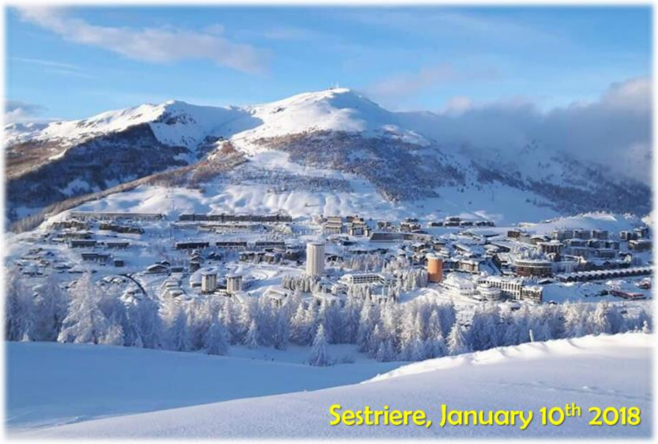
GEI 2018

PROGRAM &
BOOK OF
ABSTRACTS

GIORNATE DELL'ELETTROCHIMICA ITALIANA



1st winter edition

JANUARY 21-25
2018

OLYMPIC VILLAGE HOTEL, SESTRIERE (TO) – ITALY

Società Chimica Italiana
Divisione di Elettrochimica

POLITECNICO
DI TORINO
Dipartimento
di Scienza Applicata
e Tecnologia

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The Organising Committee kindly acknowledges the help in the organization from *Giovanni GALLO* (Coop Polisport Auxilium) and *Fabio TESSORE* (Equipe Pragelato Ski Club).

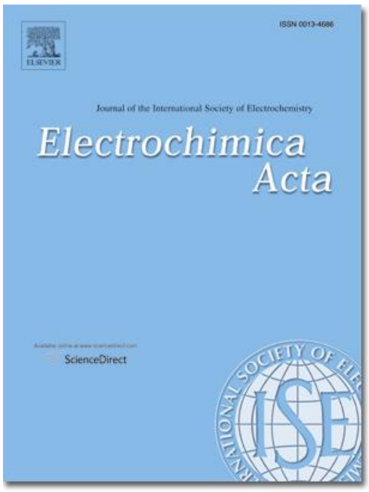
Fraz. PLAN, Via Rohrbach 13 - Pragelato (TO)

"Al Mulino" rappresenta una tappa fissa per chi frequenta l'alta valle Chisone. Un ristorante pizzeria, che, da oltre 40 anni, propone una rivisitazione di piatti tipici della cucina locale e Piemontese attraverso un'appassionata ricerca delle materie prime dai piccoli produttori locali.

"Al Mulino" restaurant pizzeria is a must try place for any tourist who loves the exquisite cuisine of Upper Chisone Valley. For over 40 years, it offers authentic local and Piamontese cuisine made of handpicked raw materials from local producers.

Special thanks to Francesca, Simone, Adriana, Alvaro and the whole "team"!

ELECTROCHIMICA ACTA VIRTUAL SPECIAL ISSUE



A selection of scientific contributions will be published in the *“Virtual” Special Issue* of *ELECTROCHIMICA ACTA* entitled *Sustainable Electrochemistry: Functional Applied Materials and Techniques for Energy Devices and Sensing*, short title *“GEI 2018 Sestriere”*, so as to "capture" timely, high quality papers and, at the same time, to build up an ensemble of contributions closely correlated to the selected theme. It will be *Edited by Federico Bella, Giuseppina Meligrana, Claudio Gerbaldi (Guests)* and *Sergio Trasatti*. All participants are invited to submit their scientific research work that are in line with the scope of the VSI.

Modern electrochemistry is cross-disciplinary in nature, recently attracting the interest of chemists, physicists, biochemists, surface and materials scientists, and engineers. It has many applications for sustainability, becoming now more and more an interdisciplinary field composed of sustainable "green" chemistry, nano-(bio-)technology, electrocatalysis, energy and sensing. The present “Sustainable Electrochemistry: Functional Materials and Techniques for Energy Devices and Sensing” Virtual Special Issue brings together the basic concepts of electrochemical discipline, materials science and engineering, from the development of innovative electroactive (nano-, bio-, hybrid-)materials, their optimization/functionalization and analysis/characterization through innovative powerful techniques to the assembly and validation in intelligent, efficient devices for energy conversion/harvesting and sensing, also focusing on how these can be applied in an industrial context. The objective is emphasizing effectively the major role that electrochemistry plays within society and industry as a fundamental discipline for key applications and technologies, which will pave the way for future cleaner, greener and more sustainable society.

Submission opens: 26th Jan 2018 (the gate will not be opened before that date)

Submission deadline: 1st May 2018

PROGRAM

Sunday, January 21st			
14:00			***Registration***
15:45			***Welcome and Opening of the winter GEI 2018***
			AFTERNOON Session – Chairmen: ARBIZZANI C. / PENAZZI N.
16:00	*Su.I01*	*VERLATO*	*Study of CO_2 reduction over nanostructured catalysts: effect of ceria as co-catalyst*
16:20	Su.Or01	SAVINO	The role of oxygen vacancies in green-synthesized TiO_2 for CO_2 photoelectroreduction
16:40	Su.Or02	FALCIOLA	Preparation and electrochemical characterization of “insulating” or mesoporous solid-templated silica films
17:00	Su.Or03	NERVI	Electrochemical reduction of CO_2 by electrodes functionalized with transition metal complexes
17:20	**Su.KN01**	**GENNARO**	**From fundamental research to industrial applications: the case of electrochemistry for ATRP**
18:00	**Su-LM**	**TARASCON**	**Award of the Galvani Medal** (Introduction by F. PAOLUCCI) **Energy storage via batteries: a dual materials-electrochemistry approach**
19:30			**Welcome party**

Monday, January 22nd

ENERCHEM joint session 1 – Chairmen: NAVARRA M. / NERVI C.

08:40	**Mo.PL01**	**FREITAG**	**Copper complexes for dye-sensitized solar cells**
09:15	*Mo.I02*	*BINETTI*	*The current status and future prospects of chalcogenide thin film solar cells*
09:35	Mo.Or04	LONGONI	A novel wet jet milling-exfoliated WS_2-graphite dual-ion battery: from lab-to-industrial scale feasibility
09:55	Mo.Or05	PAVONE	Dye-electrode interface in p-type photo-electrochemical cells: new insights from ab initio calculations
10:15	Mo.Or06	DI NOTO	New ion-exchange membranes derived from polyketone
10:35			**Coffee break**

ENERCHEM joint session 2 – Chairmen: BINETTI S. / BAROLO C.

11:00	*Mo.I03*	*BRUNETTI*	*Scaling up of organic and perovskite solar cells: an overview on lights and shadows*
11:20	Mo.Or07	NAVARRA	A systematic approach to design novel ionic liquids as electrolyte components in lithium batteries
11:40	Mo.Or08	SCALIA	Photo-capacitors: dye sensitized PV technology and carbon-based electrical double layer capacitors integration
12:00	Mo.Or09	MATTAROZZI	Electrodeposition of porous Cu-Zn alloys showing remarkable low T performances in Li-ion batteries
12:20	Mo.Or10	ARAB	Photoactive TiO_2 films by plasma electrolytic oxidation
12:40			**Lunch break & Relax**

AFTERNOON Session 1 – Chairmen: RAPINO S. / KANOUFI F.

14:35	**Mo.KN02**	**PALCHETTI**	**Nanostructured electrochemical biosensing platforms for nucleic acid determination**
15:00	*Mo.I04*	*BESTETTI*	*Entropy production rate as a tool for calculating corrosion current density*
15:20	Mo.Or11	PIFFERI	A concerted investigation of the interlayer charge transfer in silver/anatase nanocomposites
15:40	Mo.Or12	BARTOLINI	Exploring cellular interactions with 2D organic monolayers by scanning electrochemical microscopy
16:00	Mo.Or13	CINTI	Paper-based electrochemical tools for sweat analysis
16:20			**Coffee break**

AFTERNOON Session 2 – Chairmen: PIFFERI V. / GALLIANO S.

16:50	*Mo.I05*	*BARBUCCI*	*Impedance study of perovskite materials for IT-SOFCs: case of* $La_{0.8}Sr_{0.2}MnO_{3-\delta}$, $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-\delta}$ *and* $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$
17:10	Mo.Or14	VICARI	Electrochemical treatment of real wastewater with low conductivity
17:30	Mo.Or15	ARMANDI	Effect of iron addition on the catalytic activity of manganese oxides electrodeposited films in the water oxidation reaction
17:50	Mo.Or16	DURANTE	Effect of thiophenic-like functional group on Pt NPs deposition and activity towards oxygen reduction reaction
18:10		**SPONSOR TALKS**	(Biologic, Elsevier, Lithops)
19:30			**Dinner**
21:30		**POSTER SESSION 1**	– All Posters are exposed

Tuesday, January 23rd

MORNING session 1 – Chairmen: PALCHETTI I. / ISSE A.

08:40	**Tu.PL02**	**BANKS**	**Electrochemical sensors: from screen-printed electrodes to graphene**
09:15	*Tu.I06*	*VALENTI*	*Transparent carbon nanotube network for efficient electrochemiluminescence imaging*
09:35	Tu.Or17	ANTONELLO	Ordering gold nanoclusters by electrochemistry
09:55	Tu.Or18	MIOMANDRE	Electrochemical modulation of the fluorescence of tetrazines: from solution to monolayers
10:15	Tu.Or19	TESTOLIN	Functional hybrids of multilayer CVD graphene and colloidal anatase nanocrystals
10:35			**Coffee break**

MORNING session 2 – Chairmen: ANTONELLO S. / PIANA G.

11:00	*Tu.I07*	*NEGRO*	*Hierarchical "core-shell" electrocatalysts for the oxygen reduction reaction (ORR) based on graphene "cores" and metal alloy carbon nitride "shells"*
11:20	Tu.Or20	DANIEL	PGM free electrocatalyst based on Fe-Nx active sites embedded in mesoporous carbon for ORR
11:40	Tu.Or21	ZAFFORA	Electrochemical doping of mixed Nb-Ta oxides by the incorporation of electrolyte species
12:00	Tu.Or22	ISSE	Dissociative electron transfer to chain transfer agents for RAFT polymerizations
12:20	Tu.Or23	MINGUZZI	Recent advance in operando X-ray absorption spectroscopy on (photo)electrode materials
12:40			**Lunch break & Relax**

AFTERNOON Session 1 – Chairmen: MUNOZ-GARCIA A. / BANKS C.

14:35	**Tu.KN03**	**PIANA**	**Transition-metal migration upon cycling in a Li-rich layered oxide - A long-duration synchrotron in situ study**
15:00	*Tu.I08*	*BRUTTI*	*Gas release mitigation in Li-ion pouch cells*
15:20	Tu.Or24	DE GIORGIO	Sodium-alginate: an effective binder to develop eco-friendly and water-processable $Li_4Ti_5O_{12}$//$LiNi_{0.5}Mn_{1.5}O_4$ batteries
15:40	Tu.Or25	SILVESTRI	New insights on the $NaAlH_4$ based anodes inefficiency in lithium cell
16:00	Tu.Or26	ZOLIN	An innovative process for Li-ion battery ultra-thick electrodes manufacturing
16:20			**Coffee break**

AFTERNOON Session 2 – Chairmen: AMBROSIO E.P. - PIANA M.

16:50	*Tu.I09*	*MUNOZ-GARCIA*	*First-principles design of mixed proton-electron conductors for solid-oxide fuel cell electrodes*
17:10	Tu.Or27	BAGLIO	Bifunctional oxygen electrodes based on non noble metal oxides for metal-air batteries
17:30	Tu.Or28	MUSIANI	New routes to porous oxide layers
17:50	Tu.Or29	DE BON	Catalytic halogen exchange in electrochemically mediated ATRP: the case of methyl methacrylate
18:10		**POSTER SESSION 2** – All Posters are exposed	
20:00			**Dinner**

Wednesday, January 24th

MORNING session 1 – Chairmen: NICOTERA I. / NAIR J.R.

08:40	**We.PL03**	**DOMINKO**	**Metal sulphur batteries: myth or reality?**
09:15	*We.I10*	*QUARTARONE*	*Aqueous process of $Na_{0.44}MnO_2$ cathode material for the development of greener Na-ion batteries*
09:35	We.Or30	ARBIZZANI	Modified carbon paper interlayers in Li/S and Li/polysulfides batteries
09:55	We.Or31	FIORE	Improving the electrochemical behavior of highly abundant, low cost Fe(II) oxide as anode material in Na-ion rechargeable batteries
10:15	We.Or32	MORENO	Dissolved polysulfides as catholyte for high performance lithium-sulfur storage system
10:35	We.Or33	CHEN	Mixed colloidal/solid-state synthesis of crystalline pure P2-$Na_{1.7}Ni_{1.0}Mn_{2.9}O_{7.6}$ an its utilization as a stable cathode in Na-ion batteries
10:55			**Light Lunch**

MORNING session 2 – Chairmen: DOMINKO R. / FREITAG M.

11:30	*We.I11*	*NAIR*	*Polymer electrolyte: searching for new dimensions and pathways*
11:50	We.Or34	NICOTERA	Single lithium-ion conducting solid polymer electrolytes based on Nafion and functionalized graphene oxide
12:10	We.Or35	TSURUMAKI	Ionic liquids as additive salts for electrolytes of lithium ion batteries with the intent of improved stability

FREE AFTERNOON / SOCIAL EVENTS

12:30 **SKI Time**

or TOUR of the FENESTRELLE FORTRESS

18:10 *"Updates on the organization of the ISE Annual Meeting 2018"*
M. MUSIANI Lecturer

20:00 **Social Dinner, Restaurant "Al Mulino" Plan Pragelato (TO)**

BEST POSTER AWARDS & SPONSOR LOTTERY

Thursday, January 25th

MORNING session 1 – Chairmen: DELUCCHI M. / DURANTE C.

08:55	**Th.PL04**	**KANOUFI**	**Coupling electrochemistry and high resolution optical microscopies for single nanoparticle electrochemical study**
09:30	**Th.KN04**	**RICCI**	**Controlling DNA-based reactions and nanostructures assembly through electronic inputs**
09:55	*Th.I12*	*ARNABOLDI*	*Enantioselective voltammetry on achiral electrodes*
10:15	Th.Or36	POLO	Enzyme-based electrochemical biosensor for therapeutic drug monitoring of anticancer drug CPT-11
10:35	Th.Or37	MALFERRARI	Production of reactive oxygen species in cellular models of a human multisystem disorder monitored with modified microelectrodes
10:55			**Coffee break**

MORNING session 2 – Chairmen: ARNABOLDI S. / RICCI F.

11:20	*Tu.I13*	*DI FRANCO*	*Assessment of corrosion resistance of austenitic and duplex stainless steels in food industry*
11:40	Tu.Or38	DELUCCHI	Ag as brazing metal in Ti6Al4V/Ag/YAG joints: galvanic effects in seawater
12:00	Tu.Or39	PETRUCCI	How anodization conditions affect the characteristics of thin film electrodes deposited on nanostructured titanium substrates
12:20	Tu.Or40	BRANDIELE	Effect of Y salt precursor on the synthesis and activity of PtXY alloyed NPs versus oxygen reduction reaction
12:40	Tu.Or41	ZENG	Electroreduction of CO_2 on tin oxide modified copper oxide nanostructured foam
13:00			**Closing Remarks** **&** **Departures**

ORAL CONTRIBUTIONS

GALVANI MEDAL AWARD

Prof. Jean-Marie TARASCON

Lectio Magistralis (Su.LM)

Energy storage via batteries: a dual materials-electrochemistry approach

S*UNDAY, January 21*st *2018*

Prof. Jean-Marie TARASCON, Professor of Chemistry at the Collège de France in Paris and Director of the French Research Network on Electrochemical Energy Storage (RS2E), fellow of the Royal Society (2014) and the Royal Society of Chemistry (2015), ENI award (2011), Chevalier de la Légion d'Honneur (2009), Member of the French Academy of Sciences (2005).

Motivation for the GALVANI MEDAL AWARD: “distinguished for his seminal studies on high temperature superconducting materials and his most excellent contribution in the development of new high performing electrode materials and plastic architecture, which have revolutionized the way of thinking in the field of energy storage/conversion devices“.

Su.LM

Energy storage via batteries: a dual materials-electrochemistry approach

Jean-Marie Tarascon[a,b]

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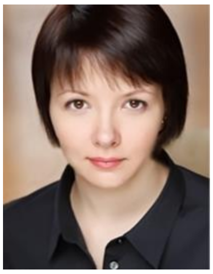
Research's progresses in rechargeable batteries are driven by ever increasing demands for portable electronic devices as well as for powering electric vehicles and providing load-leveling for mass storage of renewable energy. Li-ion batteries are the systems of choice for the aforementioned applications. Therefore, for this to fully happen, materials with higher energy densities while being sustainable and low cost must be developed. The challenges for chemists are enormous and this calls for new sustainable materials, new concepts as well as new chemistries together with a mastering of electrochemistry. These different aspects will be addressed through this presentation.
Firstly, regarding new concepts, we will show how the discovery of a new Li reaction mechanism [1-3] that involves the anionic network with the reversible formation of dimers (OO) represents a transformational approach for creating electrode materials with exacerbated capacities. Secondly, concerning new chemistry, our new findings with the Na-ion chemistry [4,5] which enlists novel materials/electrolyte designs together with the assembly of 18650 prototypes will be presented. Lastly, the implementation of electrochemical approaches towards the better understanding of alternative Li(Na)-air battery technologies will be shown.

[1] A. J. Perez, Q. Jacquet, D. Batuk, A. Iadecola, M. Saubanère, G. Rousse, D. Larcher, H. Vezin, M. L. Doublet, and J. M. Tarascon, *Nat. Energy* **2** (2017) 954-962.
[2] P. E. Pearce, A. J. Perez, G. Rousse, M. Saubanère, D. Batuk, D. Foix, E. McCalla, A. M. Abakumov, G. Van Tendeloo, M. L. Doublet, and J. M. Tarascon, *Nat. Mater.* **16** (2017) 580-586.
[3] E. McCalla, A. M. Abakumov, M. Saubanère, D. Foix, E. J. Berg, G. Rousse, M. L. Doublet, D. Gonbeau, P. Novák, G. Van Tendeloo, R. Dominko, and J. M. Tarascon, *Science* **350** (2015) 1516-1521.
[4] R. Dugas, B. Zhang, P. Rozier, and J. M. Tarascon, *J. Electrochem. Soc.* **163** (2016) A867-A874.
[5] B. Zhang, R. Dugas, G. Rousse, P. Rozier, A. M. Abakumov, and J. M. Tarascon, *Nat. Commun.* **7** (2016) art. no. 10308.

PLENARY LECTURES



MONDAY, January 22nd 2018

Mo.PL01 - Copper complexes for hybrid solar cells

Marina FREITAG

Department of Chemistry - Ångström Laboratory, Physical Chemistry, Uppsala University, Sweden

TUESDAY, January 23rd 2018

Tu.PL02 - Electrochemical sensors: from screen-printed electrodes to graphene

Craig BANKS

Faculty of Science and Engineering, Manchester Metropolitan University, UK

WEDNESDAY, January 24th 2018

We.PL03 - Metal sulphur batteries: myth or reality?

Robert DOMINKO

National Institute of Chemistry, Laboratory for Materials Electrochemistry, Ljubljana, Slovenia

THURSDAY, January 25th 2018

Th.PL04 - Coupling electrochemistry and high resolution optical microscopies for single nanoparticle electrochemical studies

Frederic KANOUFI

Paris Diderot University, Interfaces, Traitements, Organisation et Dynamique des Systèmes (ITODYS), France

Mo.PL01

Copper complexes for dye-sensitized solar cells

Marina Freitag

Department of Chemistry, Ångström Laboratory, Uppsala University, Lägerhyddsvägen 1, 75120-Uppsala Sweden
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Redox mediators in dye sensitized solar cells (DSCs) or hole transport materials (HTMs) in solid state DSCs (ssDSCs) play a major role determining the photocurrent and the photovoltage. With the introduction of new copper complexes as promising redox mediators or HTMs in DSCs both criteria are satisfied to enhance power conversion efficiencies and stability [1].

Due to the small reorganization energy between Cu(I) and Cu(II) species, this copper complexes can sufficiently regenerate the oxidized dye molecules with close to unity yield at driving force potentials as low as 0.1 V. The high photovoltages of over 1.0 V were achieved by the series of copper complex based redox mediators without compromising photocurrent densities. The solar-to-electrical power conversion efficiencies for $[Cu(tmby)_2]^{2+/1+}$, $[Cu(dmby)_2]^{2+/1+}$ and $[Cu(dmp)_2]^{2+/1+}$ based electrolytes were 10.3%, 10.0% and 10.3%, respectively, using the organic Y123 dye under AM1.5G illumination [2,3]. Solar cells that operate efficiently under indoor lighting are of great practical interest as they can serve as electric power sources for portable electronics and devices for wireless sensor networks or the Internet of Things. Our photosystem combines two judiciously designed sensitizers, coded D35 and XY1, with the copper complex Cu(II/I)(tmby) as a redox shuttle, and features a high open-circuit photovoltage of 1.1 V. The DSC achieves an external quantum efficiency for photocurrent generation that exceeds 90% across the whole visible domain from 400 to 650 nm, and achieves power outputs of 15.6 and 88.5 $\mu W\ cm^{-2}$ at 200 and 1,000 lux, respectively, under illumination from a model Osram 930 warm-white fluorescent light tube. This translates into a PCE of 28.9% [4].

Until recently, there have been no viable alternatives for Spiro-OMeTAD as a hole-transport material (HTM) for ssDSCs We show that copper coordination complexes in the solid phase can act as efficient molecular hole conductors in DSCs. We report a record 11% stable solid-state molecular photovoltaic based on copper complex HTM under standard AM1.5G conditions. We demonstrate that rapid hole hopping and the amorphous state of copper complexes are pivotal for achieving such a high conversion efficiency in the solid-state molecular photovoltaics [5].

[1] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, and H. Pettersson, *Chem. Rev.* **110** (2010) 6595-6663.
[2] Y. Saygili, M. Söderberg, N. Pellet, F. Giordano, Y. Cao, A. B. Munoz-Garcia, S. M. Zakeeruddin, N. Vlachopoulos, M. Pavone, G. Boschloo, L. Kavan, J. E. Moser, M. Grätzel, A. Hagfeldt, and M. Freitag, *J. Am. Chem. Soc.* **138** (2016) 15087-15096.
[3] S. Hattori, Y. Wada, S. Yanagida, and S. Fukuzumi, *J. Am. Chem. Soc.* **127** (2005) 9648-9654.
[5] M. Freitag, D. J. Teuscher, Y. Saygili, D. X. Zhang, D. F. Giordano, D. P. Liska, P. J. Hua, S. M. Zakeeruddin, J. E. Moser, M. Grätzel, and A. Hagfeldt, *Nat. Photonics* **11** (2017) 372-378.
[4] M. Freitag, Q. Daniel, M. Pazoki, K. Sveinbjornsson, J. Zhang, L. Sun, A. Hagfeldt, and G. Boschloo, *Energy Environ. Sci.* **8** (2015) 2634-2637.

Tu.PL02

Electrochemical sensors: from screen-printed electrodes to graphene

Craig Banks

Faculty of Science and Engineering, Manchester Metropolitan University, Chester Street, M15GD-Manchester, UK
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The glucose sensor is a billion-dollar per annum global market, which has its origins in screen-printing and electrochemistry. Screen-printing can produce economical one-shot disposable sensors which can be used for the rapid, sensitive and portable analysis of many target analytes in a plethora of areas.

However, for new sensors based on this process to be developed and implemented commercially, next generation screen-printed electrodes need to be designed. Additionally their fundamental understanding needs to be considered. In this talk, we will overview recent next generation screen-printed electrodes developed in the Banks Group and research directed at their fundamental understanding and analytical applications. Last, the talk will overview recent insights into graphene used as an electrode sensing platform.

We.PL03

Metal sulphur batteries: myth or reality?

Robert Dominko[a,b]

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Sulphur can be considered as a sustainable and cheap positive electrode material which in the combination with metallic anode (Li, Na, Mg,…) represents an attractive redox couple with several fold higher energy density compared to current Li-ion technology. For instance, a combination of lithium and sulphur corresponds to the theoretical energy density of 2600 Wh/kg. Although, use of magnesium metallic anode reduces energy density to 1330 Wh/kg, the combination is of high interest due to the ability of magnesium to provide two electrons during oxidation, due to the higher gravimetrical density of magnesium (theoretical volumetric energy reaches 2500 Wh L^{-1}) and due to non-dendritic deposition of Mg metal.

Although use of sulphur as cathode material is of high interest for different commercial applications, problems related to low electronic conductivity of sulphur and sulphides, limited number of available electrolytes, solubility of sulphur and polysulphides in the working electrolytes are postponing commercialization of metal sulphur based batteries. Electrochemical reduction of sulphur with Li or Mg proceeds through different polysulfide equilibrium states [1-3] and the mechanism of sulphur conversion into sulphide depends on the type and quantity of electrolyte used in the cell. Use of ether based electrolytes, with high polysulphides solubility requires larger amounts of electrolyte compared with the fluorinated ether based electrolytes, where the solubility of polysulphides is highly reduced. Although the solubility is lower, the appearance of different types of polysulphides during the reduction process can be detected when fluorinated ethers are used as solvents. Polysulphides can be also detected in the solid state formation, for instance conversion of sulphur confined in the ultramicropores. Such cathode composite configuration enables use of carbonate based solvents and possible further reduction of electrolyte quantity. Magnesium sulphur batteries are even more difficult from point of view of electrolyte selection due to limited compatibility of electrolytes with metallic magnesium.

Electrolyte selection has minor influence on the mechanism of sulfur conversion however it is important since it determines kinetics of sulphur conversion (power of the battery) and energy density of the battery which is highly affected with amount of added electrolyte during cell assembly.

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Th.PL04

Coupling electrochemistry and high resolution optical microscopies for single nanoparticle electrochemical studies

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Within the last decade, powerful electroanalytical strategies have been proposed to study electrochemical processes, *in operando*, at the level of individual nanoentities. They rely for example on the time-resolved detection of stochastic electrochemical collisions of individual nanoparticles, (NPs) on ultramicroelectrodes [1a,b] or the control of nanoparticle electrochemistry at nanoelectrodes [1c,d]. Such pure electrochemical strategies provide, *in situ,* much valuable information concerning NP electrochemistry, size or concentration, etc… they are however blind to a wide range of NP information.

Few groups [2,3], including ours, have proposed the coupling of different optical microscopies to the electrochemical activation of nanoobjects as promising platform for understanding the chemistry of nanoobjects. In this respect, we have proposed superlocalization optical microscopies (3D holography, spectroscopy) to give a complementary monitoring of the electrochemistry of individual NPs. Such coupled approaches define powerful tools to apprehend *in operando* the chemical activity of NPs.

This approach is illustrated (Fig. 1) here for the direct visualization of the transport-reaction processes associated to NP actuation along with complementary chemical signatures of the transformation of individual NPs during their electrochemistry [2].

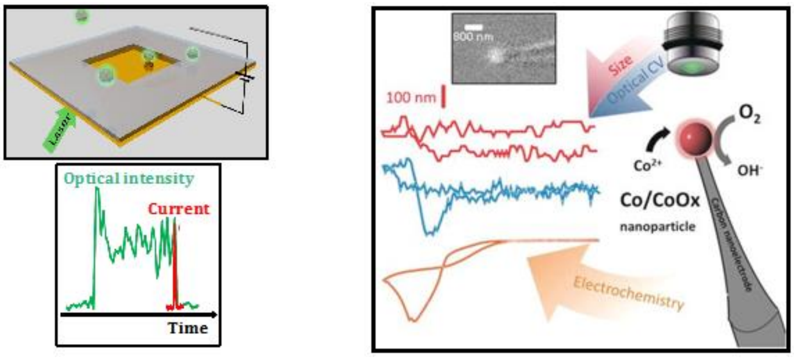

Figure 1. Optical monitoring of (left) single NP electrochemical collision on a microelectrode, (right) the electrodeposition of Co NP on a nanoelectrode.

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[3] See review in: Y. Wang, X. Shan, and N. J. Tao, *Faraday Discuss.* **193** (2016) 9-39.

KEYNOTE LECTURES

SUNDAY, January 21st 2018

Su.KN01 - From fundamental research to industrial applications: the case of electrochemistry for ATRP

Armando GENNARO

Department of Chemical Science, University of Padua, Italy

MONDAY, January 22nd 2018

Mo.KN02 - Nanostructured electrochemical biosensing platforms for nucleic acid determination

Ilaria PALCHETTI

Department of Chemistry "Ugo Schiff" - University of Florence, Italy

TUESDAY, January 23rd 2018

Tu.KN03 - Transition-metal migration upon cycling in a Li-rich layered oxide - A long-duration synchrotron in situ study"

Michele PIANA

Department of Chemistry, Technical University of Munich, Germany

THURSDAY, January 25th 2018

Th.KN04 - Controlling DNA-based reactions and nanostructures assembly through electronic inputs

Francesco RICCI

Department of Chemical Science and Technology, University of Rome "Tor Vergata", Italy

Su.KN01

From fundamental research to industrial applications: the case of electrochemistry for ATRP

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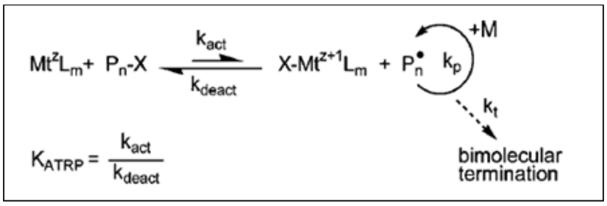
Controlled radical polymerizations or, as recommended by IUPAC, reversible deactivation radical polymerizations (RDRP), allow to produce polymers with a narrow distribution of molecular weights. Among the different RDRP techniques, Atom Transfer Radical Polymerization (ATRP) is the most versatile, investigated and applied for the synthesis of polymers and copolymers of precise architecture, which are employed in several industrial processes [1].

