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Comune di Padova

Società Chimica Italiana
*Divisione di Elettrochimica*

# Giornate dell'Elettrochimica Italiana
# GEI 2019

## *Program and Book of Abstracts*

8-12 September 2019 Padova, Italy

## WELCOME AND PREFACE

You are welcome to the **Giornate dell'elettrochimica Italiana - GEI 2019** meeting in Padova, Italy, (8 - 12 September 2019). The GEI 2019 is the annual meeting of the Electrochemical Division of the Italian Chemical Society and this year it is held in the congress center inside the magnificent Botanical Garden of Padova. The University of Padova is the second oldest university in the western world, and to mark the continuity between academic culture and technological progress, the scientific theme of the meeting is Electrochemistry: from Theory to Industrial Applications.

Among the topics of the GEI 2019 conference, biomedical sensors, synthesis of new catalysts, polymers and solvents to be used in the field of energy conversion and storage, electrosynthesis of new chemicals, and environmental care play a central role. Fundamental aspects as well as their applications to (nano)materials science, energy, environment and biomedicine are discussed.

During the five days conference, a rich scientific program is proposed including plenary and keynote speakers of international relevance, oral and poster presentations and the awarding of the best PhD and Master theses.

## CONFERENCE VENUE

The activities of the **GEI 2019** are carried out in the congress center inside the magnificent Botanical Garden of Padova (see map below). The official entrance is sited in Via Orto Botanico 15. The GEI 2019 Meeting Attenders can reach the auditorium on foot throuth the ancient part of the garden, following the indication posted on the footpaths. Attenders can freely move all around the Orto Botanico Garden, during the opening time, provided that they wear the meeting badge.

## SCI ELECTROCHEMISTRY DIVISION / DIVISIONE DI ELETTROCHIMICA

Società Chimica Italiana
*Divisione di Elettrochimica*

In line with the objectives of the Italian Chemical Society, the Electrochemistry Division proposes, in the specific disciplinary field, to advance research, promote teaching and develop profitable relationships between academia and industry. To this end, various initiatives have been activated over the years with continuity and regularity, such as the Italian Electrochemistry Days (Giornate dell'Elettrochimica Italiana - GEI), the School of Electrochemistry, Master and Doctoral Thesis Awards, the Galvani medal Award and the Newsletter.

Have a look at our website:
https://www.soc.chim.it/it/divisioni/elettrochimica/home

and follow our news on the social networks:
SCI - Divisione di Elettrochimica

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### CONFERENCE CO-CHAIR

**Prof. Abdirisak A. Isse**, University of Padua, Italy

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- Alessandro Minguzzi, Università degli Studi di Milano
- Gianluca Longoni, Research & Development Engineer at STMicroelectronics

### STUDENT HELPERS

- Riccardo Brandiele
- Giovanni Crivellaro
- Giorgia Daniel
- Alessandro Facchin
- Marco Mazzucato
- Angeloclaudio Nale
- Valentina Perazzolo
- Mattia Reato
- Jacopo Stefanelli

**DEAR ATTENDER**

To showcase some of the most recent electrochemical research being performed in Italy and within international collaborations, **Christian Durante** (University of Padova), **Flavio Maran** (University of Padova), and **Claudio Gerbaldi** (Politecnico di Torino) invite you to contribute an original research or review-type article to a Special Collection dedicated to the GEI2019 meeting. The issue will remain open for submissions until **October 31st, 2019**.

Taking advantage of the new continuous publishing workflow that we recently introduced, all invited papers are published online as soon as possible in the next available issue (meaning that there is usually very little waiting time before final citation data, including page numbers, are available). These papers will also be combined into a virtual "Special Collection" dedicated to GEI2019, which will regularly be updated and will evolve until all contributions are published.

Please let us know with a short reply to this email if you would be interested in contributing to this exciting Special Collection dedicated to GEI2019. It would also be useful if you could give an indication of the type of paper you wish to submit, for planning purposes.

We would be pleased and honored if you accepted this invitation, but if you have any questions, please do not hesitate to contact the Editorial Office!

CHEM ELECTRO CHEM

2017 Impact Factor: 4.446
*Included in Web of Science*

**Guest Editors**

Christian Durante
Uni. Padua

Flavio Maran
Uni. Padua

Claudio Gerbaldi
Politecnico di Torino

**Editor-in-Chief**

Kate Lawrence
Wiley-VCH

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The GEI 2019 meeting has been organised under the patronage of:

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The Organizing Committee wishes to thank all the Sponsors for their support to the 2019 Giornate dell'Elettrochimica Italiana; their sponsorships have helped to make this event possible.


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# MEETING PROGRAM

*Afternoon Session (chairman: Francesco Paolucci-Christian Durante)*

**14.00**: Registration

**15.00**: Opening Ceremony GEI 2019

**15.30**: Electrochemical Division Awards Ceremony

*Master's Thesis Awards*

| | | | |
|---|---|---|---|
| **15.40** | A_S01 | **Ruggero Poiana** (premio di Laurea Biologic) | *Elettrochemiluminescenza di sistemi nanostrutturati per applicazioni biosensoristiche* |
| **16.00** | A_S02 | **Martina Fracchia** (premio di Laurea Photoanalytical) | *Fotocatalisi nel water splitting: Meccanismi di reazione* |
| **16.20** | A_S03 | **Alessandro Facchin** (premio di Laurea Ametek) | *Electrochemical scanning tunnelling microscopy investigations of Fe@N-based macrocyclic molecules adsorbed on Au(111) and their implications in oxygen reduction reaction* |

**16.40**: Coffee break

*PhD Thesis Awards*

| | | | |
|---|---|---|---|
| **17.00** | A_S04 | **Davide Clematis** (premio di Dottorato De Nora) | *Among old materials and different approaches to enhance stability and electrochemical activity of solid oxide cells* |
| **17.20** | A_S05 | **Matteo Bonomo** (premio di Dottorato Engitec) | *Photo-electrochemistry of sensitized semiconducting oxides as photocathodes in p-type DSC* |
| **17.40** | A_S06 | **Noemi Colozza** (premio di Dottorato De Nora) | *The development of nano-structured printed electrochemical (bio)sensors for synergic approaches to environmental monitoring* |
| **18.00** | A_S07 | **Francesca Colò** (premio di Dottorato alla memoria Del Prof. Giovanni Davolio) | *Advanced and functional materials for sodium secondary batteries* |

*Plenary Lecture*

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|---|---|---|---|
| **18.30** | PL_S01 | **Juan-Miguel Feliu** (Universidad de Alicante, Spain) | Around the electric charge |

**19.30**: Orto Botanico Guided Tour

**20.30**: Welcome party

*Morning Session (chairman: Luigi Falciola – Giovanni Valenti)*

*Plenary Lecture*

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|---|---|---|---|
| **8.30** | PL_M02 | **Richard G. Compton** (University of Oxford, UK) | *Electrochemical studies of nanoparticles* |

*Oral Presentations*

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|---|---|---|---|
| **9.30** | O_M01 | **Andreas Lesch (INVITED)** (University of Bologna) | *Electrochemical detection of melanoma biomarkers in tissue* |
| **9.50** | O_M02 | **Sheila Sadeghi** (University of Torino) | *Human flavin monooxygenase electrodes modified with graphene oxide: a tool for personalised medicine* |
| **10.05** | O_M03 | **Valentina Pifferi** (University of Milan) | *Metal-semiconductor hybrids for electroanalytical purposes* |
| **10.20** | O_M04 | **Alessandro Minguzzi** (University of Milan) | *Monitoring real time emission from pancreatic beta cells in dependence on their substrate: a scanning electrochemical microscopy study* |

**10.35** Coffee break

*Keynote Lecture*

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|---|---|---|---|
| **11.00** | K_M01 | **Patrizia R. Mussini** (University of Milan) | *Enantiodiscrimination in electrochemistry and electroanalysis: implementing "inherent" chirality at the electrochemical interphase* |

*Oral Presentations*

| | | | |
|---|---|---|---|
| **11.40** | O_M05 | **Paolo Ugo (INVITED)** (University Ca' Foscari of Venice) | *Electrochemical sensing of non-electroactive analytes by molecularly imprinted polymer films on micro and nanoelectrodes* |
| **12.00** | O_M06 | **Alessandra Zanut** (University of Bologna) | *Probing electrochemiluminescence response through DNA sensor for the detection of specific DNA sequences* |
| **12.15** | O_M07 | **Giovanni Valenti** (University of Bologna) | *Surface-confined electrochemiluminescence microscopy of cells* |
| **12.30** | O_M08 | **Marco Malferrari** (University of Bologna) | *Spatially controlled electrochemical monitoring of reactive oxygen species production* |
| **12.45** | O_M09 | **Ornella Abollino** (University of Torino) | *A simple and rapid system for the determination of inorganic mercury and methylmercury in fish products* |

**13.00** Lunch

*Afternoon Session (chairman: Armando Gennaro – Sara Bonacchi)*

*Keynote Lecture*

| | | | |
|---|---|---|---|
| **14.30** | K_M02 | **Aldo Di Carlo** (University of Rome II) | *Dye sensitized and perovskite photovoltaics: from cells to modules* |

*Oral Presentations*

| | | | |
|---|---|---|---|
| **15.10** | O_M10 | **Andrea Listorti (INVITED)** (Università del Salento) | *Supramolecular assisted growth of organometal halide perovskites for highly efficient light-emitting and photovoltaic devices* |
| **15.30** | O_M11 | **Danilo Dini** (University of Rome "La Sapienza") | *P-type dye-sensitized solar cells with RDS NiO cathodes: improvement of the photoconversion performance following substrate treatment* |
| **15.45** | O_M12 | **Chia-Yu Lin** (National Cheng Kung University) | *Electrosynthesis, activation, and applications of nickel-iron oxyhydroxide in (photo-)electrochemical water splitting at near neutral condition* |
| **16.00** | O_M13 | **Lucia Fagiolari** (Politecnico di Torino) | *Photoanodes for aqueous dye-sensitized solar cells: effect of different $TiO_2$ pastes* |
| **16.15** | O_M14 | **Christopher Batchelor-McAuley** (University of Oxford) | *Three-dimensional nanoparticle structure, surface area and activity* |

**16.30**: Tea break

*Oral Presentations*

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|---|---|---|---|
| **17.00** | O_M15 | **Andrea Sartorel (INVITED)** (University of Padova) | *Redox catalysis for artificial photosynthesis* |
| **17.20** | O_M16 | **Alberto Vertova** (University of Milan) | *Atomically precise Pt-CO clusters for oxygen reduction reaction* |
| **17.35** | O_M17 | **Laura Calvillo** (Università di Padova) | *Insights into the Co-Fe spinels durability by following in situ transformations during the oxygen evolution reaction* |
| **17.50** | O_M18 | **Stefano Mezzavilla** (Technical University of Denmark) | *Active sites for the electroreduction of $CO_2$ with gold electrodes – a structure-sensitivity study* |
| **18.05** | O_M19 | **Monica Distaso** (Institute of Particle Technology, FAU Erlangen-Nuremberg) | *Design of highly selective Pt/C electrocatalysts for the dehydrogenation of 2-propanol* |
| **18.20** | O_M20 | **Federico Tasca** (Universidad de Santiago de Chile) | *Oxygen reduction reaction at Fe catalysts with 4 or 5 coordinated N atoms. Calculated and experimental $O_2$-Fe binding energy, activity indexes, Volcano correlations.* |
| **18.35** | O_M21 | **Nicola Cioffi (INVITED)** (Università di Bari) | *On the pros and cons of the sacrificial anode electrolysis for the preparation of transition metal colloids* |

**19.00 – 20.30**: Poster session with food and drinks

*Morning Session (chairman: Vito Di Noto – Maria Assunta Navarra)*

*Plenary Lecture*

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| **8.30** | PL_T03 | **Michel Armand** (CIC energigune, Spain) | *Novel solutes for liquid and polymer electrolytes* |

*Oral Presentations*

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| **9.30** | O_T22 | **Vittorio Pellegrini (INVITED)** (Istituto Italiano di Tecnologia) | *Graphene-based electrodes for high-power Li-ion batteries* |
| **9.50** | O_T23 | **Piercarlo Mustarelli** (University of Milano-Bicocca) | *Towards sustainable, high-performing, all-solid-state sodium-ion batteries (TRUST)* |
| **10.05** | O_T24 | **Marisa Falco** (Politecnico di Torino) | *UV-crosslinked composite polymer electrolyte for high-rate, ambient temperature Li-based batteries* |
| **10.20** | O_T25 | **Riccardo Ruffo** (University of Milano-Bicocca) | *Water in salt electrolytes for higher energy and power electrochemical energy storage devices* |

**10.35:** Coffee break

## Enerchem Special Session

*Keynote Lecture*

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| **11.00** | K_T03 | **Steven G. Greenbaum** (Hunter College-NY-USA) | *Recent liquid state and solid state NMR investigations of battery electrolytes* |

*Oral Presentations*

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|---|---|---|---|
| **11.40** | O_T26 | **Giorgia Zampardi (INVITED)** (*Universität Bremen*) | *Direct Experimental Evidences of the Electronic Character of the Positive Solid-Electrolyte Interphase in Li-ion Batteries* |
| **12.00** | O_T27 | **Catia Arbizzani** (Università di Bologna) | *Separators for the next generation batteries* |
| **12.15** | O_T28 | **Daniele Versaci** (Politecnico di Torino) | *Simply double layer approach for enhancing Li-S battery performances* |
| **12.30** | O_T29 | **Mario Branchi** (Sapienza University of Rome) | *Ionic liquids based on bis(oxalato)borate or difluoro(oxalato)borate anion as electrolyte components in high voltage lithium batteries* |
| **12.45** | O_T30 | **Francesca Lorandi** (Carnegie Mellon University) | *Polymer-based artificial solid electrolyte interphases for stable Li metal batteries* |

**13.00** Lunch

*Afternoon Session (chairman: Marco Musiani – Claudio Gerbaldi)*

*Keynote Lecture*

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| **14.30** | K_T04 | **Fabio La Mantia** (University of Bremen,) | *Lithium recovery by means of electrochemical ion pumping* |

*Oral Presentations*

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| **15.10** | O_T31 | **Davide Rosestolato (INVITED)** (S.I.A. Industria Accumulatori) | *Lead-Acid batteries for automotive. Future perspectives and objects of research: The micro-hybrid application and the EFB technology* |
| **15.30** | O_T32 | **Nicolò Pianta** (Università di Milano-Bicocca) | *High-voltage cathodic materials for sodium ion batteries* |
| **15.45** | O_T33 | **Sergio Brutti** (University of Rome La Sapienza) | *Origin of the irreversible capacity in hard carbon electrodes for sodium-ion batteries* |
| **16.00** | O_T34 | **Artem Glazkov** (University of Chemical Technology of Russia) | *Novel «chemistry» based on aqueous bromate solutions for stationary energy storage, fully electric vehicles and direct solar-to-chemical energy conversion* |
| **16.15** | O_T35 | **Gioele Pagot** (Università di Padova**)** | *Recent progresses in ionic liquid-based electrolytes for hybrid multivalent metals secondary batteries* |

**16.30**: Tea break

*Oral Presentations*

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|---|---|---|---|
| **17.00** | O_T36 | **Massimo Innocenti (INVITED)** (University of Florence) | *Electrodeposition and applied electrochemistry* |
| **17.20** | O_T37 | **Sara Politi** (University of Rome Tor Vergata) | *Role of correlation on nucleation and island growth in potentiostatic transients* |
| **17.35** | O_T38 | **Onofrio Scialdone** (Università degli Studi di Palermo) | *Electrochemical conversion of carbon dioxide in pressurized electrochemical cells* |
| **17.50** | O_T39 | **Maria Montanino** (ENEA) | *Gravure printing for printed batteries manufacturing* |
| **18.05** | O_T40 | **Lorenzo Fabbri** (University of Florence) | *Development of an efficient and green Bronze alloy electrodeposition bath* |
| **18.20** | O_T41 | **Giada Tranchida** (Università di Palermo) | *Corrosion resistance of different stainless steel grades in cleaning industrial environments* |
| **18.35** | O_T42 | **Benedetto Bozzini (INVITED)** (Università del Salento) | *In situ spectroscopic ptychography during the electrodeposition of Mn-Co/polypyrrole nanocomposites* |

**19.00 – 20.30**: Poster Session with food and drinks

*Morning Session (chairman: Vincenzo Baglio – Mariangela Longhi)*

*Plenary Lecture*

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| **8.30** | PL_W04 | **Anthony Kucernak** (Imperial College, UK) | *Measurement of electrocatalyst activity at the electrolyte-gas interface: determination of mass transport free electrocatalyst performance* |

*Oral Presentations*

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| **9.30** | O_W43 | **Carlo Santoro (INVITED)** (University of New Mexico) | *Correlations between synthesis step and performance of Fe-based PGM-free catalysts in entire pH spectrum* |
| **9.50** | O_W44 | **Pietro Giovanni Santori** (Université Montpellier) | *Effect of pyrolysis atmosphere and electrolyte pH on the oxygen reduction activity, stability and spectroscopic signature of $FeN_x$ moieties in Fe-N-C catalysts* |
| **10.05** | O_W45 | **Mariangela Longhi** (University of Milan) | *Synergistic effects of active sites nature and hydrophilicity on oxygen reduction reaction activity of Pt-Free catalysts* |
| **10.20** | O_W46 | **Jacopo Isopi** (University of Bologna) | *Graphene based electrocatalyst for oxygen reduction reaction* |

**10.35:** Coffee break

*Keynote Lecture*

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| **11.00** | K_W05 | **Isotta Cerri** (TME, Belgium) | *Toyota fuel cell development for a sustainable future* |

*Oral Presentations*

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| **11.40** | O_W47 | **Andrea Casalegno (INVITED)** (Politecnico of Milan) | *Experimental and physically based modelling analysis of electrochemical impedance to interpret limiting phenomena during PEMFC operation and ageing* |
| **12.00** | O_W48 | **Francesco di Franco** (University of Palermo) | *Performances of direct methanol fuel cells with chitosan membranes as proton conductors* |
| **12.15** | O_W49 | **Vincenzo Baglio** (ITAE-CNR-Messina) | *Towards methanol tolerant and low-cost ORR catalysts based on Metal-Nitrogen-Carbon (M-N-C) for direct methanol fuel cells* |
| **12.30** | O_W50 | **Maria Paola Carpanese** (University of Genova) | *Electrochemical behaviour of $La_{0.8}Sr_{0.2}MnO_{3-\delta}$-infiltrated $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ under anodic overpotential* |
| **12.45** | O_W51 | **Valerio C.A. Ficca** (University Tor Vergata) | *Insights into oxygen reducing activity and poisoning tolerance of platinum-group-metal-free catalysts* |

