 Reverse electro dialysis processes. Selection of redox processes and electrodes.

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The extraction of the "osmotic energy" from two salt solutions showing a large difference in salt concentration is called salinity gradient power (SGP) 1-15. The potential energy available is very high; the osmotic energy in 1 m^3 of seawater is 0.75 kWh, equal to lifting a mass of 1000 kg to a height of 270 m. For exploiting this energy: (a) pressure retarded osmosis and (b) reverse electrodialysis, have been suggested. A proper selection of redox processes and electrodes is necessary to perform successfully the reverse electrodialysis process. The appropriate redox couples and electrode materials should be characterized by high chemical and electrochemical stability, fast electrochemical reaction of the redox couple, no poisoning of electrodes and membranes, low cost and absence or minimization of waste water treatment requirements.

A large number of redox processes and electrodes has been recently studied in our laboratories by electroanalytical investigations, electrolyses in divided and undivided cells and experiments performed in small stacks in order to select proper electrode processes for a reverse electrodialyis process.

ELE-PO-15 Electrochemical deposition of different semiconductors for application in solar cells.

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Among the latest generation solar cells, those based on copper, indium, gallium and selenium (CIGS) compounds are very interesting, because they show many advantages including high efficiency of energy conversion and excellent long-term reliability [1-2]. Recently, using a CIGS thin-film [3] the world highest photovoltaic energy conversion efficiency among flexible solar cell (15.9 %) was achieved. Interest towards flexible thin-film solar cells is due to their possible installation on curved surfaces and/or structurally weak supports, but also to their possible use as a power source for mobile devices.

Goal of this work is to show the fabrication of flexible thin-film CIGS/ZnS solar cells using a very simple method, which can be extended easily to large areas. In particular, thin films were obtained on a flexible substrate (PET/ITO) by potentiostatic deposition from aqueous baths. Different deposition parameters (bath composition and temperature, deposition time) were tested in order to obtain deposits with stoichiometric composition.

Films characterization was performed using several techniques (EDS, SEM, RAMAN, XRD) giving information on both chemical composition and structure. Preliminary results on the photoelectrochemical behavior of ZnS thin films will be also presented and discussed.

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ELE-PO-16 Performance of a DEFC for PtxSny/C catalysts prepared with formic acid

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There is presently a great interest on Direct Alcohol Fuel Cells, particularly on the Direct Ethanol Fuel Cell (DEFC), because it is a renewable and low toxic fuel. Pure platinum is not the most efficient anode catalyst for DEFC, because its surface is rapidly poisoned by strongly adsorbed species coming from the dissociative adsorption of ethanol. Thus, addition of a second metal has been proposed to alleviate this problem. In this sense, tin has demonstrated to be the most effective one. However, the performance and efficient to ethanol oxidation of PtSn catalyst highly depends on its composition and structural characteristics (degree of alloying and oxide content). In this sense, this work intends to elucidate the effect of the composition of different PtSn/C catalysts prepared by reduction with formic acid, using different reducing agent (formic acid) concentration. Four different Pt:Sn ratios were studied, 9:1, 3:1, and 1:1 on 60% metal on carbon catalyst, using three different formic acid concentrations (0,5, 1 and 2 M). EDX, XRD, TEM and XPS were used for physico-chemical characterisation. Electrochemical performance was studied on an actual fuel cell setup. Studies indicate that the modification of Pt by tin1gives very interesting results leading to the oxidation of ethanol at lower potentials than on pure platinum. The presence of Sn oxides on the catalyst surface can supply surface oxygen-containing species for the oxidative removal of CO and CH_3CO species adsorbed on adjacent Pt active sites, enhancing in this way the ethanol electro-oxidation activity at low potentials.
Best electrochemical performance and efficiency was achieved for the composition PtSn/C prepared with 0,5 M formic acid, achieving a power peak of approximately 45 mW/cm^2 at 90°C and 2 relative bars in the cathode. Reasons for this arise from the small particle size achieved, and the existence of an optimum ratio degree of Sn alloyed/oxide amounts, as XRD and XPS results confirmed. Lower Sn amounts did not favour the cell performance, because of the diminution of the synergic tin effect.

An excess of Sn decrease the cell performance for two reasons: (i) probably excessive amount/formation of SnO_2 semi-conductive species, and (ii) poorer platinum distribution in the catalyst in order to perform the ethanol dehydrogenation. Formic acid concentrations mostly affect the particle size, with an increase the higher is the amount of reducing agent in the synthesis medium.

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