The core of ATRP is the following equilibrium:



The first relevant contribution that electrochemistry gave to ATRP was a more clear definition of the mechanism of the activation process.

Electrochemistry introduced efficient methods for the determination of relevant thermodynamic parameters.

In addition, relevant kinetic parameters were successfully obtained by electrochemical procedures. Electrochemical approaches allowed the determination of activation rate constants spanning about 12 orders of magnitude, which is absolutely incomparable to all other techniques previously used for kinetic investigations of ATRP.

From the synthetic point of view, the most important contribution of electrochemistry to ATRP is the development of electrochemically mediated ATRP, named *e*ATRP [2]. The concept behind *e*ATRP is that the ratio of activator to deactivator catalyst is precisely controlled by an electrochemical redox process at an electrode surface, thereby rendering the *e*ATRP process operational through an external stimulus. *e*ATRP has shown versatility in synthesizing various soft materials with well-defined polymeric architectures. Polymerizations can be carried out both under potentiostatic and galvanostatic conditions, with a three-electrode or a two-electrode setup, in both divided and undivided cells with a sacrificial anode.

[1] K. Matyjaszewski, *Macromolecules* **45** (2012) 4015-4039.
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Mo.KN02

Nanostructured electrochemical biosensing platforms for nucleic acid determination

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Electrochemical techniques, such as faradic impedance spectroscopy, amperometry, and differential pulse voltammetry, have been used by our group, for the development and characterization of different formats of genosensors. Basically, the DNA capture probes are immobilized on the electrode surfaces. Then, the target sequence is extracted from the sample, and hybridized with the specific capture probes. Different label and label-free detection methods have been optimized [1].

However, it is well known that the electrode surface nanostructuring offers suitable anchoring sites for the capture probes allowing optimal control over steric hindrance, increased surface area and increased mass transport rate. Thus, recently, we investigated different nanostructured electrochemical platforms for the sensitive detection of nucleic acids. In a first attempt, a procedure to electrochemically deposit Au nanoclusters, in order to define nanoscale immobilization Au domains over a carbon electrode surface, was optimized [2]. Then, a label-free impedimetric genosensor, using a functional polymer-modified sensor was developed [3]. Finally, the behavior of a novel AuNPs-rGO nanostructure was investigated towards electrochemical sensing of clinically relevant molecules and towards the development of a DNA-based biosensor.

[1] F. Bettazzi, E. Hamid-Asl, C. L. Esposito, C. Quintavalle, N. Formisano, S. Laschi, S. Catuogno, M. Iaboni, G. Marrazza, M. Mascini, L. Cerchia, V. De Franciscis, G. Condorelli, and I. Palchetti, *Anal. Bioanal. Chem.* **405** (2013) 1025-1034.
[2] D. Voccia, F. Bettazzi, E. Fratini, D. Berti, and I. Palchetti, *Anal. Bioanal. Chem.* **408** (2016) 7271-7281.
[3] D. Voccia, M. Sosnowska, F. Bettazzi, G. Roscigno, E. Fratini, V. De Franciscis, G. Condorelli, R. Chitta, F. D'Souza, W. Kutner, and I. Palchetti, *Biosens. Bioelect.* **87** (2017) 1012-1019.

Tu.KN03

Transition-metal migration upon cycling in a lithium-rich layered oxide – A long-duration synchrotron in situ study

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Lithium-rich layered oxides offer an extraordinarily high gravimetric capacity of more than 250 mAh g^{-1}, which makes them attractive as cathode materials in future automotive applications. However, the materials suffer from low initial coulombic efficiency, poor capacity retention and voltage fading upon cycling [1]. An uneven increase of overpotentials during charge and discharge and peak changes/shifts in the differential capacity plots suggest bulk effects as the main reason of the poor cycling stability [1]. Initially, such performance drops were ascribed to oxygen release from the host structure, but according to our recent OEMS studies, this is limited to near-surface of the particles [2].

Rietveld analysis on long-term synchrotron in-situ XRD data [3] allowed us to quantify the transition metal migration upon cycling. Our data demonstrate experimentally for the first time that the transition metal migration in such oxides proceeds from the octahedral transition metal sites via tetrahedral sites in the lithium layer into octahedral lithium sites (Fig. 1). Such migration is irreversible (at least partially) and is correlated to the irreversible discharge voltage fade. We will discuss thermodynamic or kinetic hypotheses on its origin.

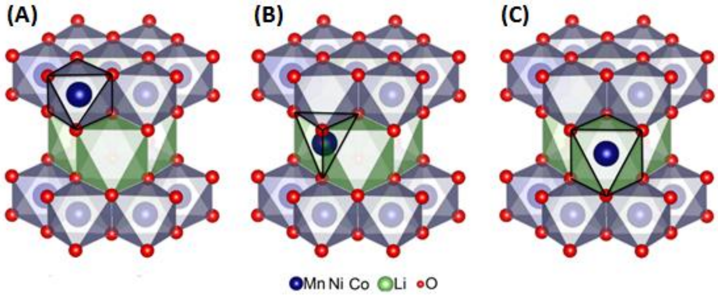

Figure 1: Transition metal migration in layered oxides from the starting position in the octahedral sites of the transition metal layer (A) via the tetrahedral sites in the lithium layer (B) finally into the octahedral sites in the lithium layer (C).

Acknowledgements: We want to acknowledge BASF SE for the support within the frame of its scientific network on electrochemistry and batteries.

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Th.KN04

Controlling DNA-based reactions and nanostructures assembly through electronic inputs

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DNA nanotechnology uses DNA (or nucleic acids) as a versatile material to rationally engineer tools and molecular devices at the nanoscale. During this presentation I will initially give an overview of the most representative and recent examples developed in our lab where we exploited the "designability" of DNA to fabricate nature-inspired DNA-based nanoswitches and nanodevices that can be used for diagnostic, drug-delivery or synthetic-biology applications. I will then focus on more recent developments where we demonstrated the use of electronic inputs as a means to remotely control DNA-based nanodevices and nanostructures assembly.

INVITED ORAL COMMUNICATIONS

Su.I01 - Enrico VERLATO, Inst. of Condensed Matter Chemistry & Technologies for Energy (ICMATE-CNR)
Study of CO_2 reduction over nanostructured catalysts: effect of ceria as co-catalyst

Mo.I02 - Simona BINETTI, Università degli Studi di Milano-Bicocca
The current status and future prospects of chalcogenide thin film solar cells

Mo.I03 - Francesca BRUNETTI, Centre for Hybrid and Organic Solar Energy (CHOSE), UniROMA-2
Scaling up of organic and perovskite solar cells: an overview on lights and shadows

Mo.I04 - Massimiliano BESTETTI, Politecnico di Milano
Entropy production rate as a tool for calculating corrosion current density

Mo.I05 - Antonello BARBUCCI, Università degli Studi di Genova
Impedance study of perovskite materials for IT-SOFCs: case of $La_{0.8}Sr_{0.2}MnO_{3-\delta}$, $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$

Tu.I06 - Giovanni VALENTI, Alma Mater Studiorum – Università di Bologna
Transparent carbon nanotube network for efficient electrochemiluminescence imaging

Tu.I07 - Enrico NEGRO, Università degli Studi di Padova
Hierarchical "core-shell" electrocatalysts for the oxygen reduction reaction (ORR) based on graphene "cores" and metal alloy carbon nitride "shells"

Tu.I08 - Sergio BRUTTI, Università degli Studi della Basilicata
Gas release mitigation in Li-ion pouch cells

Tu.I09 - Ana B. MUNOZ-GARCIA, Università degli Studi di Napoli Federico II
First-principles design of mixed proton-electron conductors for solid-oxide fuel cell electrodes

We.I10 - Eliana QUARTARONE, Università degli Studi di Pavia
Aqueous process of $Na_{0.44}MnO_2$ cathode material for the development of greener Na-ion batteries

We.I11 - Jijeesh R. NAIR, Helmholtz Institute Münster (HI MS) Ionics in Energy Storage
Polymer electrolyte: searching for new dimensions and pathways

Th.I12 - Serena ARNABOLDI, Università degli Studi di Milano
Enantioselective voltammetry on achiral electrodes

Th.I13 - Francesco DI FRANCO, Università degli Studi di Palermo
Assessment of corrosion resistance of austenitic and duplex stainless steels in food industry

Su.I01

Study of CO_2 reduction over nanostructured catalysts: effect of ceria as co-catalyst

Enrico Verlato,[a,b] Simona Barison,[a] Yasuaki Einaga,[c] Marco Musiani,[a] Keisuke Natsui,[c] Francesco Paolucci,[a,b] and Giovanni Valenti[b]

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Significant effort is being spent to limit the concentration of greenhouse gases in the atmosphere and to convert CO_2 to fuels, such as formic acid methane or ethane, by electrochemical reduction, using renewable power sources.

Ceria-based materials are well known as co-catalysts for low-temperature catalytic combustion of hydrocarbons, CO and CH_3OH [1]. We have studied the CO_2 reduction reaction (CO_2RR) on electrocatalysts consisting of ceria and different metal nanoparticles, mainly to assess the products selectivity. We have used different supporting materials: (i) boron doped diamond (BDD) [2], because of its chemical inertness, low background currents and wide potential region for water stability, which limits the HER, a process competitive with CO_2RR, and (ii) carbon nanotubes (CNTs), because of their great surface area and good conductivity.

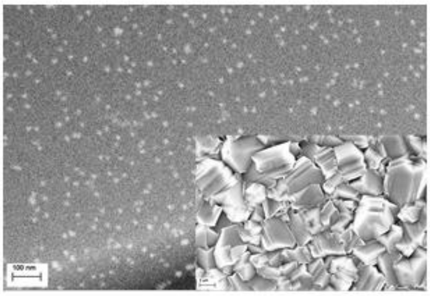

Figure 1: SEM CeO2/Pt-BDD

We deposited Pt-NP using pulsed electrodeposition, obtaining even particles distribution on the supports surface and a narrow size distribution (typically from 5 to 10 nm). Then we covered the Pt-NP with thin films of ceria, produced by an electrochemically induced precipitation. By varying the cathode potential, we obtained ceria deposits with different levels of Ce^{3+} doping.

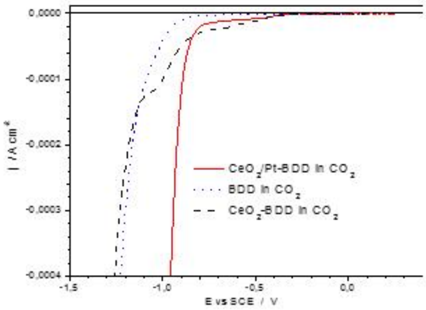

Figure 2: LSV of CO2RR

Preliminary results showed that CO_2RR on Ceria-Pt-BDD, at potential close to formate standard reduction potential, gave formate yields close to those of the best catalysts reported in literature, even if at that low overpotential the current was low. A significant formate yield was obtained for Ceria-BDD system too. These results showed that ceria enhances the selectivity for formate in the CO_2RR.

[1] E. Verlato, S. Barison, S. Cimino, L. Lisi, G. Mancino, M. Musiani, and F. Paolucci, *Chem. Eng. J.* **317** (2017) 551-560.
[2] T. A. Ivandini and Y. Einaga, *Chem. Commun.* **53** (2017) 1338-1347.

Mo.I02

The current status and future prospects of chalcogenide thin film solar cells

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A crystalline silicon (c-Si) based PV technology accounted for about 94% of the total production in 2016, while the market share of all thin film technologies amounted to about 6% of the total annual production. The reduction in PV module cost progresses with the increase of production, but we are rapidly reaching a stage where a further decrease in cost is conditional on the global availability of raw materials. Thus, PV technologies that involve the use of lesser quantities of cheaper and less refined input materials are favored. Currently, there are several low-cost thin-film solar cell options, which have potential for high efficiency. Among them, chalcogenide based thin film are very promising expecially $Cu(In,Ga)Se_2$ (CIGS) since its conversion efficiency reached 22.8% at laboratory level.

In this presentation, we will discuss the advantages and open questions related to CIGS technology and the recent results obtained at MIBSOLAR center related to a developing of a new hybrid sputtering-evaporation system for the deposition of CIGS thin-films. This procedure combines the features of both the sputtering and evaporation techniques, enabling a fine tuning of the stoichiometry and an easy transfer to industrial processes.

Despite the advantages of CIGS technology, the production of CIGS solar cells is expected to be limited as results of indium and gallium scarcity and in the last decade, much attention has been focused on I_2-II-IV-VI_4 thin films as an attractive possibility for the synthesis of In and Ga free chalcogenides. Kesterite photovoltaics utilizing Cu_2ZnSnS_4 (CZTS), $Cu_2ZnSnSe_4$ (CZTSe) and $Cu_2ZnSn(S,Se)_4$ (CZTSSe) are emerging as the most promising replacement for the chalcopyrite absorbers, through the substitution of indium and gallium in the with comparatively abundant and lower cost zinc and tin. Conventional methods for fabricating Kesterite based solar cells involve vacuum processes, e.g. co-evaporation and sputtering, even if the most performing devices based on CZTS have been realized using a solution-based methodology. In this context, at MIBSOLAR we develop a chemical procedure to obtain a superior quality CZTS films composed by highly soluble and inexpensive precursors in a non-toxic and environmentally friendly solvent. Furthermore, a new alternative to copper zinc tin sulfide/selenide is copper manganese tin sulfide (CMTS), a p-type semiconductor fully based on Earth-abundant and low-cost elements that shows an important advantage with respect to CZTS. Preliminary results also on this new absorber for solar cells will be presented.

Mo.I03

Scaling up of organic and perovskite solar cells: an overview on lights and shadows

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Photovoltaics is a fast-growing market where it is predominately dominated by silicon-based solar cells. This first generation of solar cells is a mature technology with stable efficiency, stability and lifetime but maybe difficult to recycle. Organic (OSC) and Perovskite solar cells (PSC), third generation of solar cells technology which has shown record certified efficiency above 11%in case of OSC and of 22% in case of PSC, addresses the challenge of cost, materials and productivity [1][2].

The scaling up of these two technologies based on solution processing techniques together with their durability represent fundamental aspects in the direction of their application in the real market.

In this presentation, key aspect for the realization of high efficiency and large area devices of the two type of solar cells will be shown together with some possible applications.

Furthermore, the cause of the degradation of these solar cells will be presented, highlighting critical issues and possible solutions. In particular, for the perovskite solar cells, it will be shown the result of an inter-laboratory study within the frame of the StableNextSol COST action. Here, a combination of several testing methods have been considered, both indoor under sun simulator and outdoor following the ISOS-D1, ISOS-L1, ISOS-O1 and ISOS-O2 protocols. This allowed the investigation of the role in aging of the different layers composing the perovskite solar cells and of the encapsulants, as well as identifying some critical aspects related to the characterization methodologies.

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[2] https://www.nrel.gov/pv/assets/images/efficiency-chart.png

Mo.I04

Entropy production rate as a tool for calculating corrosion current density

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According to a hypothesis attributed to Piontelli in the 1950s, in an electrochemical system, the current-distribution laws are such as to lead to the maximum exploitation rate of the internal and external sources of driving force (maximum value of the entropy production rate) allowed by the local laws of the dissipation of this driving force [1].

Based on this principle of maximum entropy production rate, a new formula for calculating the current density of uniform corrosion processes is proposed. The method will be described with reference to the case of uniform corrosion with negligible concentration gradients and ohmic drops.

The formula implies a different elaboration of potentiodynamic polarization curves from that usually adopted by Tafel analysis. Literature corrosion data for the Fe-H_2O-HCl system will be considered as example. The corrosion current density values calculated with the new formula show a better agreement with the experimental values derived from weight loss measurements than those calculated with the classical Tafel analysis [2], [3].

The case where electrode dissipative phenomena and concentration gradients are simultaneously present will be discussed. Finally, a brief mention to the problem of the ohmic drop in the electrolytic solution will be carried out.

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Mo.I05

Impedance study of perovskite materials for IT-SOFCs: case of $La_{0.8}Sr_{0.2}MnO_{3-\delta}$, $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$

Antonio Barbucci,[a,b,c] Davide Clematis,[a,c] Antonio Bertei,[b,c] Cristiano Nicolella,[b,c]
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Solid oxide fuel cells (SOFCs) are clean and efficient electrochemical devices, which can produce electricity from different practical fuels. Cathodes for SOFCs are generally based on perovskite-type oxides, such as $La_{1-x}Sr_xMnO_{3-\delta}$, $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ and $Ba_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$, whose electrocatalytical properties depend not only by the chemical composition of the materials but also by the operating conditions, such as the applied overpotentials [1].

The aim of the present work is to discuss the behavior of different cathode systems investigated by the research group under practical SOFC conditions. The analysis was pursued with combinations of modeling and high quality impedance spectroscopy experiments [2,3].

Electrochemical measurements were carried out on the following systems: $La_{0.8}Sr_{0.2}MnO_{3-\delta}/Y_{0.08}Zr_{0.92}O_{2-\delta}$, LSCF/$Sm_{0.2}Ce_{0.8}O_{2-\delta}$ and BSCF/$Sm_{0.2}Ce_{0.8}O_{2-\delta}$. Furthermore, SCF and BSCF cathodes infiltrated with an LSM nanosized discrete layer were also investigated.

The effect of temperature and cathodic overpotential was observed on different kinds of microstructures. Different approaches for the analysis of the impedance spectra were used and the results combined, in order to understand and possibly correlate the electrochemical behavior with material parameters, with the aim of get useful information for optimizing SOFC materials and devices.

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Tu.I06

Transparent carbon nanotube network for efficient electrochemiluminescence imaging

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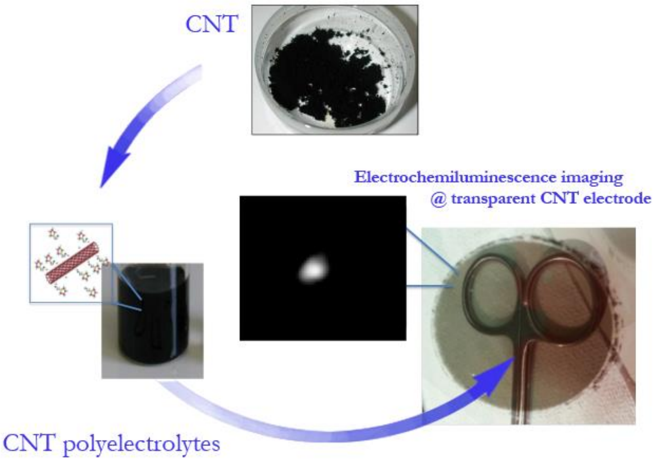
Electrochemiluminescence (ECL) is a leading technique in bioanalysis [1]. Since the excited species are produced with an electrochemical stimulus rather than with a light excitation source, ECL displays improved signal-to-noise ratio compared to photoluminescence. The peculiar analytical performances in terms of high detectability of conventional chemiluminescence (CL) are retained and, in addition, the electrochemical trigger of the reaction allows controlling the time and position of light emission from ECL probes. These properties make ECL systems particularly attractive also for microscopy imaging techniques.

In the quest for ever-increasing sensitivities, ECL can ideally be coupled to nanotechnology to develop new systems and strategies for analyte determination also in very complex matrices. In this context, the nanostructured materials such as carbon nanotubes (CNTs) and graphene are particularly promising for sensing applications [2].

Here we present the application of optically transparent electrodes based on carbon nanotubes materials to ECL, demonstrating the electrocatalytic superiority of such materials vis-à-vis ITO electrodes. The employ of carbon nanotubes resulted in a ten times higher emission efficiency compared to commercial transparent ITO electrodes. Finally, we demonstrate as a proof of principle that our CNT device can be used for the ECL imaging of micro-beads and real biological sample, such as single cell visualization [3].



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Tu.I07

Hierarchical "core-shell" electrocatalysts for the oxygen reduction reaction (ORR) based on graphene "cores" and metal alloy carbon nitride "shells"

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The sluggish kinetics of the oxygen reduction reaction (ORR) is one of the most important bottlenecks in the operation of several families of advanced energy conversion and storage devices, such as metal-air batteries and low-temperature fuel cells (*e.g.*, proton-exchange membrane fuel cells, PEMFCs and anion-exchange membrane fuel cells, AEMFCs). Accordingly, the development of efficient ORR electrocatalysts (ECs) is one of the most active research areas in this field.

This work describes the features of a new family of ECs for the ORR, exhibiting a hierarchical "core-shell" morphology; they include a graphene-based nanostructured "core" covered by a carbon nitride "shell" embedding the ORR active sites in carbon- and nitrogen-based "coordination nests". The proposed "core-shell" ORR ECs are obtained by customizing a unique and extremely flexible preparation protocol [1-3], that allows to fine-tune the morphology and the chemical composition of the ECs.

This work overviews the synthetic strategies used to obtain the ECs comprising the graphene-based nanostructured "cores" and discusses the complex correlations existing between the preparation parameters, the physicochemical properties and the electrochemical performance. Finally, the most promising avenues and new directions for the research are indicated, with the aim to obtain ECs comprising graphene-based nanostructured "cores" exhibiting an improved ORR performance and durability, and at lower costs, in comparison with state-of-the art "reference" ECs.

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Tu.I08

Gas release mitigation in Li-ion pouch cells

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A variety of Li-ion cells (LIC) formulation is currently commercialized worldwide to power mobile electronics, power tools and e-mobility or to accumulate renewable energy in stationary storage systems. This remarkable variability originates by the amazing innovations proposed by scientists in the last decades, ranging from electrode active materials, to separators, to electrolyte components. Together with the enhancement of battery performance, safety is nowadays one of the most challenging research field for LIC.

One of the key issues to mitigate the intrinsic hazard of LIC is the careful management and limitation of all parasitic processes occurring upon cycling. These side-reactions, either chemical or electrochemical, are responsible for the cycle-by-cycle performance fading and lead, in the long term, to the cell failure. Moreover, the accumulation of by-products upon cycling can unexpectedly contribute to an increase of the overall battery hazard.

Here we illustrate our recent studies about the gas release upon cycling of LTO-LFP and Graphite-NCA full LIC formulations, and the complex interplay with the other cell components. Coin cells as well as pouch cells have been assembled using commercial materials (Custom Cells Gmbh and Solvionic) and cycled at room temperature in galvanostatic conditions. The release of gaseous by-products upon cycling has been monitored by continuous in operando measurement of the internal LIC pressure and by ex situ gas chromatography. Electrodes have been recovered for post mortem analysis by SEM, XPS, FTIR and Raman spectroscopy.

Our results show the occurrence of a remarkable gas release upon cycling for both LIC formulations, occurring in parallel with the well-known parasitic surface chemistries on electrodes. This gas release has been mitigated in both LIC formulations by the incorporation of selective getters able to sequestrate specific gases released upon cycling. Moreover, the incorporation of these getters (i.e. SafeT™ and Suisorb™) improves the galvanostatic performance for both formations.

Tu.I09

First-principles design of mixed proton-electron conductors for solid-oxide fuel cell electrodes

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Electrolyzer and fuel cells based on proton-conducting solid oxides (PC-SOEC/FC) are gaining ground in the energy conversion scenario, thanks to fast proton diffusion rates at convenient operating temperatures. However, current performances are curbed by severe limitations of common electrodes [1]. Within this context, here we outline the latest work of our group on the rational design of innovative electrode materials for PC-SOEC/FC applications.

With first-principles methods, we aimed at providing unbiased explanations and predictions of materials properties and functions, so to assess new design principles based on quantum mechanics. The desired electrode materials for PC-SOEC/FCs should pair mixed proton/electron conductive (MPEC) features to good catalytic activity. We followed two design strategies: induction of proton conduction to mixed ion-electron conductors to obtain triple conducting oxides [2] or induction of electronic conduction on well-known proton conductor materials [3]. To this end, in bulk solids we evaluated oxygen vacancy formation and water uptake enthalpies, and we characterized the minimum-energy path for proton migration and the corresponding barrier heights. Then, we investigated the catalysis associated to the four proton-coupled electron transfer processes for the oxygen evolution reaction (OER) and reverse oxygen reduction reaction (ORR) at the electrode surfaces. Our calculations revealed the structural and electronic features than are needed for an effective bifunctionality towards the OER and ORR.

Our findings can trigger the targeted experimental synthesis and testing of new single-phase electrodes and can enable the deployment of reversible proton-conducting SOEC/FC devices. Moreover, our analysis can be exploited for the rational design of bifunctional electrocatalytic systems with similar key characteristics.

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We.I10

Aqueous process of $Na_{0.44}MnO_2$ cathode material for the development of greener Na-ion batteries

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The implementation of aqueous electrode processing of cathode materials is a key for the development of greener Na-ion batteries. Herein, the development and optimization of the aqueous electrode processing for the ecofriendly $Na_{0.44}MnO_2$ (NMO) cathode material, employing carboxymethyl cellulose (CMC) as binder, are reported for the first time. The characterization of such an electrode reveals that the performances are strongly affected by the employed electrolyte solution, especially, the sodium salt and the use of electrolyte's additives. In particular, the best results are obtained using the 1 M solution of $NaPF_6$ in EC/DEC (ethylene carbonate/ diethyl carbonate) 3:7 (v/v) + 2 wt % FEC (fluoroethylene carbonate).

With this electrolyte, the outstanding capacity of 99.7 mA h g^{-1} is delivered by the CMC−NMO cathode after 800 cycles at a 1C charge/discharge rate. On the basis of this excellent long-term performance, a full sodium cell, composed of a CMC-based NMO cathode and hard carbon from biowaste (corn cob), has been assembled and tested. The cell delivers excellent performances in terms of specific capacity, capacity retention, and long-term cycling stability. After 75 cycles at a C/5 rate, the capacity of the NMO in the full-cell approaches 109 mA h g^{-1} with a Coulombic efficiency of 99.9%.

We.I11

Polymer electrolyte: searching for new dimensions and pathways

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Polymer electrolytes are proposed as a safe alternative to existing and widely used organic carbonate-based liquid electrolytes [1]. In lithium-ion battery (LiB) sector, the transformation from liquid state to solid state construction is expected to improve safety concerns, architectural ease, high temperature stability and low cost of fabrication. However, several constraints have impeded their intrusion into the mainstream. The main reasons are low ionic conductivity, low cation transport properties and stringent processing conditions (use of organic solvents). Thus, the researchers have proposed several approaches including the most promising *in situ* preparation of thermoset polymer electrolytes [2] using the well-established solvent-free process such as free radical and/or ionic polymerization technique. Even though several works have been carried out via UV and/or heat induced free radical polymerization, transforming it in to an industrially viable technique is still an oasis.

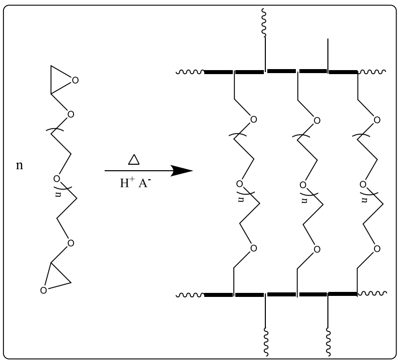

Figure 1: Schematic representation of a cross-linked polymer membrane prepared by thermal-induced CROP technique.

In this respect, we are proposing a facile production of polymer electrolyte from epoxide based oligomers using thermally induced cationic ring opening polymerization (CROP, see Figure 1). CROP has not been explored to its full potential in the field of LiBs, and we have developed an all solid-state polymer electrolyte that exhibit ionic conductivity close to 0.1 $mS.cm^{-1}$ at ambient conditions. The polymer electrolyte demonstrated an oxidation stability above 4.7V vs. Li and excellent cycling at elevated temperature for several hundreds of cycles. The results achieved in our labs confirm that CROP is viable and industrially up scalable technique with enormous potential as a primary tool for the production of all solid-state polymer electrolytes.

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Th.I12

Enantioselective voltammetry on achiral electrodes

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An attractive target in electroanalysis is the availability of chiral media affording enantioselection in terms of significant peak potential difference between the antipodes of chiral probes in voltammetry experiments on achiral electrodes.

Previous literature attempts pointed to enantioselectivity increasing with the structural order of the chiral medium; on the other hand, outstanding enantioselection performance has been recently observed working on electrode surfaces consisting in "inherently chiral" oligomer films [1-2].

Combining both strategies, we have recently developed two inherently chiral ionic liquids, ICILs, consisting of dialkylated bicollidinium salts, with an atropoisomeric bipyridinium cation featuring at least one octyl chain and bistrifilimide counteranions. They showed high enantioselectivity when tested even as low concentration additives in commercial achiral ionic liquid media [3] and also as chiral bulk media.

Importantly, similar ability was also shown by other terms of the same family, having shorter alkyl chains and/or different counteranions, solid at room temperature but of easier synthesis. As a first tentative explanation we are considering the high supramolecular order of even simple ionic liquids at the interphase with a charged surface. A chiral additive could result in chiral reorganization of this peculiar interphase, as in the case of nematic-to-cholesteric transitions induced by chiral dopants in liquid crystals.

This allowed us to include in our chiral voltammetry experiments a quite larger number of inherently chiral selectors based on different stereogenic elements, *i.e.*, the bicollidine and bibenzimidazole atropoisomeric scaffolds and the tetrathielicene helicoidal scaffold. They all proved successful.