**13.00**: Light lunch

**14.00:** General Assembly of the Electrochemistry Division of the SCI

**17.00**: Social Events: Padova & Colli Euganei Tours

**20.00**: Social Dinner

*Morning Session (chairman: Abdirisak Ahmed Isse - Sabrina Antonello)*

*Plenary Lecture*

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|---|---|---|---|
| **8.30** | PL_Th05 | **Kim Daasbjerg** (Aarhus University, Denmark) | *Developing efficient electrocatalysts for the reduction of $CO_2$ to CO: From metal porphyrin complexes to metal/nitrogen doped carbon* |

*Oral Presentations*

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|---|---|---|---|
| **9.30** | O_Th52 | **Isabella Chiarotto (INVITED)** (Sapienza University) | *A study on cathodic reactivity of caffeine: A biobased starting material for the development of new products* |
| **9.50** | O_Th53 | **Sandro Cattarin** (*ICMATE-CNR Padova*) | *Performances of compact and porous Pd-Ni electrodes in the oxidation of ethanol in alkali* |
| **10.05** | O_Th54 | **Carlo Nervi** (University of Torino) | *Electrochemical reduction of $CO_2$ by Mn and Re bipyiridine complexes: Homogeneous and hetereogeneous approaches* |
| **10.20** | O_Th55 | **Juqin Zeng** (Istituto Italiano di Tecnologia) | *Copper-based electrodes for electrochemical $CO_2$ conversion* |

**10.35:** Coffee break

*Keynote Lecture*

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|---|---|---|---|
| **11.00** | ThK06 | **Marco Panizza** (University of Genoa, Italy) | *Past and present of electrochemical treatment of organic pollutants* |

*Oral Presentations*

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|---|---|---|---|
| **11.40** | O_Th56 | **Stefano Caramori (INVITED)** (University of Ferrara) | *n-Type semiconductors for photoelectrochemical environmental remediation* |
| **12.00** | O_Th57 | **Giovanni Sotgiu** (University of Roma Tre) | *Thermally decomposed $RuO_2$-$CoO_x$ coated titanium anodes: Durability and application in environmental electrochemical processes* |
| **12.15** | O_Th58 | **Luca Casanova** (Politecnico di Milano) | *Bipolar anodic spark deposition to enhance the corrosion resistance of titanium: effect on morphology and structure* |
| **12.30** | O_Th59 | **Giulia Moggia** (*University of Antwerp*) | *On the impact of the oxidation potential on the conversion of D-glucose to D-glucaric acid in alkaline medium* |
| **12.45** | O_Th60 | **Michele Mascia (INVITED)** (Università degli Studi di Cagliari) | *Mathematical modelling of $TiO_2$ nanotubes behavior under solar light irradiation* |

Closing Remarks

# POSTER CONTRIBUTIONS

Monday Session September 9, 2019
Poster exhibition: Sunday 14:30 – Monday 20:30

| Code | Presenting author | Title |
|---|---|---|
| **P_M01** | Abdirisak Ahmed Isse | Insights into the effect of water in electrochemically-mediated ATRP in nonaqueous solvents |
| **P_M02** | Alberto Battistel | Dynamic Impedance. What shall we do with all these data? |
| **P_M03** | Alessandra Zanut | Electrochemical activity of the polycrystalline cerium oxide films for hydrogen peroxide detection |
| **P_M04** | Alessandro Facchin | Substituent effect on metal-porphyrins adsorbed on HOPG and its implications towards oxygen reduction reaction |
| **P_M05** | Anna Lielpētere | Friedel-Crafts reactions of electrochemically generated carbenium ions |
| **P_M06** | Catia Arbizzani | Study of the intercalation process and surface optimization of cathode materials for Na-ion batteries |
| **P_M07** | Massimo Innocenti | Finite elements models of galvanic cells to even the metal deposition on a cathodic bidimensional array of jewel rings |
| **P_M08** | Elisa Maruccia | Design of nitrogen containing mesoporous carbon materials for $CO_2$ up-take and sustainable electrochemistry |
| **P_M09** | Federico Morini | Exploiting plasma electrolytic oxidation to synthesize $TiO_2$ films with enhanced photoelectrocatalytic activity |
| **P_M10** | Giancosimo Sanghez de Luna | 3D Electrocatalysts for the reduction of biomass-derived compounds |
| **P_M11** | Giorgia Daniel | Effect of N- and S-doping and texture properties of carbon support on Fe-N-C catalysts performances for ORR |
| **P_M12** | Giovanni Valenti | Water-mediated electro-hydrogenation of $CO_2$ at near-equilibrium potential by undoped nanocarbon@$CeO_2$ |
| **P_M13** | José García-Antón | ZnO nanoestructures anodized under hydrodynamic conditions for hydrogen production |
| **P_M14** | José García-Antón | $WO_3$ nanostructures optimization for the photoelectrocatalytic mineralization of organic pollutants |
| **P_M15** | Lucia Fagiolari | Emerging strategies towards ambient condition fabrication of perovskite solar cells |
| **P_M16** | Maria Antonietta Baldo | Electrochemical strategy coupled with spectroscopic techniques for trace lead analysis in olive oil/RTIL mixtures |
| **P_M17** | Marijana R. Pantović Pavlović | Influence of process parameters of simultaneous anodization/anaphoretic electrodeposition synthesis of hydroxyapatite/titanium oxide composite coatings on adhesion |
| **P_M18** | Meng Liu | Versatile decoration of carbon composites with metal nanoparticles for electrocatalytic application |
| **P_M19** | Miroslava Varničić | Synthesis and electrochemical performance of multicomponent oxide materials toward oxygen reduction reaction |
| **P_M20** | Patrick Marcantelli | Electrochemical impedance spectroscopy techniques for quality control on electroplated metals |
| **P_M21** | Piercarlo Mustarelli | $^{17}O$ NMR and electrochemical characterization of super-concentrated solutions |
| **P_M22** | Riccardo Brandiele | Mesoporous carbon characterized by different carbon structures and modulable density of thiophenic groups: effect on platinum NPs activity for oxygen reduction |
| **P_M23** | Rita Petrucci | Study of theophylline anodic oxidation products in organic solvents by μHPLC-PDA-ESI-MS/MS analysis |

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|---|---|---|
| **P_M24** | Ruggero Poiana | Investigation on the cathode capacity gain in high voltage spinel structures |
| **P_M25** | Sara Rebeccani | Electrochemiluminescence meets nanotechnology: nanomaterials for enhance the signals |
| **P_M26** | Simelys Hernàndez | Syngas production by electrocatalytic reduction of $CO_2$ by using Ag-decorated $TiO_2$ nanotubes |
| **P_M27** | Valentina Perazzolo | Laser ablation synthesis in solution of AgCo alloy nanoparticles for oxygen reduction reaction |
| **P_M28** | Vincenzo Baglio | Counter electrodes based on Fe-N-C materials for low cost dye-sensitized solar cells |
| **P_M29** | Zoran Milojevic | Electro-thermal behaviour of large size Li-Ion batteries from end of life (EOL) EV module |
| **P_M30** | Artem Glazkov | Measurement of exchange current for redox-pair $Br_2/Br^-$ on platinum electrode |
| **P_M31** | Anna Testolin | Voltammetric characterization of gold-based bimetallic (AuPt; AuPd; AuAg) nanoparticles |
| **P_M32** | Antonio Barbon | Oxidation of water by oxammonium cations |
| **P_M33** | Francesca Colò | Safe polymer electrolytes and high performing anode materials for Na-based secondary batteries |
| **P_M34** | Irene Facchinetti | Thermally regenerable redox-flow batteries |
| **P_M35** | Isaac Capone | Effect of the particle-size distribution on the electrochemical performance of a red phosphorus-carbon composite anode for sodium-ion batteries |
| **P_M36** | Martina Fracchia | Operando hard and soft X-ray absorption spectroscopy in (photo)-electrochemistry |
| **P_M37** | Matteo Bonomo | Electrochemical impedance spectroscopy: a powerful tool to unveil the charge transport/recombination processes in aqueous dye-sensitized solar cells |
| **P_M38** | Roman Pichugov | High performance vanadium redox flow battery incorporating graphite foil as bipolar plates |
| **P_M39** | Walter Giurlani | Electrodeposition of Cadmium Selenide on n-Si (100) |
| **P_M40** | Binbin Huang | $Fe_3O_4$ nanoparticles with dual electromagnetic functions for highly efficient catalytic advanced oxidation processes |
| **P_M41** | Claudia Paoletti | Process scale-up for pilot scale production of lithium-ion electrode materials |
| **P_M42** | Flaminia Rondino | Si-NWs grown by Cu-catalysed CVD for lithium-ion batteries |
| **P_M43** | Mélanie François | Fabrication and electrochemical characterization of Sm-doped ceria (SDC) electrolyte for IT-SOFC and study of complete cells |
| **P_M44** | Angeloclaudio Nale | Hierarchical *"Core-Shell"* low-loading Pt electrocatalysts for the oxygen reduction reaction based on a graphene *"core"* and a carbon nitride *"shell"* |
| **P_M45** | Mattia Reato | Tailoring the conductivity and chemosensing properties of monolayer-protected gold nanoclusters films |
| **P_M46** | Giovanni Crivellaro | Elucidation of the interplay between vanadium species and charge-discharge processes in VRFBs by raman spectroscopy |
| **P_M47** | Margherita Moreno | PEO-polysulfides composite cathodes: towards solid lithium/sulphur batteries |
| **P_M48** | Wafa Aidli | Graphene quantum dots@Benzoquinone@β-cyclodextrin systems for a dual mode sensing |

# POSTER CONTRIBUTIONS

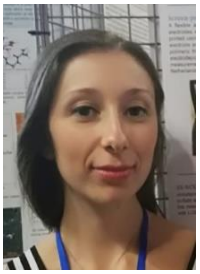
Tuesday Session September 10, 2019
Poster exhibition: Tuesday 8:30 – Thursday 11:00

| Code | Presenting author | Title |
|---|---|---|
| **P_T01** | Angela Maria Stortini | Plasma activation of copper nanowires arrays for electrocatalytic sensing of nitrate in food and water |
| **P_T02** | Alberto Battistel | Volterra Series and the Generalization of the Equivalent Circuits |
| **P_T03** | Chiara Ferrara | $FeTiO_3$ as anode material for sodium ion batteries: from morphology control to decomposition |
| **P_T04** | Claudio Gerbaldi | EnABLES: European infrastructure powering the internet of things |
| **P_T05** | Daniele Versaci | Facile synthesis of $SnO_2$/carbon anode material for high performance Li-ion battery |
| **P_T06** | Federica Proietto | Electrochemical conversion of carbon dioxide to formic acid at Sn and BDD cathodes |
| **P_T07** | Federico Brombin | High valence transition metals doping of olivine cathode for superior energy and fast cycling lithium batteries |
| **P_T08** | Francesca Lorandi | Pros and cons of highly active Cu-catalysts for atom transfer radical polymerization |
| **P_T09** | Gabriele Lingua | Innovative single-ion conducting solid electrolytes for safe, high performing energy storage devices |
| **P_T10** | Giuseppina Meligrana | Graphene-modified $LiFePO_4$ cathodes for advanced Li-/Na-ion secondary batteries |
| **P_T11** | Lourdes Vázquez-Gómez | Preparation of catalytic anodes for oxygen evolution by oxide-oxide galvanic exchange reactions |
| **P_T12** | Stefano Caporali | Aluminium anodization from ionic liquid and deep eutectic solvent: alternative routes to traditional surface treatment |
| **P_T13** | Stefano Caporali | Electrodeposition and characterization of nanosized metallic copper from deep eutectic solvent |
| **P_T14** | Leonardo Mattiello | Electrochemical studies of new donor-acceptor oligothiophenes |
| **P_T15** | Lorenzo Fabbri | Study of the oxygen reduction reaction in alkaline media of functionalized carbon nanotubes |
| **P_T16** | Lubomír Pospíšil | Chiroptical redox switching of azoniahelicenes |
| **P_T17** | Luca Mattarozzi | Electrodeposition of compact Ag-Ni alloys from concentrated chloride baths |
| **P_T18** | Abdirisak Ahmed Isse | Electrochemically mediated atom transfer radical polymerization of *N,N*-dimethylacrylamide |
| **P_T19** | Luigi Falciola | Anodic titanium dioxide nanotube arrays for electroanalytical purposes |
| **P_T20** | Magdaléna Hromadová | Single molecule conductance of electroactive helquats. Solvent effect |
| **P_T21** | Marco Lunardon | $MoS_{2(1-x)}Se_{2x}$/Graphene hybrids for electrochemical hydrogen evolution reaction |
| **P_T22** | Maria Assunta Navarra | A sub-stoichiometric calcium titanate $CaTiO_{3-\delta}$ additive to enhance the oxygen reduction reaction catalytic activity |
| **P_T23** | Mariarita Santoro | Nickel-based structured catalyst for indirect internal reforming of methane in solid oxide fuel cells |
| **P_T24** | Walter Giurlani | Cobalt electrodeposition on chars obtained from pyrolysis of waste tires: a study on the catalytic efficiency in ORR via hydrodynamic voltammetry |

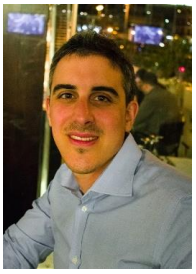
| | | |
|---|---|---|
| **P_T25** | Miroslav Pavlović | Influence of A' cation substitution on promotion of supercapacitance of rare earth/$CoO_3$-based spray pyrolytic perovskite microspheres |
| **P_T26** | Morteza Rahmanipour | High-surface area carbon materials as alternative counter electrode for electrochemical characterization of electrode materials for sodium-ion cells |
| **P_T27** | Nicola Comisso | New evidences on the growth of oxide layers via oxide-oxide galvanic exchange reactions |
| **P_T28** | Patrick Marcantelli | Experimental study for environmentals friendly silver electroplating for the production of jewels |
| **P_T29** | Roman Pichugov | Bromate-ion ($BrO_3^-$) reduction in acidic solution at RDE. Theoretical predictions vs. experimental data for maximal current density |
| **P_T30** | Sanja Eraković | Long-lasting oxygen evolving titanium anodes activated by Mn and Sn oxides by hydrothermal air-pyrolytic brushing |
| **P_T31** | Siddharth Gadkari | Can biofilm be modelled as a porous conductive layer? |
| **P_T32** | Valentina Perazzolo | Synthesis of micro- and mesoporous carbons from PEO-b-PS soft template and resorcinol-formaldehyde resins for the *in situ* generation of hydrogen peroxide |
| **P_T33** | Antonio Gentile | Structure properties correlation in MXenes: 2D anodic materials for sodium ion batteries |
| **P_T34** | Chia-Yu Lin | n-p $BiVO_4$-$CuBi_2O_4$ nano-heterojunction as an efficient photoanode in photoelectrochemical water oxidation |
| **P_T35** | Davide Clematis | Interaction between $La_{0.6}Sr_{0.4}FeO_3$ and $La_{0.6}Ba_{0.4}CoO_3$ and investigation of $Ba_{0.99}Sr_{0.297}La_{0.594}Co_{0.8}Fe_{0.2}O_{3-\delta}$ as cathode for intermediate temperature solid oxide fuel cells |
| **P_T36** | Giorgia Daniel | Plastic derived carbon materials for oxygen reduction reaction: effect of pre- and post- treatments |
| **P_T37** | | Promoted to oral presentation |
| **P_T38** | Marco Musiani | Preparation of electrodes for the reduction of $CO_2$ to formic acid at low overpotential by electroprecipitation of nanostructured $CeO_2$ onto BDD electrodes |
| **P_T39** | Riccardo Brandiele | Exploiting N-doped carbon spheres for supercapacitors |
| **P_T40** | Riccardo Brandiele | $Pd_3Y$ alloyed NPs synthetized by laser ablation: toward zero platinum in PEMFC cathode catalysts |
| **P_T41** | Sara Bonacchi | A new monolayer-protected clusters: the 145$^{th}$ gold atom matters |
| **P_T42** | Simelys Hernández | Catalytic vs. electrocatalytic reduction of $CO_2$ to added-value products |
| **P_T43** | Simone Bonizzoni | PEO-grafted $TiO_2$ filler as solid polymer electrolyte for lithium rechargeable batteries |
| **P_T44** | Alessandro Facchin | Behavior of Fe(III)-octaethyl porphyrin adsorbed on HOPG towards ORR probed by electrochemical scanning tunneling microscopy |
| **P_T45** | Yi-Hsuan Lai | Electrodeposited nickel molybdenum sulfide for electrochemical and photoelectrochemical hydrogen generation in near-neutral medium |
| **P_T46** | Arcangelo Celeste | Lithium rich transition metal oxides as high capacity positive electrode materials in Li-ion cells |
| **P_T47** | Chuanyu Sun | Hybrid inorganic-organic proton-conducting membranes based on SPEEK doped with $WO_3$ nanoparticles for application in vanadium redox flow batteries |
| **P_T48** | Yannick H. Bang | Interplay between activation processes, physicochemical properties and electrochemical performance of *"core-shell"* carbon nitride Pt-Ni ORR electrocatalysts based on hierarchical graphene supports |

# ELECTROCHEMICAL DIVISION PHD THESIS AWARDS

**Davide Clematis**
Premio di Dottorato Fondazione Oronzio e Niccolò De Nora



**Noemi Colozza**
Premio di Dottorato Fondazione Oronzio e Niccolò De Nora



**Matteo Bonomo**
Premio di Dottorato Engitec Technologies

**Francesca Colò**
Premio di Dottorato alla memoria del Prof. Giovanni Davolio

# ELECTROCHEMICAL DIVISION MASTER THESIS AWARDS

**Alessandro Facchin**
Premio di Laurea Ametek

**Martina Fracchia**
Premio di Laurea Photo Analytical S.R.L.

**Ruggero Poiana**
Premio di Laurea Biologic Sas

# Electrochemiluminescence of nanostructured systems for biosensor applications

## Premio di Laurea 2019 “Bio-Logic S.a.s.”

Ruggero Poiana,[a] Elena Villani,[a] Andrea Fiorani,[a] Giovanni Valenti,[a] Stefania Rapino,[a] and Francesco Paolucci[a]

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Electrogenerated chemiluminescence (ECL) is a redox induced light emission [1]. As a light emission technique, ECL possesses unique properties over the other light emission methods. Therefore, ECL is a powerful transduction technique and allows wide applications in particular in the bioanalysis for the determination of important markers.

Here, we propose a protocol for the direct quantification of cells, based on ECL technology. The cells recognition and quantification were performed taking the advantage of the double functionalization of multiwalled carbon nanotubes (MWCNTs). The nanomaterials were chemically modified *(i)* with an antibody, specific for the selective capturing of cells that overexpress the EGFR membrane protein, and *(ii)* filled with ferromagnetic core for cell separation (Fe@*f*-MWCNTs) [2]. EGFR is a typical protein of epithelial cells and is overexpressed in human mammary epithelial cancer cells (MCF10A). In this work we used MCF10A as a model for circulating tumor cells (CTC). CTC are epithelial cells detached from the primary tumor and transported by the blood vessels triggering metastatization process. For this reason, the evaluation of CTC concentration in blood samples can give informations about tumor proliferation and diagnosis.