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

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Th.I13

Assessment of corrosion resistance of austenitic and duplex stainless steels in food industry

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Due to their surface physico-chemical properties and their high corrosion resistance, stainless steels (SS) seem to be the most promising candidates for food and fine-chemical industry, for nuclear power industries and for maritime development [1-2]. The corrosion resistance of austenitic and duplex SS markedly depends on the composition, thickness, structure and electronic properties of the passive films covering their surface. It is commonly accepted that the native film on stainless steel surface is a chromium rich few nanometers thick oxide layer [1-2]. However, SS are usually exposed for long time to aggressive media such as chloride containing solution, or highly concentrated organic and inorganic acidic solutions, hot alkaline solutions, therefore it is necessary to understand how passive films change as a consequence of the interaction with the environment. There is a large number of papers in the literature reporting on the characterization of passive films of Austenitic and Duplex stainless steels with a special focus on their electronic properties [1-2]. Several authors base their conclusion on the interpretation of the dependence of the capacitance on electrode potential in the frame of Mott-Schottky theory with an approach sometimes questionable [2].

In this work, we report the results of a physico-chemical characterization of passive films on different stainless steel grades (two austenitic 304L/EN 1.4307 and 316L/EN 1.4404, and a duplex 2507/EN 1.4410). For comparison, we have also investigated the behaviour of a pure magnetron sputtered chromium electrode. Passivation was performed electrochemically by potentiostatic polarization below and above O_2 evolution potential at several pH values, as well as by immersion at open circuit potential in solutions simulating environments typical of food and beverage industry. The latter were prepared according to the CoE protocol recently published by the European council [3], and to the prescriptions necessary to maintain an acceptable hygiene level in the plant.

The experimental investigation was mainly based on photoelectrochemical and impedance measurements, which provide information on the passive films composition and on their electronic properties (band gap, conductivity type, polarization resistance). The experimental results were used to gain insight into the passivation mechanism of stainless steel in the different environments.

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LIST OF ORAL COMMUNICATIONS

Su.Or01	U. SAVINO	The role of oxygen vacancies in green-synthesized TiO_2 for CO_2 photoelectroreduction
Su.Or02	L. FALCIOLA	Preparation and electrochemical characterization of “insulating” or mesoporous solid-templated silica films
Su.Or03	C. NERVI	Electrochemical reduction of CO_2 by electrodes functionalized with transition metal complexes

Mo.Or04	G. LONGONI	A novel wet jet milling-exfoliated WS_2-graphite dual-ion battery: from lab-to-industrial scale feasibility
Mo.Or05	M. PAVONE	Dye-electrode interface in p-type photo-electrochemical cells: new insights from ab initio calculations
Mo.Or06	V. DI NOTO	New ion-exchange membranes derived from polyketone
Mo.Or07	M.A. NAVARRA	A systematic approach to design novel Ionic Liquids as electrolyte components in lithium batteries
Mo.Or08	A. SCALIA	Photo-capacitors: dye sensitized PV technology and carbon-based electrical double layer capacitors integration
Mo.Or09	L. MATTAROZZI	Electrodeposition of porous Cu-Zn Alloys showing remarkable low T performances in Li-ion batteries
Mo.Or10	H. ARAB	Photoactive TiO_2 films by plasma electrolytic oxidation
Mo.Or11	V. PIFFERI	A concerted investigation of the interlayer charge transfer in silver/anatase nanocomposites
Mo.Or12	L. BARTOLINI	Exploring cellular interactions with 2D organic monolayers by scanning electrochemical microscopy
Mo.Or13	S. CINTI	Paper-based electrochemical tools for sweat analysis
Mo.Or14	O. SCIALDONE	Electrochemical treatment of real wastewater with low conductivity
Mo.Or15	M. ARMANDI	Effect of iron addition on the catalytic activity of manganese oxides electrodeposited films in the water oxidation reaction
Mo.Or16	C. DURANTE	Effect of thiophenic-like functional group on Pt NPs deposition and activity towards oxygen reduction reaction

Tu.Or17	S. ANTONELLO	Ordering gold nanoclusters by electrochemistry
Tu.Or18	F. MIOMANDRE	Electrochemical modulation of the fluorescence of tetrazines: from solution to monolayers
Tu.Or19	A. TESTOLIN	Functional hybrids of multilayer CVD graphene and colloidal anatase nanocrystals
Tu.Or20	G. DANIEL	PGM free electrocatalyst based on Fe-Nx active sites embedded in mesoporous carbon for ORR
Tu.Or21	A. ZAFFORA	Electrochemical doping of mixed Nb-Ta oxides by the incorporation of electrolyte species

Tu.Or22	A. ISSE	Dissociative electron transfer to chain transfer agents for RAFT polymerizations
Tu.Or23	A. MINGUZZI	Recent advance in operando X-ray absorption spectroscopy on (photo)electrode materials
Tu.Or24	F. DE GIORGIO	Sodium-alginate: an effective binder to develop eco-friendly and water-processable $Li_4Ti_5O_{12}$//$LiNi_{0.5}Mn_{1.5}O_4$ batteries
Tu.Or25	L. SILVESTRI	New insights on the $NaAlH_4$ based anodes inefficiency in lithium cell
Tu.Or26	L. ZOLIN	An innovative process for Li-ion battery ultra-thick electrodes manufacturing
Tu.Or27	V. BAGLIO	Bifunctional oxygen electrodes based on non noble metal oxides for metal air batteries
Tu.Or28	M. MUSIANI	New routes to porous oxide layers
Tu.Or29	F. DE BON	Catalytic halogen exchange in electrochemically mediated ATRP: the case of methyl methacrylate

We.Or30	C. ARBIZZANI	Modified carbon paper interlayers in Li/S and Li/polysulfides batteries
We.Or31	M. FIORE	Improving the electrochemical behavior of highly abundant, low cost Fe(II) oxide as anode material in Na-ion rechargeable batteries
We.Or32	M. MORENO	Dissolved polysulfides as catholyte for high performance lithium-sulfur storage system
We.Or33	L. CHEN	Mixed colloidal/solid-state synthesis of crystalline pure P2-$Na_{1.7}Ni_{1.0}Mn_{2.9}O_{7.6}$ an its utilization as a stable cathode in Na-ion batteries
We.Or34	I. NICOTERA	Single lithium-ion conducting solid polymer electrolytes based on Nafion and functionalized graphene oxide
We.Or35	A. TSURUMAKI	Ionic liquids as additive salts for electrolytes of lithium ion batteries with the intent of improved stability

Th.Or36	F. POLO	Enzyme-based electrochemical biosensor for therapeutic drug monitoring of anticancer drug CPT-11
Th.Or37	M. MALFERRARI	Production of reactive oxygen species in cellular models of a human multystem disorder monitored with modified microelectrodes
Th.Or38	M. DELUCCHI	Ag as brazing metal in Ti_6Al_4V/Ag/YAG joints: galvanic effects in seawater
Th.Or39	E. PETRUCCI	How anodization conditions affect the characteristics of thin film electrodes deposited on nanostructured titanium substrates
Th.Or40	R. BRANDIELE	Effect of Y salt precursor on the synthesis and activity of PtXY alloyed NPs versus oxygen reduction reaction
Th.Or41	J. ZENG	Electroreduction of CO_2 on Tin oxide modified copper oxide nanostructured foam

	M. DESTRO	A new European player perspective on Li-ion cell production: the “E-Lithium” project

Su.Or01

The role of oxygen vacancies in green-synthesized TiO_2 for CO_2 photoelectroreduction

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Carbon dioxide (CO_2) is a greenhouse gas; its concentration in atmosphere is 400 ppm, mostly due to the anthropic activity. It is possible to reduce CO_2 to obtain added-value chemicals, such as methane, carbon monoxide, methanol or formic acid through photo/electro catalysis. In this work, we present the role of oxygen vacancies in sub stoichiometric titanium dioxide (TiO_{2-x}) [1] realized via simple green synthesis, as catalytic sites for the CO_2 reduction.

A foil of titanium was oxidized via thermal process in hydrogen peroxide at 80°C on hotplate for 48 hours. The as-prepared sample was then reduced to TiO_{2-x} via calcination in vacuum, at 450°C for 1 hour. The absorption spectrum was characterized by an UV-VIS spectrometer with integrated sphere. According to Tauc relation, the energy gap decreased from (2.08 ± 0.08) eV for TiO_2 to (1.43 ± 0.02) eV for TiO_{2-x}. This drop is due to the change in the density of states of the valence band. The electrochemical properties and the stability of TiO_{2-x} in solution of $KHCO_3$ (0.1 M) saturated with CO_2 were assessed in a three electrodes configuration via Cyclic Voltammetry (CV) and Chrono-amperometry (CA). In order to have information about the photo-catalytic activity of TiO_{2-x}, the CV was performed both in dark condition and irradiating the system with a visible light source. As shown in Fig. 1, the current density is slightly higher, in absolute value, under illumination than under dark conditions. CA was performed irradiating the system with the light source and applying a constant bias voltage of -1.4 V vs Ag/AgCl. The obtained products were analyzed through gas chromatography and high-performance liquid chromatography, revealing the promising catalytic activity of green-synthesized TiO_{2-x}.

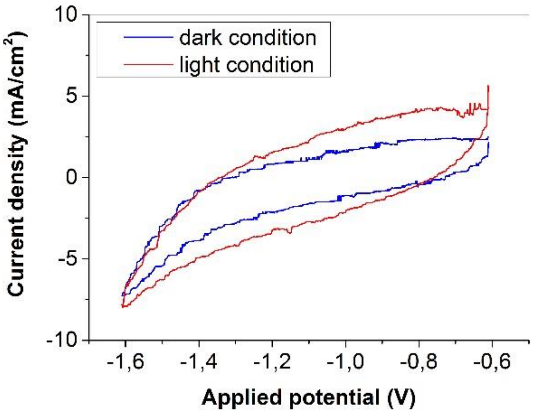

Figure 1: CV under dark (blue line) and light (red line) condition.

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Su.Or02

Preparation and electrochemical characterization of “insulating” or mesoporous solid-templated silica films

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Mesoporous silica materials characterized by well-ordered microstructure and size- and shape-controlled pores have attracted much attention in the last years. These systems can be used for the development of functional thin films for advanced applications in catalysis and electrocatalysis, sensors and actuators, separation techniques, micro- and nano-electronic engineering [1-2].

In this work, “insulating” and mesoporous silica films were prepared by spin coating a home-made silica sol on a cleaned ITO glass. The mesoporosity was controlled by the use of Polystyrene (PS) latex beads with different dimensions (30-60-100 nm) as template. The number of successive multi-layered depositions was varied (1-2-3-5 layers) and after the template removal, stable, homogeneous and reproducible transparent films were obtained, characterized by an interconnected porous structure. The morphological features and the physicochemical and optical properties of the films and/or precursors were studied by DLS, FE-SEM, AFM, UV-vis transmittance spectroscopy and wettability analyses. Moreover, a deep electrochemical characterization was also performed by Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS). In particular, the use of two redox mediator probes [($K_4Fe(CN)_6$) and ($Ru(NH_3)_6Cl_3$)], presenting opposite charge and different diffusional behaviour, allowed the comprehension of the mass transport and charge transfer phenomena, evidencing the effects of spatial confinement and charge selection.

In the case of “insulating” films prepared without the use of PS latex, we proved an experimental evidence for theoretical models [3] concerning electroinactive layer-modified electrodes, with a scan-rate-dependent variation of the CV shape due to a progressive increase in the diffusion coefficient inside the insulating layer. A complex balance between diverging effects (higher hydrophilicity and insulating behavior effects of silica) when increasing the numbers of layers is also observed. In the case of mesoporous layers, a better electrochemical response of smaller pores and of thicker layers was found, due to two main cooperative phenomena: a diffusion modification from fully planar to radial-convergent at the pore-silica interface due to surface porosity; the presence of pores in a hydrophilic matrix which leads to a capillary pull effect, stronger in the case of smaller pores.

The easiness of preparation and the interesting properties of these devices pave the way towards their use in many fields, particularly trace electroanalysis.

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Su.Or03

Electrochemical reduction of CO_2 by electrodes functionalized with transition metal complexes

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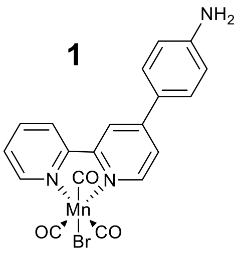
The electrochemical conversion of carbon dioxide into value-added chemicals mediated by transition-metal complexes has attracted growing interest in recent years [1]. Transition metal complexes immobilized on electrode surfaces can represent promising catalysts to be utilized in a large-scale process for CO_2 reduction. Our approach consists into design the transition metal catalyst and covalently attaches it on the electrode surface, bridging the two world of homogeneous and heterogeneous catalysis [2]. We recently reported the electrocatalytic properties of Mn^I complexes in homogeneous solutions towards the conversion of CO_2 in the absence and in the presence of Brønsted acids [3].

Herein we extend our approach to the immobilization by chemical bond on the electrode surface. Two rhenium and manganese complexes (**1** and **2**), containing a substituted bipyridine ligand bearing an amino group have been synthesized and their catalytic activities tested towards electrochemical CO_2 reduction. The two complexes were chemically bonded on Glassy Carbon Electrode (GCE) surface by two methods: a) direct electrochemical oxidation of a terminal amino group with formation of C-N bonds, and b) electrochemical reduction of the corresponding diazonium salts with formation of C-C bonds [4]. Electrocatalytic activities of complexes **1** and **2** were compared in both homogeneous and heterogeneous phases. The chemically modified GCEs show efficient conversion of CO_2 into CO, with turnover numbers (TONs) about 60 times higher than those of the corresponding catalysts in homogeneous solutions, and in a relative much shorter time. The heterogeneous surfaces modified by the catalyst are much more efficient than the corresponding homogeneous solutions. The functionalized electrodes obtained by reducing the diazonium salts display better durability than the ones obtained by oxidizing the amino moiety, this is particularly evident in the case of **1**.

1



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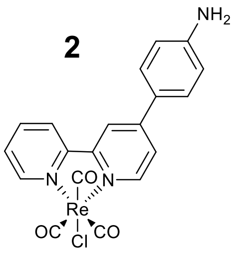

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Mo.Or04

A novel wet jet milling-exfoliated WS_2-graphite dual-ion battery: from lab-to-industrial scale feasibility

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Dual-ion batteries are an intriguing technological alternative to standard single-ion rocking-chair batteries. They offer, indeed, notable advantages in terms of insertion kinetics, low-cost host materials, and higher operational potentials [1]. Their fundamental working principle is hinged on both the cation and anion intercalation in host crystalline structures. Original prototypes of this configuration were also known as dual graphite batteries, since a symmetric configuration of graphite-based electrodes were employed [2]. Provided this geometry, lithium cations were reversibly store in the anode while, at considerably more oxidative potential, PF_6^- anions could intercalate in graphite layers of the cathode. Practical challenges of the illustrated device, are mainly related to stability of cathode material and electrolyte solution, subjected to electrode potential often exceeding 4.5 V vs. Li/Li^+. With the present contribution we provide a thorough description of a Dual-ion battery assembly based on exfoliated WS_2 anode and a graphite cathode. A novel Wet-Jet Milling exfoliation technique of bulk WS_2 has been here adopted and its advantages in terms of reliability and scalability have been thoroughly described. The effects on lithium uptake electrochemistry, of reduction of bulk WS_2 to few-layers nano-flakes has been assessed as well. The assembled dual-ion battery demonstrated capable of improved cycling ability and stability when tested in a $LiPF_6$ containing electrolyte solution. In particular an output voltage of 2.4 V has been achieved, taking advantage of the anion intercalation mechanism happening at 4.5 V vs. Li/Li^+.

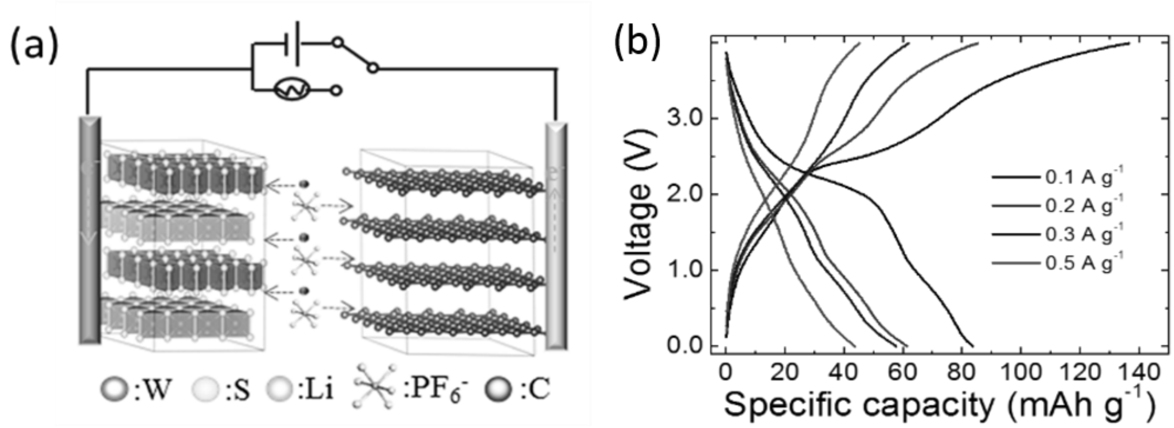

Figure 1: (a) schematic representation of a dual-ion battery, (b) WS_2-graphite dual ion battery performance in $LiPF_6$ ethylene carbonate:ethyl methyl carbonate electrolyte.

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Mo.Or05

Dye-electrode interface in p-type photo-electrochemical cells: new insights from ab initio calculations

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For the last decades, dye-sensitized solar cell (DSSC) technologies have been challenging solid-state photovoltaics for solar energy conversion into electricity. Remarkably performances have been recently achieved with conventional n-type DSSCs, thanks to great experimental and theoretical efforts devoted to understanding and tuning the n-DSSC materials properties and functions [1]. The research on p-type DSSC, instead, is still in its infancy and, so far, their poor performances have hindered the foreseen development of tandem cells, i.e. solar cells with a photo-anode (from n-DSSC) and a photo-cathode (from p-DSSC). A deeper and more comprehensive understanding of structure-property-function relationships in photocathode device is thus crucial for further advancements.

In this contribution, we will discuss our first-principles studies on state-of-the-art photocathodes based of nickel oxide and prototypical dyes (e.g., C343) [2]. We will highlight the p-NiO electrode features, the dye molecular properties and how overall properties are affected by their mutual interactions. We will discuss the design principles for new push-pull dyes [3] and for new electrodes that can substitute NiO for achieving better efficiencies.

Our quantum-mechanical analyses of the p-DSSC model will provide new insights on the dye-electrode interface, paving the route to an effective, rational design of new and better performing photocathodes for photovoltaics and photoelectrochemical cells.

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Mo.Or06

New ion-exchange membranes derived from polyketone

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Anion-exchange membrane fuel cells (AEMFCs) provide significant advantages over their proton-exchange membrane counterparts. In the alkaline environment, the oxygen reduction reaction (ORR) is more facile, there is diminished fuel crossover, and a greater flexibility regarding fuel and catalyst choice. The membrane at the heart of AEMFCs not only facilitates the ion exchange but also separates the fuel feedstocks and acts as a support for the membrane-electrode assembly (MEA). However, to date there are still no membrane materials that satisfy all the needs (long-term stability in alkaline environment, high ionic conductivity, low swelling and good structural integrity) for use in AEMFCs and this remains one of the larger obstacles for further AEMFC development.

The amination and subsequent quarternisation of polyketone leads to a new family of ionomers containing N-substituted pyrrole moieties. The degree of amination can be controlled by manipulating reaction conditions, allowing the composition and resulting structural properties of the polymer to be tuned [1,2]. Membrane fabrication results in thermally stable (T_D > 250 °C), structurally robust polymer electrolytes that exhibit ionic conductivity (> 10^{-3} S cm^{-1}). These new solid-state ion-conducting materials have the potential to be used in a variety of applications including AEMFCs.

Here we present an in-depth study focusing on the structure-property relationships of this new polypyrrole/polyketone polymer.

A variety of analytical techniques are used to probe the thermal and structural properties of the polymers, these include highresolution thermogravimetric analysis, modulated differential scanning calorimetry, dynamic mechanical analysis, vibrational, NMR and UV-Vis spectroscopies. In addition, broadband electrical spectroscopy is used to gauge the interplay between the structural properties and electrical response [3].

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Mo.Or07

A systematic approach to design novel Ionic Liquids as electrolyte components in lithium batteries

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The flammability of the organic electrolyte commonly used in lithium batteries hinders the great potentiality of such devices for large-scale applications, where the battery is expected to operate over a wide temperature range without compromising safety. To combat flammability, highly stable ionic liquids (ILs), having negligible vapour pressure, have been widely investigated as electrolytes.

The main issues affecting the applicability of ILs in lithium batteries are their viscosity and the relatively narrow range of temperatures where they exist in the liquid state, both impacting the ionic conductivity. Thus, the goal of this work was to develop highly conductive, stable IL compounds, with reduced viscosity and suppressed crystallization. Tailored, in-house synthesized new ILs, based on cyclic quaternary ammonium cations, with ether or sulfur functionalization [2,3], and bis(trifluoromethanesulfonyl)imide (TFSI) or bis(fluorosulfonyl)imide (FSI) anion, will be here described. Their thermal and electrochemical properties, including the definition of the stability window, interface characteristics towards carbon-based and lithium electrodes, will be discussed. Electrochemical performances in advanced lithium-ion configurations, adopting electrolytes based on the proposed ILs, will be presented.

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Mo.Or08

Photo-capacitors: dye sensitized PV technology and carbon-based electrical double layer capacitors integration

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The rising power demand in off-grid conditions and the unstable nature of solar radiation are forcing the scientific and industrial community to investigate the feasibility of integrated harvesting storage devices, capable to convert the electromagnetic radiation coming from the sun into power and directly store it into a storage media. Among the third generation PV technologies a good compromise between cost, relatively high efficiency and medium-long life stability is represented by the so called Dye sensitized solar cells (DSSCs), which work well also with diffuse radiation or under low illumination conditions [1]. Regarding the storage section, the majority of work reported in literature deals with a supercapacitor (SC) instead of a battery. This is mainly related to the simpler configuration and less restrictive technical specifications required by SC with respect to batteries. In addition, SCs have a consistently longer cycle life, a much higher power density and appear also intrinsically safer than batteries because no redox reactions occur during operation, and the power is just electrostatically stored in the storage media. In the last year different photo-capacitors (PCs) structure regarding DSSCs and carbon-based SCs integration were proposed. Here we present a highly flexible photo-capacitor [2], fabricated with metallic grids as current collectors and polymer electrolyte both for the DSSC and SC section. Integration was performed testing photo-charge curve under different illumination conditions and subsequently discharging the SC section with imposed constant current. Here we also present innovative solutions regarding high energy PCs and new possible smart PCs configurations.

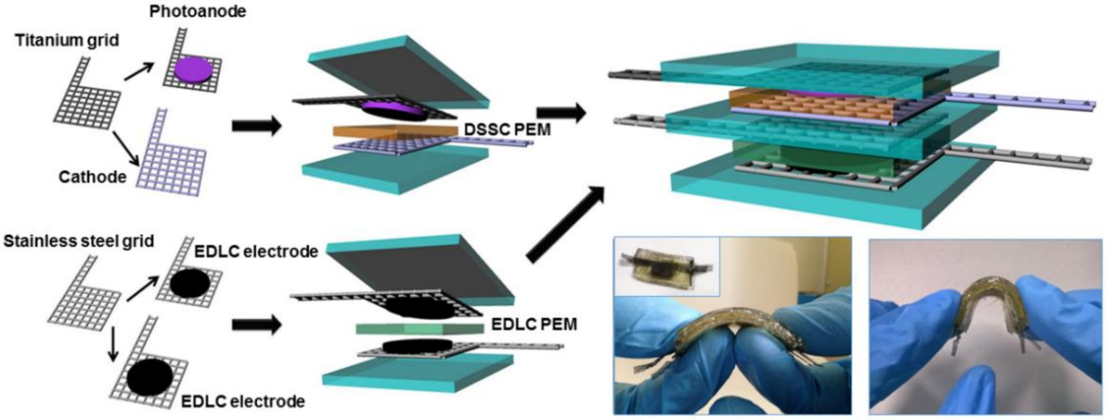

Figure 1: Architecture and characteristics of the photo-capacitor.

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Mo.Or09

Electrodeposition of porous Cu-Zn alloys showing remarkable low *T* performances in Li-ion natteries

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Zinc is an interesting alloying material for use as anode in Li-ion batteries due to its good theoretical performance, natural abundance, low cost and toxicity. However, its large volume change and, thus, tendency to flake upon lithiation-delithiation makes it unsuitable for practical applications. It is known that intermetallic compounds can better manage the strain associated with Li insertion/de-insertion. This consideration prompted us to investigate porous Cu-Zn alloys, in the range of Zn-rich compositions, made via electrodeposition using the Dynamic Hydrogen Bubble Template (DHBT) method, which has been already applied with success to the preparation of Cu-rich compositions [1].

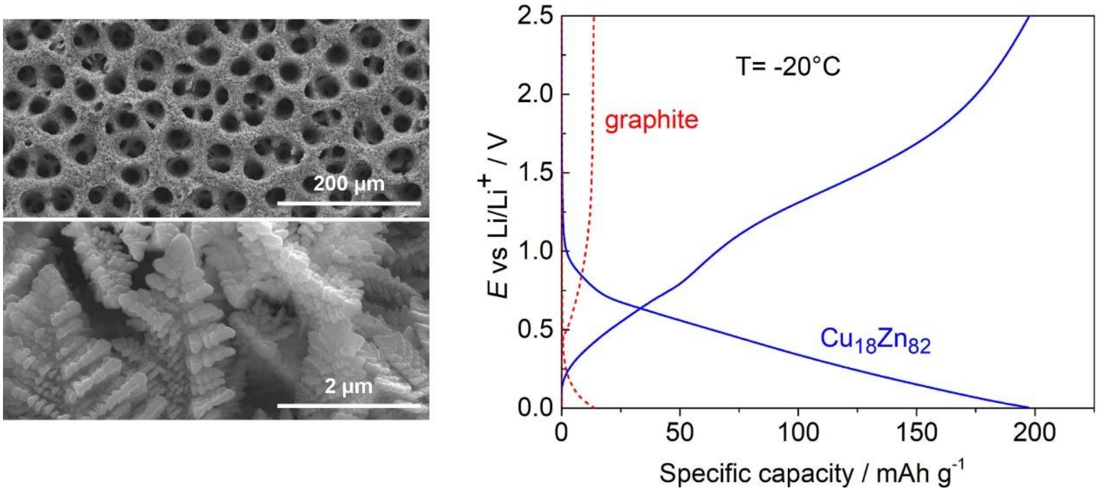

Figure 1: SEM images of a 30 C cm^{-2} $Cu_{18}Zn_{82}$ deposit (left) and voltage profiles upon lithium insertion and extraction at -20 °C (right).

The SEM images (Figure 1, left) show the 3D porous structure of $Cu_{18}Zn_{82}$, warranting easy electrolyte permeation and fast interface charge transfer. Tested as anode for Li batteries at room *T*, the material shows nice performance and mechanical stability, unlike pure Zn. Even more interesting, it retains good performance even at subambient temperatures [2], whereas graphite, i.e., the state of the art material for Li-ion batteries, fails (Figure 1, right) due to unfavorable intercalation thermodynamics. The open issues for material improvement will be indicated and discussed.

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Mo.Or10

Photoactive TiO_2 films by plasma electrolytic oxidation

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Titanium dioxide is considered the most practical photocatalytic material for applications in environmental remediation, self-cleaning of surfaces and light-assisted hydrogen generation [1]. Photoactive TiO_2 films can be obtained by a number of techniques including sol-gel, CVD, RF Magnetron Sputtering, Plasma Spray, Electron Beam Evaporation, Anodic Oxidation [2] and Plasma Electrolytic Oxidation (PEO) [3]. In the present study, the focus is on PEO of Ti carried out in H_2SO_4 at temperatures from -5 to 20 °C, and constant cell voltages ranging from 100 to 200 V. The obtained films were characterized by SEM, AFM, XRD, GDOES, XRD and GI-XRD. The photoelectrochemical activity of the TiO_2 coatings was assessed by measuring the incident photon to current efficiency (IPCE) with and without applied voltage. Depending on the cell voltage, either pure anatase (100-130 V), a mixture of anatase and rutile (140-170V), or pure rutile (180-200 V) were obtained. By tuning phase composition and film thickness, IPCEs higher than 90% were measured (Figure 1).

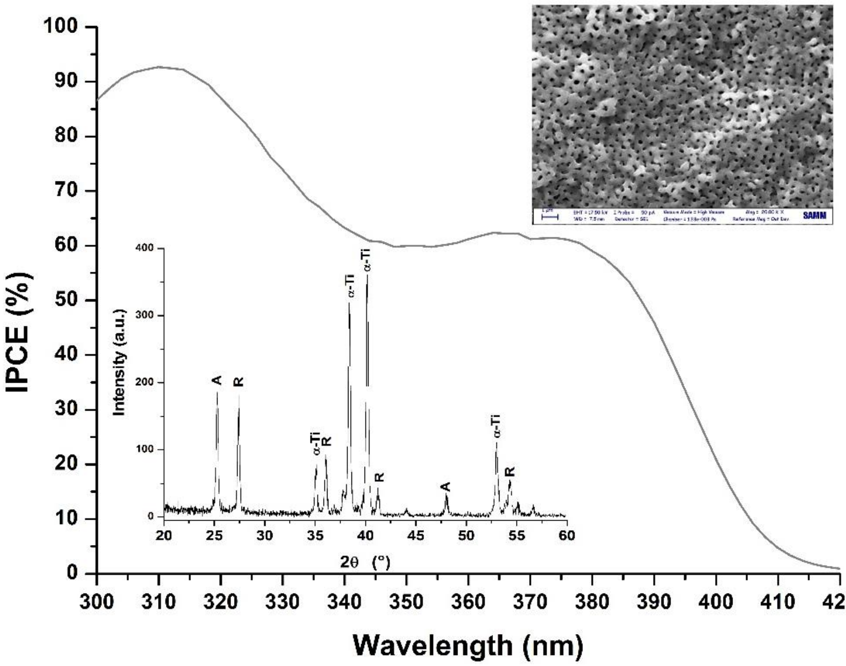

Figure 1: IPCE, XRD pattern and SEM micrograph of TiO2 films by PEO.