The lack of aspecific signal was demonstrated by the comparison between our materials, Fe@*f*-MWCNTs, and others with the same functionality but without a capturing antibody. In addition, analytic parameters were calculated obtaining a *limit of detection* of 11 cells/mL.

Finally, the role of carbon nanotubes, in signal enhancement [3], was confirmed by the comparison with commercial magnetic beads. The results showed an increase of the analytical signal thanks to carbon nanotubes electronic properties. For further studies on this project, cell detection will be performed on blood samples in order to evaluate the effect of complex biological matrix.

[1] W. Miao, J.-P. Choi, and A. J. Bard*, J. Am. Chem. Soc.*, 2002, **124**, 14478–14485.
[2] R. Marega, F. De Leo, F. Pineux, J. Sgrignani, A. Magistrato, A. D. Naik, Y. Garcia, L. Flamant, C. Michiels, and D. Bonifazi, *Adv. Funct. Mater.*, 2013, **23**, 3173–3184.
[3] Z. Guo, Y. Sha, Y. Hu, Z. Yu, Y. Tao, Y. Wu, M. Zeng, S. Wang, X. Li, J. Zhou, and X. Su, *Anal. Bioanal. Chem.*, 2016, **408**, 7203–7211.

# Operando X-ray absorption spectroscopy for the study of photocatalytic water splitting

## Premio di Laurea 2019 "Photo Analytical S.R.L."

Martina Fracchia,[a] Tomasz Baran,[b] Alberto Visibile,[b] Alberto Vertova,[b,c] Sandra Rondinini,[b,c] Alessandro Minguzzi[b,c] and Paolo Ghigna[a,c]

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The progressive lack of fossil fuels together with the growing awareness of the environmental problems has led to an extensive research of renewable and sustainable energy sources. In this sense, the photocatalytic water splitting has been extensively studied as a way to produce hydrogen in a sustainable way by exploiting the solar energy. While much attention has been devoted to the development of new materials, a comprehensive understanding of the mechanism of this reaction is still necessary to rationalize the choice of the photocatalytic materials, with the final aim to reach higher water-to-hydrogen efficiency.

Operando X-Ray absorption spectroscopy (XAS) represents a powerful and versatile technique which allows getting information on the electronic and structural properties of a given material, while simulating the real operating conditions of a reaction. In the recent years we have developed different strategies [1] to apply operando XAS on photoelectrodes and photoarchitectures, in order to study the generation and the fate of the photogenerated carriers (recombination/charge transfer), and to clarify the role of the overlayer in composite electrodes.

Here I will present two applications of operando XAS, respectively on a composite photoanode ($\alpha$-$Fe_2O_3$ /$IrO_x$) and on photocathodes systems ($Cu_xO$). In the first case, the composite electrode was investigated through a pump&probe XAS experiment with a time resolution of 600 ns [2]. This allowed the observation of a hole transfer process occurring between the semiconductor and the overlayer at potentials suitable for the water splitting reaction, with the $IrO_X$ accumulating holes for at least 600 ns.

Regarding the $Cu_xO$-based photocathodes [3], these were investigated through a novel differential scan acquisition of spectra in dark/light and through the FEXRAV (Fixed-Energy X-ray Absorption Voltammetry), a technique developed by our research group. It was demonstrated that a CuO-$Cu_2O$ core-shell combination presents an exceptional stability and the ability to retain good photocatalytic activity for many hours. The reasons behind this stability and the role of $Cu_xO$ in the water splitting process will be shown.

[1] E. Achilli, A. Minguzzi, A. Visibile, C. Locatelli, A. Vertova, A. Naldoni, S. Rondinini, F. Auricchio, S. Marconi, M. Fracchia and P. Ghigna, *J. Synchrotron Rad.*, 2016, **23**, 622-628.
[2] T. Baran, M. Fracchia, A. Vertova, E. Achilli, A. Naldoni, F. Malara, G. Rossi, S. Rondinini, P. Ghigna, A. Minguzzi and F. D'Acapito, *Electrochim. Acta*, 2016, **207**, 16-21
[3] T. Baran, S. Wojtyla, C. Lenardi, A. Vertova, P. Ghigna, E. Achilli, M. Fracchia, S. Rondinini and A. Minguzzi, *ACS Appl. Mater. Interfaces*, 2016, **8**, 21250-21260

# EC-STM investigations of $FeN_4$ macrocycles adsorbed on Au(111) and their implications in oxygen reduction reaction

## Premio di Laurea 2019 "Ametek"

Alessandro Facchin and Christian Durante

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$FeN_x$ sites, where a single iron atom is coordinated to nitrogen atoms, are known to exert a catalytic effect towards oxygen reduction reaction (ORR) [1]. For this reason, they can be conveniently dispersed in mesoporous carbon matrixes to obtain Fe-N-Mc catalysts to be employed in fuel-cells and metal-air batteries. Notwithstanding the lot ongoing investigations [2], there still exists a general lack of information about the main factors governing the ORR electrocatalysis promoted by $FeN_x$ sites. Electrochemical Scanning Tunnelling Microscopy (EC-STM) is a powerful technique, which allows to directly visualize the electrochemical behaviour of a system at the molecular scale. The STM unit probes the surface of a sample, which in the same time acts as working electrode in a so-called "four-electrodes setup". In this paper, an Au(111) single crystal was systematically functionalized with Fe(II)-phthalocyanine (Fe(II)Pc) or Fe(III)-phthalocyanine chloride (Fe(III)Pc-Cl) solutions, allowing self-assembly to occur at the solid/liquid interface. Ordered monolayers were observed, especially in the case of Fe(II)Pc, whereas Fe(III)Pc-Cl shown short-range or disordered arrangements.
By analysing the EC-STM image of figure 1.a, the Fe(II)Pc adlayer shows a protrusion of $\Delta Z_{(Ar)} \approx 0.25$ Å in Ar purged electrolyte (0.1 M $HClO_4$), whereas it becomes $\Delta Z_{(O2)} \approx 0.9$ Å in $O_2$ saturated electrolyte, as shown in fig. 1.b, where the higher protrusion appears shifted from the molecular centre, indicating a probable end-on $O_2$ adsorption geometry at the iron centre. This particular protrusion disappears when the $FeN_4$/Au electrode is polarised at sufficiently large potentials suitable for ORR, indicating that adsorption no longer occurs, and ORR is proceeding at high rate.

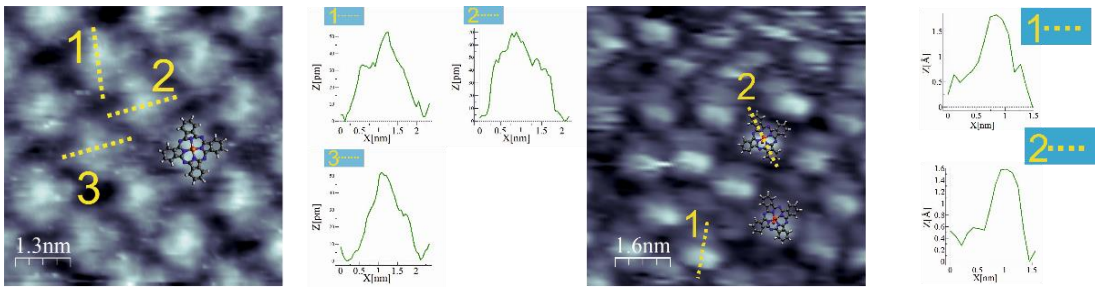


**Figure 1**: a) High-resolution EC-STM image of Fe(II)Pc adlayer on Au(111) in deaerated 0.1 M $HClO_4$. Parameters: $I_t$= 1.05 nA; $U_b$= –352 mV; $E_{app}$= 625 mV vs RHE. The insets show the corresponding topographic profiles. b) High-resolution EC-STM image of Fe(II)Pc adlayer on Au(111) in $O_2$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

[1] G. Wu, K.L. More, C. M. Johnston, P. Zelenay, *Science*, **2012**, 332, 443-448.
[2] W. Xu, Z. Wu, S. Tao, *J. Mater. Chem. A.* 4, **2016**, 16272–16287.
[3] M. Wilms, M. Kruft, G. Bermes, K. Wandelt, *Rev. Sci. Instrum.*, **1999**, 70, 3641-3650

# Among old materials and different approaches to enhance stability and electrochemical activity of solid oxide cells

## Premio di Dottorato 2019 " Fondazione Oronzio e Niccolò De Nora"

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Perovskite materials are widely studied as cathode materials for intermediate-temperature solid oxide fuel cells (IT-SOFC) for their relevant properties regarding electrocatalytic activity or stability. Nevertheless, a material that combines both it is not yet available. Among them, $La_{1-x}Sr_xMnO_3$ (LSM), $La_{1-x}Sr_xCo_{1-y}Fe_yO_3$ (LSCF), $Ba_{1-x}Sr_xCo_{1-y}Fe_yO_3$ (BSCF), $La_{1-x}Sr_xFeO_3$ (LSF), $La_{1-x}Ba_xCoO_3$ (LBC), were deeply investigated but their properties are not completely exploited or optimized.

The study starts from LSM – based electrodes, which show a change in kinetic mechanism over a overpotential threshold. These results [1,2] open new horizons about the employment of this material, up today considered not suitable for IT-SOFC temperature range. A first application, with promising results, is proposed here with a LSM infiltration in LSCF and BSCF scaffold [3].

Promising results are obtained also by mixing BSCF and LSCF powders [4]. Three different BSCF:LSCF ratio are considered to produce three different cathodes. All the new compositions show an improvement of activity for oxygen reduction reaction, with very competitive values of polarization resistance. Moreover, one of these new electrodes has also a lowering of degradation rate compared with reference materials

In the last year of this project, other two materials are combined and their interactions investigate. LSF, providing a high stability, is coupled with LBC, which has a really high surface electrocatalytic activity. The two materials are tested in different thin film systems. When they are mixed before the sintering stage react forming a new perovskite phase ($Ba_{0.099}Sr_{0.297}La_{0.594}Fe_{0.8}Co_{0.2}O_3$), with a higher activity. The reaction is avoided producing a bilayer system, and the presence of LBC top layer over a LSF dense thin film drastically reduces polarization resistance, highlighting promising results.

Moreover a particular attention has been paid to deeper integrate different approach to analyze electrochemical impedance spectroscopy results, such as equivalent circuit modeling, distribution of relaxation time and physically based model [5].

[1] M.P. Carpanese, D. Clematis, A. Bertei, A. Giuliano, A. Sanson, E. Mercadelli, C. Nicolella, A. Barbucci, Solid State Ionics 2017, **301**, 106-115
[2] A. Bertei, M.P. Carpanese, D. Clematis, A. Barbucci, M.Z. Bazant, C. Nicolella, Solid State Ionics 2017, **303**, 181-190
[3] A. Giuliano, M.P. Carpanese, D. Clematis, M. Boaro, A. Pappacena, F. Deganello, L.F. Liotta, A. Barbucci, J. Electrochem. Soc., **2017**, 164, F3114-F3122
[4] D. Clematis, A. Barbucci, S. Presto, M. Viviani, M.P. Carpanese, Int. J. Hydrog. Energy, 2019, **44**, 6212-6222
[5] D. Clematis, S. Presto, M.P. Carpanese, A. Barbucci, F. Deganello, L.F. Liotta, C. Aliotta, M. Viviani, Catalysts, 2019, **9**, 441**.**

# Photo-electrochemistry of sensitized semiconducting oxides as photocathodes in p-type DSCs

## Premio di Laurea/Dottorato 2019 “Engitec Technologies”

Matteo Bonomo[a,b] and Danilo Dini[a]

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It has becoming ever clearer that climate change caused by carbon emissions is a serious threat to the world. Therefore, it is of great importance that novel carbon neutral ways of energy production are developed. The present work is a typical example that aims to develop novel carbon free solar driven energy devices. In this contribution, it is discussed the development of p-type semiconductors that are coated with appropriate sensitizers and capable of absorbing sunlight as photocathodes for Dye-Sensitized Solar Cells (DSCs) [1]. The design of such assemblies is far from straightforward, since they are dependent on a range of components such as well-developed electrode surfaces, i.e. p-type semiconductor, sensitizers, electrolytes and appropriate electrodes. In the present work these individual components in great detail together with their mutual interaction and the results obtained in these studies have been discussed thoroughly.

The most interesting result was obtained by the implementation of a mixed $ZrO_2$/NiO photocathode [2]. The insertion of $ZrO_2$ nanoparticles in the NiO matrix allow to reduce the recombination phenomena limiting the overall efficiency of the devices. The optimization of both deposition method (i.e. spray deposition) and sintering procedure (i.e. Rapid Discharge Sintering) allow to sensibly enhance the overall efficiency of the (+144% compared to pristine device). The reported efficiency, i.e. 0.164%, is the highest ever obtained with a P1-sensitized p-DSSC.

Different classes of sensitizers were investigated: squaraine dyes (as NIR-sensitizers) [3]; pyran-based dyes which allows to outperform P1-sensitized device [4]; quinone-based molecules, in which the anchoring group is not conjugated with the aromatic structure. Additionally, the optimization of a range of electrolytes were also investigated, by means of XPS and EIS, in order to enhance the photocurrent powered by the cell.

Finally, the most effective photocathode was implemented in a tandem device (in which the anode is photoactive) leading to an overall conversion efficiency close to 2% opening doors for further amelioration.

[1] M. Bonomo and D. Dini *Energies* 2016, **9**, 373
[2] M. Bonomo, P. Mariani, F. Mura, A. Di Carlo and D. Dini *J. Electrochem. Soc.* 2019, **166**, D290-D300
[3] M. Bonomo, N. Barbero, F. Matteocci, A. Di Carlo, C. Barolo and D. Dini *J. Phys. Chem C.* 2016, **120**, 16340-16353
[4] M. Bonomo, R. Centore, A. Di Carlo D. Dini and A. Carella *Solar Energy* 2018, **169**, 237-242

# The development of nano-structured printed electrochemical (bio)sensors for synergic approaches to environmental monitoring

## Premio di Dottorato 2019 “Fondazione Oronzio e Niccolò De Nora”

Noemi Colozza[a]

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The necessity to monitor toxic chemicals in the environment has become increasingly urgent during the last century. For this purpose, electrochemical sensors play a noteworthy role, being particularly suitable for the planning of innovative and sustainable analytical monitoring programmes. Herein, I present the development and characterization of miniaturised electrochemical screen-printed sensors and their application to the detection of some among the most toxic and persistent long-term threats for the environment and livings: heavy metals and chemical warfare agents.

In detail, a bismuth-based and Nafion-coated sensor on a flexible polyester support was developed for the voltammetric detection of cadmium and lead ions in water samples (LOD = 0.3 ppb for $Pb^{2+}$; LOD = 1.5 ppb for $Cd^{2+}$), as a more sustainable and alternative to the conventional mercury-based sensors. The high versatility of such sensors was proved by their application to $Cd^{2+}$ and $Pb^{2+}$ monitoring within a bioremediation experiments in the presence of a filter-feeding organism (*Styela plicata*) [1]. The heavy metal content was measured both in the polluted waters and in the biotic tissues. Moreover, the sensor electroanalytical performances upon different storage and working conditions were studied in order to improve the reliability of the detection, highlighting a strong dependence on storage humidity conditions as well as on bismuth electrodeposition conditions.

Besides, enzymatic inhibition sensors were realised using paper supports for the detection of mustard agents, toxic substances used as airborne chemical weapons in the military field and in terrorist activities [2,3]. Office and filter paper were chosen as supports for the electrode serigraphic printing, to develop sustainable and easy-to-dispose sensors. Particularly, the filter paper porosity was harnessed to pre-load the reagents on the sensor, allowing for the realisation of a reagent-less origami-like sensor. Mustard agent detection was performed by measuring their inhibitory activity toward choline oxidase enzyme, through the amperometric detection of the enzymatic by-product $H_2O_2$. A carbon black/Prussian blue nanocomposite was employed to enhance the electrochemical performances toward $H_2O_2$ reduction. The resulting sensors represent sustainable and easy-to-use analytical tools for the detection of mustard agents (i.e. bis(2-chloroethyl) sulphide) in liquid samples (LOD = 0.9 mM and 0.4 mM for office and filter paper sensors, respectively) as well as in aerosol phase (origami sensor: LOD = 0.019 g/m$^3$), paving the way for the on-site and real-time monitoring of mustard agents in high-risk areas.

[1] N. Colozza, M. F. Gravina, L. Amendola, M. Rosati, D. E. Akretche, D. Moscone, F. Arduini. *Sci. Tot. Environ*., 2017, **584-585**, 692-700.

[2] N. Colozza, K. Kehe, G. Dionisi, T. Popp, A. Tsoutsoulopoulos, D. Steinritz, D. Moscone, F. Arduini, *Biosensor Bioelectron*., 2019, **129**, 15-23.

[3] N. Colozza, K. Kehe, T. Popp, D. Steinritz, D. Moscone, F. Arduini, *Environ. Sci. Pollut. Res*., 2018, https://doi.org/10.1007/s11356-018-2545-6

# Advanced and functional materials for sodium secondary batteries

## Premio di Dottorato 2019 “alla memoria del Prof. Giovanni Davolio”

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In modern energy economy, particularly for large-scale stationary electric energy storage systems, is crucial to find a valid alternative to lithium-ion batteries (LIBs), in order to develop devices with similar characteristics in terms of energy densities and performances, but cheaper than the existing ones, and with a better look at the sustainability of the all of the cell components. Amongst the post-LIBs technologies under development, sodium-ion batteries (NIBs) appear to be the most appealing and ready-to-use systems. Clearly, technological advances, particularly in materials science viewpoint, must be effectively implemented.

Taking into account the abovementioned challenges and expectations for large-scale energy storage devices in the near future, the target of this PhD Thesis was the study and the development of novel polymer electrolytes and organic electrodes to fabricate high energy, safe and ecofriendly NIBs and the assessment of their physico-chemical characteristics and electrochemical behaviour. Different systems were prepared, carefully characterized and tested in lab-scale cell configuration, comprising cellulose-based hybrid polymer electrolytes [1], and innovative crosslinked quasi-solid polymer membranes, both methacrylate-based and PEO-based ones [2,3], produced by UV-induced photopolymerization strategies. The final part of the PhD thesis work was then focused on the development and electrochemical characterization of a carboxylate organic electrode for NIBs, the disodium benzenediacrylate ($Na_2BDA$), with a vision towards all polymeric NIBs.

Overall, the efficient implementation of safe and ecofriendly polymer electrolytes in sodium based rechargeable batteries was effectively demonstrated by exploiting UV-induced photopolymerization that, compared to other techniques, is simple, fast, eco friendly and energy saving, thus easily scalable to the industrial level. Moreover, the promising prospects of organic materials were successfully demonstrated as valid alternatives to common inorganic electrodes in NIBs, especially when the severe solubility issues in common liquid electrolytes are prevented, which can lead to different beneficial effects, not only from the environmental point of view, but also for the realization of flexible, lightweight and low-cost Na-ion battery electrodes.

[1] F. Colò, F. Bella, J. R. Nair, M. Destro and C. Gerbaldi, *Electrochim. Acta*, 2015, **174**, 185–190.
[2] F. Bella, F. Colò, J. R. Nair and C. Gerbaldi, *ChemSusChem,* 2015, **8**, 3668-3676.
[3] F. Colò, F. Bella, J. R. Nair and C. Gerbaldi, *J. Power Sources*, 2017, **365**, 293/302.

# PLENARY LECTURES

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**Richard G. Compton**
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(PL_M02)

**Michel Armand**
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**Anthony Kucernak**
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# Around the electric charge

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Electric charge is one of the most important magnitudes to be determined in Electrochemistry, as it relies with the amount of matter involved in the reaction through Faraday laws. Coulometry is a well stablished analytical technique to quantify different species. Incidentally, it is widely used to evaluate the real surface of the electrocatalysts. Charge density on well-defined surfaces can be used to identify the surface stoichiometry of atomic level processes, such those taking part in underpotential deposition, which is the first stage of building of metallic layers on single crystal substrates. Indeed, this also includes the initial state of platinum surfaces at low potentials, which contain a monolayer of adsorbed hydrogen prior to hydrogen evolution.
In this presentation, I would like to discuss surface charge density as a characterization tool on atomically defined platinum single crystal electrodes. The aim would be to point out apparent discrepancies in evaluating coulometry of different adsorbate layers and the validity of Faraday laws in Surface Electrochemistry. Special emphasis will be dedicated to define the potential at which the charge is zero at platinum single crystals. The implications in the anion adsorption processes and the thermodynamic analysis of adsorbed layers at positive or negative charges will be discussed. It is possible to evaluate acid-base properties at the interface and compare with the values in bulk solution. It will be shown that surface pK values are higher than in bulk solution, even at the zero charge potential [1], thus suggesting that water at the interface is more alkaline [2]. The concept of neutral pH at the interface will be also discussed [3].

[1] R. Martínez-Hincapié, A. Berná, A. Rodes, V. Climent, J.M. Feliu, J. Phys. Chem. C 120 (2016) 16191-16199.
[2] J.K. Beattie, A.M. Djerdjev, G.G. Warr, Faraday Discuss. 141 (2009) 31-39.
[3] R. Rizo, E. Sitta, E. Herrero, V. Climent, J.M. Feliu, Electrochim. Acta 162 (2015) 138-145.

# Electrochemical studies of nanoparticles

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First the analytical need for nanoparticle detection will be introduced and electorchemical studies of nanoparticles showen to allow for and electrochemical studies on suspensions of nanoparticles shown to allow the detection and characterisation of diverse nanoparticles at the single entity level. For electroactive nanoparticles such as those of silver, Ag, or iron oxide, $Fe_3O_4$, quantification of the charge associated with single collisional impacts, allows the sizing of the particles in the range from ca 100nm down to less than 5nm. The frequency of impact events permits particle concentrations to be estimated and the potential dependence indicates the chemical nature of the impact particles.

In many cases the electrochemistry reveals agglomeration or aggregation of the particles and since the monomers and agglomerated diffuse at different speeds the kinetics of de-agglomeration can be inferred in cases such as that of uncapped $Bi_2O_3$ particles where the electrochemical signals are dominated by the monomer signal whilst independent evidence shows significant agglomeration in bulk solution. A models for the extent of agglomeration will be discussed.

Second the extension to the study, at the single entity, will; be described in terms of the detection of bacteria, red blood cells, the doping of particles of solids and polymers and in nano-droplets will be reported.

Finally the possible nano-toxicity of silver will be discussed

# Novel solutes for liquid and polymer electrolytes

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The race for high energy density batteries being at the same time sustainable and safe is becoming frantic. Today's batteries of the LIB type use mostly cobalt-containing positive electrode materials and a flammable liquid electrolyte based on organic carbonate solvents in which $LiPF_6$, a relatively unstable salt, is dissolved. On the other hand, lithium metal (Li°) batteries using a polymer electrolyte reach comparable energy densities, even with the lower voltage but green $LiFePO_4$ electrode [1]. The system however operates at ≈ 70°C. The electrolytes controls thus the type of (electro)chemistries that can be harnessed, and the solute is critical.

The traditional salt for polymer electrolytes has been $Li[(CF_3SO_2)_2N]$ (LiTFSI) due to its high dissociation and outstanding stability. The more conductive lower homolog $Li[(FSO_2)_2N]$ is not used industrially as it is not thermally stable enough for extrusion at high temperature (≈ 250°C), though it gives better SEI with Li°. The drawback of both salts is their low cation transference number (≤ 0.25) resulting in strong concentration gradients during operation.

We hypothesized that introducing some protons in the structure of the anion would result in the formation of hydrogen bonds either with the other surrounding anions or with the donating oxygens in the polymer (solvent), slowing them. Thus $Li[CF_2HSO_2NSO_2CF_3]$ (LiDFTFSI) and $Li[CH_3SO_2NSO_2CF_3]$ (LiMTFSI) were synthesized through routes that could be scaled-up. Both salts are thermally and hydrolytically stable. The conductivity in PEO 20:1 at 70°C and the transference numbers (Bruce & Vincent method) are summarized in table 1:

| | TFSI | DFTFSI | MTFSI |
|---|---|---|---|
| $\sigma_{total}$ (mS cm$^{-1}$) | 6.97 | 5.66 | 3.87 |
| $T_+$ | 0.23 | 0.35 | 0.49 |
| $\sigma_{Li^+}$ (mS cm$^{-1}$) | 1.58 | 1.98 | 1.90 |

The results confirm the hindered mobility of the proton-containing anions, resulting in a net cation-only conductivity superior to that of LiTFSI, the reference salt. As expected, the anodic stabilities measured in PC decrease with the increasing concentration of protons, but stay well above 4.5 V for practical applications.

The different implications of the discovery of these novel salts, for polymers, but also for liquid electrolytes will be discussed, and other strategies for reaching high transference numbers will be detailed.

[1] http://www.bollore.com/en-us/activities/electricity-storage-and-solutions/blue-applications.

# Measurement of electrocatalyst activity at the electrolyte-gas interface: Determination of mass transport free electrocatalyst performance

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The vacuum deposited catalyst method is an approach which allows development of ultra low loading electrodes (<1 $\mu g_{pt}$ $cm^{-2}$) with very high mass transport performance ($k_{MT}$ > 10 cm $s^{-1}$ c.f for rotating disk electrode $k_{MT}$ <0.005 cm $s^{-1}$) optimised for gaseous reactant transport[1]. This new approach has allowed a range of observations of the hydrogen evolution and oxidation and oxygen evolution and reduction reactions hitherto unseen, as it allows access to ***specific*** current densities much higher than achievable in electrolysers or fuel cells (~A $cm^{-2}$)[2]. In this presentation we consider the effect of spectator species on the electrocatalytic performance of the above reactions and also consider the application of the approach to produce ultra-low loading fuel cell electrodes. We also consider the combination of this approach with a range of different secondary measurement techniques such as SECM, mass spectrometry and FTIR.

One of the important aspects of this approach is its ability to deconvolute the activity of facets and edges on nanoparticles. By considering the performance of the hydrogen reactions as a function of Pt particle size (2.1 – 15 nm) using a set of well characterised catalysts, we find that the activity is composed of two components which vary in a defined way with particle size[3] figure 1(a). Geometrical considerations and electrokinetic modelling suggest that those two components correspond to (a) the response of edges/vertices, and (b) the response of facets (Pt(100) and Pt(111)), Figure 2(b). Edges and vertices are much more active towards the hydrogen reaction close to the equilibrium potential than facets, Figure 2. This suggests that for the hydrogen reaction, the ideal catalysts are highly defective with few facets. For the oxygen reduction reaction we find the opposite case – facets are more active than edges.

By modelling the individual performance of each of the two different sites, we obtain parameters for the exchange current densities on both sites. We find that the edge sites have an exchange current density which is about two orders of magnitude greater than the facet sites, but that the performance of the facet sites are still reasonable considering the results on single crystal electrodes.

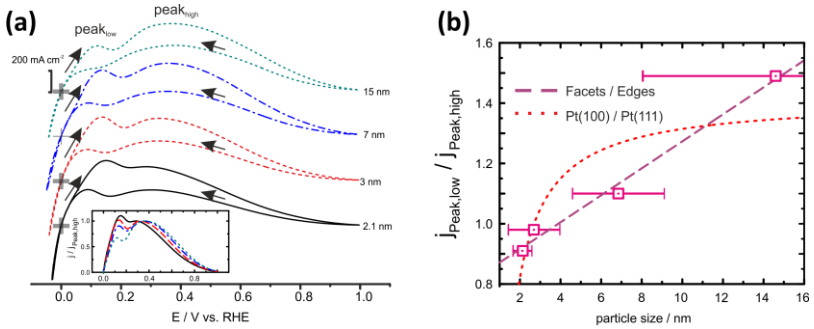


Figure 1. (a) Voltammograms (corrected to surface specific current density) of the HOR for Pt/C of different particles sizes with targeted loading to give a roughness factor in the range 0.7 – 1. Inset: Anodic scan in normalised to the height of the second peak. (b) Plot of ratio of peak current densities for the low and high peaks as a function of platinum particle size along with best fit curves for the response expected if the peaks are due to facets and edges or just different facets (Pt100 vs Pt111). The CVs were run in 4 mol $dm^{-3}$ $HClO_4$ at 10 mV $s^{-1}$ at 298 K. 1 bar hydrogen.

[1] Zalitis CM, Kramer D, Kucernak AR. , *Phys. Chem. Chem. Phys*. 15 (2013) 4329-4340.
[2] Zalitis CM, Kramer D, Sharman J, Wright E, Kucernak AR., *Polymer Electrolyte Fuel Cells* 132013. p. 39-47.
[3] Zalitis, CM; Kucernak, AR; Sharman, J; Wright E, *J. Mat. Chem. A,* 5 (2017) 23328-23338

# Developing efficient electrocatalysts for the reduction of $CO_2$ to CO: From metal porphyrin complexes to metal/nitrogen doped carbon

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Rising concentrations of $CO_2$ in the atmosphere is a huge concern since it is one of the main contributors to global warming. In the Carbon Dioxide Activation Center (CADIAC) we believe that $CO_2$ can be used for not only storing intermittent electrical energy but also as a valuable feedstock for production of important chemicals. Electrochemical reduction of $CO_2$ is one of the most important methods for accomplishing this. However, the use of high-performing catalyst materials for lowering the large overpotential associated with the direct electroreduction is needed to drive the process.

We develop efficient catalysts, including metal porphyrin complexes and single metal atoms incorporated in nitrogen doped carbon materials, for the electrochemical conversion of $CO_2$ to CO in aqueous media. Metal porphyrin complexes are electrocatalytically active themselves but once they are immobilized on a carbon support, they exhibit both enhanced activity and long-term stability [1]. The electrocatalytic performance can be further improved for materials where single metal atoms are supported in a nitrogen doped carbon material [2]. Importantly, these materials may be produced using pyrolysis of a common bio source such as amino acids. Advanced structural analysis along with theoretical calculations suggest that the coordination environment of the individual metal atoms is much more multi-faceted than that of the well-defined metal porphyrin complexes. Finally, we have been able to demonstrate that iron carbide, which usually is very active for the hydrogen evolution reaction, can boost the $CO_2$ reduction activity of nitrogen doped carbon significantly, once it is wrapped by carbon layers [3].

[1] X.-M. Hu, M. Rønne, S. U. Pedersen, T. Skrydstrup and K. Daasbjerg, *Angew. Chem. Int. Ed.* **56** (2017) 6468–6472.
[2] X.-M. Hu, H. H. Hval, E. T. Bjerglund, K. J. Dalgaard, M. R. Madsen, M.-M. Pohl, E. Welter, P. Lagmani, K. B. Buhl, M. Bremholm, S. U. Pedersen, T. Skrydstrup and K. Daasbjerg, *ACS Catal.* **8** (2018) 6255–6264.
[3] J.-J. Shi, X.-M. Hu, M. R. Madsen, P. Lamagni, T. E. Bjerglund, S. U. Pedersen, T. Skrydstrup and K. Daasbjerg, *ACS Appl. Nano Mater.* **1** (2018) 3608–3615.

# KEYNOTE LECTURES

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**Aldo Di Carlo**
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**Steve G. Greenbaum**
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**Fabio La Mantia**
University of Bremen, Germany
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**Isotta Cerri**
Toyota Motor Europe, Belgium
(K_W05)

**Marco Panizza**
Università degli Studi di Genova
(K_Th06)

# Enantiodiscrimination in electrochemistry and electroanalysis: implementing "inherent" chirality at the electrochemical interphase

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All electrochemical processes are intrinsically "intelligent" on account of the selectivity achievable by controlling the electrical potential, also providing a convenient tool for transduction of recognition events. However, chirality can make electrochemical processes even smarter, implying to discriminate between enantiomers of a given electroactive chiral molecule in terms of potential difference, for advanced analytical, synthetic or device applications.

To achieve enantioselective electrochemistry and electroanalysis, electron transfer processes at the interphase must take place in the presence of a suitable enantiopure chiral selector, resulting in energetically different diastereoisomeric conditions for the two probe enantiomers [1]. Particularly effective are molecular selectors endowed with "inherently chirality", *i.e.* with chirality and key functional properties originating from the same structural element (in our case coinciding with the main molecular backbone, featuring a tailored torsion). Actually large enantiomer peak potential differences have been observed in voltammetry:

*(i)* working in achiral media, on electrode surfaces modified with thin films of inherently chiral electroactive oligomers [1,2]; they can be electrodeposited from enantiopure monomers consisting of an atropoisomeric biheteroaromatic core with oligothiophene wings, or of a thiahelicene scaffold. Such films also exhibit attractive chiroptical properties (also electrochemically modulable) as well as impressive results in magnetoelectrochemistry experiments, and can be detached and tested as self-standing chiral membranes;

*(ii)* working on achiral electrodes, implementing inherent chirality in their interphase with an ionic liquid IL medium, exploiting the latter's peculiarly high order [1,3]. We developed inherently chiral ionic liquids ICILs consisting in double salts of atropoisomeric bipyridinium scaffolds with long alkyl chains. Very conveniently, enantiodiscrimination is observed not only working in a bulk ICIL, but also using it, or other inherently chiral selectors, as low-concentration chiral additives in commercial achiral ILs. Less remarkable enantiodiscrimination was observed working with chiral (not "inherently" chiral) biobased ionic liquids CILs.

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[1] S. Arnaboldi, M. Magni and P.R. Mussini, *Curr. Opin. Electrochem.*, 2018, **8**, 60–72.
[2] F. Sannicolò, S. Arnaboldi, T. Benincori, V. Bonometti, R. Cirilli, L. Dunsch, W. Kutner, G. Longhi, P.R. Mussini, M. Panigati, M. Pierini and S. Rizzo, *Angew. Chem. Int. Ed.* 2014, **53**, 2623-2627.
[3] S. Rizzo, S. Arnaboldi, V. Mihali, R. Cirilli, A. Forni, A. Gennaro, A.A. Isse, M. Pierini, P.R. Mussini and F. Sannicolò, *Angew. Chem. Int. Ed.* 2017, **56**, 2079-2082.

# Dye sensitized and erovskite photovoltaics: from cells to modules

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Photovoltaic (PV) technologies are facing an exciting and stimulating development due to the use of organic and hybrid organic-inorganic solution process materials. In this so called III-Generation PV, the electrochemical cell named Dye Sensitized Solar Cells (DSSCs) laid the foundation for the development of the Perovskite Solar Cells (PSCs) that permit to achieve certified efficiency exceeding 24%.
DSSCs have revealed important features in terms of cost, lightning conditions and lifetime, with respect to other photovoltaic (PV) technologies. Processing of DSSC enables a full customization of the photo-active area of the devices that allows for achieving aesthetical requirements partially disabled by traditional photovoltaic technologies. In the first part of this talk, I will focus on this technology and its application in Building Integrated PV (BIPV).
The second part of the talk is devoted to Organometal Lead Halide Perovskites, such as $CH_3NH_3PbI_3$ (MAPI), which have opened up new directions to fabricate cost effective and high efficient PV devices. I will focus in particular in the recent developments in the use of Graphene and related 2D materials in conjunction with PSCs. Many factors can influence the efficiency and stability characteristics of PSCs. In this perspective, 2D nanomaterials, such as graphene and related materials can play a primary role owing to their 2D nature and the large variety of 2D crystals, whose complementary opto/electronic properties, can be on-demand tuned by chemical functionalization and edge modification. Here, we show the use of graphene and 2D materials as an effective way to control the morphology [1] and to stabilize the device's interfaces. Several strategies have been used to master interface properties both at the anode and cathode parts of the cell. By dispersing graphene flakes into the mesoporous TiO2 layer and by inserting graphene oxide (GO) [2] or $MoS_2$ as interlayer between perovskite and Spiro-OMeTAD layers, we show that PCE exceeding 20% with a two-step MAPI deposition can be achieved also for process in air. This approach can been exploited for the fabrication of state-of-the-art large area perovskite modules with a PCE > 15% on an active area exceeding 80 cm2. The use of 2D materials permitted to increase the PCE by more than 10% with respect to "conventional" modules.[3]. A discussion on the relation between 2D interface engineering and stability of the PSC will be presented.

[1] F. Biccari et al. Adv. Energy Mat. 2017, 7, 1701349
[2] A. Agresti et al. ChemSusChem 2016, 9, 2609
[3] L. Najafi et al. ACS nano, 2018, 12, 10736-10754
[4] A. Agresti et al. ACS Energy Lett. 2017, 2, 279−287

# Recent liquid state and solid state NMR investigations of battery electrolytes

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Our laboratory is focused on application of various nuclear magnetic resonance (NMR) techniques to help understand structure and dynamics of energy storage materials. In this presentation we discuss three recent collaborative efforts. The first topic, in collaboration with Oak Ridge National Lab (R. Ruther, J. Nanda), is on glyme-based sodium electrolytes being developed for Na ion batteries and electrolytic double layer capacitors, in which similarities and differences in ion solvation and cation-anion pairing, compared to the corresponding Li electrolytes, are highlighted. The study of ion pairing tendencies in the glymes led us to do a deeper dive in commercial-type liquid carbonate electrolytes, in collaboration with the U.S. Army Research Lab (K. Xu, O. Borodin, A. von Cresce), where we employ NMR spectroscopy and diffusometry to shed additional light on ion solvation and transport. Next, in joint work with Tel Aviv University (M. Lifschitz, E. Cohen, D. Golodnitsky), we analyze local structure and Li+ ion transport in composite polymer/ceramic electrolytes prepared by electrophoretic deposition for 3-D microbatteries. Finally, in collaboration with Ionic Materials, Inc., we discuss recent results for a solid polymeric electrolyte with room temperature conductivity > 1 mS/cm based on inexpensive semicrystalline polyphenylene sulfide and Li salts such as LiTFSI. This solid polymer can be reliably extruded into thin films, is non-flammable, has attractive mechanical properties for lithium dendrite suppression, is electrochemically stable against Li, and is compatible with a variety of cathodes, including NMC with low cobalt content.