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Mo.Or11

A concerted investigation of the interlayer charge transfer in silver/anatase nanocomposites

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The use of hybrid nanomaterials, characterized by unprecedented behaviors and features, has now paved the way toward promising applications in many fields, such as electrocatalysis, photocatalysis, electroanalysis, and environmental chemistry, impacting on the everyday life [1].

Suitably designed nanoheterojunctions enhance synergistic functionalities and allow one to obtain "brave new materials" with physicochemical properties that are not simply the addition of the precursors' ones but are completely new, different, and unexpected. However, research on such devices is most often dominated by trial and error procedures, while a deep atomistic understanding of the phenomena inside of the junction region driving appropriate design of the final device is missing.

Here, a concerted theoretical and electrochemical investigation is proposed to gain insights into the important class of heterojunctions made by metal-semiconductor interfaces. Specifically, this approach is applied to the case of silver/anatase hybrid nanocomposite, a very promising material for advanced sensing applications [2].

In particular, we measure the exceptional electrochemical virtues of the Ag/TiO_2 junction in terms of current densities and reproducibility, providing their explanation at the atomic-scale level and demonstrating how and why silver acts as a positive electrode [3]. Using periodic plane-wave DFT calculations, we estimate the overall amount of electron transfer toward the semiconductor side of the interface at equilibrium. Suitably designed (photo)electrochemical experiments strictly agree, both qualitatively and quantitatively, with the theoretical charge transfer estimates. The unique permanent charge separation occurring in the device is possible because of the synergy of Ag and TiO_2, which exploits in a favorable band alignment, in a smaller electron–hole recombination rate and in a reduced carrier mobility when electrons cross the metal–semiconductor interface. Finally, the hybrid material is proven to be extremely robust against aging, showing complete regeneration, even after 1 year [3].

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Mo.Or12

Exploring cellular interactions with 2D organic monolayers by scanning electrochemical microscopy

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The morphology of cells changes consistently with the surface where they adhere [1]. As reported in literature, surfaces with micrometric and nanometric patterns affect the cell morphology, as well as surfaces with peculiar chemical functionalities [2]. In order to control both morphology and chemistry of the surface, mono-molecular layers of small organic molecules (specifically Pentacene, α-Sexithiophene and PDI8-CN_2) were deposited on SiO_x substrates by means of Organic Molecular Beam Epitaxy (OMBE). Through the partial annealing method, SiO_x substrates were fully covered with a mono-molecular layer, as confirmed by Atomic Force Microscopy measurements (surface coverage of about 98%). The roughness of the prepared monolayers is very low and the chemical functionalities of the surface are well controlled. Epithelial cells were cultivated on such samples and their shape was investigated by optical and fluorescence microscope and Scanning Electrochemical Microscopy (SECM).

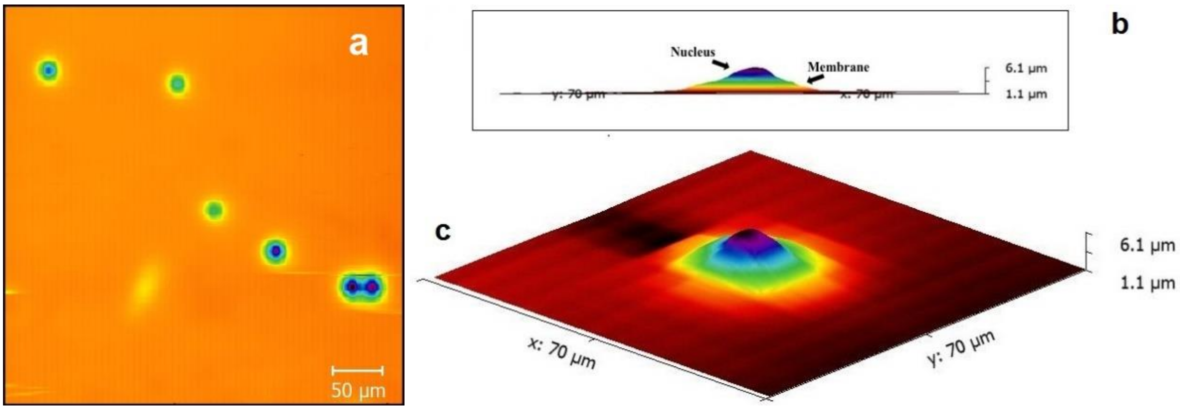

Figure 1: a) SECM image of cells on Pentacene; b) single cell profile and c) 3D image.

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Mo.Or13

Paper-based electrochemical tools for sweat analysis

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Albeit a whole panel of species can be measured in blood, saliva or urine, none of the techniques involved are used for analyses in the field or can evaluate in real-time the physiological status (with the exception of glucose monitoring strips). Sweat offers a valuable matrix that contains a plethora of information, allowing for continuous non-invasive measurements. Regarding the analytical methodologies that can be adopted to detect the analytes present in the sweat composition, the electroanalytical ones require non-sophisticated equipment, small amount of sample, and are suitable for measurements out of the laboratory; also the screen-printed electrodes own high adaptability such as customizing shape, dimension, conductive-ink material, and substrate. In addition, being in the era of sustainability, we are required to reduce both the environmental and the economic impact related to mass-scale processes. A sustainable analytical method should minimize the production of hazardous waste during the analysis to reduce environmental impact and it should provide a more sustainable use of recyclable materials. Furthermore, the measurement should be cost-effective allowing for cost-effective analysis. However, even if glucose strips represent a keystone as self-monitoring devices, drawbacks related to their production cost and waste removal need to be carefully evaluated.

Herein, paper-based substrates are proposed as novel materials for the sustainable production of printed electroanalytical platforms with application to sweat analysis. The combination of screen-printing, wax printing, and paper-based substrates, has been successfully applied to detect zinc and chloride ions directly in sweat. An explanation about the manufacturing processes will be provided, and the properties of both filter and office papers will be showed, highlighting the different experimental setup that are adopted depending on the type of paper, respectively for chloride and zinc detection. The analytical relevance of the proposed approach will be proposed in terms of healthcare applications. The analytical performances of the two electrochemical sensors will be discussed, highlighting the development of real-time, in-process monitoring, and environmental friendly analysis, that meet positively with the required features of sustainability. The two developed sensors have been interrogated towards the detection of zinc and chloride in real samples of sweat, and they have been capable to detect the analytes in the physiological range of 0.08-2 μg/mL and 10-200 mM, with detection limit of 25 ng/mL and 1 mM, respectively for zinc and chloride.

Mo.Or14

Electrochemical treatment of real wastewater with low conductivity

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In the last years, many efforts have been devoted to the development of electrochemical processes for the effective treatment of wastewater contaminated by organic pollutants resistant to conventional biological processes and/or toxic for microorganisms [1–5]. It was shown that some electrochemical approaches, including the direct anodic oxidation at suitable anodes such as boron-doped diamond (BDD) and/or electro-Fenton (EF) at suitable operating conditions and cells [1–6] could allow treating effectively a very large number of organic pollutants. However, most of the investigations were performed using synthetic wastewater. Hence, it is now mandatory to study the problems connected to the passage from synthetic wastewater to the real ones.

The treatment of a real wastewater characterized by low conductivity was here performed by anodic oxidation at boron-doped diamond (BDD) in both conventional and microfluidic cells. The electrolyses carried out in conventional cells without supporting electrolyte were characterized by very high TOC removals but excessively high energetic consumptions and operating costs. The addition of sodium sulphate, as supporting electrolyte, allowed to strongly reduce the cell potentials and consequently the energetic consumptions and the operating costs. The best results in terms of both TOC removal, energetic consumptions and operating costs were obtained using a cell with a very low inter-electrode distance with no addition of a supporting electrolyte.

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Mo.Or15

Effect of iron addition on the catalytic activity of manganese oxides electrodeposited films in the water oxidation reaction

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There is currently a great interest towards the water splitting (WS) reaction as a promising means to store solar energy [1]. Out of the two half-reactions involved in WS, water oxidation (WO) is the most challenging one, and it is usually considered as the bottleneck of the whole WS process. Manganese oxides (MnOx), being active, earth-abundant and low-toxicity materials, are currently considered as promising water oxidation catalysts [2].

In this context, we firstly report on the optimization and characterization of mixed Fe/Mn oxide films as catalysts for the WO reaction at neutral pH (0.1 M buffer phosphate). Cathodic electrodeposition at constant current density allows a facile and rapid synthesis and a homogeneous coverage of the electrode. The optimal range of $Fe(NO_3)_3$ concentration in a $KMnO_4$ deposition solution was investigated, showing the beneficial effect of Fe addition both in terms of activity and stability of the catalyst.

Electrochemical Impedance Spectroscopy (EIS) measurements showed that both electrode charge-transport properties and electrode–electrolyte charge transfer kinetics are enhanced for optimal iron content.

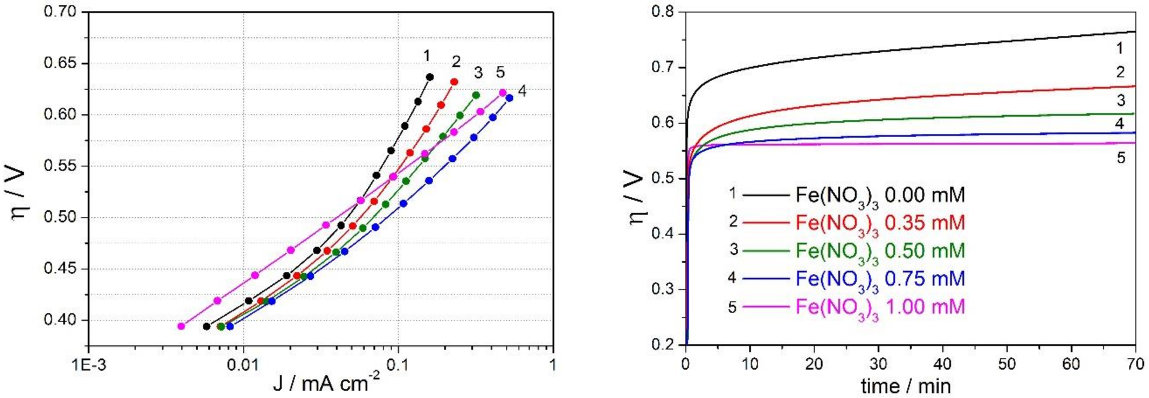

Figure 1: Tafel Plot (left) and Chronopotentiometry at 0.1 mA cm^{-2} (right) for samples electrodeposited from 1.5 mM $KMnO_4$ solutions containing different Fe(III) amounts.

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Mo.Or16

Effect of thiophenic-like functional group on Pt NPs deposition and activity towards oxygen reduction reaction

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Mesoporous carbons (MCs) are highly porous materials, which offer high surface area and a porous network able to improving mass transfer in chemical or electrochemical reactions [1]. In previous papers we demonstrated that Pt NPs on nitrogen or sulfur doped mesoporous carbon are highly active and show high mass activity towards oxygen reduction reaction (ORR) [2,3].

In this work, sulfur doped mesoporous carbons (S-MCs) were synthetized with four different content of dopant heteroatoms (4%, 6%, 8% and 12%). Successively, the four S-MCs were modified with Platinum nanoparticles (Pt@S-MC) by solid-state reduction with H_2 at high temperature. The aim of the paper is to define whether the sulfur heteroatoms present as thiophenic like group affect the Pt nucleation and growth, and afford better material in terms of dimension and dispersion of Pt nanoparticles and better electrocatalytic activity towards oxygen reduction. On this regard, DFT calculations on three thiophenic groups sited close to each other are indicative of a clear stabilization of Pt nucleus of at least 50 KJ/mol with respect to a perfect graphene layer (Fig. 1). Electrochemical characterization showed that Pt@S-MC are highly catalytic materials for ORR in term of both $E_{1/2}$ and mass activity

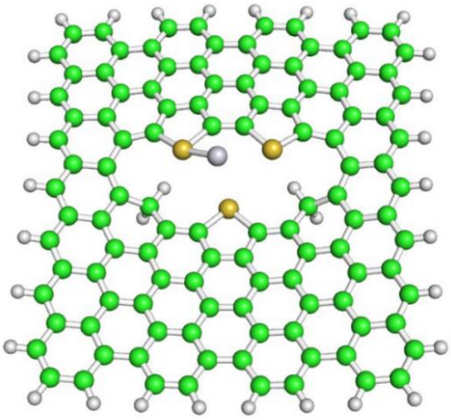

Figure 1: DFT optimized structure of Pt atom on S-MC.

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

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Tu.Or17

Ordering gold nanoclusters by electrochemistry

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Gold nanoparticles and, particularly, the smaller monolayer-protected clusters (MPCS) are materials of ever-growing importance in fundamental and applied research due to their distinct optical, magnetic [1], electrochemical [2], and catalytic properties. In MPCs with a gold core diameter of <1.6 nm quantum confinement effects make these gold clusters display features very much alike those of molecules. This borderline behavior between actual molecules and larger nanoparticles makes the study of their fundamental properties particularly important. If properties are understood well, the capability of devising novel applications is greatly enhanced.

Recently we have demonstrated that single crystals of thiolate-protected $Au_{25}(SR)_{18}$ clusters can be grown in large quantity and very high quality by an electrochemical approach (electrocrystallization) [3]. This approach allowed, for example, tuning the crystals dimensions and, consequently, studying how the sample morphology affects magnetic properties and to shed some light on this puzzling aspect of nanocluster behavior [1]. Single-crystal X-ray crystallographic analysis revealed also the formation of a structure that contains parallel chains of interconnected gold nanoclusters, just like a multiple-strand necklace made of gold "pearls" of only 1 nm. The individual cluster are linked with single Au-Au bonds and stabilized by interlocking of ligands. Within this structure the otherwise unpaired electrons of the paramagnetic $Au_{25}(SR)_{18}$ clusters pair up, with generation of an unprecedented antiferromagnetic system. In this communication, the electrochemical details of the electrocrystallization process and the main results about the analysis of magnetic behavior will be presented.

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Tu.Or18

Electrochemical modulation of the fluorescence of tetrazines: from solution to monolayers

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The electrochemical control of fluorescence, called electrofluorochromism, has recently proven an interesting way of reversibly switching on and off the luminescence of various systems (see fig. 1), to make among others new high contrast smart displays[1,2]. Our group has shown that among a shortlist of luminophores emitting in the visible range and being easily oxidized or reduced into a stable form, tetrazines were very promising, because of their small size and long excited state lifetime [3]. The first ever-designed electrofluorochromic window was made from this molecule [4].

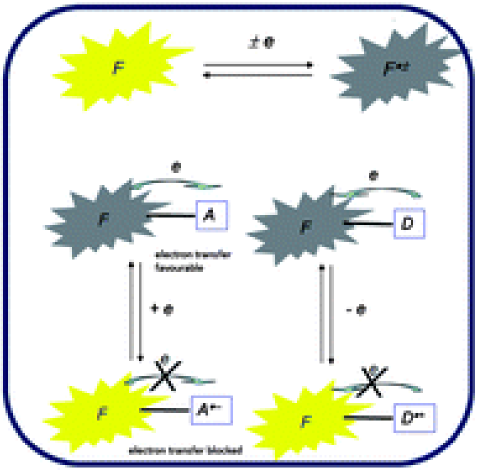

Figure 1: Principle of electrofluorochromism

After having demonstrated that the luminescence of tetrazines in solution can be fully electrochemically controlled [3], we were interested in investigating the possibility to switch on and off this molecule once covalently grafted on the electrode surface. Tailored derivatives with anchoring functions were synthesized to graft either on ITO or on gold. The electrochemical characterization shows that monolayers can be obtained on both surfaces. The luminescence properties and their electrochemical control at the monolayer scale were investigated using fluorescence microscopy coupled to electrochemistry. The results will be discussed in this communication.

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Tu.Or19

Functional hybrids of multilayer CVD graphene and colloidal anatase nanocrystals

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UV-light photoactive hybrids based on CVD graphene (from 1 to 5 layers) decorated with TiO_2 nanocrystals (NC) surface functionalized with 1-pyrene butyric acid (PBA), were prepared by a simple solution-based procedure. PBA functionalization was obtained by a capping exchange procedure onto pre-synthesized organic-capped NCs [1].

An in-depth physico-chemical characterization demonstrated the successful immobilization of the colloidal NCs on the graphene multilayers, which preserves or even enhances the graphene intrinsic structural properties: the electrical conductivity is higher than that measured for bare graphene, due to a p-doping effect, related to a hole transfer from the nano-objects to graphene, mediated by the short aromatic ligand acting as a charge channel.

The hybrids properties are strongly dependent on the number of layers of CVD graphene. The use of two redox probes [inner-sphere, surface sensitive ($K_4Fe(CN)_6$) and outer-sphere, surface insensitive ($Ru(NH_3)_6Cl_3$)], in a CV and EIS study, allowed to understand these features, showing a strong difference between the mono-, the bi- and the other multi-layers, in terms of different diffusional mechanism and redox active sites [2]. Moreover, the stacked layers of the pyrene-coated TiO_2 NCs are found to increase the electroactivity, the capacitive behavior, as well as the photo-electrical response of graphene, concomitantly maintaining its high charge mobility. The photoelectrical conversion of the hybrid is enhanced of 50% with respect to the bare graphene, with a long recombination lifetime of the photogenerated electron-hole pairs.

For all the above reasons, the photoactive composite has a great potential as an optically transparent component for manufacturing photoanodes to be integrated in solar cells or photodetectors and in FETs or (photo)electrochemical sensors, also exploiting the possibility of photorenovating the sensor surface [3].

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Tu.Or20

PGM free electrocatalyst based on Fe-N_x active sites embedded in Mesoporous Carbon for ORR

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The low disposability and high cost of platinum-based catalysts are serious obstacles to the scale-up and commercialization of PEMFCs. Nitrogen doped mesoporous carbons containing small amount of transition metals, such as Fe, are innovative materials to obtain Pt free catalyst for Oxygen Reductio Reaction (ORR) [1]. It was demonstrated that these carbons could catalyze the O_2 reduction to H_2O at overpotentials comparable to that of the most active Pt catalyst.

In this paper, nitrogen doped mesoporous carbons containing small amount of Fe (Fe-N-MC), were prepared from a low-cost carbon source polysaccharide. The synthesis consists in the formation of a hydrogel embedding an iron salt and a nitrogen compound, which should assure an optimal Fe dispersion and mesoporosity after pyrolysis. After the freeze-drying of the gel, the material was subjected to a first thermal treatment at 400 °C and a second one at 900 °C to obtain a discrete product, which was further activated with KOH at high temperature. XPS analysis reveals the presence of various form of iron oxides and a defined peak due to the Fe-N_x bond at 708.6 eV (Fig. 1a).

The catalytic performance of a catalyst ink prepared from Fe-N-MC was investigated by cyclic voltammetry and by rotating ring-disk electrode in 0.5 M KOH attesting that O_2 is reduced, following an almost $4e^-$ pathway, at very positive potential (0.9 V vs. RHE) (Fig 1b). The peroxide production is greater than in acid solution, because of different catalytic-active sites [2].

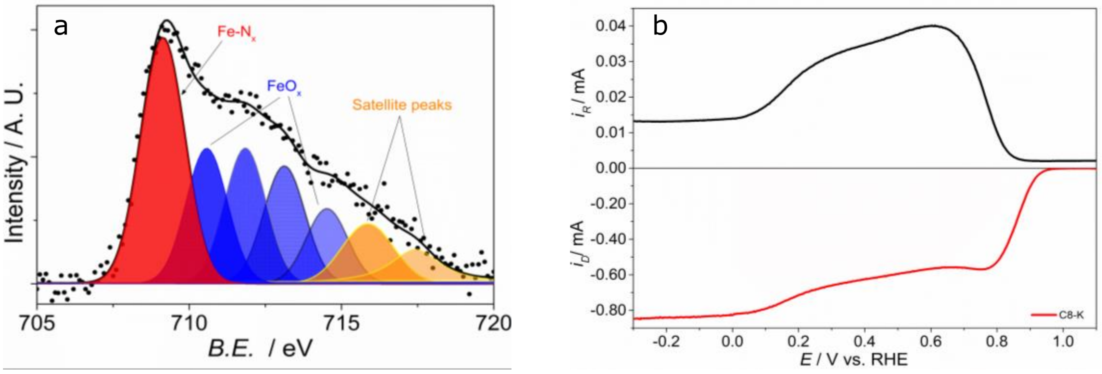

Figure 1. (a) Fe 2p XPS signal, and (b) RRDE in 0.5 M KOH.

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

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Tu.Or21

Electrochemical doping of mixed Nb-Ta oxides by the incorporation of electrolyte species

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Amorphous and/or nanocrystalline oxide films can be easily prepared by anodizing, a low-cost and low-temperature electrochemical technique that allows growing oxide layers with controlled structural and compositional features. The choice of the process parameters (such as current density and formation voltage) has a direct influence on the film thickness and on its crystalline or amorphous nature, while the electrochemical bath composition as well as the metallic substrate strongly affect the composition of the oxides. Regarding the electrochemical bath, it is important to consider that species coming from the electrolyte can be incorporated into the growing oxide leading to changes in structural as well as electronic properties of the anodic layers. In previous papers [1,2], it has been shown that foreign species, such as N or organic anions, can be incorporated into the oxides during the anodizing of valve metal (e.g. Nb) or valve metal alloys (e.g. Al-Ta) with a notable change in the electronic properties of the films.

In this work, we want to study whether anodizing sputtering-deposited Nb-Ta alloys in acetate buffer electrolyte has any effects on the optical and dielectric properties of resulting Nb_2O_5, Ta_2O_5 and mixed Nb-Ta oxides.

Photoelectrochemical measurements were carried out in order to estimate anodic oxides electronic properties, such as band gap and flat band potential, whilst differential capacitance measurements and electrochemical impedance spectra were performed to have information about the dielectric constant of the oxides.

According to differential capacitance curves as well as according to the electrochemical impedance spectra, anodizing in acetate electrolyte does not change appreciably the dielectric properties of the investigated anodic films. Nevertheless, the photoelectrochemical behavior of mixed Nb-Ta oxides is notably influenced from the anodizing bath composition; in fact, a redshift in the light absorption threshold of the anodic oxides is detected with respect of the same oxides grown in different electrolyte [3]. This difference in the optical response is supposed to be due to the incorporation of anions from the electrolyte that induce the generation of localized states into the band gap of the anodic oxides.

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Tu.Or22

Dissociative electron transfer to chain transfer agents for RAFT polymerizations

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Reversible addition-fragmentation chain transfer (RAFT) polymerization is a powerful technique to obtain well-defined macromolecular architectures. Photoinduced electron transfer (PET) RAFT [1] and the newborn electrochemically mediated RAFT (*e*RAFT) attracted our attention on the redox properties of chain transfer agents (CTAs) that mediate these processes [2].

CTAs include dithioesters, trithiocarbonates, dithiocarbamates, and xanthates. We present the electrochemical study of some compounds in these categories (Fig. 1a). The mechanism of dissociative electron transfer was investigated by cyclic voltammetry, controlled-potential coulometry and convolution analysis in the absence and presence of a strong acid or base (Fig. 1b). The transfer coefficient, α, or the kinetic competition parameter, κ, was used to discriminate between stepwise and concerted mechanisms [3].

This study represents the first electrochemical analysis of CTAs, intended to guide the selection of these compounds and broaden the understanding of RAFT polymerization mechanism.

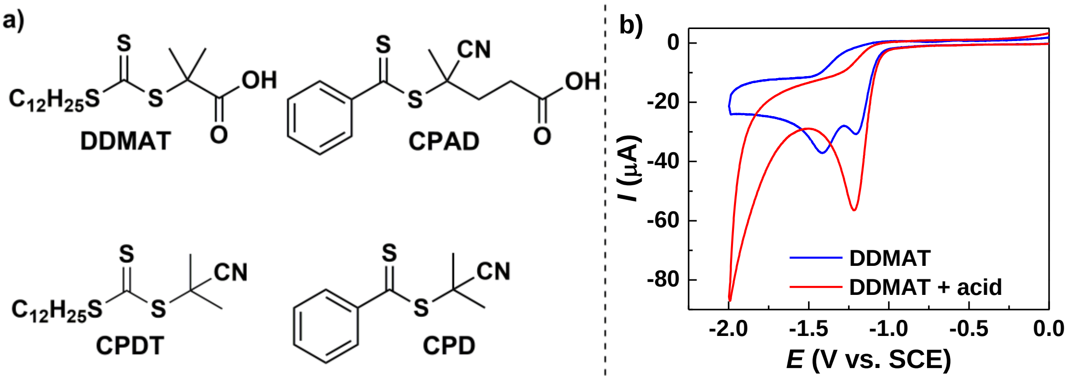

Figure 1: a) chemical structures of analyzed CTAs. b) CVs recorded on a GC electrode of 10^{-3} M DDMAT in CH_3CN + 0.1 M Et_4NBF_4, in the absence and presence of 0.02 M acetic acid. υ = 0.2 V s^{-1}, r.t.

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Tu.Or23

Recent advance in operando X-ray absorption spectroscopy on (photo)electrode materials

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

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

We extended operando XAS approaches to the study of photoelectrodes adopting a novel differential spectra acquisition approach [2], that allows the direct comparison of spectra acquired in the dark and under UV-Vis illumination.

More recently, we have been carried studies by time-resolved XAS out with the aim of studying the time-dependence of interfacial phenomena. To this aim, we developed methods based on pump-and-probe [3] as well as energy dispersive XAS [4,5] to gain new insights on charge transfer phenomena dynamics.

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

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Tu.Or24

Sodium-alginate: an effective binder to develop eco-friendly and water-processable $Li_4Ti_5O_{12}//LiNi_{0.5}Mn_{1.5}O_4$ batteries

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Natural polysaccharide sodium alginate (SA) is a promising binder, commonly extracted from brown algae, for advanced, eco-friendly lithium-ion batteries based on in-water-made electrodes [1]. The use of water-processable binder is not only an effective strategy to reduce the electrode processing costs of 80% [2], but also to improve the stability upon long-term cycling of lithium-ion batteries [3].

The beneficial effect of SA on the electrochemical performance of $Li_4Ti_5O_{12}$ (LTO)//$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) cells featuring two electrodes with SA binder is discussed. In particular, the rate capability and cycling stability of different LTO electrode formulations featuring SA binder is reported.

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Tu.Or25

New insights on the $NaAlH_4$ based anodes inefficiency in lithium cell

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Sodium alanate ($NaAlH_4$) recently emerged as a promising material for application as anode in lithium ion battery [1]. In our previous works, we proved that this material is able to react in a lithium cell through a reversible conversion mechanism, achieving almost all the theoretical capacity (1985 mAh/g) upon first discharge.

Despite this encouraging result, issues related to low cell efficiency and cyclability are still unsolved. Such drawbacks are partly due to the big volumetric expansion observed during conversion reaction (for instance, ≈ 72%). The development of alanate/carbon composites such as those obtained by the use of mechanochemical treatments [1] or nanoconfinement strategies [2] demonstrated some improvements in terms of reversibility of the electrochemical process. However, even in this case, the cell performance quickly drops in few cycles.

On the other hand, two other factors should be taken into account to understand the mechanism behind the failure of the alanate in lithium cell: i) the chemical reactivity toward the electrolyte and ii) hydrogen desorption upon alanate charge process.

Regarding the reactivity with the electrolyte, it is well-known that thanks to the liability of the Al-H bond, alanates are strong reducing agents, typically used in organic chemistry for carbonyl reduction. Standard electrolyte used for electrochemical tests as LP30 is based on alkyl carbonates, and thus, it may be easily reduced as soon as it comes into contact with the alanate electrode.

Concerning the hydrogen evolution, thermodynamic studies revealed that alanate electrochemical oxidation can occur in potential ranges that matches those exploited for conversion reactions in lithium cells [3].

Here, we report a study focused on the comprehension of the above mentioned factors and suggest possible strategies to adopt to overcome these issues.

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Tu.Or26

An innovative process for Li-ion battery ultra-thick electrodes manufacturing

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One of the biggest challenge of the 21th century is to achieve a decrease of fossil fuels consumption by increasing the use of energies produced by "green" methods. In this framework, the development of energy storage system is crucial. In fact, energy produced by renewable sources is, usually, intermittent. Therefore, it is really important to establish a reliable, economic and high-performing electric energy storage grid. Nowadays, advanced devices that convert and store energy are the focus of intensive research and lithium-ion batteries are a commercially established reality that is able to ensure an effective solution for a green electric future.

Nevertheless, different research strategies are encouraged by the needs to enhance performance and reduce costs of Li-ion batteries. One of the most efficient one consists in increasing the surface capacity of electrodes [1, 2]. Indeed, the latter allows to increase both volumetric and mass energy density and to reduce the cost by reducing the relative amount of passive elements. Today, the maximum loading achievable by current industrial reference process, the "slot die coating", is limited at around 5 mAh cm^{-2} owing to the binder migration phenomena during solvent evaporation [3].

This communication deals with the production of ultra-thick negative and positive electrodes by an innovative process based on filtration. Upon optimization, ultra-thick electrodes with loading between 10 and 25 mAh cm^{-2} were achieved. In addition, this approach was also found to be versatile as it can be readily transferred to post Li-ion technologies and to different materials. Despite their unconventional thickness (around 1 mm before compression), electrodes show robust mechanical properties. Electrochemical performance of full ultra-thick prototypes will be disclosed along with the analysis of advantages and limitations of this innovative process.