# Lithium recovery by means of electrochemical ion pumping

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The development and the spreading of lithium-ion batteries for stationary energy storage and of (hybrid and fully) electrical vehicles will led in the next years to an increase of the demand of lithium and consequently of its price. According to the UE, lithium is above threshold of criticity in terms of economic importance and slightly below it for the supply risk. However, it is forecast that in the next two decades the request of lithium will overcome six to ten times the potential of its mineral deposit [1], thus endangering the supply. The easiest and most economically competitive production is currently carried out through the lime-soda evaporation process, which mostly uses the brines of salt lakes, the so-called salar, located at the borders of Chile, Bolivia and Argentina [2]. This method produces a large amount of chemical waste and causes a sever environmental impact [2].

In 2012, Pasta et al. have developed a new process for the lithium extraction, using the principle of electrochemical ion pumping [3]. Here, I will present the working principle of the technique, the fundamental advancements in materials [4,5], and reactor design and control [6]. By proper choice of materials, current density, and mass loading, it was possible to concentrate lithium chloride from a 1.5 L source solution of 1 mM LiCl in a 5 mL recovery solution of 100 mM LiCl in 9 capture / release cycles (See Figure 1). The economic feasibility of the process will be briefly discussed.

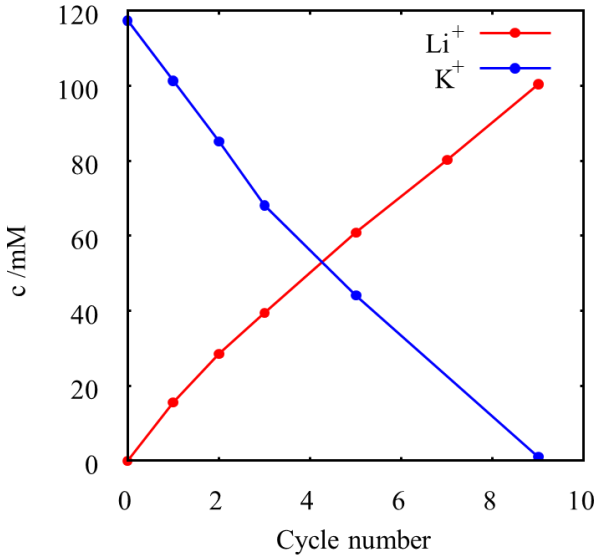


**Figure 1**: $Li^+$ and $K^+$ concentration in the recovery solution for each cycle.

[1] D. Kushnir and B. A. Sandén, *Resour. Policy*, 2012, **37**, 93–103.
[2] V. Flexer, C. F. Baspineiro, and C. I. Galli, *Sci. Total Environ.*, 2018, **639**, 1188–1204.
[3] M. Pasta, A. Battistel, and F. La Mantia, *En. & Environ. Sci.*, 2012, **5**, 9487-9491.
[4] R. Trócoli, A. Battistel, and F. La Mantia, *ChemSusChem*, 2015, **8**, 2514-2519.
[5] R. Trócoli, C. Erinmwingbovo, and F. La Mantia, *ChemElectroChem*, 2017, **4**, 143-149.
[6] M.S. Palagonia, D. Brogioli, and F. La Mantia, *J. Electrochem. Soc.*, 2017, **164**, E586-E595.

# Toyota fuel cell development for a sustainable future

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Toyota believes that the hydrogen fuel cell system is a technological breakthrough with the potential to deliver sustainable, zero-emissions mobility as part of a low carbon society. This forms an important part of Toyota long-term Environmental Vision 2050 and the desire to create true harmony between society and nature.
Believing that hydrogen will be a leading energy carrier Toyota started the development of fuel cell technologies in 1992 and, through several model changes and 'limited market' introduction, launched the hydrogen fuel cell electric vehicle ('Mirai' that means future in japanese) around 2015. In addition to a very attractive drivability the vehicle features a cruising range of more than 500km, a cold-start capability at -30°C and about 3 minutes refuelling time. The system integrates in-house made components such as the fuel cell stack, the boost converter and the high-pressure hydrogen tanks.
With a maximum power of 114 kW the Toyota fuel cell stack [1] achieves a volumetric power density of 3.1 kW/L thanks to the design and manufacturing of a unique separator consisting of 3D fine mesh flow channels and an internal water circulation system that eliminate the use of any external humidifiers.
Toyota is now looking at the future plan to decrease the cost of the technology with no compromise of performance and life-time, for instance by reducing the amount of PEMFC stack materials. Significant R&D efforts and advancements have been made and will be presented
The technical prospects and R&D approaches for the remaining technical challenges on performance and durability for the next generation FCEVs will be introduced and discussed.

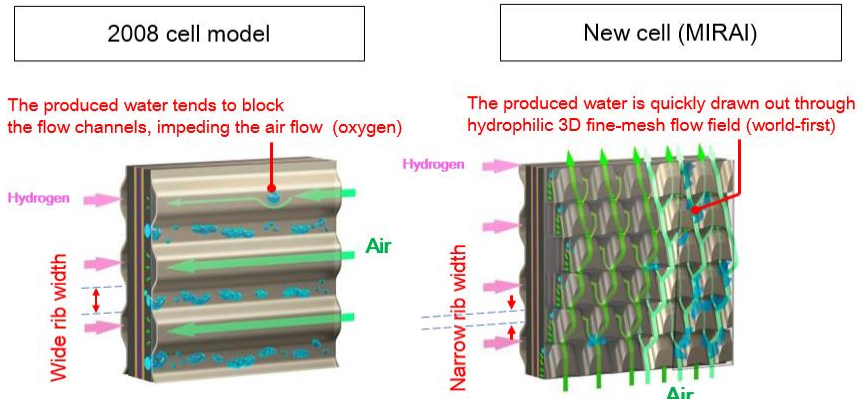


**Figure 1**: Design modification of fuel cell separator. Left: conventional straight channel design, Right: 3D fine mesh flow channel design

[1] T. Yoshida and K. Kojimaa, Electrochem. Soc. Interface Summer, 2015, **24**, 2, 45-49

# Past and present of electrochemical treatment of organic pollutants

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Oxidative electrochemical technologies offer an alternative solution to many environmental problems in the process industry, because electrons provide a versatile, efficient, cost-effective, easily automatable, and clean reagent. In electro-oxidation, organic pollutants can be removed by different methods:

(i) Direct electrolysis: the pollutants (R) are oxidized after adsorption on the anode surface without the involvement of any substance other than electrons:
$R_{ads} \rightarrow P_{ads} + ze^-$

(ii) Oxidation via intermediates of oxygen evolution: organic compounds are oxidised near the anode surface (M) at high potentials in the region of water discharge due to the participation of intermediates of oxygen evolution:
$M + H_2O \rightarrow M(^\bullet OH) + H^+ + e^-$
$R + M(^\bullet OH) \rightarrow M + CO_2 + H_2O$
Anodes with high oxygen evolution overpotential, such as $SnO_2$, $PbO_2$ or boron-doped diamond (BDD) are ideal electrodes for the complete oxidation of organics to $CO_2$ in wastewater treatment.

(iii) Indirect electrolysis mediated by oxidizing agents generated anodically: organic pollutants are removed through the mediation of some electroactive species generated at the anode surface, which act as intermediaries for electrons shuttling between the electrode and the organic compounds. The main oxidizing chemicals electrogenerated anodically are active chlorine and persulfates, that are produced by the oxidation of chloride and sulphates ions commonly present in wastewaters:
$2Cl^- \rightarrow Cl_2 + 2e^-$
$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2H^+ + 2e^-$

(iv) Electro-Fenton processes: the pollutants are removed by the $^\bullet OH$ produced in the bulk of the solution using the electrogenerated Fenton's reagent where $H_2O_2$ is supplied in situ from the two-electron reduction of $O_2$ on cathodes such as gas diffusion electrodes (GDE), reticulated vitreous carbon (RVC) or graphite-felt, and $Fe^{2+}$ is continually regenerated from $Fe^{3+}$ reduction:
$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^\bullet OH$
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$
$Fe^{3+} + e^- \rightarrow Fe^{2+}$

(v) Coupled anodic and cathodic Processes: using an undivided cell, the contaminants are treated by $H_2O_2$ generated on the cathode and oxidizing agents or $^\bullet OH$ generated at the anode.

Process selection depends on the nature of the electrode material, experimental conditions, and electrolyte composition. This lecture focuses on recent progress in the most promising electrochemical tools for the treatment of wastewater contaminated by organic pollutants.

# ORAL PRESENTATIONS

# Electrochemical detection of melanoma biomarkers in tissue

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In this talk, the electrochemical detection of melanoma, the most dangerous form of skin cancer, is presented using Soft-Probe Scanning Electrochemical Microscopy (Soft-Probe-SECM). Skin samples from humans and mice were obtained either by biopsy or non-invasively by using adhesive patches [1, 2]. The melanoma biomarker tyrosinase (TYR), a sensitive and specific melanoma-associated antigen, was addressed by antibodies labelled with horseradish peroxidase (HRP, Fig. 1a). The HRP labels catalyzed the oxidation of ferrocene methanol, which was detected by soft microelectrodes that were gently brushed over the skin samples. Soft microelectrodes (inset in Fig. 1a) have been demonstrated to be powerful tools for scanning in contact mode square millimeter-sized biological specimens with low risk of damaging the sample, making the soft probes very attractive for cancer research and diagnostics [3]. Measured TYR levels in melanoma tissue were compared with those in normal skin. Increasing TYR values were found with progression of the tumor (Fig. 1b) [2]. Melanoma staging was further achieved by imaging with micrometric resolution the heterogeneous TYR activity, which is a result of immuno-suppression at higher melanoma stages [1]. The results on tissue were confirmed by analyzing samples made of *in vitro* grown human melanoma cell lines representing three different stages of tumor growth.

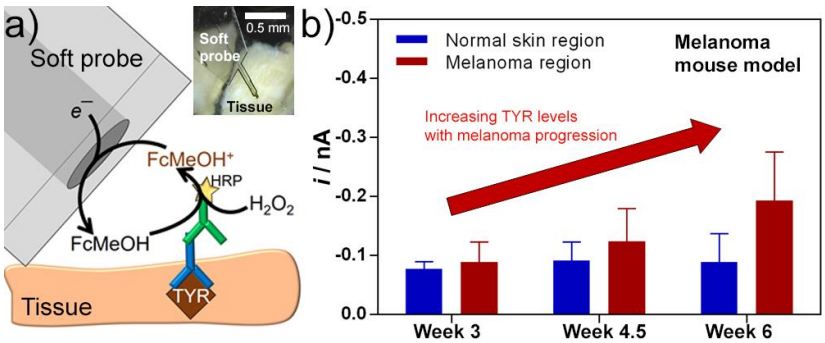


**Figure 1**: a) Electrochemical detection of the melanoma biomarker TYR using antibodies with HRP labels and FcMeOH as electro-active substrate [3]. b) Bar plot with averaged currents over normal and melanoma skin regions from skin with increasing tumor growth [2].

[1] T.-E. Lin, A. Bondarenko, A. Lesch, H. Pick, F. Cortés-Salazar and H. H. Girault, *Angew. Chem. Int. Ed.* 2016, **55**, 3813–3816.
[2] S. Darvishi, H. Pick, T.-E. Lin, Y. Zhu, X. Li, P.-C. Ho, H. H. Girault and A. Lesch, **submitted**.
[3] T.-E. Lin, S. Rapino, H. H. Girault and A. Lesch, *Chem. Sci.* 2018, **9**, 4546–4554.

# Human flavin monooxygenase electrodes modified with graphene oxide: a tool for personalised medicine

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Human flavin-containing monooxygenase 3 (hFMO3) is a membrane-bound hepatic protein which belongs to phase-1 drug metabolising enzymes. This enzyme catalyses the selective oxygenation of drugs containing a soft nucleophile (mainly nitrogen or sulphur) by incorporation of one atom of molecular oxygen, a detoxification process whereby the drugs are transformed into polar and excretable molecules.

Previously, we had successfully immobilised hFMO3 on both gold and carbon electrodes [1]. Here, in order to enhance the electrochemical response of hFMO3 it was immobilised in the presence of graphene oxide (GO). Oxygen-containing groups of GO, allow it to be suspended in water and make it compatible with biological applications not available to graphene. Electrochemical characterisation of the immobilised enzyme with GO and didodecyldimethylammonium bromide (DDAB) on glassy carbon electrodes was carried out by cyclic voltammetry where several parameters including redox potential, electron transfer rate and surface coverage were determined. This system's application in drug screening was demonstrated by the N-oxidation of two therapeutic drugs [2], benzydamine (anti-inflammatory) and tamoxifen (breast cancer), by the immobilised enzyme (Fig. 1).

The use of GO in the presence of DDAB is a clinically relevant biotechnological approach with potential application in not only high throughput screening of new chemical entities, but also deciphering the implications of hFMO3 polymorphism in drug metabolism [3], i.e. Personalised Medicine.

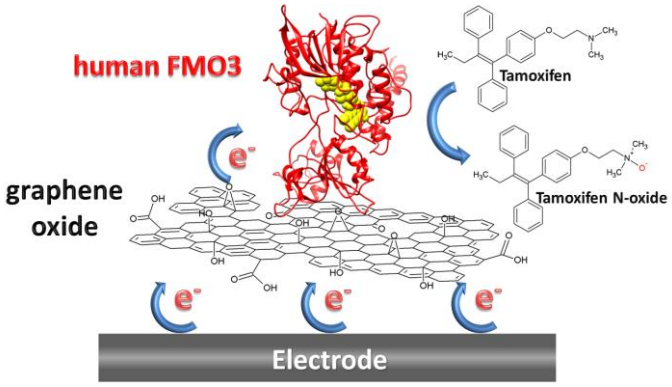


**Figure 1**: Immobilisation of hFMO3 on carbon electrodes in presence of graphene oxide for possible applications in drug discovery and metabolism.

[1] S. Sadeghi, R. Meirinhos, G. Catucci, V. Dodhia, G. Di Nardo and G. Gilardi, *J. Am. Chem. Soc.* 2010, **132**, 458-459.
[2] S. Castrignanò, G. Gilardi and S. J. Sadeghi, *Anal. Chem.* 2015, **87**, 2974-2980.
[3] S. Castrignanò, S. Bortolussi, G. Catucci, F. Valetti, G. Gilardi and S. J. Sadeghi, *Electrochim. Acta* 2017, **228**, 611-618.

# Metal-semiconductor hybrids for electroanalytical purposes

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The use of hybrid nanomaterials is increasing in the recent research since they can act as "brave new materials" with physico-chemical properties different and often enhanced with respect to the relative single components. In fact, hybrid nanocomposites are not the simple sum of the precursors, due to the introduction of the so-called "heterojunction".

The unprecedented characteristics paved the way towards the application of the hybrids in many fields such as sensing, catalysis and electrocatalysis, photocatalysis, environmental chemistry and electroanalysis [1]. However, the study and application of these materials are often done simply by trial and error procedures, rarely accompanied by an investigation on the phenomena that are deeply located at the interfaces.

In the present work, the properties of metal-semiconductor hybrids are studied in depth, starting from a silver-anatase nanocomposite, for which the electrochemical virtues are proved both from experimental evidences (in terms of current densities and reproducibility) and from theoretical explanations at an atomic-scale level. The application of such device in the detection of neurotransmitters is verified, also focusing on the abatement of fouling and passivation. The material is so proven to be extremely robust against aging, showing complete regeneration even after years [2-3].

The interest is then moved towards a gold-anatase nanocomposite, in order to highlight any relevant difference with the correspondent Ag/$TiO_2$ hybrid. At a first glance, it can be claimed that while in the case of Ag/$TiO_2$ composite it is silver that adapts to titania, in the case of Au/$TiO_2$ the effect is not so clear. Gold is a more stable and a less adaptable metal than silver and this aspect reflects in big differences in the electrochemical response of the devices. Different dimensions of gold nanoparticles are considered and the effect of aging time on the $TiO_2$ sol is investigated. Finally, also this hybrid device is applied for electroanalytical purposes in the field of emerging contaminants analysis.

[1] A. V. Emeline, V. N. Kuznetsov, K. Ryabchuk, and N. Serpone, *Environ. Sci. Pollut. Res.* 2012, **19**, 3666-3675.
[2] G. Soliveri, V. Pifferi, G. Panzarasa, S. Ardizzone, G. Cappelletti, D. Meroni, K. Sparnacci, and L. Falciola, *Analyst* 2015, **140**, 1486-1494
[3] G. Di Liberto, V. Pifferi, L. Lo Presti, M. Ceotto, and L. Falciola, *J. Phys. Chem. Lett* 2017, **8**, 5372-5377

# Monitoring real time emission from pancreatic beta cells in dependence on their substrate: a scanning electrochemical microscopy study

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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 exocytosis. 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 addition, the progressive loss of activity of electrodes during the oxidation of these species is well documented.
This work is motivated by recent observation of the dependence on the metabolism of pancreatic cells on their growth substrate.
We approach the problem by monitoring the release of 5-HT by living cells stimulated by different species (glucose, KCl and anti-diabete drugs) by means of a microelectrode. This is paralleled by the study of cell growth substrates by scanning electrochemical microscopy in order to evaluate possible effects of the morphology on the availability of oxidizing species.

[1] C. Amatore, S. Arbault, M. Guille, F. Lemaitre, *Chem. Rev.*, 2008, **108**, 2585
[2] L. Huang, H. Shen, M. A. Atkinson, R.T. Kennedy, Proc. Natl. Acad. Sci. USA, 1995, **92**, 9608.

# Electrochemical sensing of non-electroactive analytes by molecularly imprinted polymer films on micro and nanoelectrodes

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Molecularly Imprinted Polymers (MIPs) are promising materials being explored extensively as recognition elements for sensors since they offer improved stability, cost effectiveness and rapid fabrication. In this study, we present the preparation and application of electrochemical sensors for the detection of non-electroactive analytes. The electropolymerization of a suitable monomer performed in the presence of the target analyte produces an imprinted scaffold deposited as a thin film on the surface of a metal electrode. After stabilization of the MIP and removal of the template, molecular cavities remain. When the MIP is exposed to the target analyte solution, the cavities are filled again. The blocking level of the cavities can be monitored voltammetrically by using a redox probe able to compete with the analyte for the active sites within the cavities.

In particular, we focused the study on the development of MIP based sensors suitable for the trace detection of two non-electroactive analytes, namely an emerging pollutant that is perfluorooctane sulphonate (PFOS) [1] and a sugar of interest for the food industry, that is L-arabitol [2].