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Tu.Or27

Bifunctional oxygen electrodes based on non noble metal oxides for metal-air batteries

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Metal-air batteries are envisaged as next-generation batteries, with extraordinary high energy densities (depending on the metal used, Li, Na, Zn, Al, Mg, Fe…), among other advantages, being promising systems for portable, mobile or stationary applications [1]. In the last few years, research has been focused on the development of highly efficient oxygen reduction/evolution catalysts based on transition metals, such as Co, Fe, Mn, La, etc, in the form of mixed oxides (perovskites, spinels, etc), or advanced carbon materials, such as N or S-doped carbon materials, like graphene, or macrocycles incorporating transition metals, such as porphyrins and phtalocyanines [2,3]. In this work, electrospun carbon nanofibers decorated with Co-based oxides have been tested as bi-functional catalysts for both the reduction of oxygen and the oxidation of water in an alkaline medium to combine performance and stability. The durability of the catalyst has been investigated by carrying out accelerated stress tests.

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Tu.Or28

New routes to porous oxide layers

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Porous electroactive oxides are potentially interesting materials for electrochemical applications, e.g. as electrocatalysts, intercalation materials and supercapacitors. Our group has recently proposed the oxygen bubble templated anodic deposition as a route to achieve PbO_2 layers with void fractions up to 0.7 [1] (Figure 1a). Those layers, when cycled in H_2SO_4 aqueous solutions, exchange much larger charges than compact PbO_2 deposits with the same mass [2] (Figure 1b). In the oxygen bubble templated deposition, PbO_2 is obtained by oxidation of Pb^{2+} ions at currents higher than the diffusion limited current. Thus, O_2 is evolved in a side reaction and the deposits grow around the bubbles.

The extension of the same methodology to other oxides, endowed with an electrical conductivity significantly lower than that of PbO_2, is not straightforward because they cannot sustain the flow of large currents. To obtain other porous oxides, one can exploit galvanic displacement reactions between PbO_2 and some cations, like Mn^{2+}, Co^{2+} or Sn^{2+} [3]. This approach leads to the formation of MnO_2 and Co_3O_4 layers a few μm thick and much thinner SnO_2 oxide layers that coat PbO_2. Figure 1c shows a cross sectional SEM image of a Co-modified PbO_2 deposit. The modified PbO_2 deposits acquire the electrocatalytic properties of the outer oxide layer, e.g. Co_3O_4.

A new route based on the deposition of nanostructured porous Pb, its oxidation to PbO_2 and conversion of the latter through galvanic displacement is being explored.

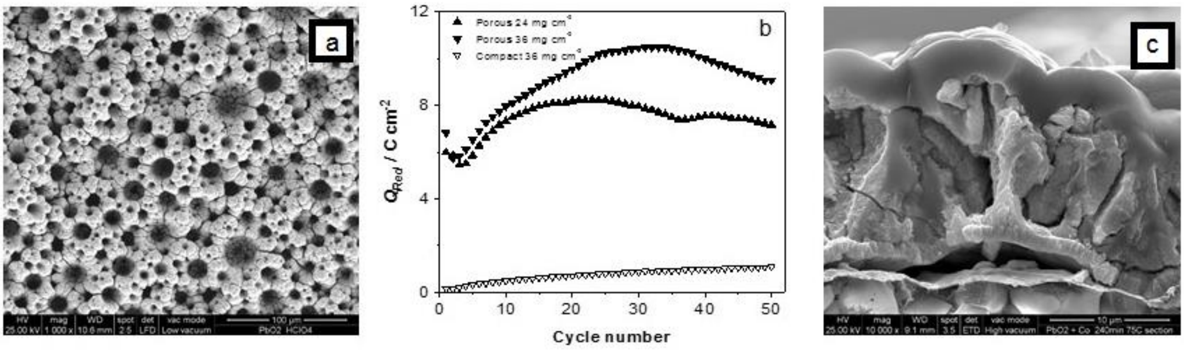

Figure 1: (a) SEM image of porous PbO_2. (b) Cycling behavior of porous and compact PbO_2. (c) Cross-sectional SEM image of Co-modified PbO_2.

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Tu.Or29

Catalytic halogen exchange in electrochemically mediated ATRP: the case of methyl methacrylate

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Atom transfer radical polymerization (ATRP) is a powerful polymerization technique for the synthesis of polymers and copolymers of precise architecture. A reversible exchange of a halogen atom between a dormant species P_n-X and a Cu^I complex with an amine ligand, $[Cu^IL]^+$, which produces the propagating radical $P_n^\bullet$ and $[XCu^{II}L]^+$, is at the heart of the process. The equilibrium is strongly shifted toward the dormant state ($K_{ATRP} << 1$), thus the concentration of $P_n^\bullet$ is very low and terminations are negligible [1].

Electrochemically mediated ATRP (*e*ATRP) is an advanced ATRP technique allowing fast (re)generation of Cu^I from Cu^{II}, easy control of the distribution of Cu^I and Cu^{II} species and the possibility of switching between active and dormant states [2]. In the framework of a research project on the application of *e*ATRP in ionic liquids, we studied polymerization of methyl methacrylate (MMA) in [BMIm][OTf]. Initial attempts were unsuccessful probably because of the use of improper catalysts and/or initiators, leading to excessive propagation rate, inefficient initiation and, hence, excessive viscosity. Poor initiation efficiency was a consequence of both termination of radicals and penultimate effect. The latter, typical of short MMA oligomers (DP < 5), increases (re)activation rate of dormant R-MMA_n-X by a factor of 2-3.

Two strategies were applied to increase initiation efficiency, avoid fast termination and preserve chain-end fidelity. *e*ATRP was triggered in the presence of a more active initiator such as 2-bromopropionitrile (BrPN) and an excess of chloride anions. The higher k_{act} of BrPN reduced the reactivity mismatch between initiator and short oligomers while the excess of chlorides catalytically switched the end-functionality from C–Br to C–Cl. Indeed, chlorinated alkyl halides are more difficult to (re)activate, being 10-100 times less active than the corresponding brominated ones. Better initiation in combination with catalytic halogen exchange provided a fast and well-controlled *e*ATRP of methyl methacrylate in [BMIm][OTf]. This procedure worked also in ethanol: in this case, the chloride salt acted also as the supporting electrolyte.

Halogen exchange with large amounts of Cu is a valuable tool for all those polymerizations affected by chain-end instability, excessive propagation or reactivity mismatch during chain extension and copolymerization [3]. Herein we show that a ppm level of Cu is enough if *e*ATRP is employed.

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We.Or30

Modified carbon paper interlayers in Li/S and Li/polysulfides batteries

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The intermittent nature of renewable energy sources requires the use of large-scale energy storage systems. Electrochemical storage is the most flexible in terms of scalability and performance, with several chemistries available. Given that low cost, high energy and long cycle life are key features, Li/S batteries can be suitable systems. However, the utilization of sulfur as cathode material is crucial in solid-state Li/S batteries given the poor electronic conductivity of sulphur. It also limits the active mass loading on the electrode and in turn, the battery energy. One approach to increase the sulfur loading is to realize 3D cathodes [1], the other is to use lithium polysulfide dispersed in the electrolyte [2].

Another drawback of Li/S batteries is the polysulfide shuttle effect. Long chain lithium polysulfides dissolve in the electrolyte and diffuse from the cathode to the lithium metal anode, where they are reduced to short chain lithium polysulfides that can deposit on the anode or transport back to the cathode. This shuttle phenomenon is detrimental for the battery performance and cycle life and can be mitigated by suitable separators or interlayer barriers [3]. This approach can also be effective for Li/polysulfide batteries.

A carbon paper interlayer has been electrochemically modified in situ and its effect on the electrochemical performance of batteries with sulfur-based, 3D cathodes presented and discussed.

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We.Or31

Improving the electrochemical behavior of highly abundant, low cost iron (II) oxide as anode material in sodium-ion rechargeable batteries

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Sodium ion batteries are a realistic alternative to the lithium ion technology with similar performances and intrinsic advantages thanks to the larger distribution and lower price of the sodium raw materials. Their full development depends on the design of electrode materials, which should made of cheap and high abundant elements. Iron oxides are potentially good candidates as negative electrodes for their high specific capacity, but they suffer of low electronic transport properties and large volume change during sodiation/de-sodiation cycles. Therefore stable performances in hematite or magnetite based electrodes require the synthesis of Fe/C composites made by expensive carbon precursors. However, the intrinsic limits of iron (II) oxide can also be tackled using a different approach by combining the advantages of the nanostructured morphology and the doping with aliovalent element. In the present work, we present for the first time the use of Si-doped Fe_2O_3 nanofibres as negative electrodes for sodium batteries, obtained by an easy scalable electrospinning method. The Si-doped does not just increase the transport properties but induces also changes in the structure and morphology of the resulting fibers.

The electrochemical results show that the Si-doped Fe_2O_3 fibers are able to deliver an anodic capacity of 350 $mAh\cdot g^{-1}$ after 70 cycles never achieved for iron oxide based electrode standard formulation (Fig.1). The mechanism of the reaction has been investigated as well by means of a combination of electrochemical, X-Ray and Raman micro-spectroscopy.

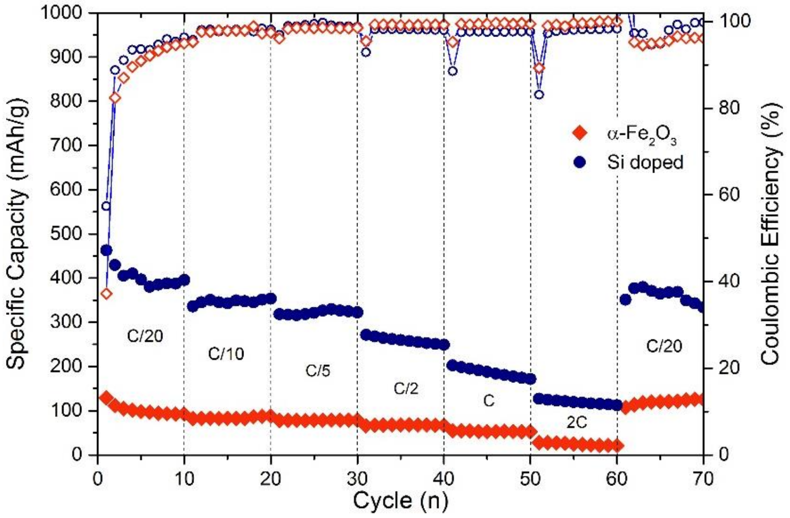

Figure 1: Anodic capacity resulting from the iron oxide based electrodes.

We.Or32

Dissolved polysulfides as catholyte for high performance lithium-sulfur storage system

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The lithium-sulfur (Li-S) battery represents one of the most interesting electrochemical storage system due to the high theoretical energy density (2567 Wh kg^{-1}), high theoretical cathode capacity (1675 mAh g^{-1}), low cost and high abundancy of sulfur. Unfortunately there are still some issues to overcome; one for all the polysulfide shuttle effect that reduces the capacity and lowers the Coulombic efficiency [1]. Many approaches has been introduced to avoid the polysulfide shuttle.

In this work, we concentrate our attention on the use of polysulfide "additives" as actual active material in a Li/dissolved polysulfides configuration. This catholyte needs several step of optimization, such as the choice of the best solvent able to stabilize long chain polysulfides, a suitable electrolyte composition for improve capacity retention and a proper lithium metal protection. A cell cycled between 1.7 and 2.8 V at C/10 rate showed a specific capacity of 925 mAh g^{-1} after 50th cycle with a Coulombic efficiency higher than 99.5% [2]. In order to overcome the safety issues that could rise by the interaction of lithium with organic solvents, we also exploit a solid polymer electrolyte [3] acting as anolyte to possibly obtain an all solid state Li/S battery.

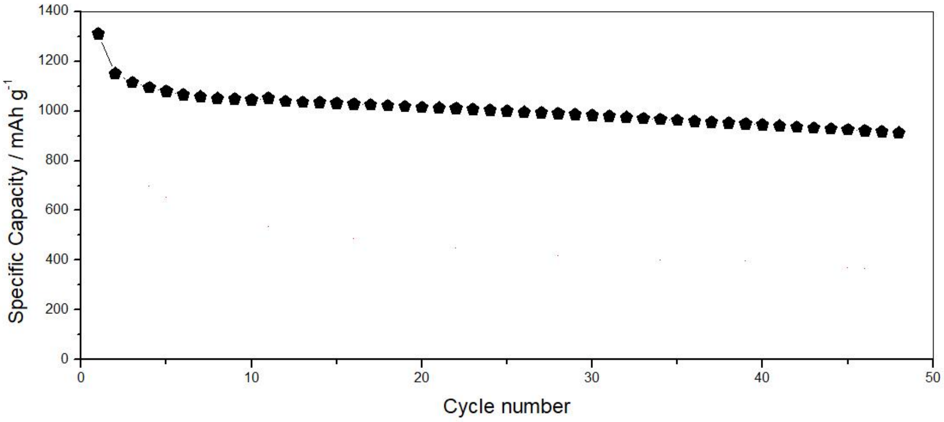

Figure 1: Cell capacity as a function of the cycle number. The test was conducted in the potential window from 1.7 to 2.8 V at C/10 rate.

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We.Or33

Mixed colloidal/solid-state synthesis of crystalline pure P2-$Na_{1.7}Ni_{1.0}Mn_{2.9}O_{7.6}$ an its utilization as a stable cathode in Na-ion batteries

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P2-$Na_{2/3}[Ni_xMn_y]O_2$-based [1] cathode materials are promising candidates for Na-ion batteries. The cycling performance of these cathodes was usually reported to drop at working voltages above 4.2 V, due to the deleterious P2/O2 irreversible phase transition [2]. Diverse approaches have been proposed to overcome this limitation such as the selective Mg doping of a $Na_{0.67}Ni_{0.67}Mn_{0.33}O_2$ P2 phase [3] or a systematic study aiming at defining the role of oxygen anion during the very first sodiation. Here we propose a two-steps colloidal-solid state synthesis for the preparation of P2-$Na_{1.7}Ni_{1.0}Mn_{2.9}O_{7.6}$. The adopted synthetic route and the peculiar Na:Ni:Mn stoichiometric ratio (1.7:1:3) leads to a cathode material that can withstand repeated charge/discharge cycles at working voltages as high as 4.4 V vs. Na/Na^+. The in-operando XRD pattern recorded on the de-sodiated electrode (4.4 V vs. Na/Na^+) does not evidence the disappearance of P2 phase while incursion of alien phases is limited, corroborating the effective suppression of the P2/O2 phase transition upon Na^+ intercalation/deintercalation. Further insight into the mechanisms at the basis of the phase transition suppression will be provided by means of theoretical study. The discharge capacity delivered at relatively low current (C/10) is 109 mAh g^{-1}, with a capacity retention exceeding 93% after 20 cycles. At the high current of 1C the delivered discharge capacity is 94 mAh g^{-1}.

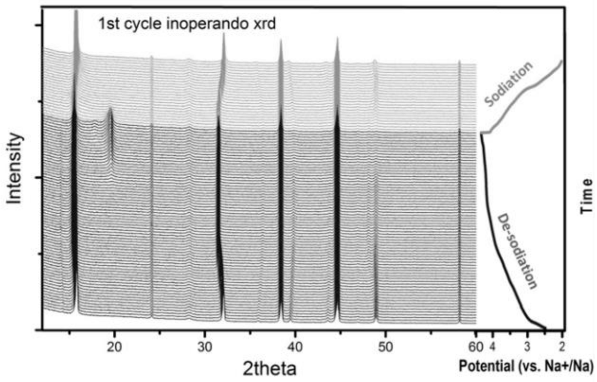

Figure 1: *in-operando* XRD measurements performed during the first de-sodiation/sodiation cycle of P2-$Na_{1.7}Ni_{1.0}Mn_{2.9}O_{7.6}$ electrode vs metallic sodium.

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We.Or34

Single lithium-ion conducting solid polymer electrolytes based on Nafion and functionalized graphene oxide

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The solid-state polymer electrolytes (SPEs) have attracted great interest because they might improve lithium-battery technology by replacing the liquid electrolyte currently in use and thereby enabling the fabrication of flexible, compact, laminated solid-state structures, free from leaks and available in variety of geometries. They are typically based on various polymers (PEO is the most studied), into which several ionic salts are readily dissolved. In these systems are thus dual-ion conductors, in which both cations and anions are mobile and will cause a concentration polarization leading to poor performances of batteries.

More recently, a new concept for polymer electrolytes has been proposed based on a single lithium-ion conducting-SPEs, which have anions covalently bonded to the polymer, inorganic backbone, or immobilized by anion acceptors [1]. For this purpose, polymer electrolytes based on ionomers such as Nafion, with perfluorinated ionizable groups ($-CF_2SO_3^-$), are interesting due to the presence of weak coordinating anions, providing a high concentration of counter ions in nonaqueous media, which in turn favours the ion transport. Such types of solid electrolyte based ion-selective membranes are also particularly interesting in the Lithium-metal cells (e.g. Li-O_2, Li-S, Lithium-LFP) for a variety of beneficial effects ranging from the limited oxygen crossover, the immobilization of the lithium polysulfides to the mitigation of the lithium dendrites growth, and at the same time to enhance the lithium transference number.[2-3]

In this work, lithiated Nafion and Nafion-nanocomposites membranes based on sulphonated graphene oxide (sGO) were synthesized and their ionic conductivity and lithium transference number investigated in common nonaqueous solvents. Besides, jointly with a extensive electrochemical analysis (lithium stripping/plating tests, galvanostatic cycling vs. $LiFePO_4$), a thorough and systematic study of the lithium-ions transport mechanisms in such systems was conducted by Pulsed Field Gradient (PFG) NMR spectroscopy. Finally, the mechanical properties of the film electrolytes were investigated by dynamic mechanical analysis (DMA) in a wide temperature range.

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We.Or35

Ionic liquids as additive salts for electrolytes of lithium ion batteries with the intent of improved stability

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With a growth of the energy density required to be supplied by lithium ion batteries, there are strong demands on improvement of credibility and safety. The electrolyte is a critical component in realizing the theoretical capacity of electrodes and determining safety specifications. The electrolyte generally contains flammable carbonates as a solvent to dissociate lithium salts, and this reduces the thermal stability of batteries. There are a lot of challenges in replacing carbonates with non-volatile ionic liquids (ILs) to control the flammability [1]. We have been proposed *N*-butyl-*N*-methylpyrrolidinium hexafluorophosphate ($[Py_{14}]PF_6$) as an additive salt for 1M $LiPF_6$ in ethylene carbonate - dimethyl carbonate (commercially so called LP30) [2]. The structure of this IL was considered to be one of the most suitable for adding to LP30, because of its anion structure analogous to that of LP30 as well as the high electrochemical stability of the cation.

In the present research, $[Py_{14}]PF_6$ was used in two ways: (1) as an additive (IL-in-LP30) and (2) as a main component of electrolytes (LP30-in-IL). Physical and electrochemical properties in terms of thermal stability, ionic conductivity, viscosity, and electrochemical stability are compared to review the role of the IL in LP30 both at high and low concentrations. Selected LP30-IL mixtures have been used in lithium metal half-cells and lithium-ion full cells containing a high voltage cathode such as $LiNi_{0.5}Mn_{1.5}O_4$.

Acknowledgements: A.T. acknowledges to the Avvio alla Ricerca 2017, Sapienza University of Rome. S.P. acknowledges to Ricerca di Sistema Elettrico - PAR 2016.

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Th.Or36

Enzyme-based electrochemical biosensor for therapeutic drug monitoring of anticancer drug CPT-11

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Therapeutic drug monitoring (TDM) is the clinical practice of measuring pharmaceutical drug concentrations in patients' biofluids at designated intervals allowing a close and timely control of their dosage. To date, TDM in oncology is performed within specific clinical research programs, still far from the routine practice, in centralized laboratories employing instruments (e.g. mass spectrometer) that can be run only by trained personnel. An innovative, fast and user-friendly analytical tool would help medical doctors to routinely monitor and control chemotherapeutic dosage. In fact, antineoplastic drugs often show a narrow therapeutic range (the concentration range in between non-efficacy and toxicity), which might cause under dosage and subsequent therapeutic failure, or over dosage and therefore severe adverse effects [1]. CPT-11 is an antineoplastic drug that inhibits topoisomerase type I, causing cell death, and is widely used in the treatment of colorectal cancer. However, CPT-11 was also found to directly inhibit the enzyme acetylcholine esterase (AChE) [2], which is involved in neuromuscular junction. Taking advantage of such inhibition, we developed an enzymatic biosensor, based on a platinum electrode functionalized with AChE and Choline oxidase (ChOx), which is capable of detecting CPT-11 in the concentration range 10-10,000 ng/mL, which is usually found in human plasma [3]. We believe that these findings could open new routes towards a real-time TDM in oncology, thus improving the therapeutic treatments, which might have tremendous fallouts into the clinical practice, the Healthcare System and, most importantly, the quality of life of oncological patients.

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Th.Or37

Production of reactive oxygen species in cellular models of a human multisystem disorder monitored with modified microelectrodes

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Modified microelectrodes have been successfully employed to detect the production of reactive oxygen (ROS) and nitrogen (RNS) species by various cellular types, as a consequence of physiological and artificial stimuli on adherent cultures [1]; as respiratory complexes are a main source of ROS inside cells, hydrogen peroxyde production was punctually studied also in mitochondria purified from rat liver [2].

We employed modified platinum microelectrodes and Dropsens Screen-Printed Electrodes to quantify hydrogen peroxyde produced by activation of the respiratory chain in cell suspensions. Specifically, it was investigated in cybrids, i.e. cellular models of mitochondrial disease, representative of a multisystem disorder due to a microdeletion on the cytochrome *b* subunit of respiratory complex III [3]. In this cellular model, it has been previously showed a strong impairment of activities of respiratory chain complexes; in this view, a higher production of ROS and an alteration of oxydative homeostasis was proposed to take place in mutant cybrids. To test this hypothesis, we developed a protocol to measure on digitonized cells time-dependent hydrogen peroxyde production, which follows respiratory chain activation triggered by adenosine diphosphate (ADP). As instability of electrochemical measurements resulted from adhesion of cells to the active microlectrode surface, platinized platinum microlectrodes were covered with an antifouling matrix; this latter procedure strongly stabilized hydrogen peroxide chronoamperometric signals and allows for quantification of ROS production in mutant as compared to wild type cybrids.

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Th.Or38

Ag as brazing metal in Ti6Al4V/Ag/YAG joints: galvanic effects in seawater

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The electrochemical behavior of Ag and AgCu, used as brazing material, was compared in Ti6Al4V/YAG (Yttrium-Aluminium garnet) joints. The concern was about galvanic effects in seawater, which can cause possible sources of weakness of the interlayer. Ag and AgCu brazed Ti6Al4V/YAG joints have been already tested in terms of wettability and interfacial reactivity elsewhere [1].

In the present work, Ti6Al4V/Ag/YAG and Ti6Al4V/AgCu/YAG samples were initially immersed for four weeks in a seawater mesocosm. SEM observations showed that the interlayer resulting from AgCu brazing was locally corroded due to Cu depletion. On the other hand, Ag-based interlayer appeared integer. Hence, Ag behavior, as brazing material, was further investigated. Although Ag and Ti6Al4V can be regarded as noble-behaving materials, in case of Ag behaving as an anode, possible worsening effects due to coupling it with Ti6Al4V can be related to the geometry of the system, since Ti6Al4V has a more extensive area than the interlayer, and the environment of application, since Ti6Al4V can enhance cathodic effects due to its ennoblement induced by biofilm growing [2]. Therefore, the study of the Ag interlayer was performed using Ti6Al4V and Ag electrodes, coupled and not coupled, immersed in seawater. Biofilm induced ennoblement was investigated by comparison with 254 SMO/Ag systems. After 4 weeks, the couples were disconnected, open circuit potential was monitored for 1 hour, potentiodynamic polarization curves were performed. Freely corroding electrodes were polarized as well. Results show that Ag behaved initially as a cathode in 254 SMO/Ag and Ti6Al4V/Ag couples; after few days, reversal of polarization was observed, making Ag behaving as an anode. This event was a stable feature only for the 254 SMO/Ag couples, and this trend was consistent with freely corroding electrode behaviors: the corrosion potential of 254 SMO electrodes shifted to potentials larger than that of Ag, with sigmoidal kinetic, typical of biofilm ennoblement; on the other hand, Ti6Al4V potential shifted to potentials comparable to Ag ones, with a saturation kinetic typical of passivation layer strengthening.

Important evidences about Ti6Al4V/Ag couples were: a) Ti6Al4V did not undergo biofilm induced ennoblement, b) galvanic current densities on Ag were about 10^{-6} A cm^{-2}, whatever the sign of the current. Then, Ag, better than AgCu, can be used as brazing metal for Ti6Al4V/interlayer/YAG joints in seawater, since no appreciable galvanic effects occur.

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Th.Or39

How anodization conditions affect the characteristics of thin film electrodes deposited on nanostructured titanium substrates

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Although manganese oxide-based electrodes exhibit promising electrocatalytic activity, a reduced electrogeneration of chlorinated by-products in the presence of chlorides and low cost, they have been little explored in the anodic oxidation of recalcitrant pollutants. This is partially due to their limited durability caused by a low adherence of the oxides to the investigated substrates. Nonetheless, the characteristics of these materials encourage further studies to improve both stability and durability by adopting more efficient preparation techniques.

In previous research, by comparing the performance of MnOx films grown on both untreated and microstructured substrates we have verified that the morphological and electrochemical properties of the electrodes can be improved by a surface texturization [1].

Recently, a new approach for the production of anode materials has been developed and applied. The method involves the oxide deposition on substrates modified at a nano-scale with significant increase in the life time of the electrode without impacting the electrocatalytic properties [2]. The enhanced performance can be attributed either to the increase in the electrode surface area or to the improved inclusion of the oxide particles inside the nanostructures.

The present work investigates the possibility to improve the durability of electrodes obtained by deposition of a mixed oxides thin film on a nanostructured titanium substrate by optimizing the main operative conditions of anodization procedure. The manganese and ruthenium mixed oxide layer has been obtained by thermal decomposition of alcoholic solutions of the precursor salts. The electrodes obtained have been characterized in terms of morphological and electrochemical properties by scanning electron microscopy (SEM) and cyclic voltammetry (CV). The factors investigated were fluoride concentration (0.25-0.75 %), anodization voltage (15–45 V) and anodization time (45-135 min). The response variable was the durability of the anode assessed by accelerated life tests.

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Th.Or40

Effect of Y salt precursor on the synthesis and activity of Pt_XY alloyed NPs versus oxygen reduction reaction

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The preparation of Pt bimetallic systems for Oxygen Reduction Reaction (ORR) is a topic extremely important because the amount of Pt could be reduced, while the catalytic activity and stability may be maintained or even improved, due to the so called "*geometric effect*" and "*ligand effect*". Pt_3Y has a catalytic activity greater than pure platinum and it exhibits the second highest ORR activity ever measured on a polycrystalline electrode, surpassed only by single crystal Pt_3Ni [1].

In this paper, we describe the synthesis and characterization of Pt_xY nanoparticles (NPs) supported on a graphitized Carbon Black. In the past, we unveiled the effect of Pt precursor and carbon support on Pt_XY formation; here we report the effect of different Y salt precursors on the Pt_3Y NPs properties synthesized by means of thermal reduction [2]. The synthesis temperature has been chosen according to the decomposition temperature of yttrium salt, determined by TGA analysis. This study is crucial to unravel how yttrium precursor influences the formation of the alloy and the growth and shape of the NPs. It was observed that different yttrium salts afford Pt_xY NPs of different size, in fact nanoparticles of 6.12 nm mean diameter were obtained using YCl_3 (Figure 1a). The electrochemical characterization showed that Pt_xY catalyst prepared from $Pt(acac)_2$ and YCl_3 shows high mass activity for ORR and stability after long lasting durability tests (figure 1b).

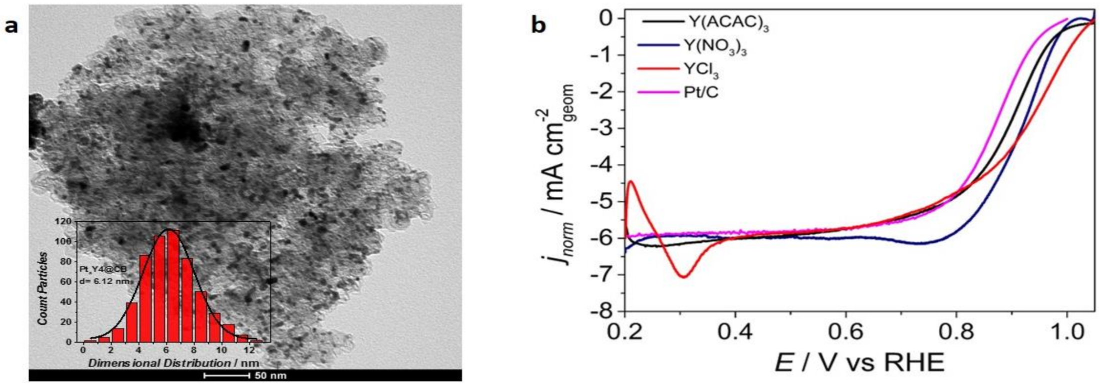

Figure 1. Catalysts prepared from $Pt(acac)_2$ and yttrium salt: a) TEM image of Pt_xY obtained by YCl_3; b) LSVs recorded at scan rate of 20 mV s^{-1} in O_2 saturated 0.1 M $HClO_4$ at 25 °C, rotation rate 1600 rpm.

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Th.Or41

Electroreduction of CO_2 on tin oxide modified copper oxide nanostructured foam

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The electrochemical conversion of CO_2 to value-added products is of great interest since it could use electricity from renewable source as input. As well known, a properly designed electrocatalyst is essential to selectively yield a desired product from CO_2 reduction [1]. In this work, a low-cost and eco-friendly electrode comprised of copper oxide (CuO_x) foam and sparse Tin oxide (SnO_x) was prepared through a simple two-step electrodeposition route.

Before each electrochemical measurement, the as-prepared electrode was in-situ reduced at -1.0 V vs. reversible hydrogen electrode (RHE) for 20 min until a constant current was achieved. Unless otherwise specified, all the potentials were referred to RHE in this work.

The electrocatalytic performance of SnO_x@CuO_x electrode was firstly studied using cyclic voltammetry (CV) at room temperature with a CHI760D electrochemical workstation. A Pt wire was used as counter electrode and Ag/AgCl (3 M NaCl) was used as reference electrode. As shown in Fig. 1a, SnO_x@CuO_x displays a higher current density and positively shifted onset potential in CO_2-saturated electrolyte, exhibiting its promising activity and selectivity toward CO_2 reduction. Chronoamperometric measurements (CAs) were also carried out on SnO_x@CuO_x in CO_2-saturated electrolyte, as exhibited in Fig. 1b. CO is the only detected CO_2 product, with a faradaic efficiency of about 80 % at low-moderate overpotentials (E= -0.6 V and -0.8 V). High CO partial current densities on SnO_x@CuO_x electrode are observed and likely attributed to its highly porous structure (data not shown), which allows large surface area accessible for electrochemical reactions.

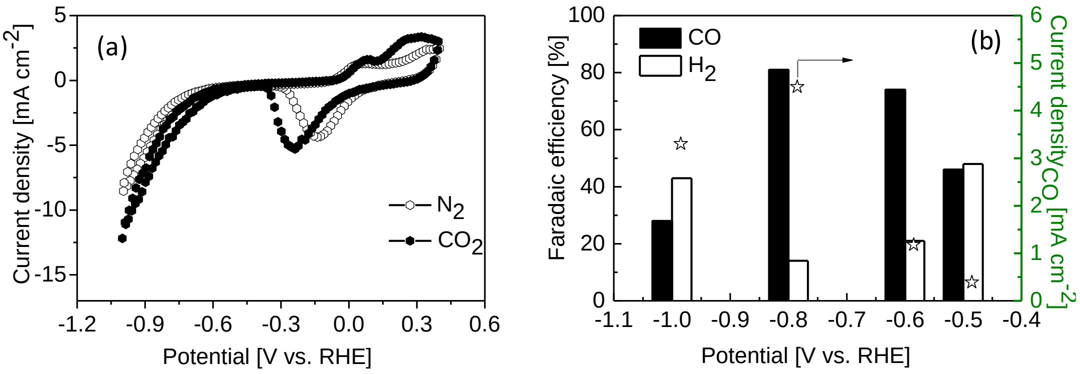

Figure 1: (a) CVs on SnO_x@CuO_x electrode in N_2 or CO_2- saturated 0.1M $KHCO_3$ at a scan rate of 10 mV s^{-1};(b) CAs on SnO_x@CuO_x in CO_2-saturated 0.1M $KHCO_3$

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SPONSOR TALK

A new European player perspective on Li-ion cell production: the "E-Lithium" project

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As important as they are, evolutionary technology improvements achieved through European R&D activities, are not sufficient to drive EU competitiveness in the battery sector, without a stable and secure battery manufacturing base. The lack of a domestic cell manufacturing base makes the EU dependent on the supply of foreign battery technology, and, over time, the current EU capabilities in high-quality R&I at worldwide level will decline, compromising the ability for EU to compete for and catch the market of the next generation of batteries. Recently the European Commission expressed its intention to support industry-led initiatives to develop a full battery value chain in the EU [1].

Within this context, Lithops is developing a Li-ion cells 200 MWh/y manufacturing plant (based in South Italy) for ESS and industrial traction market. Lithops plans to exploit the know-how gained during several years of R&D activities within its pilot plant for the production of Li-ion pouch cells (based in Turin), covering from active material treatments to cell testing. Together with Seri Group (Lithops holder) and Faam, Lithops aim to set a vertically integrated production, from raw materials to second-life battery re-usage and materials recycling. The manufacturing plant is designed to mainly produce (ramping-up in Q3 2018) 40 Ah Li-ion pouch cells for Energy Storage Systems (ESS) and industrial traction application, with an expecting output of approx. 1.5M cells/y. Regarding the raw materials Lithops has recently subscribed an agreement with Jemse, the Argentinean mining company of Jujuy region, this partnership will grant strategic access to raw materials at competitive prices, enabling strong saving in the cell production costs, and access to the South American market. Great effort will be made also on R&D activities, particularly on materials and recycling. The group plan is to produce the cathodic active material (LFP), by exploiting a cost-competitive synthesis method. Moreover, working together with Game Lab research group, Lithops is developing solid-polymer-electrolyte membranes (replacing liquid electrolyte) with interesting performance, through a promising process that could be easily up-scaled in the production line.

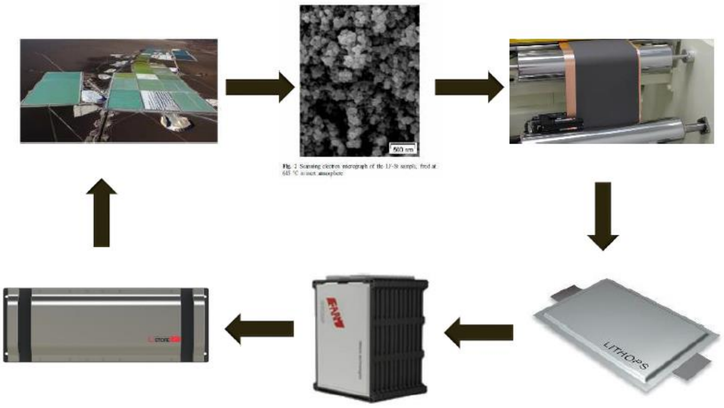

Figure 1: E-Lithium project overview

[1] http://setis.ec.europa.eu/system/files/integrated.../action7_declaration_of_intent_0.pdf

POSTER CONTRIBUTIONS

LIST OF POSTER COMMUNICATIONS

P01	M. ALIDOOST	Embedded silicon in cyclodextrin nanosponges as Li-ion cell anode
P02	J. AMICI	Study of transition metal phtalocyanines as ORR catalysts for Li-O_2 cells and their interactions with different binders
P03	C. ARBIZZANI	Novel catholyte formulation towards high energy semi-solid Li/O_2 flow battery
P04	C. BAROLO	New ligand and device designs towards stable LEC based on copper(I) complexes
P05	A. BARBUCCI	Kinetics of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$-$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ composite as cathode for IT-SOFCs
P06	F. BELLA	Addressing the controversial mechanism of Na^+ reversible storage in TiO_2 nanotube arrays: amorphous, anatase and rutile TiO_2
P07	A. BERTEI	Do electrochemical reactions really take place at the three-phase boundary in solid oxide fuel cells?
P08	L. CHEN	Bi-functional layered P2-$Na_{0.67}Ni_{0.33}Ti_{0.67}O_2$ as electrode material for symmetric Na-ion full battery
P09	F. COLO’	Innovative polymer electrolytes for safe, low-cost and durable sodium-ion batteries
P10	G. DANIEL	The effect of post-pyrolisis treatment on PGM free electrocatalyst for ORR based on Fe-N_x
P11	C. DURANTE	Soft template assisted synthesis of mesoporous carbon as electrode support for Pt_xM NP catalysts for fuel cell
P12	L. FALCIOLA	Photo-renewable conductivity and pH electroanalytical sensors for on-line monitoring of drinking water quality
P13	M. FALCO	Towards solid batteries operating at ambient temperature: composite polymer electrolytes based on LLZO in a cross-linked PEO matrix
P14	C. FRANCIA	PEEK-WC / nanosponge membranes as anode protective layers for rechargeable Li-O_2 batteries
P15	S. GALLIANO	Investigation on bio-derived hydrogel electrolytes for dye-sensitized solar cells
P16	A. GENNARO	Electrochemical reduction of CO_2 to formic acid - from bulk to supported Sn NPs electrocatalysts
P17	C. GERBALDI	High performing single-ion conducting block copolymer electrolytes based on poly(ethylene oxide) and specifically designed methacrylic sulfonamide
P18	A. ISSE	Novel TPMA-modified ligands for atom transfer radical polymerization
P19	M. IURLO	Electrostatics vs. self-assembly
P20	P. JAGDALE	Carbon fibers from waste cellulose for Li-ion batteries
P21	L. MATTAROZZI	Electrodeposition of Ag-Rh Alloys
P22	L. MAZZAPIODA	Titanium-based oxide nanoparticles as electrode and electrolyte components in PEM Fuel cells and Electrolyzers
P23	G. MELIGRANA	Carbon from waste: pyrolysed hazelnut shells as efficient active electrode materials for Li-/Na-ion batteries

P24	A. MINGUZZI	Observing single exocytosis events from β pancreatic cells
P25	P. MUSTARELLI	Novel photosynthetic microbial fuel cells (PMFCs) for efficient wastewater treatment and microalgae production
P26	C. NERVI	Development of solid-state electrolytes by anion substitutions in lithium borohydride
P27	N. PENAZZI	Li-ion Cell Anode using 2090-T8 Al Alloy
P28	G. PIANA	Photocured polymer electrolytes for lithium-based batteries
P29	V. PIFFERI	Preconcentration effect of ion-exchange polymers in lead electroanalytical determination
P30	G. RIVEROS	Electrodeposition and characterization of SnS-reduced graphene oxide composite
P31	O. SCIALDONE	Electrochemical conversion of carbon dioxide to formic acid: on the road to applicative scale
P32	L. SILVESTRI	Silicon nanoparticles incorporated in graphene sheets for high capacity anode in Li-ion batteries
P33	A. TESTOLIN	Electrochemical characterization and electroanalytical applications of RGO-AuNPs Hybrids
P34	G. VALENTI	Driving the selectivity of electrochemical CO_2 reduction to formic acid: synergic effects in a C-based heterostructure
P35	D. VERSACI	Facile synthesis of SnO_2/g-C_3N_4 hybrid compound for Li-ion anode applications
P36	O. YILDIRIM	Enzymatic electrochemical biosensor based on a 2D-covalent triazine framework
P37	A. ZANUT	Electrochemiluminescent detection of sarcosine using nanostructed cerium oxide for early diagnosis of prostate cancer
P38	U. ZUBAIR	Carbon wrapped black titanium oxides for the effective suppression of polysulfides shuttling process

P01

Embedded silicon in cyclodextrin nanosponges as Li-ion cell anode

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Silicon is one of the most promising anode materials for lithium-ion but also post lithium-ion batteries: it shows a low working potential and is the second abundant element on the earth crust. The theoretical capacity of silicon at room temperature is 4200 mA h /g based on the fully alloyed form of $Li_{4.4}$ Si [1].

However, the semiconducting nature of silicon restricts its use as anode material. In addition, its large volume change during cycling, more than 300%, causes a serious pulverization of electrode and loss of electrical contact between Si and the current collector which leads to rapid capacity decay during cycling [2].

This contribution reports the initial results of Si@CNS-rGO anode obtained by embedding silicon nanoparticles in pyrolised cyclodextrin based nanosponges (CNS) and consequently wrapping with rGO sheets.

The promising results obtained (Fig.1) and the synthesis characteristics, being simple and low cost, make this an interesting new way to obtain an anode alternative to graphite, which can be easily scalable at industry level.

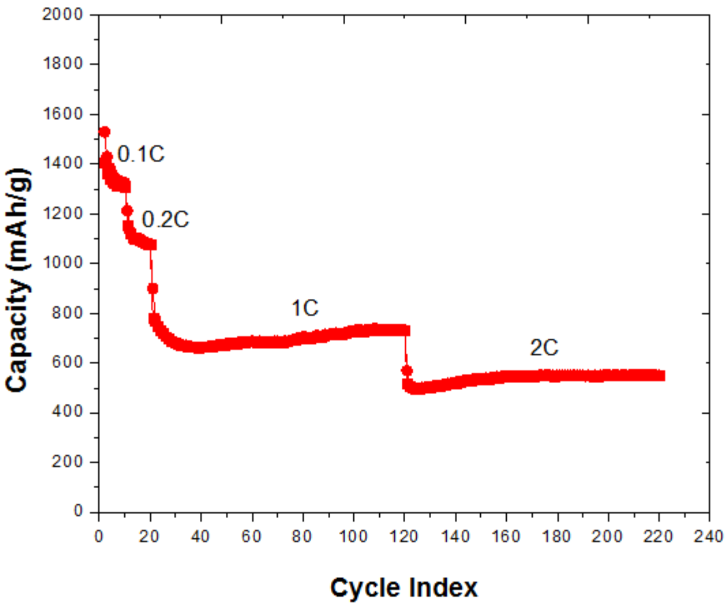

Figure.1-Delithiation capacity profile of a Li-ion cell with Si@CNS-rGO as anodic active material. The capacity values are referred to the Si mass.

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P02

Study of transition metal phtalocyanines as ORR catalysts for Li-O_2 cells and their interactions with different binders

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Global warming and reduction of fossil-fuel supplies demand the pursuit of renewable energy sources and sustainable storage technologies. The rechargeable Li-air battery, coupling the light Li metal with the inexhaustible source of O_2 of the surrounding air, represents an exciting opportunity.

This kind of cell presents a very high energy density (1000 kWh/kg), close to the theoretical density of gasoline. However, actual efficiency is much lower than the theoretical value mainly because of different major issues such as the high recharge potentials needed to decompose Li_2O_2, which is an insulator, and the parasitic products formed from the electrolyte and/or binder decomposition during cell discharge. To date, the most widely used binder for Li batteries is polyvinylidene fluoride, PVDF.

However, recent papers reported that this type of binder undergoes decomposition reactions due to superoxide ion attack during discharge. Hence, new binders are under study, among them, lithiated Nafion is the one showing the most promising results. On the other hand, noble metals have extensively been considered the best performing catalysts for oxygen reduction reaction (ORR), though their high cost and limited reserves in nature poses serious limitations. Increasing efforts have thus been made to explore cost-effective and stable noble metal free materials and recent breakthroughs in the synthesis of non-noble group metal catalysts for efficient ORR have been made.

It has been demonstrated that supported transition metal phthalocyanines displayed an enhanced electrocatalytic performance towards ORR. Hence, these materials were tested at the cathode of Li-O_2 cells, coupled with different binders in order to study the interaction and identify the best combination of materials to achieve optimal performance.

P03

Novel catholyte formulation towards high-energy semi-solid Li/O_2 flow battery

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Li/O_2 batteries are considered very attractive due the theoretical specific energy of 3500 Wh kg^{-1}, more than 10-fold higher than that of lithium-ion batteries (LIBs).

In Li/O_2, cathode passivation by Li_2O_2 discharge products is one of the most serious drawback with the slow O_2 mass transport, which in air breathing cells limits current densities. Replacing solid electrodes with semi-solid slurries has been demonstrated to be an effective strategy to improve rate response and we have pursued such approach to demonstrate a new concept, a non-aqueous Semi-Solid Lithium Redox Flow Air (O_2) Battery (SLRFAB) that operates with a flowable semi-solid O_2-saturated carbon-based catholyte [1].

The design optimization of the SLRFAB lab-scale prototype has been also reported, which highlighted how the increase of catholyte carbon content permits to achieve outstanding specific energy and power value [2].

However, increasing the carbon percentage in the SLRFAB catholyte for an high energy content is a challenging approach because the carbon particles affect the viscosity of the catholyte.

Here a set of catholytes for a SLRFAB have been studied, using different carbons and carbon contents. Catholytes based on Super-P and Pure Black in O_2-saturated glyme-based electrolyte have been investigated [3].

The electrochemical results are presented and discussed according to the morphological properties of the carbons and of the carbon aggregates, along with the rheological and electrical conductivity data of the semi-solid catholytes.

Acknowledgments: The work was funded by Alma Mater Studiorum –Università di Bologna (RFO, Ricerca Fondamentale Orientata).

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P04

New ligand and device designs towards stable LEC based on copper(I) complexes

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The final goal in thin-film lighting technologies is to fabricate highly efficient, air-stable, low-cost, and single-layer lighting sources using up-scalable solution-based techniques. Those requirements are fulfilled by the light-emitting electrochemical cell (LEC) technology.[1] Among the different Cu-iTMC families applied in LECs, heteroleptic complexes – i.e., [Cu(N^N)(P^P)]+ where N^N and P^P are diimine and diphosphine ligands, respectively are the most studied ones.

This work reports on the positive impact of i) attachment of methoxy groups at the ortho position of the bipyridine ligand (6,6’-OMe2bpy) in heteroleptic copper (I) complexes belonging to the $[Cu(bpy)(POP)]^+$ family, and ii) a new device design comprising a multilayered architecture to decouple hole/electron injection and transport processes on the performance of LEC. In short, the substituted complex showed enhanced thermal- and photo-stability as well as photoluminescence and ionic conductivity features in thin films compared to those of the archetypal complex without substitution. These beneficial features led to LEC outperforming in terms of luminance and efficacy the reference devices. Furthermore, the new device design resulted in a 10-fold enhancement of the lifetime without negatively affecting the other figures-of-merit. Here, hole / electron injection and transport processes are performed at two different layers, while electron-hole recombination occurs at the copper (I) complex layer. As such, this work provides further insights into a smart design of N^N ligands for copper(I) complexes and opens the path to a simple device architecture towards enhanced electroluminescence response.

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P05

Kinetics of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$-$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ composite as cathode for IT-SOFCs

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Cathodes in solid-oxide fuel cells have to meet numerous requirements, primarily high catalytic activity for oxygen exchange reduction at intermediate-low temperature (≤600 °C) and chemical/structural stability. Perovskite-type oxides such as $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) are considered promising materials in terms of electrical performance at intermediate temperature conditions, but problems related to their degradation have not still been resolved [1].

This work dealt with the LSCF-BSCF composite system as cathode for intermediate temperature soli oxide fuel cells (IT-SOFCs). Based on preliminary results obtained previously by the authors [2], the aim of this study was to investigate the effect of composition on long-term stability, and then three volume ratios were considered: BSCF-LSCF 70-30 v/v% (BL70), 50-50 v/v% (BL50) and 30-70 v/v% (BL30). Composite cathodes were deposited on a $Ce_{0.8}Sm_{0.2}O_{2-\delta}$-electrolyte system and impedance spectroscopy was applied in different working conditions, by varying temperature (500 to 650 °C) and cathodic overpotential (50 to 300 mV).

Excellent values for polarization resistance were observed: 0.021 Ω cm^2 at 650°C and 0.26 Ω cm^2 at 500°C for BL70 composition, these resistances being much lower than the ones found for pure BSCF [3]. Analyses of the impedance results, carried out by distribution of relaxation time (DRT) and equivalent circuit models indicated a change in the kinetic regime, passing from a co-control of the surface oxygen exchange and bulk diffusion at low temperature (< 500 °C), to a different rate-determining step at high temperature (650 °C).

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P06

Addressing the controversial mechanism of Na^+ reversible storage in TiO_2 nanotube arrays: amorphous, anatase and rutile TiO_2

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Titanium dioxide (TiO_2), in its amorphous as well as most common polyphases including anatase, rutile, brookite and various metastable phases, is under intense investigation as anode candidate for advanced sodium-ion electrochemical energy storage. Na-ion batteries (NiB) are attracting the widespread interest of the scientific community because they may offer the most convenient alternative to current leading-edge Li-ion technology (LiB) for large-scale grid energy storage, where size does not matter and cost, safety and reliability are the most stringent requirements [1,2].

In the recent years, various hypotheses have been proposed on the real mechanism of reversible insertion of sodium ions into the TiO_2 structure and literature reports are often controversial in this respect. Interestingly, we experienced peculiar, intrinsically different electrochemical response between amorphous, rutile and anatase TiO_2 nanotubular arrays, obtained by simple anodic oxidation, when tested as binder- and conducting additive-free electrodes in lab-scale sodium cells. In particular, after the initial electrochemical activation, anatase TiO_2 showed excellent high rate capability and very stable long-term cycling performance at larger specific capacity values, thus definitely outperforming the amorphous and rutile counterparts.

To reach deepen insights into the subject, materials were thoroughly characterized by means of scanning electron microscopy and *ex-situ* X-ray diffraction, and the mechanism of sodium ion insertion in the TiO_2 bulk phases was systematically modelled by density functional theory (DFT) calculations. The results we obtained may significantly contribute to get a more systematic selection of proper active material configurations for highly efficient sodium-based energy storage systems [3].

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P07

Do electrochemical reactions really take place at the three-phase boundary in solid oxide fuel cells?

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Within composite electrodes for solid oxide fuel cells (SOFCs), electrochemical reactions between gas species and charge carriers take place in the proximity of the three-phase boundary (TPB), which is the contact perimeter among the electron-conducting phase, the ion-conducting phase and the porous phase. The TPB reaction zone is conventionally regarded as a mono-dimensional line and efforts have been made to increase its length to reduce the activation losses.

In this study, by using physically-based modelling, 3D tomography and impedance spectroscopy, we show that the electrochemical reactions take place within an extended region around the geometrical TPB line, as in Fig. 1. Such an extended region is in the order of 4 nm in Ni-YSZ anodes [1] while approaches ca. 200 nm in LSM-YSZ cathodes [2]. These findings have significant implications for preventing the degradation of nano-structured anodes, which is due to the coarsening of the fractal roughness of Ni nanoparticles [1], as well as for the optimisation of composite cathodes, indicating that the adsorption and surface diffusion of oxygen limit the rate of the oxygen reduction reaction (ORR) [2]. In both anodes and cathodes, the results point out that the surface properties of the materials are key in determining the performance and lifetime of SOFCs, demonstrating that the three-phase boundary paradigm must be abandoned.

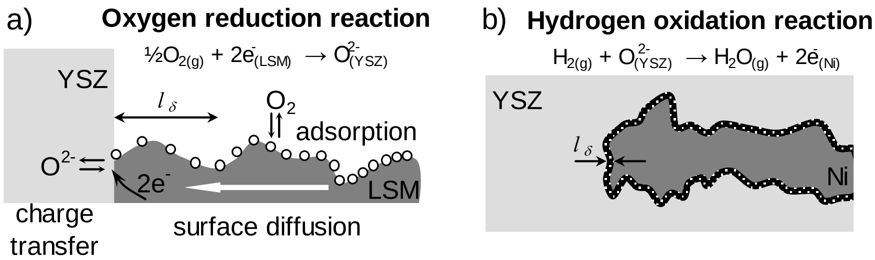

Figure 1: a) Oxygen reduction reaction within a composite LSM-YSZ SOFC cathode; b) hydrogen oxidation reaction in a Ni-YSZ SOFC anode.

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P08

Bi-functional layered P2-$Na_{0.67}Ni_{0.33}Ti_{0.67}O_2$ as electrode material for symmetric Na-ion full battery

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Sodium-ion batteries (SIB), based on the low cost and naturally abundant mineral sources, have been regarded as promising candidate for next-generation energy storage, especially addressed to mid- to large-scale stationary applications. In this landscape, full sodium battery with a symmetric configuration, namely with the same compound employed as both cathode and anode electroactive material, became very attractive and promising from a commercial standpoint. Vanadium or titanium-based $Na_3TM_2(PO_4)_3$ (TM = V or Ti) NASICON represented notable example in this sense [1,2].

Layered P2-$Na_{0.67}Ni_{0.33}Ti_{0.67}O_2$ [3] is proposed in this contribute as a valid and environmentally safer alternative to the vanadium-containing species. P2-$Na_{0.67}Ni_{0.33}Ti_{0.67}O_2$ relies on two electrochemical active transition metals with sufficiently separated RedOx potentials: Ni^{4+}/Ni^{2+} (3.5 V vs. Na^+/Na) and Ti^{4+}/Ti^{3+} (0.7 V vs. Na^+/Na). In this work, a stable symmetric full sodium ion battery, based on P2-$Na_{0.67}Ni_{0.33}Ti_{0.67}O_2$, is proposed and its optimization procedure, in terms of electrode balancing and electrodes potential cut-offs systematically presented. The final optimized P2-$Na_{0.67}Ni_{0.33}Ti_{0.67}O_2$-based symmetric SIB exhibits an average potential of 2.8 V with an energy density of 54 Wh kg^{-1} based on the cathode and anode materials. We herein also present the results of *in-operando* XRD measurement performed on the compound to better understand the structure changes occurring during the sodiation/de-sodiation processes.

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P09

Innovative polymer electrolytes for safe, low-cost and durable sodium-ion batteries

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In the recent years, large-scale and high-energy storage systems are becoming extremely important to realize the load leveling of intermittent renewable energy sources, such as wind and solar, into the grid. Secondary (rechargeable) sodium-based batteries represent the most promising technology in this respect, because of their high-energy density, low-cost, simple design, and easiness in maintenance. However, standard batteries use liquid electrolytes as ion transport media; these are based on toxic and volatile organic carbonate solvents, and their flammability clearly raises safety concerns. The most striking solution at present is to switch on all solid-state designs exploiting polymer materials, films, ceramics, etc.

Here, we offer an overview of our recent developments on innovative polymer electrolytes for sodium-ion batteries. Polymer electrolytes were prepared through different techniques, including simple solvent casting [1] and UV-induced photopolymerization (UV-curing) [2,3], being simple, low-cost and easily scalable to an industrial level. All samples were thoroughly characterized in the physico-chemical and electrochemical viewpoint. They exhibited excellent ionic conductivity and wide electrochemical stability window, which ensure safe operation at ambient conditions. Electrochemical performances in lab-scale devices were evaluated by means of cyclic voltammetry and galvanostatic charge/discharge cycling exploiting different electrode materials (prepared by water-based procedures exploiting green carboxymethylcellulose as binder).

Work on Na-ion polymer batteries for moderate temperature application is at an early stage, only lab-scale cells were demonstrated so far. Nevertheless, with the appropriate choice and optimisation of electrode/electrolyte materials (and successful combination thereof), the intriguing characteristics of the newly developed polymer electrolytes here presented postulates the possibility of their effective implementation in safe, durable and high energy density secondary Na-based solid-state devices conceived for green-grid storage and operating at ambient and/or sub-ambient temperatures.

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P10

The effect of *post*-pyrolisis treatment on PGM free electrocatalyst for ORR based on Fe-N$_x$

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Nowadays, platinum is the best catalyst used in PEMFC, because it allows to obtain great catalytic performance for Oxygen Reduction Reaction (ORR). On the contrary, the high cost and easy poisoning of platinum-based catalysts prevent the large-scale commercialization of PEMFCs. Nitrogen doped mesoporous carbon are a new class of Pt free materials for ORR [1,2]. In particular, it was observed that doped carbons with small amount of Fe can catalyze the O_2 reduction to H_2O at overpotentials comparable to that of the most active Pt catalyst [3].

In this paper, nitrogen doped mesoporous carbon containing small amount of Fe was prepared from agarose through a hydrogel embedding an iron salt. After the freeze-drying of the gel, the material was subjected to two thermal treatments to obtain a product, which was ball milled and further activated with different methods (H_2SO_4, CO_2, KOH, steam treatments). TEM images and BET measurements revealed changes on carbon structure (Fig. 1a,b) and increment of BET surface area and mesoporosity. Moreover, *post*-pyrolisis treatments modified the graphitization grade, through the reduction of amorphous carbon, visible from Raman spectra (Fig. 1e).

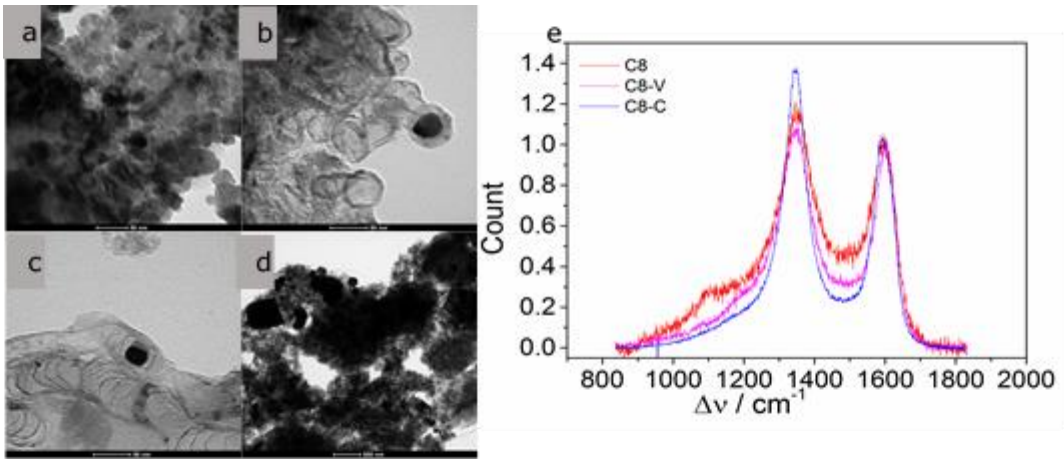

Figure 1. (a-d) TEM images of different catalysts after post pyrolysis treatments; (e) Raman spectra.

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

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P11

Soft template assisted synthesis of mesoporous carbon as electrode support for Pt_xM NP catalysts for fuel cell

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Mesoporous carbons (MCs) are highly porous and promising materials, which find wide application in electrocatalysis, sensing, drug deliver and separation technologies [1]. In this paper, novel MCs were prepared according to a soft template approach based on the templating action of a PEO-PS copolymer. The copolymer was synthetize according to a SARA-ATRP polymerization from the precursors PEO-Br and styrene, and Cu/$CuBr_2$/TPMA (TPMA = tris(2-pyridylmethyl)amine) as catalyst. The adopted synthesis resulted in an efficient way to diminish the amount of Cu catalyst and therefore the metal contamination in the resulting carbon material. The carbon was obtained by the pyrolysis of a resorcinol-formaldehyde-copolymer adduct prepared under hydrothermal condition at 100 °C in a homemade autoclave. The elemental analyses attested the purity of the resulting carbon with nitrogen and sulfur present only in very small traces. The MC morphology was investigated by SEM techniques (Fig. 1) revealing the presence of small carbon particle (<100 nm) and wide mesopores (>10 nm) resulting from the decomposition of the templating copolymer, whereas a surface area of 500 m^2/g was evaluated by BET method.

Pt_xM NPs (M = Ni, Co) were deposited on the new support by solid state reduction with H_2 at high temperature and the catalytic performances towards ORR were investigated by electrochemical techniques.