Contamination of waters by perfluorinated alkyl substances (PFAS) is a problem of global concern. Because of its suspected toxicity and bioaccumulation, perfluorooctane sulfonate (PFOS) is perhaps the perfluorinated compound of major concern, for which the lowest alarm concentration limits (30 ng/L i.e. 6 x $10^{-11}$ M) have been indicated. The here proposed sensor is based on a gold electrode modified by a thin coating of a molecularly imprinted polymer (MIP), prepared by anodic electropolymerization of o-phenylenediamine (o-PD) in the presence of PFOS as the template. Ferrocenecarboxylic acid is exploited as electrochemical probe suitable to compete with PFOS, generating analytically useful voltammetric signals. The sensor is characterized by a low detection limit (4 x $10^{-11}$ M), satisfactory selectivity, reproducibility and repeatability, furnishing analytical results in agreement with those obtained by HPLC-MS/MS analyses, also in real water samples.

L-arabitol is classified as one of the top 12 biomass-derivable building block chemicals, with low-calorific, low-glycemic, anticariogenic, and prebiotic character. In humans, abnormal concentrations of arabitol indicate the existence of infections by *Candida spp*. or other pathological conditions. A highly selective and sensitive sensor for L-arabitol is developed combining the high sensitivity offered by three-dimensional nanostructured electrodes, namely, 3D-ensembles (3DNEE) of gold nanowires, with the recognition capability of MIPs. The MIP/3DNEE is prepared by controlled etching of polycarbonate templated nanoelectrode ensembles, followed by electropolymerization of o-PD on the gold nanowires in the presence of L-arabitol as molecular imprinting template. In this case, the redox probe used to compete with the analyte is the ferrocenyl-methytrimethylammonium cation. The sensor is characterized by a detection limit as low as 7.5×$10^{-10}$ M. The applicability of the MIP/3DNEE in real samples is demonstrated by successfully quantifying L-arabitol concentration in sugarcane vinasse.

[1] N. Karimian, A.M. Stortini, L.M. Moretto, C. Costantino, S. Bogialli, P. Ugo, *ACS Sens.*, 2018, **3**, 1291-1298.
[2] M. A. Beluomini, N. Karimian, N. R. Stradiotto, P. Ugo, *Sensor Actuat. B-Chem.* 2019, **284**, 250–257.

# Probing electrochemiluminescence response through DNA sensor for the detection of specific DNA sequences

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Electrochemiluminescence (ECL) is a powerful transduction technique that has rapidly gained importance as a sensitive and selective transduction technique in analytical science gathering the advantages of the electrochemical sensitivity and the spatial resolution.[1]

Methods for the detection of specific DNA sequences have attracted significant attention due to possible applications in different fields such clinic diagnostics, food safety, environmental pollution analysis, and forensic identification. DNA sensors, the electrochemical equivalent of molecular beacons, appear to be a promising tool to detect oligonucleotides. [2,3]

In this work, the electrochemiluminescent behaviour of a DNA sensor was investigated through the use of a system comprised of a luminophore-reporter-modified stem-loop DNA probe (receptor) attached to an interrogating gold electrode via self-assembled monolayer chemistry. ECL is generated according to the "oxidative-reduction" strategy using Tripropylamine (TPA) as co-reactant and Ru(bpy)32+ as luminophore. Upon hybridization with a complementary oligonucleotide target we observe a change of the conformation of the stem-loop probe arising in a variation of the ECL signals.

Here we investigate the effect of probe density on the electrode surface and the variation of ECL signal at a nanometric distance from electrode using different set of stem–loop probes.

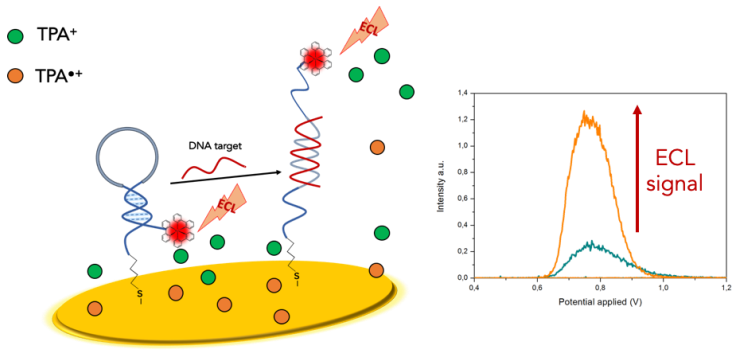


**Figure 1**: Schematic representation (left) and ECL response (right) of the DNA sensor using DNA beacon probe before and after the addition of complementary DNA target.

[1] G. Valenti, A Fiorani, H. Li, N. Sojic, F. Paolucci, *ChemElectroChem*, 2016, **3**, 1990–1997.
[2] W. Yao, L. Wang, H. Wang, X. Zhang, L. Li, N. Zhang, L. Pan, N. Xing, *Biosensors and Bioelectronics*, 2013, **40,** 356–361.
[3] F. Ricci, R. Y. Lai, A. J. Heeger, K. W. Plaxco, James J. Sumner, *Langmuir*, 2007, **23**, 6827-6834.

# Surface-confined electrochemiluminescence microscopy of cells

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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.[1]

Here we present the application of ECL imaging for the visualization of single cells and we show the potential diagnostic applications of our approach thought the direct ECL imaging of overexpressed proteins on tumor cells. [2]

We also demonstrated the efficient generation of ECL at the level of the entire basal membrane of single cells.[3] In contrast to the classic wide-field fluorescence microscopy, we observed that the ECL emission is confined to the immediate vicinity of the electrode surface and generated only at the level of the basal membrane. Finally, ECL microscopy allows observing membrane details, which are difficult to resolve by classic PL microscopy.

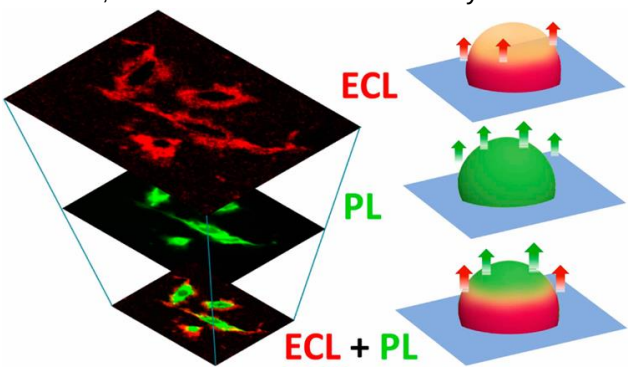


**Figure 1**: PL (green), ECL (red) and overlay of both luminescence signals cell

[1] A. Zanut, A. Fiorani, S. Rebeccani, S. Kesarkar, G. Valenti, *Anal. Bioanal. Chem.*, 2019, DOI: https://doi.org/10.1007/s00216-019-01761-x
[2] G. Valenti, S. Scarabino, B. Goudeau, A. Lesch, M. Jovic, E. Villani, M. Sentic, S. Rapino, S. Arbault, F. Paolucci, N. Sojic, *J. Am. Chem. Soc.* 2017, **139**, 16830-16837.
[3] S. Voci, B. Goudeau, G. Valenti, A. Lesch, M. Jović, S. Rapino, F. Paolucci, S. Arbault, N. Sojic, *J. Am. Chem. Soc.* 2018, **140**, 14753−14760.

# Spatially controlled electrochemical monitoring of reactive oxygen species production

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Reactive oxygen species are produced in living cells in several physiological and pathological processes [1,2]. Reactive oxygen species production by organic polymer upon light illumination is gaining more and more interest for its high throughput capability, selectivity and resolution. The exploitation of visible light requires the presence of photo-transducers; organic copolymers are generally good photo-transducers as they show easily tunable optical properties, good photocatalytic efficiency and they are characterized by excellent biocompatibility properties. Recently it has been showed that the organic copolymer poly-3-hexyl-thiophene (P3HT), once internalized as P3HT nanoparticles within the cell cytosol, generate ROS upon photo-stimulation [3].

By means of electrochemical approaches, such as Scanning ElectroChemical Microscopy (SECM), we measured ROS production by P3HT thin films and explored the impact on $H_2O_2$ production in the presence of relevant cellular redox proteins. Spatially-controlled illumination of substrates and simultaneous detection of hydrogen peroxide production at the micrometric scale were achieved by coupling Scanning ElectroChemical Microscopy (SECM) with a fluorescence inverted microscope. The hydrogen peroxide oxidation was specifically measured employing platinized-microelectrodes. The currents were recorded in dark and upon illumination in close proximity of the P3HT thin film substrate as compared to bare ITO substrates employing the modified electrode as SECM probes. We resolved the profile of $H_2O_2$ production by P3HT thin films upon photostimulation at the micrometric scale.

The interaction between P3HT thin films and a model redox protein (in the dark or upon photostimulation) was investigated exploiting our SECM/fluorescence microscope apparatus.

[1] M. Malferrari, M. Becconi, S. Rapino. *Anal. Bioanal. Chem.* 2019, in press. DOI: https://doi.org/10.1007/s00216-019-01734-0
[2] M. Malferrari, A. Ghelli, F. Roggiani, G. Valenti, F. Paolucci, M. Rugolo, S. Rapino. *ChemElectroChem.* 2019, **6**, 627–33.
[3] E. Zucchetti, M. Zangoli, I. Bargigia, C. Bossio, F. Di Maria, G. Barbarella, C. D'Andrea, G. Lanzani, M.R. Antognazza. *J. Mater. Chem. B* 2017, **5**, 565-574.

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# A simple and rapid system for the determination of inorganic mercury and methylmercury in fish products

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Fish represent a critical source of mercury into human diet. It is therefore evident how important is to constantly monitor the levels of total mercury (HgTOT) and to differentiate among forms of different toxicity in the fish products placed on the market.
In the present work, the analytical technique chosen to determine HgTOT and to distinguish between inorganic mercury (HgIN) and methylmercury (MeHg, the most toxic mercury form), in fish was anodic stripping voltammetry with the square-wave potential scan mode (SW-ASV) using a solid gold electrode (SGE). A procedure for the mineralization of the sample with a commercial food warmer, suitable for field operation, was developed. Mercury speciation was carried out with disposable cartridges obtained by modifying a commercial resin with a ionic liquid. The new modified resin was called CYXAD (*Patent Pending*).

An aliquot of each sample was treated with a mixture of $HNO_3$:$H_2O_2$ (1:1) in the food warmer, to extract HgTOT. Another aliquot was treated with HCl and the solution so obtained was passed through a cartridge packed with the CYXAD solid phase: the latter holds HgIN quantitatively, while MeHg is eluted. The eluate containing MeHg is discarded because its high $Cl^-$ content would damage the surface of the SGE. Recovery of HgIN immobilized on the CYXAD takes place by elution with $HNO_3$.
Aliquots of the two solutions, containing HgTOT and HgIN respectively, were transferred into a measuring cell and mercury was determined by SW-ASV with the SGE, using a portable potentiostat (PalmSens3, PalmSens BV). HgTOT and HgIN were determined, and MeHg was obtained by difference.

The method was tested on a certified fish sample, namely ERM 464 (European Reference Material - Tuna Fish), in order to evaluate its accuracy: the results were satisfactory, since the recovery was higher than 98% of the certified value.
Subsequently, the analysis of fish samples commonly found and widely consumed (canned tuna, swordfish, anglerfish, dogfish fillets, mussels, ...) was carried out and differentiation between HgTOT, HgIN and MeHg was obtained. These samples were also analyzed in parallel using Direct Mercury Analyser, DMA[1] (official method used by the Istituto Zooprofilattico del Piemonte, Liguria e Valle d'Aosta which made the instrument available to us) coupled to another speciation scheme.

The results obtained with the procedure developed in this work were consistent with those obtained by DMA, as well as with those found using a conventional microwave digestion followed by SW-ASV.

The proposed procedure is very simple, fast and low-cost; it can be used also by unqualified personnel. It is suitable for the determination of both HgIN and MeHg on site, so it can be applied for fast screening tests allowing the increase of controls on fish batches, with a view to reducing consumer health risks.

[1] S. Squadrone, E. Chiaravalle, S. Gavinelli, G. Monaco, M. Rizzi, M.C. Abete, *Chemosphere* 2015; **138,** 633–641.

# Supramolecular assisted growth of organometal halide perovskites for highly efficient light-emitting and photovoltaic devices

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The control over Organometal Halide Perovskites (OHPs) formation is a fundamental requirement foreseeing the exploitation of these outstanding, eclectic materials in optoelectronics. OHPs, extensively used in solar cells and light emitting diodes (PeLEDs) are deposited from solution on a target substrate and formed throughout a self-assembly process of their chemical precursors [1]. The resulting polycrystalline film shows often a far from ideal behaviour, due to unsuitable morphology and high defect density, direct consequences of a scarcely controllable assembly. We present here the exploitation of a tailored biopolymer, starch, as beneficial additional component of formamidinium (FA)- and methylammonium (MA)-based tri-iodide perovskite films. We prove how the macromolecule by establishing specific supramolecular interactions with OHPs precursors allows the deposition of an optimal film via single-step deposition method. Noticeably this is a fundamental technological advantage in comparison to standard multistep deposition approaches. Furthermore, it allows a fine tuning of i) solution viscosity (making it compatible with different large area deposition techniques), of ii) perovskite grain size and of iii) film thickness, parameters that all depends to the polymer:perovskite:solvent relative concentrations. Very importantly the presence of the biopolymer is also improving the stability of the polycrystalline film thanks to two fundamental properties. The polymer being an electronic insulator reduce the impact of the internal electric field over OHPs mobile ions; in addition the polymer is also permeable to ions (ionic conductor), thus by buffering those prevent ions migration/segregation across perovskite grains, one of the most important material degradation mechanism under device working conditions.

We validated our approach by embedding these composites in photovoltaic (PV) and light-emitting (PeLED) devices. As result we obtained an inverted, planar, low-temperature processed solar cell showing a remarkable 17% efficiency [2] and a highly efficient LED (EQE of ~5%) exhibiting outstanding radiance values above 200 $W/sr \bullet m^2$ obtained at very high currents (about 1000 $mA/cm^2$) which are among the highest reported radiances for NIR PeLEDs [3].

[1] Green, M. A.; Ho-Baillie, A. Perovskite Solar Cells: The Birth of a New Era in Photovoltaics. ACS Energy Lett. 2017,2(4), 822; Colella, S.; Mazzeo, M.; Rizzo, A.; Gigli, G.; Listorti, A. The bright side of perovskites. J. Phys. Chem. Lett.2016, 7(21).
[2] A. Giuri, S. Masi, A. Listorti, G. Gigli, S. Colella, C. Esposito Corcione, A. Rizzo, Polymeric rheology modifier allows single-step coating of perovskite ink for highly efficient and stable solar cells, Nano Energy, 2018, 54, 400-408.
[3] A. Giuri, Z. Yuan, Y. Miao, J. Wang, F. Gao, N. Sestu, M. Saba, G. Bongiovanni, S. Colella, C. Esposito Corcione, G. Gigli, A. Listorti, and A. Rizzo Ultra-Bright Near-Infrared Perovskite Light-Emitting Diodes with Reduced Efficiency Roll-off, Scientific Report, 2018, 8 (1), 15496.

# P-type dye-sensitized solar cells with RDS NiO cathodes: improvement of the photoconversion performance following substrate treatment

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The dye-sensitized solar cells of *p*-type (pDSCs) with NiO cathodes deposited via rapid discharge sintering (RDS) in plasma atmosphere constitute a class of light-conversion devices with generally efficacious, stable and very reproducible performance.[1] The RDS procedure affords electroactive NiO layers with mesoporous features and low optical self-absorption when NiO film thickness is comprised between 1.5 and 4.5 μm. In a precedent comparative study it was shown that the pDSCs assembled with many different types of NiO cathodes reached a maximum of overall photoconversion efficiency of 0.145% when P1 was the colorant and $I^-/I_3^-$ the redox mediator [2]. The present contribution considers novel procedural aspects in the preparation of NiO films when RDS is the sintering method. In particular, we have considered the adoption of additional thermal, UV-ozone irradiation and particle bombardment pre-treatments for the transparent metallic substrate (FTO or, less frequently, ITO) on which NiO nanoparticles (NPs) are sprayed prior to the step of sintering. The heating of the substrate at 70 °C during NPs spray deposition represented the most efficacious treatment with an average increase of 15 % in the overall conversion efficiency of the corresponding pDSCs. Such an improvement was mainly ascribed to two factors: i) the enhancement of the connectivity between NiO NPs; ii) the increase of the efficiency of charge collection at the NiO/substrate interface. Particle bombardment of the ITO/FTO substrate in plasma atmosphere prior to NiO NPs coverage led to an increase in the porosity of the overlying NiO films but this feature was accompanied by a poorer performance of the corresponding device due to the worsening of the conduction properties of the substrate. Finally, the effect of UV-ozone irradiation of NiO-coated substrates on the electronic properties of NiO films was analysed. UV treatment was intentionally considered to induce a shift of the band edges, the alteration of the work function of mesoporous NiO as well as the eventual modification of its charge capacity properties. In fact, no considerable changes in the performances of the corresponding photoelectrochemical cells could be recorded as a consequence of the UV-ozone treatment of the mesoporous photocathodes. The insensitiveness of mesoporous NiO to UV-ozone treatment is expected to be a consequence of the over-oxidized state of non-stoichiometric, nanostructured NiO.

[1] E.A. Gibson, M. Awais, D. Dini, D.P. Dowling, M.T. Pryce, J.G. Vos, G. Boschloo and A. Hagfeldt, *Phys. Chem. Chem. Phys.* 2011,**15**,2411-2420.
[2] C.J. Wood, G.H. Summers, C.A. Clark, N. Kaeffer, M. Braeutigam, L.R. Carbone, L. D'Amario, K. Fan, Y. Farré, S. Narbey, F. Oswald, L.A. Stevens, C.D.J. Parmenter, M.W. Fay, A. La Torre, C.E. Snape, B. Dietzek, D. Dini, L. Hammarström, Y. Pellegrin, F. Odobel, L. Sun, V. Artero and E.A. Gibson, *Phys. Chem. Chem. Phys.* 2016,**18**, 10727-10738.

# Electrosynthesis, activation, and applications of nickel-iron oxyhydroxide in (photo-)electrochemical water splitting at near neutral condition

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We present the pulse-current electrosynthesis, structural characterization, and OER electrocatalytic properties of nickel-iron oxyhydroxide borate thin film (Fe:Ni-Bi), and Fe:Ni-Bi pretreated under different anodic conditions. It was found that the intentionally-added iron ions in the plating solution promotes OER at surface of the as-deposited Fe:Ni-Bi, resulting in lower current efficiency for film deposition and change in surface morphology and crystal structure; the deposition in absence of intentionally-added iron resulted in the formation of porous dendrite-structured Ni-Bi with γ-NiOOH phase, whereas that deposition in presence of Fe resulted in the formation of aggregation of β-NiOOH Fe:Ni-Bi nanoparticles (~20 nm). In addition, through the systematic assessments on effects of electrosynthetic conditions and conditions in anodic activation step, the factors in determining the OER activity of Fe:Ni-Bi are uncovered, including (i) Fe incorporation to modify OER mechanism, (ii) applied turnover frequency to affect the extent of phase transition to OER active γ-NiOOH, and (iii) pretreatment in alkaline electrolyte to enlarge the electrochemically effective surface area. After optimizing these factors, the OER activity of Fe:Ni-Bi can significantly enhanced (Figure 1). Finally, the developed electrosynthetic approach can effectively translate the high OER activity of Fe:Ni-Bi from a flat FTO substrate to a porous $BiVO_4$ photoanode, facilitating the interfacial hole transfer and improving photostability of $BiVO_4$.