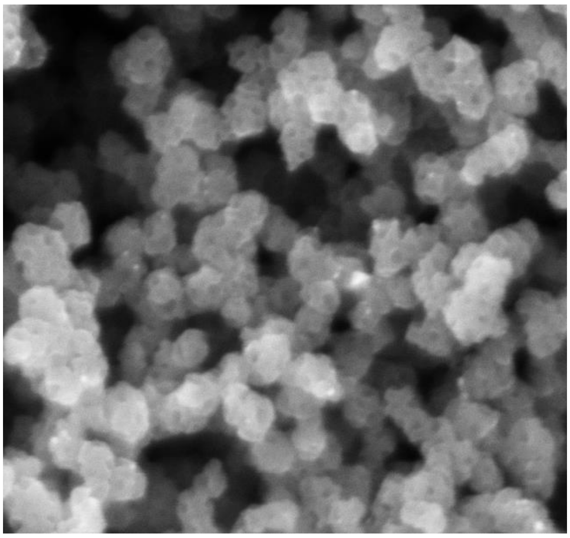

Figure 1: SEM picture of mesoporous carbon

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

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P12

Photo-renewable conductivity and pH electroanalytical sensors for on-line monitoring of drinking water quality

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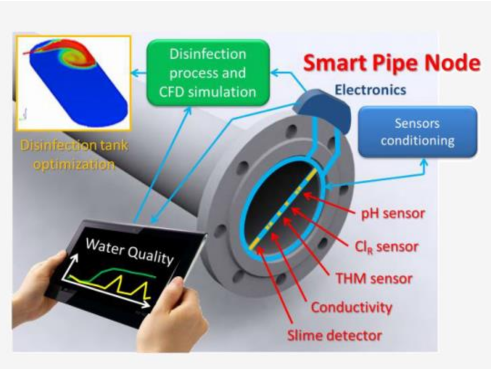
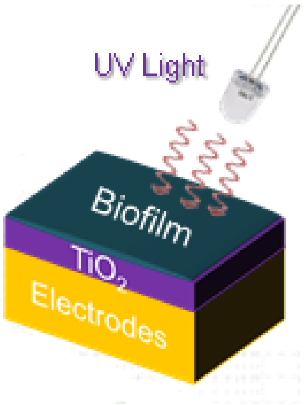
This presentation is embedded in the framework of the DrinkAble (DRINKing wAter resilient management comBining process anaLyses, CFD and innovative sEnsor monitoring) Project (funded by Fondazione Cariplo) [1], whose aim is the construction of the so called "Smart Pipe Node": a compact flange hosting several miniaturized sensors for quantitative, continuous and distributed monitoring of the parameters assessing water quality, risks for health and the efficacy of disinfection. These nodes, are supposed to be installed both in treatment plants (for instance for the optimization of disinfection processes), as well as across the whole distribution network.



In this context, one of the major problems encountered by the on-line sensors is the fouling and passivation of the sensing surface, preventing their use for prolonged times without the need of maintenance and substitution.



Here, we presented the optimization of low-cost renewable electroanalytical sensors for the determination of two main parameters in drinking water control: conductivity and pH. The innovative aspect of these devices is their photo-renewable transparent surface made of photocatalytic TiO_2 coating [2], which can be activated by UV-LEDs integrated in the system.

Both the conductivity and pH measurements were performed before and after a forced fouling process, underlying changes in the response of the sensors and subsequent UV-light recovery, allowing the use of these sensors in remote integrated monitoring systems and flow analysis, where short detection time is crucial.

Acknowledgements: The authors acknowledge the Fondazione Cariplo, grant no. 2014-1285 for financial support.

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P13

Towards solid batteries operating at ambient temperature: composite polymer electrolytes based on LLZO in a cross-linked PEO matrix

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Possible concerns about the safety of rechargeable lithium metal batteries has postponed their introduction into the smart electronics or automotive industries and have promoted advances in the field of non-flammable solid electrolytes. Among the oxide ceramic super lithium ion conductors, garnet-type $Li_7La_3Zr_2O_{12}$ (LLZO) has recently attracted much attention because of its relatively high ionic conductivity at room temperature (>10^{-4} S cm^{-1}), negligible electronic conductivity and absence of harmful decomposition products upon contact with atmospheric moisture. Anyway, processing LLZO in pellets by sintering, results in brittle and more or less porous electrolytes, which often display poor interfacial contact with Li metal electrodes. Moreover, there are some reports of lithium dendrite growth and instability towards the cathode material - especially while processing of the electrode at high temperature - referred to cells assembled with this electrolyte family [1,2]. To circumvent these problems, recent efforts have been dedicated to the formulation of composite hybrid polymer electrolytes (CPEs), where the ceramic material is embedded in a polymeric matrix. As compared to the pristine components, CPEs are stiff while preserving flexibility, are easily processed, and can be conceived to attain improved ionic conductivity and interfacial contact with the electrodes [3].

In this work, a polymer based matrix containing poly (ethylene oxide) (PEO), lithium bis (trifluoromethylsulphonyl) imide (LiTFSI), tetra (ethylene glycol dimethyl ether) (G4) and a photoinitiator was added with LLZO particles, thoroughly mixed, formed into a film and cross-linked under UV radiation to obtain a composite hybrid electrolyte [4]. This easy procedure allows obtaining self-standing CPEs with desirable properties of flexibility, shape retention upon thermal stress, improved interfacial contact with the electrodes and ionic conductivity suitable for practical application. Lab-scale lithium metal cells assembled with the CPEs and lithium iron phosphate (LFP) cathodes demonstrated specific capacities up to 125 mAh g^{-1} at 1C rate and could work for hundreds of cycles at ambient temperature.

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P14

PEEK-WC / nanosponge membranes as anode protective layers for rechargeable Li-O_2 batteries

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Nanosponges are innovative cross-linked cyclodextrin polymers nanostructured within a three-dimensional network [1]. An amorphous polyetheretherketone known as PEEK-WC and dextrin-based nanosponges are used to prepare flat sheet membranes. The presence of nanosponges in membrane changes PEEK-WC features. PEEK-WC/nanosponge membranes display very low oxygen permeability, fairly good ionic conductivity, high electrolyte uptake and assure suitable interfacial stability with Li metal.

For these properties, such membranes are used to protect highly reactive Li metal anode from oxygen cross-over and from side reactions due to oxygenated DMSO based electrolyte. Li-O_2 lab-scale cells are assembled with the membrane sandwiched between Li and separator soaked by electrolyte, with continuous oxygen flow of 3 ml/min at the cathode side. XRD, XPS and FESEM analyses demonstrate that membranes do not interfere with formation and decomposition of Li_2O_2. Membranes assure long cell cycle life at curtailed capacity and better capacity retention during cycling in full discharge/charge conditions.

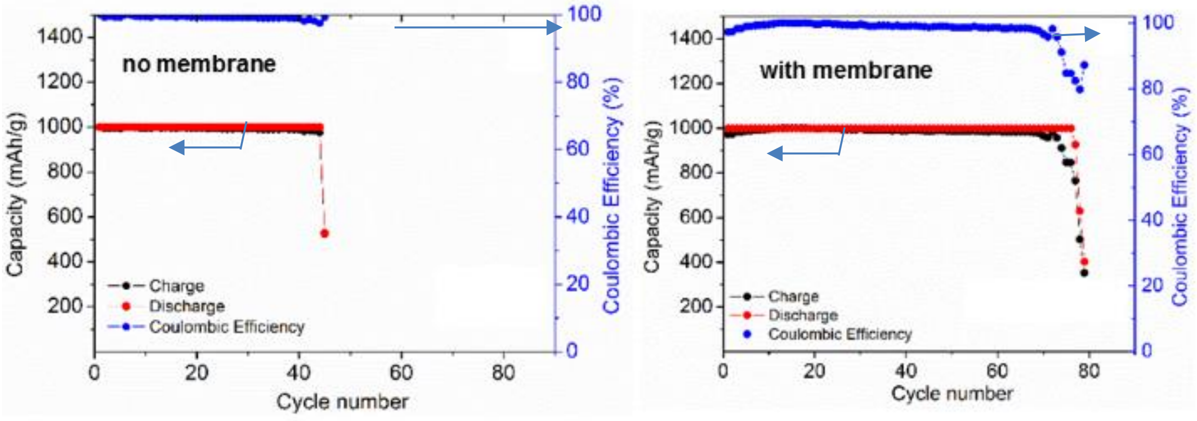

Figure 1: Capacity vs. Cycle number of Li-O_2 cells with unprotected Li anode (left) and protected Li anode (right).

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P15

Investigation on bio-derived hydrogel electrolytes for dye-sensitized solar cells

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Dye-sensitized solar cells (DSSCs) with water-based electrolytes are considered as one of the possible breakthrough towards DSSCs large-scale diffusion. If opportunely developed and optimized, aqueous solar cells can be considered a truly low impact photovoltaic device and no toxic components [1,2]. Moreover, the possibility of gelling the electrolyte into a polymeric matrix can reduce the leakage outside the device, thus increasing the long-term stability. Above all, bio-derived polymers appear promising being renewable and easy available with low cost [3].

In this contribution, the investigation on bio-derived hydrogel electrolytes for dye-sensitized solar cells is proposed. Moreover, the use of design of experiments (DoE) is demonstrated to be a useful chemometric technique for the concurrent investigation of a series of experimental factors that directly influence the photovoltaic performances of solar cells. Results obtained enlighten that a solid mathematical-statistical approach is fundamental to support the researchers and effectively drive the experiments towards the achievements of optimal operating conditions for aqueous solar cells.

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P16

Electrochemical reduction of CO_2 to formic acid – from bulk to supported Sn NPs electrocatalysts

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Converting carbon dioxide to value-added chemicals or fuels through electrocatalysis is an appealing approach to tackle both CO_2 emission and energy storage challenges. The process requires a suitable catalyst that can drive the electrochemical transformation towards desired products with minimal energy loss. Interestingly, SnO_2 can selectively reduce CO_2 to formate or formic acid. This catalytic system is very attractive because Sn is earth abundant and cheap, and the product, if separated out efficiently, can be used in formic acid fuel cells or as the hydrogen carrier. However, the process occurs at relatively high overpotentials (~0.7 V), potential at which SnO_2 catalyst suffers from deactivation, due to reduction to metallic Sn, or metal leaching. The present paper aims at the synthesis and characterization of Sn/SnO_2 NPs, and to explain the effect of the material morphology and selectivity when supported on next generation mesoporous carbon, e.g. nitrogen and sulfur doped mesoporous carbons [1]. This latter approach appears promising, as it has recently been observed that SnO_2 NPs supported on N-doped and S-doped mesoporous carbons show much high stability during operational condition.

Several synthesis conditions were tuned so that to obtain Sn/SnO_2 NPs different in size. All the synthesized materials were characterized by TEM and XPS spectroscopies. The catalytic activity was confirmed by cyclic voltammetry whereas selectivity to formic acid production was evaluated by rotating ring-disk electrode e by HPLC analysis in long lasting electrolysis experiments (Fig. 1).

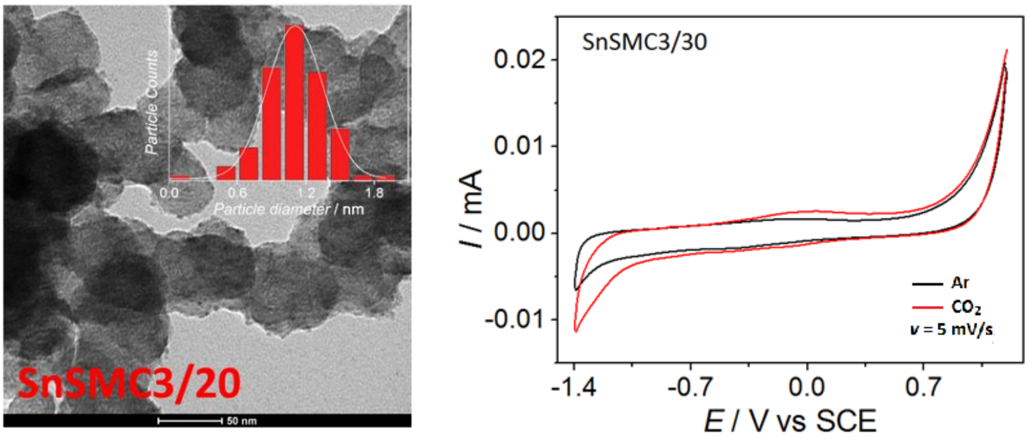

Figure 1. TEM image of Sn/SnO_2 NPs on sulfur doped mesoporous carbon and CV characterization.

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

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P17

High performing single-ion conducting block copolymer electrolytes based on poly(ethylene oxide) and specifically designed methacrylic sulfonamide

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In the field of polymer electrolytes, new single-ion conductors have attracted increasing interest in recent years, mainly because of their intrinsic safety and peculiar chemical structure that can be tailored as desired to display unique properties, such as $t_{Li}^{+} \approx 1$. Nevertheless, their practical application is still limited by low ionic conductivity (σ, far below 10^{-5} S cm^{-1} at 25 °C).

Herein, the preparation and characterization of new families of single-ion conducting copolymers based on the specifically designed lithium 1-[3-(methacryloyloxy)propylsulfonyl]-1-(trifluoromethylsulfonyl)imide (LiMTFSI) anionic monomer is described [1,2]. RAFT polymerization was employed to prepare well-defined anionic di- and tri-block copolymers comprising poly(LiMTFSI) and poly(ethylene oxide) blocks [1].

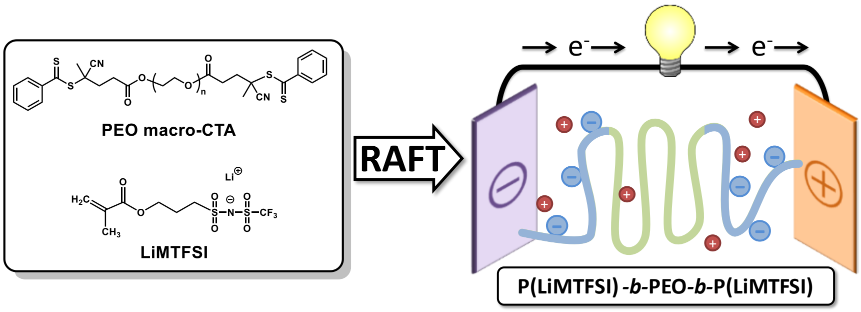

Figure 1: Schematics of RAFT polymerization of block copolymers [3].

Block copolymers were semi crystalline with a single T_g. They showed very high σ (≈ 10^{-4} S cm^{-1} at 70 °C), impressive $t^{+} \approx 0.91$ and wide 4.5 V electrochemical stability, combined with long lifetime up to 300 cycles and outstanding rate performance in $LiFePO_4$/Li cells at different temperatures.

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P18

Novel TPMA-modified ligands for atom transfer radical polymerization

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The design of new ligands is the most effective way to tune the reactivity of catalysts for atom transfer radical polymerization (ATRP). A copper complex with tris-2(pyridilmethyl)amine (Fig. 1a) is largely used for this polymerization process, mainly in aqueous media where it is stable even at acidic pH [1].

Herein, we present structural and electrochemical characterizations of 4 novel ligands in which the TPMA skeleton was modified by adding *m*-functionalized phenyl substituents (Fig. 1b) [2]. Their Cu complexes had more positive standard potentials (*i.e.* lower reducing power) than $[Cu^{II}TPMA]^{2+}$ under identical conditions. However, comparable results were obtained in electrochemically mediated ATRP (*e*ATRP) of methyl methacrylate in DMF. Similarly, *e*ATRPs of oligo(ethylene glycol)methyl ether methacrylate (OEOMA) and methacrylic acid (MAA) in water were fast and well-controlled (Fig. 1c,d).

The relatively low activity of these catalysts was found to be beneficial for highly reactive systems, where they facilitate polymerization control. Different synthetic modifications of TPMA skeleton can be envisioned as a useful approach to influence polymer growth or suppress harmful side-reactions.

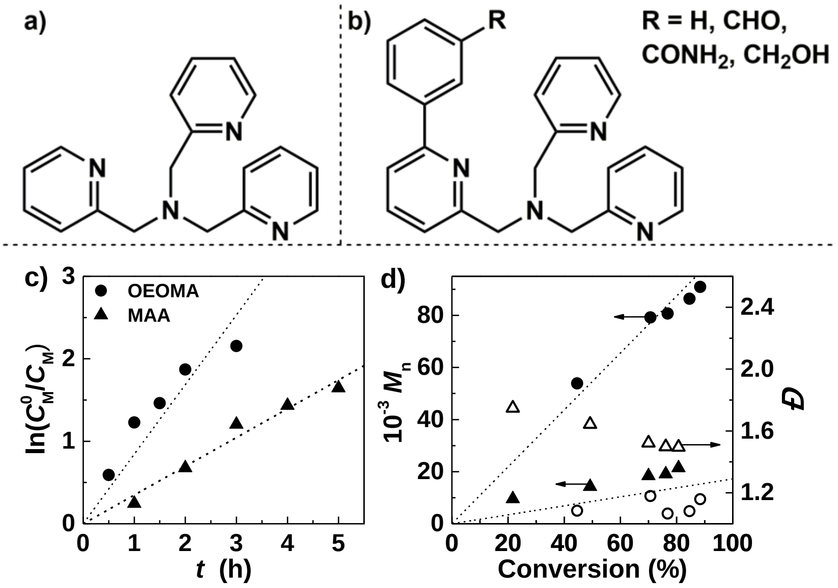

Figure 1: chemical structures of a) TPMA, b) TPMA-modified ligands. c) Kinetic plot and d) molecular weights and dispersity evolution vs. conversion, in *e*ATRPs of OEOMA (20% vol.) and MAA (10% vol., pH 0.9) in water, r.t.

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P19

Electrostatics vs. self-assembly

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In this work, we report the assembly of a new class of compounds based on naphthalenediimide (NDI) that form helical nanotubes in nonpolar solutions and in the solid state. They are simple to prepare, and possess a uniform core with the potential to bind a variety of guests and display externally a range of side chains that currently are derived from α amino acid residues. If the side chains are able to form hydrogen bonds, the NDI species may form helical nanotubes, otherwise the supramolecular structure is inhibited.

The electrochemical and photophysical study of the above species was aimed to investigate their behaviour following the introduction, via electrochemical reduction, of negative charges into the NDI core assessing in particular (i) the stability of the supramolecular structure and (ii) the possibility to switch its disassembling via an electrochemical stimulus.

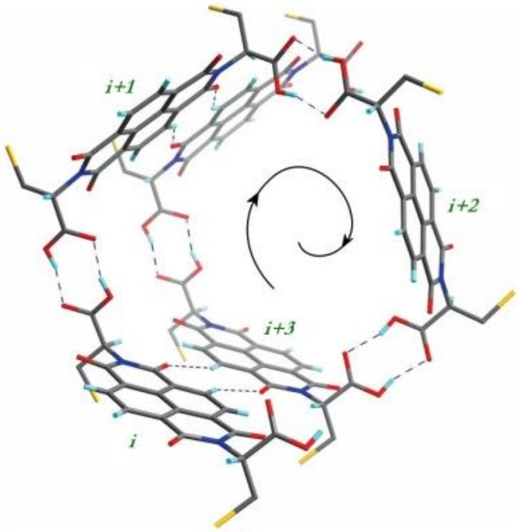

Figure 1: Supramolecular structure through hydrogen bond [1].

Our compounds have been studied not only with electrochemical techniques but also with spectroelectrochemical studies (absorption and emission); for the first time these compounds have been studied with Cicular Dicroism (CD) coupled with absorption spectroelectrochemistry.

[1] G. D. Pantoş, P. Pengo, and J. K. M. Sanders, *Angew. Chem. Int. Ed.* **46** (2007) 194-197.

P20

Carbon fibers from waste cellulose for Li-ion batteries

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Reversible cycling of lithium (Li) metal anodes with an organic electrolyte often results in non-uniform passive film formation on the electrode surface. This effect causes dendrite growth of Li metal, which detrimentally affects cell performance and safety upon long-term charge/discharge cycling. Advantageously, electrochemical intercalation of lithium ions (Li^+) into various carbonaceous materials can solve these issues. Precursor and preparation method are controlling the structure and orientation of mesostructured carbon, which is one of the major factors governing the intercalation of Li^+. Recently, the scientific community reconsidered disordered carbon materials. They may store Li^+ differently from e.g. graphite, which provides evident advantages in some specific applications. So far, many anode materials have been investigated including graphitic/amorphous carbons, nitrides, tin oxides and tin-based alloys. However, according to recent literature reports, carbon is still the dominant material, which enlightens the importance of carbonaceous anode materials in the field [1,2].

In this study, the key innovation is the use of micro-fibrillated carbonised cellulose. Controlled pyrolysis in inert atmosphere was adopted for carbonization of cellulose waste. Constant current charge/discharge cycles and Li intercalation on carbon structural orientation are thoroughly investigated and reported. Carbon fibers demonstrated remarkable galvanostatic cycling with $LiPF_6$-based electrolyte, delivering specific capacities of > 230 mAh g^{-1} at ambient temperature at a cycling rate of 1C, very stable for several hundreds of cycles. Noteworthy, the battery components used can be almost completely recovered after operation. Such an approach opens up a new way of thinking for advanced sustainable batteries.

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[3] L. Zolin, J. R. Nair, D. Beneventi, F. Bella, M. Destro, P. Jagdale, I. Cannavaro, A. Tagliaferro, D. Chaussy, F. Geobaldo, and C. Gerbaldi, *Carbon* **107** (2016) 811-822.

P21

Electrodeposition of Ag-Rh alloys

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The Ag-Rh system is characterized by the presence of a large miscibility gap, especially by a total insolubility of Rh in Ag in the solid state. Nonetheless, the preparation of Ag-Rh nanoparticles by the polyol method has been recently reported [1]. We explore here the possibility to obtain a metastable $Ag_{50}Rh_{50}$ alloy by electrodeposition, in analogy to Cu-Rh alloys [2].

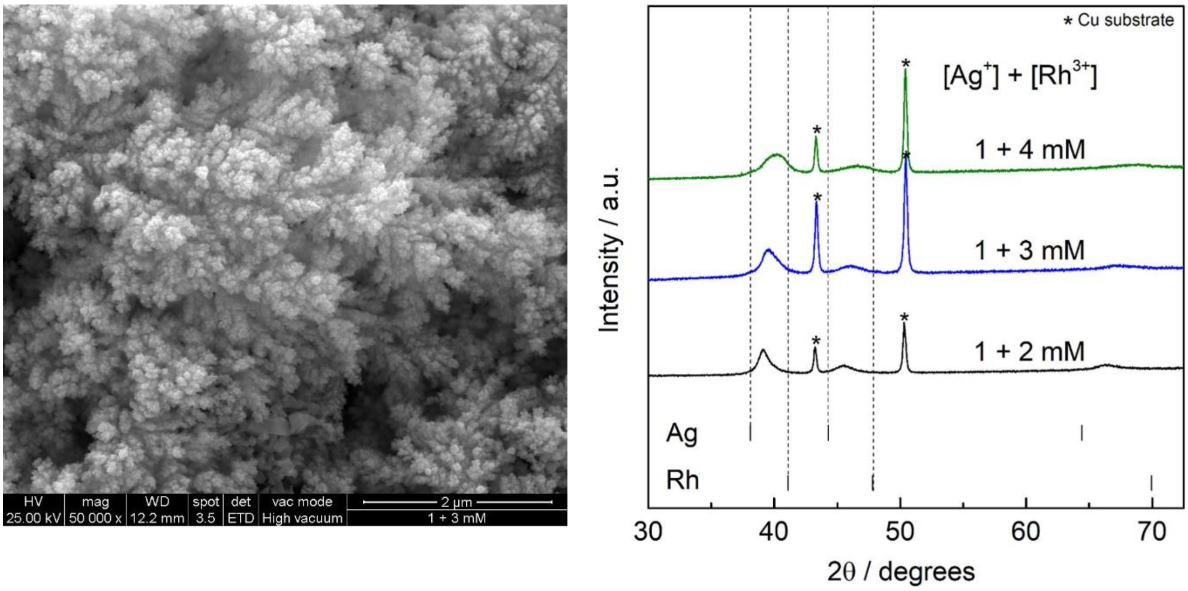

Figure 1: SEM image of typical morphology of Ag-Rh deposit (left) and X-ray diffractograms of selected compositions (right).

SEM investigations of an Ag-Rh deposit show a spongy material made of aggregates of submicron crystals (Fig. 1, left). The diffraction peaks are located between typical reflections of pure Ag and Rh, and shift with bath composition (Fig. 1, right). The dependence of lattice parameter on EDS composition is close to Vegards' law. Cyclic voltammograms are performed on Ag-Rh alloys with the aim to clarify their ability to absorb hydrogen, in analogy to Pd, as reported in literature [1, 3]. Preliminary results do not confirm literature claims.

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P22

Titanium-based oxide nanoparticles as electrode and electrolyte components in PEM Fuel cells and Electrolyzers

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The aim of this work is the development of advanced materials for the production and the conversion of hydrogen in order to reduce costs, improve efficiency, performance and durability of the final device, whether electrolyzer or fuel cell, both based on a polymer electrolyte membrane (PEM).

Titanium-based oxide nanoparticles are considered very attractive, thanks to their tunable physical-chemical properties [1]. Here we propose a study about Sulfated Titania oxide (S-TiO_2) and $CaTiO_3$ perovskite nanoparticles (CTO).

S-TiO_2 was used as additive in Nafion membranes. It was prepared by a sol-gel template method and characterized by means of X-ray diffraction (XRD), Scanning electron microscopy (SEM), Specific surface area, Thermogravimetric analysis (TGA) and Ionic exchange capacity (IEC). Hydration properties of composite membranes were also evaluated and their performance as electrolytes in hydrogen fuel cells was carefully investigated. Polarization curves and impedance spectra, recorded at low humidification level (31%RH) will be shown.

$CaTiO_3$ perovskite nanoparticles were originally considered as both co-catalysts and membranes' additive. CTO was prepared through sol-gel methods [2] and characterized by XRD, TGA and infrared spectroscopy. Its electrochemically active surface area and performance towards O_2 evolution/reduction reaction were evaluated by rotating disk electrode (RDE) measurements.

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P23

Carbon from waste: pyrolysed hazelnut shells as efficient active electrode materials for Li-/Na-ion batteries

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Looking beyond the current "take, make and dispose" extractive industrial model, the circular economy is restorative and regenerative by design. Relying on system-wide innovation, it aims to redefine products and services to design waste out, while minimising negative impacts. Food industry, paper industry and agriculture produce by-products and waste that currently are not properly exploited in both environmental and economic terms. In order to reduce and/or recycle and re-evaluate such waste, new processes can be envisaged and developed that may ensure an innovative use of these materials (waste), outside the same product sector. For example, you can think of processes based on new approaches, which harness this waste through the development of reuse and recycling chains in the energy sector. Indeed, one of the possible strategies concerns the preparation of electrodes and electrolytes to be implemented in electrochemical devices (solar cells, batteries, supercapacitors) made from the abovementioned waste, after appropriate functionalization and/or treatment [1].

In this work, we report our very recent results about the synthesis of carbonaceous materials from the hazelnut shell bio-waste. We show how the carbonisation temperature influences the structural-morphological features of the resulting materials and their electrochemical behaviour in terms of lithium or sodium ion reversible storage. In particular, high-temperature carbonization (~2000 °C) of compactly packed cellulose egg cells in the rigid hazelnut shell leads to a highly graphitic dense carbon material with low specific surface area, which is particularly advantageous in Li-ion cells due to limited SEI formation, thus lower initial capacity loss. Conversely, hard carbon materials produced by low-temperature pyrolysis (~800 °C) possessed clear turbostratic structure with large amorphous domains alternated to sufficiently separated micro graphene-like sheets in the semigraphitic domains to act as an ideal anode material for Na-ion cells. Excellent reversible capacities were obtained in both Li- and Na-based lab-scale cells along with very stable cycling at ambient temperature. An almost ideal capacity retention is observed even after 500 reversible charge/discharge cycles. Furthermore, all of the carbonaceous materials developed show a remarkable rate performance with ~99% retention after cycling at high current rates of up to 5C.

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P24

Observing single exocytosis events from β pancreatic cells

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The use of microelectrodes for the real time detection of discrete exocytosis events from single cells is a well-established approach for the study of cell physiology and metabolism. In fact, the "artificial synapsis" made of a micro (or nano) electrode faced on top of a single cell allows to monitor the stimulated release of a defined substance (e.g., a neurotransmitter or a hormone) by applying a constant potential while recording the current intensity [1].

Among the several cases considered so far, the study of exocytosis from β-pancreatic cells is of particular importance for investigating the mechanisms behind diabetes mellitus, a pathology that is one of the main causes of death, particularly in western countries. Diabetes is due to the lack or insufficient release of the hormone insulin from β-cells in response to increased blood glucose concentrations.

After the first, seminal studies by Kennedy [2], no reports have appeared in the literature regarding the detection of insulin or 5-hydroxytryptamine (serotonin), the two being co-released by exocitosis. The main obstacles are both the sluggish kinetics of insulin oxidation at an electrode and the very low concentration of both molecules in exocytosis vesicles.

In this poster we show the first encouraging results obtained studying the release of 5-HT by single (or small groups of) β-pancreatic living cells by means of Pt and Au microelectrodes. A constant potential is applied and, after a stabilization period, a stimulating solution of glucose or KCl is added. Afterwards, the observation of current spikes indicates single exocytosis events.

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P25

Novel photosynthetic microbial fuel cells (PMFCs) for efficient wastewater treatment and microalgae production

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In this work, we propose a novel dual-chamber PMFC for cost-effective wastewater treatment and efficient production of microalgae, useful for the concurrent production of biodiesel and other co-products, as integrators, pigments and nutraceutical substances of commercial value. It includes: i) bio-anode and biocathode composed by innovative electrocatalysts based on graphene and graphene related materials (GRMs); ii) a ion exchange membrane (IEM), based on Polybenzimidazoles, more cheaper and more performing than Nafion^{TM}; iii) different families of microalgae, as *Scenedesmus acutus* and *Ematococcus pluvialis*.

The work aims at improving the PMFC performances, in order to enhance the treatment efficiency, the power output and the algae growth rate. This was obtained by an optimal choice of the microalgae, a careful analysis of the involved electrochemical reactions and by the use of materials, innovative in terms of compatibility with the biological environment, cost and electrochemical and functional performances.

P26

Development of solid-state electrolytes by anion substitutions in lithium borohydride

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Solid-state electrolytes could improve the safety and capacities of Li-ion batteries. Less than 10 years ago, complex hydrides (e.g., $LiBH_4$) were suggested as solid-state electrolytes [1]. $LiBH_4$ shows different polymorphs, the stable phase at room temperature is orthorhombic and it has a low ionic conductivity. However, the hexagonal phase, which is stable at temperatures above 110 °C, has a remarkable high ionic conductivity ($\sim 10^{-3}$ S cm^{-1} at 120 °C). For real application in batteries, high ionic conductivities at room temperature are required. Many studies showed that substitution of BH_4^- anion with halide or complex anions can stabilise the hexagonal structure at lower temperatures or can provide to the formation new compounds, leading to high ionic conductivity at room temperature [1].

In this work, the novel complex hydrides to be used as solid-state electrolytes have been investigated. Mixtures of $LiBH_4$ and Li_2NH have been prepared by ball milling, showing the formation of a new compound, $Li_5(BH_4)_3NH$, and its structure has been confirmed by DFT. Electrochemical impedance spectroscopy measurements shown a Li-ion conductivity close to 10^{-6} S·cm^{-1} at room temperature for this compound [2].

Increasing the number of mixed components, by entropy effect, the presence of multiple anions in the structure is expected to promote the mutual solubility, leading to highly substituted complex hydrides. An extensive study of complex ternary and quaternary systems containing $LiBH_4$, lithium halides and $LiNH_2$ has been performed. Mixing two and three lithium halide with $LiBH_4$, in equimolar concentration, two novel solutions, with the hexagonal structure of $LiBH_4$, have been stabilized with a molar composition $Li(BH_4)_{0.39}Br_{0.33}Cl_{0.28}$ and $Li(BH_4)_{0.36}Br_{0.28}Cl_{0.06}I_{0.31}$, respectively. The study of the thermodynamic of these systems allowed the understanding of phases stability as a function of composition and temperature. Further studies in this field are expected to develop and improve the design of novel electrolytes for all solid-state batteries.

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P27

Li-ion Cell Anode using 2090-T8 Al Alloy

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This work contributes to solving the problem of the fast capacity decay of pure aluminium anodes for lithium batteries [1,2]. The phase transformations during lithium insertion and lithium extraction have been studied and the electrochemical behaviour of pure aluminium and 2090-T8 aluminium-copper-lithium alloy powders has been compared (Fig.1). The chemical composition of the alloy, which was verified by means of mass spectrometry (SPECTRO LAB S), was the following: 2.72 Cu, 2.07 Li, 0.12 Zr, 0.090 Fe and 0.10 Si (mass percentage). It has been found that, at low current density, the rapid capacity decay of pure aluminium is prevalently due to the incomplete reversibility of the lithiated phase, Li_9Al_4, during the delithiathion of the anode. Partially reversible Li_9Al_4 is also present in the 2090-T8 aluminium alloy, together with fully reversible crystals of the Al_5CuLi_3 phase. In this case, the anode capacity fade after the second galvanostatic cycle is modest.

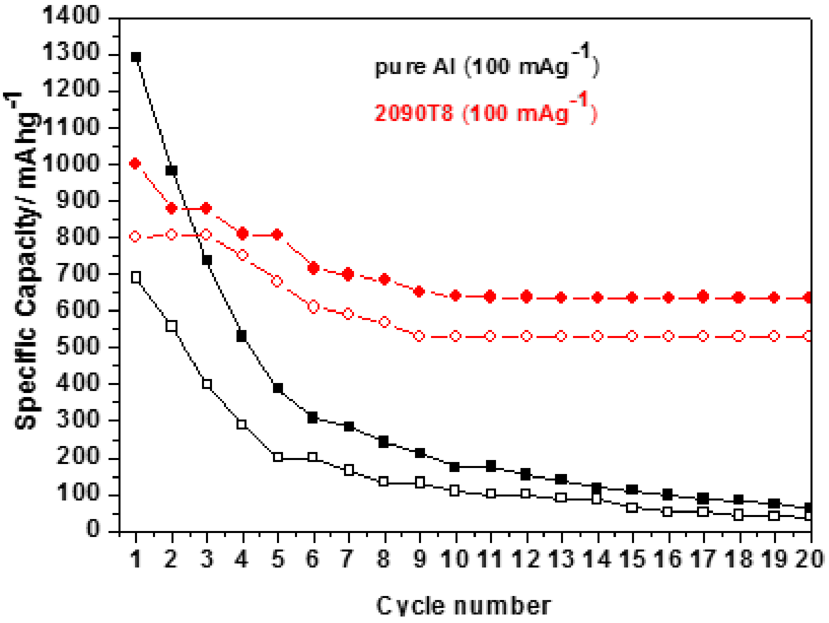

Figure 1: Capacity profiles of a pure Al (square points) and a 2090-T8 alloy (diamond points) anode at a constant current density of 100 mA g^{-1}.The solid symbols correspond to cell charging (anode lithiation) and the open symbols refer to cell discharging (anode delithiation).

Because of its size and composition, the ternary phase Al_5CuLi_3 performs a buffering function for the introduction of Li during anode charging, thus inducing cycling stability.

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P28

Photocured polymer electrolytes for lithium-based batteries

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We all desire a long-lasting, non-explosive, flexible and small lithium-ion battery (LIB) for our portable electronic devices and (future) electric vehicles. The use of a solid polymer as electrolyte, instead of a flammable solvent, is currently the most promising solution for thinner and safer LIBs. Poly(ethylene oxide)-based polymers (PEO) are widely used, even commercially, thanks to their good ability to transport lithium ions at temperatures over 60 °C [1].

In our Lab, we focus on the structuring of classic −EO− based backbones by photo-polymerization, a fast, cost-effective and solvent-free technique. Solid polymer electrolytes (SPEs) based on different monomers/oligomers are prepared. By incorporating high amounts of plasticizers [2,3] and lithium salts, outstanding ionic conductivities are obtained ($\sigma > 10^{-4}$ S cm^{-1} at 20 °C) along with wide electrochemical stability window (>5 V vs. Li^+/Li) as well as good interfacial stability. Besides, SPEs have remarkable morphological characteristics in terms of homogeneity, flexibility and robustness (Fig. 1).

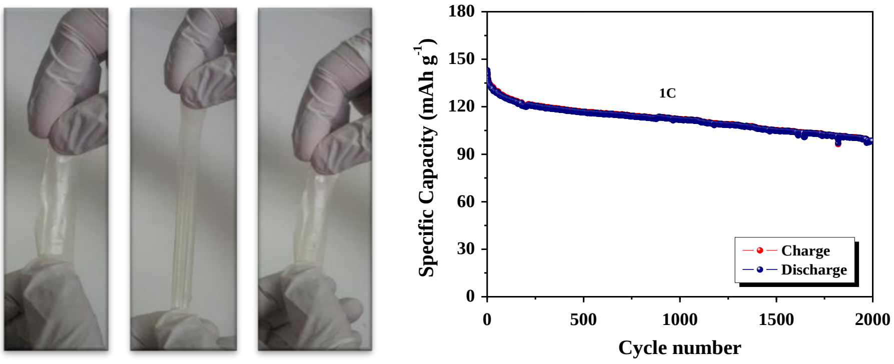

Figure 1: Appearance of a cross-linked polymer electrolyte (left) and long-term cycling at ambient temperature in $LiFePO_4/Li$ lab-scale polymer cell (right).

All-solid lithium-based polymer cells show very good cycling behavior in terms of rate capability and stability over a wide range of operating temperatures, which confirms the promising prospects of photocured polymer electrolytes for practical application at ambient/sub-ambient temperatures.

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

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P29

Preconcentration effect of ion-exchange polymers in lead electroanalytical determination

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In the last couple of decades, electrode coatings based on proton conducting polymers were extensively adopted in the electroanalytical field for the preparation of modified electrodes to be used as highly performing sensors. These devices offer several advantages: they reduce adsorption phenomena, suppress the inclusion of interfering species, protect the electroactive surface from passivation and fouling, act as pre-concentrating agents towards selected analytes, modify the process kinetics and diffusion yielding to high sensitivity and selectivity [1-2].

In this context, in this presentation, we would like to show some results on the use of sulphonated poly(aryl ether sulphone) (SPAES) [2-3], an innovative polymer in this field, whose properties can be appropriately designed, tailored and used in the preparation of modified electrodes for electroanalytical applications. Since connectivity and morphology of the modifier polymer are critical factors in controlling conductivity, stability, active surface and diffusion mechanism of the modified electrode, much attention is devoted to the polymer casting conditions on the glassy carbon support. In particular, the effect of the use of different casting solvents [dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), N-methylpyrrolidone (NMP)] is evaluated. On the other hand, polymers prepared with different IEC (Ion exchange Capabilities) are also tested. A Principal Component chemometric Analysis is also employed for the results rationalization.

Finally, the performances of the different membranes are evaluated in the electroanalytical determination of lead, focusing on the analyte adsorptive preconcentration capability of the casted polymers. For this purpose, linear sweep voltammetry with and without the stripping preconcentration step is employed and the best conditions for lead determination are discussed.

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P30

Electrodeposition and characterization of SnS-reduced graphene oxide composite

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Photoelectrochemical water splitting is promising for hydrogen production through charge carriers using appropriate semiconductor photoelectrodes. Thus, diverse materials have been studied as photoanodes and photocathodes in order to carry out one or both of two the water splitting half reactions [1]. In this way, SnS (p-type semiconductor) is a promising material to be used in these systems due to its optimal band gap (1–1.3 eV), non-toxicity nature and low cost [2]

In this study, the electrosynthesis and characterization of SnS-ERGO (electrochemically reduced graphene oxide) composite is shown. The synthesis is carried out in two electrochemical steps: Electrochemical reduction of graphene oxide (GO) from a GO suspension on a FTO electrode followed by the electrodeposition of SnS from a $SnSO_4$ and $Na_2S_2O_3$ acid solution. The effect of electrodeposition temperature and solution composition have been studied. The characterization was carried out through SEM images, EDS analyses, XRD, and photoelectrochemical measurements.

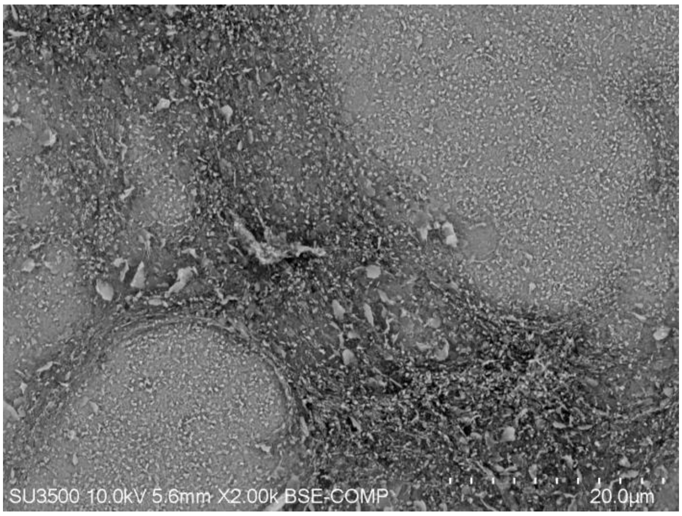

Figure 1: SEM image of a SnS-ERGO composite electrodeposited at 70°C. The light-grey zone corresponds to the SnS film. The darker zone revels the presence of ERGO in the SnS film.

Acknowledgements: This study was supported by Fondecyt (Chile) project 1160952.

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P31

Electrochemical conversion of carbon dioxide to formic acid: on the road to applicative scale

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To curb the negative effect of carbon dioxide as a greenhouse gas, an interesting approach is the utilization of Carbon Capture and Conversion (CCC) technology, which is focused on the use of CO_2 waste as a feedstock to produce added-value products by using the excess electric energy from renewable source [1].

In this context, electrochemical reduction of CO_2 is considered one of the more attractive pathway to convert CO_2, because the products can be selectively controlled by changing the operative conditions of the electrolysis. In the last years, an increasing attention has been devoted on the electrochemical conversion of CO_2 to formic acid in water [2,3]. The main hurdle of the reduction of CO_2 from water solution is the low CO_2 solubility in water. In this work, the effect of some operating parameters, including pressure, current density, and flow rate, on the conversion of CO_2 at tin flat cathodes to formic acid was studied using a pressurized filter-press cell with a continuous recirculation of the solution (0.9 L).

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P32

Silicon nanoparticles incorporated in graphene sheets for high capacity anode in Li-ion batteries

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One of the major challenge today is the development of an energy storage system able to provide high efficiency, safety and inexpensiveness. Rechargeable lithium batteries could play a key role but, at present, their use is mainly restricted to the field of electronic portable devices with a few applications in electric mobility. To extend their use further improvements are required in terms of energy density and cycle life performance.

Silicon represents a feasible candidate for the next generation Li-ion batteries. The main advantages are related to high capacity values (≈4200 mAh g^{-1} for the fully lithiated alloy $Li_{4.4}Si$) and low discharge potential (0,37 V vs. Li/Li^+). Furthermore, it is abundant and non-toxic.

Unfortunately, many issues prevent its practical application in lithium devices. Specifically, lithiation/de-lithiation processes are associated with a large volume expansion-contraction changes (> 300 %) that can induce cracks and as consequence pulverization of the electrode, which eventually leads to rapid capacity fading in few cycles. Nanometrization of silicon particles or their encapsulation in an inactive matrix are some of the commonly adopted strategies to control the volumetric changes, reduce the lithium diffusion length and prevent the agglomeration of silicon particles, thus improving the performance of the electrode in terms of both life and rate capability [1].

In this context, graphene represents a suitable substrate to host active nanoparticles such as those of silicon, thanks to its unique chemical and physical properties such as high conductivity, mechanical flexibility and chemical stability [2,3].

In this communication, we will present the results related to a silicon/graphene composite prepared by a mechanochemical approach. The obtained composite is investigated in terms of structure and morphology. We will present its electrochemical behavior studied by potentiodynamic cycling with galvanostatic acceleration (PCGA) and galvanostatic measurement (CG).

Acknowledgements: This work has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No. 696656-GrapheneCore1.

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P33

Electrochemical characterization and electroanalytical applications of RGO-AuNPs hybrids

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A novel synthetic route for the synthesis of gold nanoparticles (AuNPs) modified graphene electrodes has been developed: Reduced Graphene Oxide (RGO) sheets are functionalized with pyrene linkers acting as growing sites for gold nanoparticles (AuNPs) of different dimensions (approximatively 5, 10 and 20 nm). The Au surface is functionalized with oleylamine or 3,4-dimethylbenzenethiol as capping agents. The hybrid material is deposited onto Carbon Screen Printed Electrodes (C-SPEs) for a deep physico-chemical and electrochemical characterization, using Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) measurements.

The role played by every single hybrid counterpart has been investigated, showing a synergistic effect, which is responsible of the enhancement of the system properties. The charge transfer from gold nanoparticles to graphene, assisted and stimulated by the pyrene linker, seems to be the key point to understand the peculiarities of this innovative material.

The as prepared RGO-AuNPs hybrids have been used in the electroanalytical detection of both inorganic and organic species (arsenic, H_2O_2, dopamine), showing promising results in terms of sensitivities and detection limits. In particular, regarding the detection of the neurotransmitter dopamine by means of Differential Pulse Voltammetry in Phosphate Buffer Solution, a LOD of (3.3 ± 0.2) ppb has been reached, comparable with other electroanalytical results in the literature and in accordance with the benchmark for this molecule [1]. For arsenic detection, the hybrid devices show increased performances in comparison with bare gold or gold NPs, also allowing speciation between arsenic (III) and (V), appropriately adjusting the experimental conditions. In the case of H_2O_2, the hybrid devices display high electrocatalytic activity and fast electron-transfer kinetics, representing an ideal platform for developing oxidoreductase-based electrochemical biosensors as well as for detecting H_2O_2 in real samples.

Acknowledgements The authors acknowledge the MIUR National Project PRIN 2012 (prot. 20128ZZS2H).

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P34

Driving the selectivity of electrochemical CO_2 reduction to formic acid: synergic effects in a C-based heterostructure

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CO_2 concentration in the atmosphere increased from 320 ppm in the early 60's, to more than 400 ppm in 2014, with an exponential trend never observed before. It is thus not surprisingly that recently a lot of efforts were focused in the research and improvement of new/existing materials, catalysts, methods, and technologies, able to capture and to convert CO_2 in useful products.[1] The design of new electrocatalysts that reduce CO_2 in a selective and efficient fashion is a key step for future exploitation of this technology.

In this work we present how the combination of different building blocks in a single nanostructure might be a good strategy to achieve a good selectivity in the CO_2 reduction process.

Combining the unique physico-chemical properties of functionalized f-MWCNTs and nanocrystalline cerium dioxide (CeO_2) we revealed faradaic efficiency for formic acid production as high as 55% at an overpotential as low as 0.02V in acid solutions. These performances have been possible by the *in-operando* formation of partially reduced ceria (CeO_2-X), responsible of an increased CO_2 adsorption and a more efficient electron transfer at the surface.[2] The fundamental role of MWCNTs to increase electrons availability at the semiconductor surface was also evidenced.[3] In the nanocomposite, where the MWCNTs are covered by nanometric-thick CeO_2, the oxide layer is thin enough to allow efficient charge transport through it and fast electron transfer at the surface where CO_2 is adsorbed.

The interconnection of the various components has been shown to be fundamental for the efficient CO_2 reduction to formic acid with this new metal-free nanocomposite, and opens new possibilities in the design of optimized electrocatalytic materials.

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P35

Facile synthesis of SnO_2/g-C_3N_4 hybrid compound for Li-ion anode applications

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Tin-based materials, especially tin oxide, have been widely investigated as potential graphite substitutes in the anodes of Li-ion batteries, because SnO_2 anode shows higher theoretical capacity in comparison to graphite anode. Tin dioxide is also inexpensive, exhibits low toxicity and is environmentally friendly [1]. Unfortunately, during the lithiation process (i.e., conversion and alloying reaction), tin dioxide suffers from a drastic volumetric expansion, that induces surface cracking accompanied by an electrical contact loss with the current collector and subsequent capacity fading [2].

In this work, we synthetized SnO_2/g-C_3N_4 (graphitic carbon nitride) composites via a facile solid-state method, with the aim of studying and identifying the effect of carbon nitride on the cycling performances of the oxide and to optimize the lithium storage capability of the composite. For this reason, all the materials have been morphologically and electrochemically characterized in order to investigate the influence of crystal structure, particle size, morphology and surface area on the cell cyclability. The reported figure shows the first galvanostatic cycling data regarding the SnO_2/g-C_3N_4 hybrid compound as an anodic active material economically feasible and industrially scalable. The capacity values are markedly higher than those for a pure SnO_2 sample.

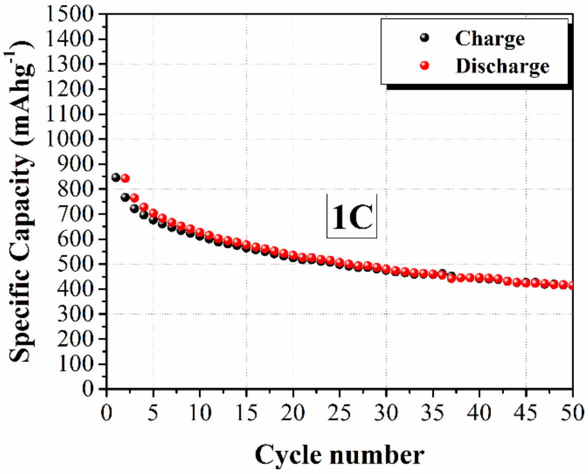

Figure 1: Specific Capacity at 1C for the SnO_2/g-C_3N_4 hybrid compound.

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P36

Enzymatic Electrochemical Biosensor Based on a 2D-Covalent Triazine Framework

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Ordered two dimensional porous materials have been attracted a lot of attention due to their huge potential applications. Several nanoporous frameworks have been obtained such as Zeolites, Metal Organic Frameworks (MOFs) or Covalent Organic Frameworks (COFs). While researchers have studied these materials for energy storage, optoelectronics or even drug delivery, just few studies have been reported on biosensor applications. In addition, MOFs have just been used as electrochemical substrate [1, 2], however, to the best of our knowledge, no study have been reported yet using COFs as a biosensor matrix.

In this study, we have carried out synthesis and characterization of triazine-based COF (CTF-1), and the subsequent application on an electrochemical enzymatic biosensor. Electrochemical impedance spectroscopy measurements indicated that the charge transfer resistance (Rct) of gelatine-CTF-1 modified electrode was nearly 20% lower than that the standard gelatine modified electrode (Figure 1). This result shows the conductive nature of the synthesized CTF-1. On the other hand, chronoamperometric measurements were carried out showing that the gelatine-CTF-1-SOD electrode has an amperometric response 25% higher respect to the standard. These findings clearly show that CTF-1 is a promising candidate as electrochemical enzymatic biosensor component.

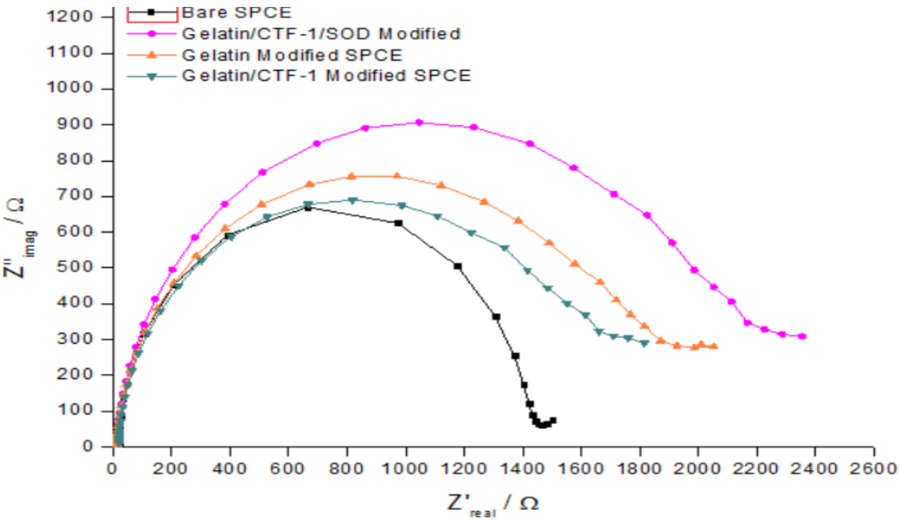

Figure 1: EIS spectra.

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P37

Electrochemiluminescent detection of Sarcosine using nanostructured Cerium Oxide for early diagnosis of prostate cancer

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Recently, Sarcosine has been identified as a key metabolite marker for the monitoring and early diagnosis of metastatic prostate cancer (PCa). Electrochemiluminescence (ECL) is the most commonly used transduction methodology for early PCa diagnosis for both research and commercial applications [1].

In this work, we describe a method for the quantification of Sarcosine, obtained by ECL approach, in which Sarcosine acts as co-reagent in a $Ru(bpy)_3^{2+}$ ECL process. In fact, Sarcosine is a secondary amine, capable of generating ECL according to the "oxidative-reduction" strategy. As electrode, we used polycrystalline ceria films (20 nm thick), prepared ex-situ by nonreactive magnetron sputtering of a CeO_2 target. Here, we also demonstrated that CeO_2 is far superior electrode material for ECL application compared with the commercial GC electrode [2]. Thanks to this approach we were able to detect sarcosine in Phosphate Buffer (pH=7) solutions at different concentration (50-5000 μM).

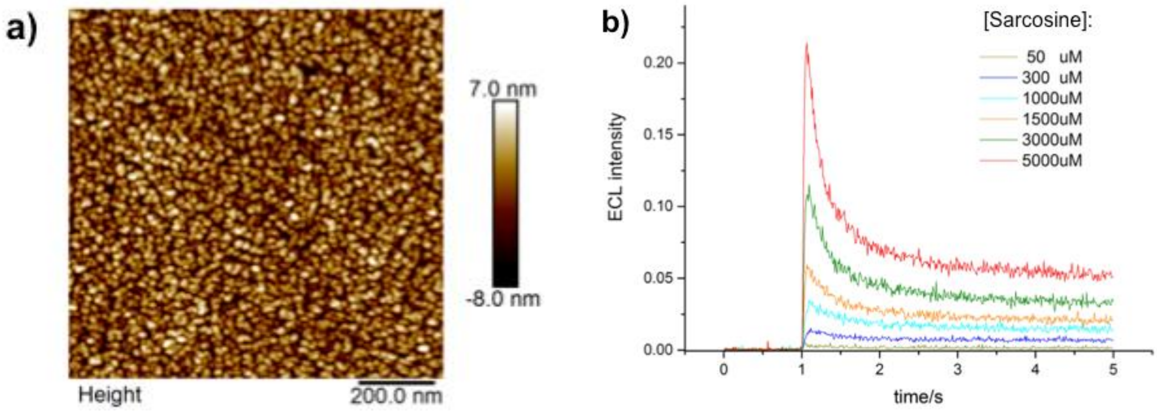

Figure 1: a) AFM image of CeO_2 on Glassy Carbon; b) ECL signal recorded using nanostructured Ceria after addition different concentration of Sarcosine (50-5000 μM).

[1] G. Valenti, E. Rampazzo, E. Biavardi, E. Villani, G. Fracasso, M. Marcaccio, F. Bertani, D. Ramarli, E. Dalcanale, F. Paolucci, and L. Prodi, *Faraday Discuss.* **185** (2015) 299-309.
[2] G. Valenti, A Fiorani, H. Li, N. Sojic, and F. Paolucci, *ChemElectroChem* **3** (2016) 1990-1997.

P38

Carbon wrapped black titanium oxides for the effective suppression of polysulfides shuttling process

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Lithium sulfur (Li/S) - a post Li ion technology - offers a high-energy density storage system. But the insulating nature of both sulfur (S_8) and Li_2S, and the solubility of intermediate Lithium polysulfides (LiPS) seriously prevent the capacity retention and high rate capabilities [1, 2]. Conductive Magneli Phase Ti_nO_{2n-1} decorated carbon matrices are synthesized to host sulfur for long life Li-S batteries. The longevity and greater capacity retention of so obtained sulfur cathodes can be referred to both physical confinement and chemical bonding of LiPS. The experimental characterizations are speaking of strong Magneli Phase Ti_nO_{2n-1} interaction with LiPS supported by surge in local concentration of LiPS as a result of the absorptivity of carbon matrix. These cathodes allowed working at low electrolyte to sulfur ratio to target high gravimetric and volumetric capacities in comparison to their highly porous carbon counterparts. The assembled cells from as obtained cathodes exhibited the initial discharge capacity of 1100 mA h g^{-1} at 0.1 C and maintained its reversible capacity to 520 mA h g^{-1} at 0.2 C for more than 500 cycles. The molecular interaction of LiPS with Magneli Phase Ti_nO_{2n-1} is also examined that actually results in suppression of polysulfides shuttle.

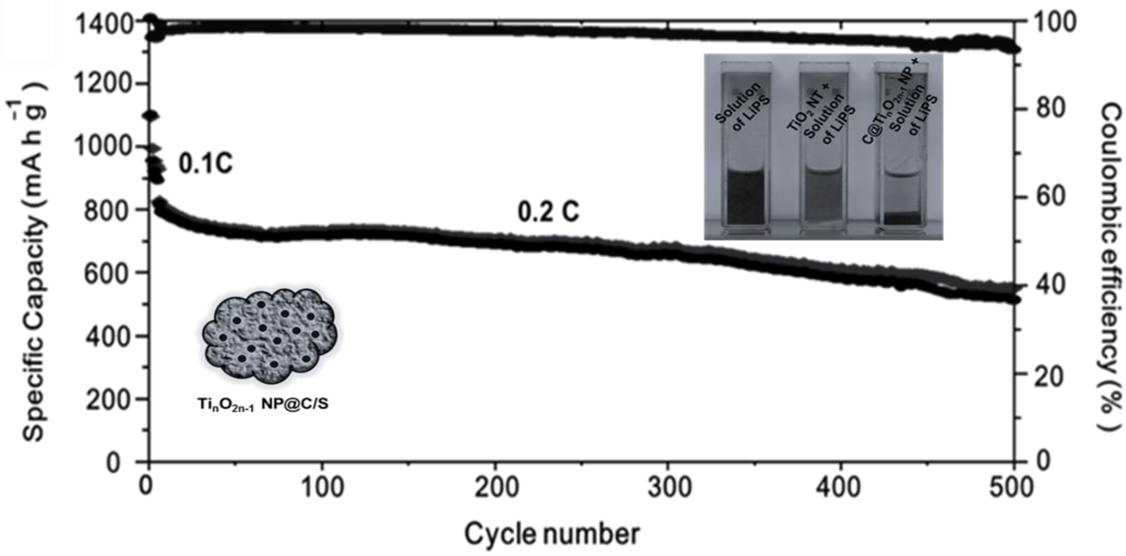

Figure 1: Effective containment of polysulfides by Carbon wrapped black titanium oxides for long Galvanostatic charging and discharging.

[1] A. Manthiram, S. H. Chung, and C. X. Zu, *Adv Mater.* **27** (2015) 1980-2006.
[2] S. Evers and L. F. Nazar, *Acc. Chem. Res.* **46** (2013) 1135-1143.

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