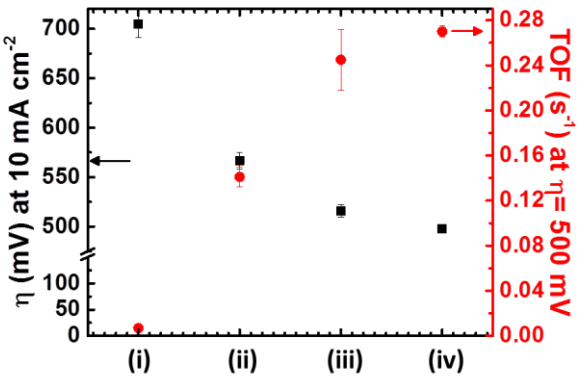


**Figure 1**: The overpotential (η), required to achieve 10 mA $cm^{-2}$, and turnover frequency (TOF) at an applied η of 500 mV of (i) the as-prepared Ni-Bi, (ii) as-prepared Fe:Ni-Bi (Fe composition:~40%), (iii) Fe:Ni-Bi (Fe composition:~40%) anodically pretreated at TOF of 0.13 $s^{-1}$ in 0.1 M NaOH, and (iv) Fe:Ni-Bi (Fe composition:~40%)anodically pretreated at TOF of 0.13 $s^{-1}$ in 1.0 M NaOH.

# Photoanodes for aqueous dye-sensitized solar cells: effect of different $TiO_2$ pastes

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In the photovoltaics field, dye-sensitized solar cells (DSSCs) have aroused much interest due to their low cost and unique possibility of diffuse light conversion [1]. A key aspect to be considered is the stability under real outdoor conditions, as well as the sustainability of materials and components. To this purpose, water-based electrolytes are considered as one of the possible breakthroughs toward large-scale diffusion DSSCs [2]. Moreover, the possibility of gellyfing the electrolyte into a solid matrix reduces its leakage outside the device, thus increasing long-term stability [3]. Consequently, the dye-sensitized $TiO_2$ photoanode should be wettable, allowing electrolyte penetration in its bulk, and at the same time must prevent the water-induced desorption of dye molecule.

Herein, we report morphologic modifications of $TiO_2$ photoanodes, introduced by adding various kinds of additives to the commercial Dyesol $TiO_2$ paste, typically used for screen printing DSSC electrodes onto conductive glass. It was found out that the addition of polyethylene glycol (PEG) modified both the morphology and thickness of photoanodes. As a result, PEG-based cells showed an increased short-circuit current density (+18%) and power conversion efficiency (48%) with respect to the pristine counterpart.

[1] M. Freitag and G. Boschloo, *Curr. Opin. Electrochem*., 2017, **2**, 111-119.
[2] F. Bella, C. Gerbaldi, C. Barolo, and M. Grätzel, *Chem. Soc. Rev*., 2015, **44**, 3431-3473.
[3] F. Bella, S. Galliano, M. Falco, G. Viscardi, C. Barolo, M. Grätzel, and C. Gerbaldi, *Green Chem*., 2017, **19**, 1043-1051.

# Three-dimensional nanoparticle structure, surface area and activity

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Aggregation-based crystal growth is an important synthetic pathway in the production of a variety of metal (including platinum) and metal oxide nanostructures. Seed particle coalescence leads to the production of larger semi-disordered mesoporous structures. In order to study the possible catalytic activity of these materials we need to fully characterize their atomic structure and surface areas. This presentation starts by showcasing some advanced transmission electron microscopy techniques, such as tomography (Fig. 1) and quantitative 2D image analysis, and demonstrating to what extent these tools can give us insight in the internal structure of the nanomaterial.

Building on work focused on the measurement of single nanoparticle surface areas[1,2], two example catalytic reactions are studied and the rate shown to directly reflect the measured surface area of the material, validating and demonstrating the use of this single nanoparticle electrochemical technique.

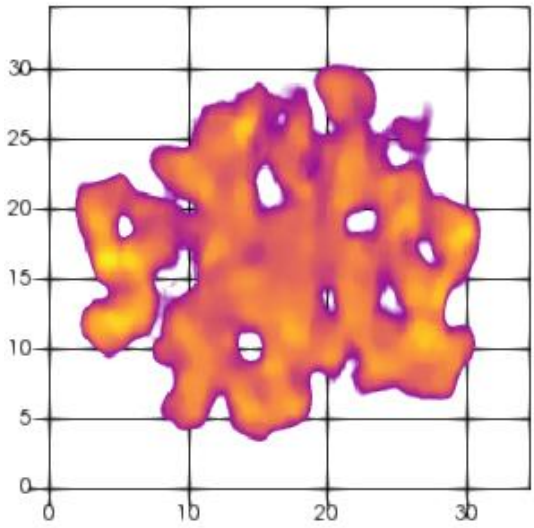


**Figure 1**: Reconstructed tomographic slice through a ca. 30nm mesoporous platinum nanoparticle, showing the internal structure of the nanomaterial. Image provided by and with thanks to Y. Wang and S. Haigh of Manchester University, UK.

[1] X. Jiao, C. Batchelor-McAuley, C. Lin, E. Kätelhön, E.E.L. Tanner, N.P. Young, R.G. Compton, *ACS Cat.* 2018, **8**, 6192-6202.
[2] X. Jiao, C. Batchelor-McAuley, N.P. Young, R.G. Compton, *Phys. Chem. Chem. Phys.* 2018, **20**, 23847-23850.

# Redox catalysis for artificial photosynthesis

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Artificial photosynthesis aims at the conversion of solar light into chemical energy, and is thus considered a promising route towards the production of renewable fuels [1]. Typical photosynthetic schemes require the integration of different functional modules for light harvesting, charge separation, and ultimately redox reactions for the activation of small molecules such as water and carbon dioxide. These transformations are however characterized by multielectronic mechanisms associated to bond breaking / formation, and are thus associated to high kinetic barriers, requiring the presence of suitable electrcatalysts in order to proceed with sustainable rates.

Biological metalloenzymes are the natural inspiring platform for the development of efficient metal based redox catalysts [2]: following these bioinspired guidelines, our recent achievements in the development of transition metal complexes as electrocatalysts for proton reduction to hydrogen, $CO_2$ reduction to CO and water oxidation to oxygen will be presented, Figure 1. Perspectives towards the development of photoelectrochemical devices will be finally discussed [3].

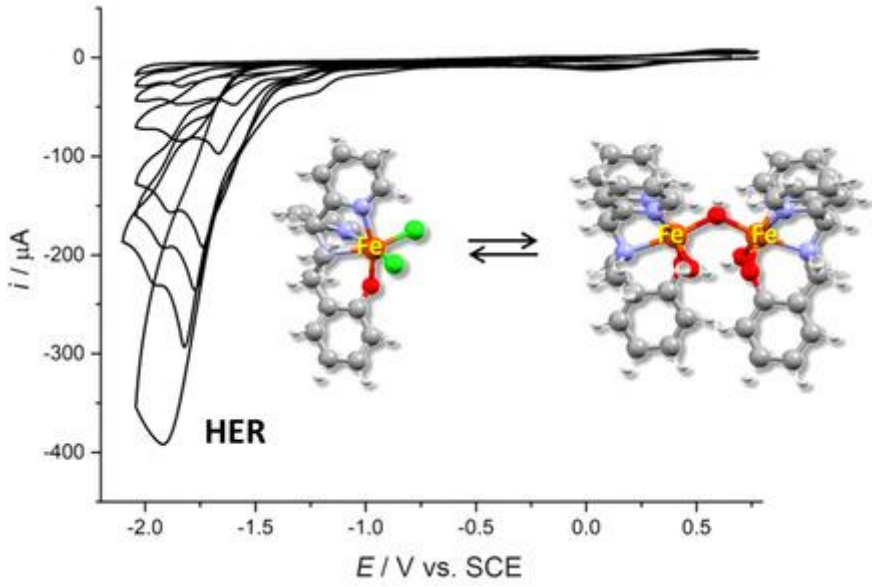


**Figure 1**: Electrocatalytic hydrogen evolution reaction with iron complexes with $N_3O$ ligands, interconverting between mononuclear and dinuclear species [2].

[1] A. Sartorel, M. Bonchio, S. Campagna, F. Scandola, *Chem. Soc. Rev.,* 2013, **42**, 2262-2280.

[2] M. Tagliapietra, A. Squarcina, N. Hickey, R. De Zorzi, S. Geremia, A. Sartorel, M. Bonchio, *ChemSusChem* 2017, **10**, 4430-4435.

[3] M. Bonchio, Z. Syrgiannis, M. Burian, N. Marino, E. Pizzolato, K. Dirian, F. Rigodanza, G. A. Volpato, G. La Ganga, N. Demitri, S. Berardi, H. Amenitsch, D. M. Guldi, S. Caramori, C. A. Bignozzi, A. Sartorel, M. Prato, *Nat. Chem.*, 2019, **11**, 146-153.

# Atomically precise Pt-CO clusters for oxygen reduction reaction

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Global warming and the huge production of the greenhouse gases are very actual concerns. A new paradigm for energy production must be proposed, and in this context also the possibility to reduce the dependence on fossil fuel should be pursued. To date different solution are adopted: lithium storage, flywheels, water basins and $H_2$ production and storage. Also metal-air batteries have been largely investigated, in recent years, as possible very attractive alternatives as energy source/storage, especially for their low environmental impact and versatility: low cost, low emissions, light weight, and relatively high specific capacity and energy density. When chemical energy is converted to electrical energy in these devices, at cathode the Oxygen Reduction Reaction (ORR) must occur at as low as possible overpotential. This ask for a strong improvement of the ORR sluggish kinetics, about 5 orders of magnitude slower than hydrogen reaction, reducing, at the same time, the use of platinum and/or Platinum Group Metals as cathode material. In this context, Pt complexes, chosen in order to minimize the metal loading tough maintaining the same performance in term of specific activity, $mA \cdot cm^{-2}$, and mass activity, $mA \cdot g^{-1}$, as possible cathode material must be investigated. In this work, molecular metal clusters (MMC) based on Pt-CO complexes, with different CO/metal ratios, are synthetized and electrochemical characterized for ORR in alkaline media. These complexes date back to Chini compounds [1], already studied via electrochemical measurements in aprotic organic solvent to discuss their oxidation state and stability, and correlation between spectroscopic CO behaviour and electrochemical induce modifications [2]. Moreover, very recently, the carbonyl chemical route has been largely used to prepare very active electrocatalysts, due to the possibility of tailoring the surface electrode chemical composition and the shape and size of the nanoparticles [3]. In any case, the carbonyl moieties have been used to both control the metallic nanoparticles size and shape, in order to mix them with other metal particles to prepare bimetallic electrocatalysts, and fix them on a suitable carbon support. The research outcomes are discussed in term of electrochemical activity, stability and durability of the prepared cathodes.

[1] Longoni, G. & Chini, P. Synthesis and chemical characterization of platinum carbonyl dianions [Pt3(CO)6]n2- (n = .apprx.10,6,5,4,3,2,1). A new series of inorganic oligomers. *J. Am. Chem. Soc.* **98**, 7225–7231 (1976).
[2] Roth, J. D. *et al.* Exploration of the ionizable metal cluster-electrode surface analogy: infrared spectroelectrochemistry of [Pt24(CO)30]N, [Pt26(CO)32]N, and [Pt38(CO)44]N (n = 0 to -10) and comparisons with potential-dependent spectra of carbon monoxide adlayers on platin. *J. Am. Chem. Soc.* **114**, 6159–6169 (1992).
[3] Gago, A. S., Habrioux, A. & Alonso-Vante, N. Tailoring nanostructured catalysts for electrochemical energy conversion systems. *Nanotechnol. Rev.* **1**, (2012).

# Insights into the Co-Fe spinels durability by following in situ transformations during the oxygen evolution reaction

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The design of highly active and durable catalysts for the oxygen evolution reaction (OER) is crucial for the development and large-scale commercialization of the water splitting technology. The research on this topic is mainly focused on the search of active materials; however, less attention is paid to their long-term structural/chemical stability that, in the end, determine the lifetime of the catalyst, that is, their durability. The use of advanced techniques that allow investigation of the materials under *operando* conditions is especially important because they allow observation of both the reversible and irreversible changes experienced by the materials during the catalytic process, whereas the analysis of the samples after the catalytic work (*post-mortem*) can only show the irreversible ones. In this work, the atomic reorganisation and oxidation state changes of key active sites in Co-Fe spinels are investigated by *quasi in situ* X-ray photoemission spectroscopy (XPS) and *operando* X-ray absorption spectroscopy (XAS) under oxygen evolution operating conditions. The combination of the two techniques allow to identify both the surface and bulk modifications of the oxides and relate them to the activity loss during extended cycling. The results show that Co-Fe spinels experience a surface irreversible phase evolution under oxygen evolution reaction (OER) conditions, resulting in the formation of an amorphous layer composed of new stable Co(III) and Fe(III) species (Figure 1).

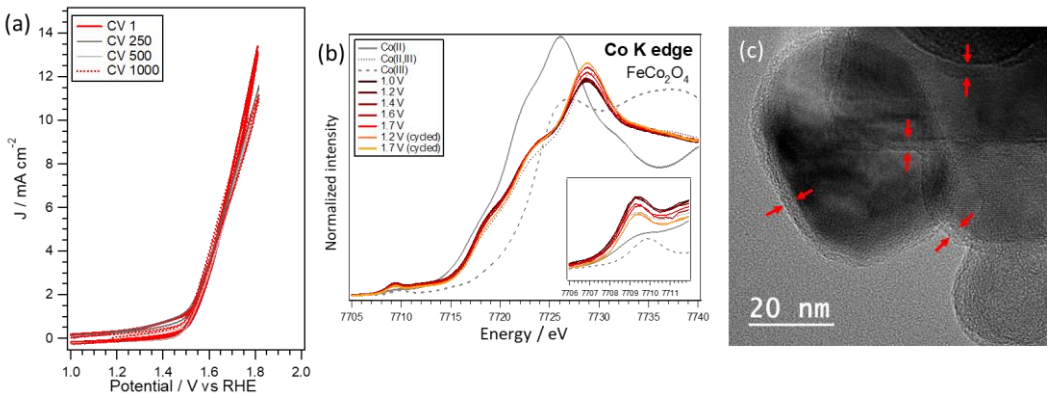


**Figure 1.** CVs in $O_2$-saturated 0.1 M KOH after 1, 250, 500 and 1000 potential cycles (a); operando XANES spectra at Co K edge recorded at different applied potentials; and TEM image after the ageing treatment (c) for the $FeCo_2O_4$ sample.

# Active sites for the electroreduction of $CO_2$ with gold electrodes – a structure-sensitivity study

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The electrocatalytic reduction of $CO_2$ to CO and syngas, which underpin multi-million tons scale processes such as olefin synthesis, methanol synthesis and Fischer-Tropsch, is a promising strategy to convert $CO_2$ into value-added chemicals and to foster the introduction of renewable electricity in the chemical industry. Gold is the most active electrocatalysts capable to produce CO at low overpotentials and with excellent selectivity [1]. Many strategies, such as nanostructuring [2] and grafting with organic ligands, have been proposed to further enhance its performance. However, the fundamental knowledge of how the atomistic structure of the catalyst surface influences reaction rates and selectivity remains a very important missing fundamental insight.

In this work, we experimentally established – for the first time – that atomic steps and undercoordinated sites control the activity of Au for $CO_2$ reduction [3]. We performed a thorough experimental investigation of gold single crystals having well-defined surface orientations. Low-index single crystals, such as (111), (100) and (110), were compared to a steps-rich (211) surface. The electrochemical reduction of $CO_2$ to CO was found to exhibit a pronounced structure sensitivity: the CO partial current density registered with the most active catalysts (i.e., (110) and (211)) is ca. 20-fold higher than the one measured with Au (100), see Figure 1.

We further established the dominance of steps by selective poisoning experiments: the reaction was found to be largely suppressed if surface defects, such as atomic steps, were selectively blocked with inert (poisoning) Pb atoms.

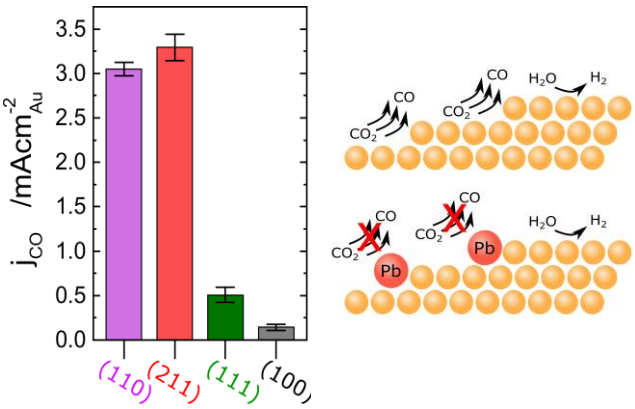


**Figure 1.** (left) CO partial current densities measured with Au single crystals in $CO_2$ sat. 0.1 M $KHCO_3$ at -0.6 $V_{RHE}$. (right) schematic representation of the Pb poisoning experiments.

The findings obtained with these model electrodes provide important targets for the design and synthesis of more efficient nanostructured catalysts. Furthermore, they offer elements to optimize the theoretical description of the electrochemical interface and reaction kinetics, which in turn may strengthen the prediction accuracy of future screening investigations.

[1] Z. P. Jovanov, H. A. Hansen, A. S. Varela, P. Malacrida, A. A. Peterson, J. K. Nørskov, I. E. L. Stephens, I. Chorkendorff, *J. Catal.* **2016**, *343*, 215–231.
[2] W. Zhu, Y.-J. Zhang, H. Zhang, H. Lv, Q. Li, R. Michalsky, A. A. Peterson, S. Sun, *J. Am. Chem. Soc.* **2014**, *136*, 16132–16135.
[3] S. Mezzavilla, S. Horch, I. E. L. Stephens, B. Seger, I. Chorkendorff, *Angew. Chem. Int. Ed.* **2019**, 58,3774–3778.

# Design of highly selective Pt/C electrocatalysts for the dehydrogenation of 2-propanol

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The intrinsic intermittent character of the energy produced from renewable sources such as sun and wind, requires the development of strategies to store the surplus electricity and use it when and where needed. Electrochemical reactions pave the way towards the sustainable synthesis of industrially relevant substrates and the storage of electricity in high energy molecules such as hydrogen. In this context, the design of selective and robust electrocatalysts plays a crucial role.

In the current contribution, a facile impregnation method is used to deposit Pt nanoparticles onto carbon support synthesized from biomass (Fig. 1). Pt nanoparticles deposited onto conventional VulcanX72 (Pt/Vulcan) were prepared under similar experimental conditions and used as reference. A first screening of the catalytic properties of the as-synthesized Pt/C and Pt/Vulcan particles is carried out using in situ UV-Vis spectroscopy to follow the reduction of para-nitro-phenol to para-amino-phenol. Finally, the de-hydrogenation of 2-propanol to acetone (Fig. 1) is used as a model reaction to test the electrocatalytic activity of selected samples of Pt/C and Pt/Vulcan particles and assess a structure function relation. In situ electrochemical infrared spectroscopy revealed excellent selectivity towards acetone formation when Pt/C particles were used as electrocatalysts, with only traces of carbon dioxide formed at higher voltages (Fig. 1). The results reveal a successful design strategy towards highly selective electrocatalysts.

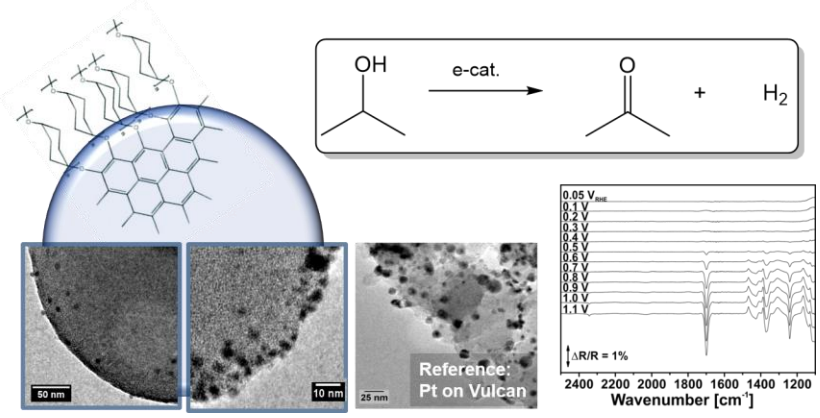


**Fig. 1**: Pt nanoparticles deposited onto the surface of spherical, biomass derived carbon support were tested as electrocatalysts for the dehydrogenation of 2-propanol. Pt on Vulcan prepared under similar experimental conditions was used as reference.

[1] M. Distaso, O. Brummel, F. Waidhas, P. Wasserscheid, J. Libuda, W. Peukert, manuscript in preparation.

# Oxygen reduction reaction at Fe catalysts with 4 or 5 coordinated N atoms. Calculated and experimental $O_2$-Fe binding energy, activity indexes, Volcano correlations

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The oxygen reduction reaction (ORR) is a fundamental chemical reaction in industrial processes as well as in living systems, being $O_2$, the final electron (e-) acceptor of many reactions. Since then its importance in the fuel cell technology where energy would be stored in the form of $H_2$ to be oxidized in conjunction with the reduction of the cheap and abundant $O_2$. However, the ORR is a complicated reaction which involves the transfer of 4 electrons and 4 protons and for its nature, it proceeds through the consequent formation of more than one intermediate accounting for the so-called "scaling correlations" [1]. The complexity of the reaction determines the slow kinetics and the difficulties into finding an adequate catalyst for it to proceed without energy losses.

In our research group, we are adopting various strategies to increase the activity and the stability of metal phthalocyanines like the substitution of planar neutral residues with more electron-negative ones, and the addition of axial back ligands [2,3]. In this research work we studied the electrocatalytic activity towards the ORR of a new compound i.e. the iron hexadeca(fluoro) phthalocyanine (16(F)FePc) in the absence and in the presence of a fifth pyridine axial ligand (FeN5). Interesting the 16(F)FePc appears to be the most active among all the FeN4 studied to the moment. The very high redox potential of the active Fe(III)/Fe(II) redox couple (-0.075 V and 0.44 V vs. SCE at pH 13 and at pH 1 respectively) confirms the correlation between the activity of the catalyst vs. redox potential of the active redox couple of the metal in the catalyst. 16(F)FePc was so active towards the ORR that the production of $H_2O_2$ measured at rotating ring electrodes was nil at pH 13 and very low at pH 1. In the presence of pyridine axial ligand, the redox potential increased of almost 60 mV and catalytic currents and stability of the catalyst also drastically increased. The catalysts were characterized with electrochemical techniques and by EPR and high resolucion XPS spectroscopy in the presence and in the absence of $O_2$. We could therefore experimentally evaluate the binding energy of $O_2$ to the Fe metal centre. Ab initio calculations, confirm the experimental data and the importance of the pyridine axial ligand to lower the binding energy of $O_2$ to the Fe metal centre because of decoupling of the Fe from the carbon support and changes in the geometrical and electronic structure.

[1] Reactivity Descriptors for the Activity of Molecular MN4 Catalysts for the Oxygen Reduction Reaction. Angew. Chem. Int. Ed., 55 (2016) 14510-14521. J.H. Zagal, M.T.M. Koper.

[2] Adsorption of 4,4´-dithiodipyridine axially coordinated to Iron(II) phthalocyanine on Au(111) as a new strategy for oxygen reduction electrocatalysis. Chemphyschem, (2018), 19(13), 1599-1604.S. Herrera, F. J. Williams, E. J. Calvo, F. Tasca.

[3] Biomimetic reduction of O2 in acid medium on iron phthalocyanines axially coordinated to pyridine anchored on carbon nanotubes". Journal of Material Chemistry A. (2017), 5(24), 12054-12059. R. Venegas, F. J. Recio, J. Riquelme, K. Neira, J. F. Marco, I. Ponce, J. H. Zagal, F. Tasca.

# On the pros and cons of the sacrificial anode electrolysis for the preparation of transition metal colloids

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Electrochemical synthesis of transition metal nanocolloids (NCs) and related oxides is highly appealing, since it affords for nanomaterials of high purity and good dimensional control by properly setting few experimental parameters. The resurgence of electrochemical routes to NCs can be traced back to the seminal works from the Reetz's group, about 25 years ago [1]. Briefly, in the so-called sacrificial anode electrolysis, a bulk metal sheet is anodically dissolved in an electrolyte solution (usually a mixture of acetonitrile and tetrahydrofuran, in the presence of quaternary ammonium salts, QUATs, used as base electrolyte) and the intermediate metal ions are reduced at the cathode, giving rise to QUAT-capped metal nanophases. Our group has a long-term experience in the production of antibacterial NCs by this cathodic-stabilization (CS) procedure [2-3]. Despite of many advantages, such as size tuning and inexpensive experimental set-up, this SAE/CS method has intrinsic limitations, mainly related to the use of potentially dangerous organic solvents, which may limit real-life applications of the as-prepared NCs [4]. That is why an important issue in the electrochemical synthesis of metal NPs regards the preparation of aqueous and long-lived colloids. We then moved from the CS approach to aqueous anodic stabilization (AS) processes, aiming at the controlled growth of metal oxide nanophases from specific precursors. AS-based production of ZnO nanophases was firstly reported by Chandrappa et al., who combined a preliminary 2-electrode electrolytic production of gel-like metal-based precursors, with further thermal decomposition to stoichiometric ZnO nanomaterials [5]. This procedure was further refined in our group, under the form of a fully scalable electrochemical-sol-gel method, providing a higher morphological control on the produced nanostructures. Both anionic [6] and cationic [7-8] stabilizers dispersed in the electrochemical media were tested, resulting in different morphologies, ranging from spheroidal particles to rice-grain, rod-like or nano-sea-urchin structures. In this communication, we will provide an overview of the aforementioned approaches and we will critically evaluate their performance level in terms of NPs composition and properties (as per detailed spectroscopic and morphological analyses). Device applications of NPs will be thoroughly discussed, as well.

[1] M.T. Reetz, W. Helbig, *J. Am. Chem. Soc.* 1994, **116**, 7401–7402.
[2] N. Cioffi, L. Torsi, N. Ditaranto, G. Tantillo, L. Ghibelli, L. Sabbatini, T. Bleve-Zacheo, M. D'Alessio, P.G. Zambonin, E. Traversa, *Chem. Mater.* 2005, **17**, 5255–5262.
[3] N. Cioffi, L. Colaianni, R. Pilolli, C.D. Calvano, F. Palmisano, P.G. Zambonin, *Anal. Bioanal. Chem.* 2009, **394**, 1375–1383.
[4] M.C. Sportelli, R.A. Picca, N. Cioffi, *TrAC* 2016, **84A**, 131–138.
[5] K.G. Chandrappa, T.V. Venkatesha, *Nano-Micro Lett.* 2012, **4**, 14–24.
[6] R.A. Picca, M.C. Sportelli, D. Hötger, K. Manoli, C. Kranz, B. Mizaikoff, L. Torsi, N. Cioffi, *Electrochim. Acta* 2015, **178**, 45–54.
[7] R.A. Picca, M.C. Sportelli, R. Lopetuso, N. Cioffi, *J. Sol-gel Sci. Tech.* 2017, **81**, 338–345.
[8] R.A. Picca, M.C. Sportelli, M. Izzi, G. Palazzo, M. Innocenti, L. Torsi, N. Cioffi, *submitted.*

# Graphene-based electrodes for high-power Li-ion batteries

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In this talk I will first discuss an hybrid anode material for lithium-ion batteries, encompassing silicon nanoparticles embedded onto graphene and synthesized via a scalable wet-jet milling method [1]. This synthesized composite, reinforced by a network of conductive carbon black exhibited electrochemical behavior that significantly supersedes the performance of a Si-dominant electrode structures [2,3]. On the cathode side, I will address a Lithium Iron Phosphate (LFP)-graphene nanohybrid obtained by a direct LFP crystal colloidal synthesis on few-layer graphene (FLG) flakes produced by LPE [4] offering a specific capacity exceeding 110 mAh/g at 20 C, with no electrode damaging. If time allows I will cover our recent work on Lithium Sulphur batteries. I will present a facile, non-aggressive and environmentally friendly strategy to create a sulfur carbon composite material by simply dry a dispersion of elemental sulfur and graphene in ethanol solvent. The sample powder shows a suitable micrometric morphology exhibited a rate capability with a stable trend till current rate of 2C and a Coulombic efficiency approaching 100% for more than 300 cycles [5]. These results highlight the impact of graphene in bringing novel technologies for energy storage closer to the market [6].

[1] A. Del Rio Castillo et al., *Materials Horizonts* **5**, 890 (2018)
[2] S. Palumbo, et al. *ACS Appl. Energy Mater.,* **2** 1793 (2019)
[3] R. Malik et al. submitted
[4] G. Longoni, et al., *Nano Energy* **51** 656 (2018)
[5] L. Carbone, et al. submitted.
[6] F. Bonaccorso et al. *Science* **347**,1246501 (2015)

# Towards sustainable, high-performing, all-solid-state sodium-ion batteries (TRUST)

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Energy storage is one of the key challenges of the 21st century. In fact, renewable energy production is expected to grow largely in the coming years, and efficient massive storage is required to improve large-scale grid integration of intermittent electricity sources.

At present, the state-of-the-art in the field is represented by lithium-ion (Li-ion) batteries. However, near future global battery market might be so large that problems regarding materials supply will rise not only for lithium (viz. $Li_2CO_3$), but also for electrode (e.g. cobalt-based) raw materials. Cheaper batteries based on sodium-ion (Na-ion) chemistry can refresh the renewable energy sector and supply more flexibility/balancing to the grid, providing proper back up to intermittent renewable sources. This chemistry might be strategic for electrified road transportation as well, which has stringent requirements in terms of safety and durability. Therefore, the development of new Na-ion based technologies requires: i) the discovery/investigation of new materials/components being widely distributed in large amount and without strategic contingencies, and ii) the search for high energy/power density, and safe battery configurations.

In this context, the MIUR-PRIN TRUST project will deliver a fully integrated innovation chain based on the material-to-end-use approach. The target of TRUST is to develop new materials for next-generation, highly performing and sustainable, all-solid-state, secondary Na-ion batteries. TRUST will explore the entire value chain including: i) computationally-assisted investigation of new materials for both the electrode and the electrolyte compartments; ii) application of advanced in situ and operando characterization tools; iii) "green" fabrication of electrode/electrolyte materials; iv) their assembly and electrochemical testing in lab-scale half-cells, finally aiming at fabricating a 100 mAh full-cell prototype in pouch configuration with the best materials, validated upon prolonged cycling at ambient temperature. The project is intended to start at TRL-2/3 and reach TRL-4 in 36 months, and its targets are in sound consonance with EU call HORIZON 2020.

In this communication, we will briefly describe the development strategy of the project and will discuss some preliminary and early-stage results.

**Acknowledgements**

Financial support from the Italian Government, Ministry of Education, Universities and Research – MIUR (PRIN N° 2017MCEEY4 funding) is gratefully acknowledged.

# UV-crosslinked composite polymer electrolyte for high-rate, ambient temperature Li-based batteries

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Among the ceramic oxide 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. Recent efforts have been dedicated to the formulation of composite hybrid polymer electrolytes (CPEs), where the ceramic material is embedded in a polymeric matrix. CPEs are stiff while preserving flexibility, are easily processed, and can be conceived to attain improved ionic conductivity and interfacial contact with the electrodes [1].

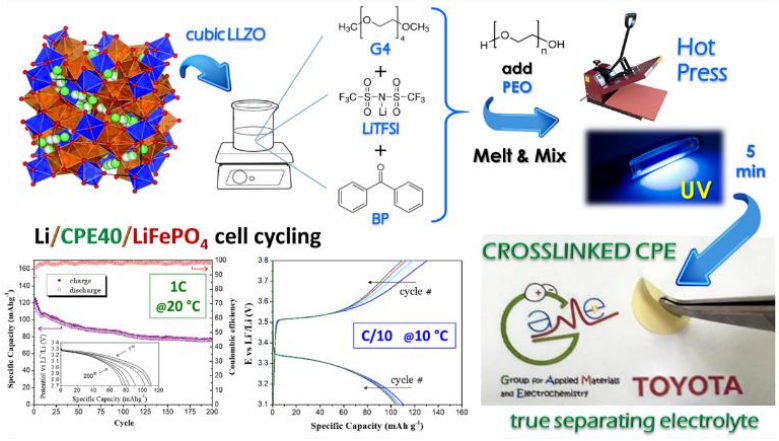


**Figure 1**: Crosslinked LLZO/PEO composite polymer electrolyte in Li metal cells at 1C-rate and < 25 °C.

Here, 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 crosslinked under UV radiation to obtain a composite hybrid electrolyte [2]. 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 $LiFePO_4$ cathodes demonstrated full specific capacity at 0.1C rate and specific discharge capacities up to 115 mAh $g^{-1}$ at 1C rate and could work for hundreds of cycles at ambient temperature [3].

[1] C.K. Chan, T. Yang, and J.M. Weller, *Electrochim. Acta* 2017, **253**, 268-280.
[2] L. Porcarelli, C. Gerbaldi, F. Bella, and J.R. Nair, *Sci. Rep.* 2016, **6**, 19892.
[3] M. Falco, L. Castro, J. R. Nair, F. Bella, F. Bardé, G. Meligrana, and C. Gerbaldi, *ACS Appl. Energy Mater.* 2019, **2**, 1600-1607.

# Water in salt electrolytes for higher energy and power electrochemical energy storage devices

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As a result of the increased energy production from renewable sources, as well as the development of electric or hybrid vehicles, energy storage is poised to play a considerable importance in the near future. At the forefront of electrical energy storage systems, are batteries and electrochemical capacitors (ECs). However, the demand for better electrochemical energy storage systems has set new standards in terms of performance, which are beyond the realm of a conventional devices. In the design for the next generation electrochemical energy storage, the pivotal role of the electrolytes should not be neglected as they affect the life-length and the realistically possible performance in terms of practically accessible capacity, rate capability, safety, etc. Superconcentrated (known also as solvent in salt) solutions are emerging as a new class of highly concentrated liquid electrolytes with various unusual functionalities beneficial for advanced lithium, post-Lithium and supercapacitor applications in both aqueous and aqueous electrolytes. When water is used as a solvent a peculiar characteristic of this kind of mixtures, is the solvation shell that is significantly different from classical aqueous electrolytes. The structure of the electrochemical interfacial region is such that with a properly designed electrolyte, it is possible to strongly limit or suppress water splitting in an extended potential window. In the present contribution a low-cost water in salt electrolyte, based potassium acetate is for the first time characterized. The extended electrochemical window of the electrolyte (as large as 2,54V using a glassy carbon working electrode, current density limit 0,01mA/cm$^2$, Figure.1b) is analyzed by cyclic voltammetry, and the conductivity at different concentrations and temperatures is studied. Finally, the advantage of using this electrolyte is exemplified using an active carbon as active material for ECs; in the supercentrated electrolyte the energy increased of a factor of 10 compared to common aqueous electrolytes (Figure.1b).

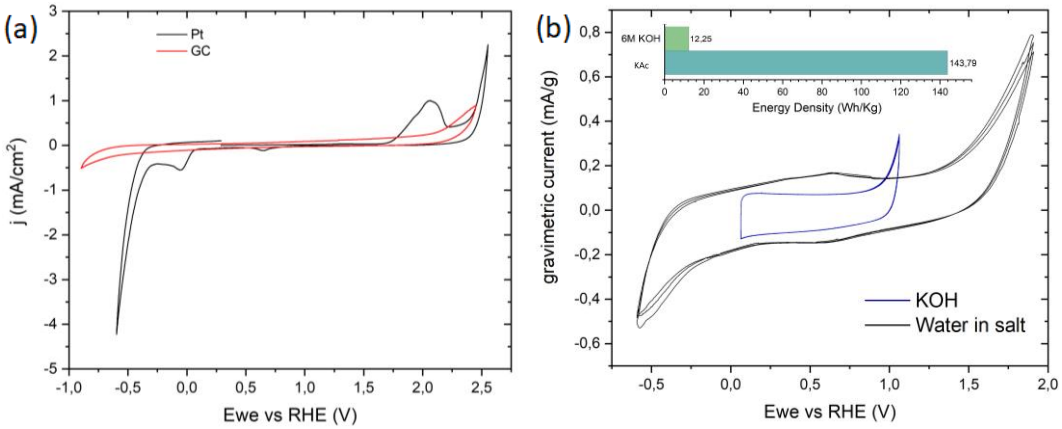


**Figure 1**: (a). Electrochemical window of the 25m electrolyte using glassy carbon (GC) or platinum (Pt) as a working electrode (scan rate 10mV/s); (b) cyclic voltammetry (CV) test of active carbon in 6M KOH and 25m potassium acetate in a three-electrode cell (scan rate 1mV/s). In the inset is reported the corresponding energy density as calculated form the CV.

[1] Y. Yamada, J. Wang, S. Ko and A. Yamada, *Nature energy*, 2019, **4**, 269–280.

# Direct experimental evidences of the electronic character of the positive solid-electrolyte interphase in Li-ion batteries

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In Li-ion batteries (LIBs), the solid-electrolyte interphase (SEI) is an electronic insulating and ionic conducting layer, which is generally formed at the negative electrode due to the strong reduction of the electrolyte occurring during the initial stage of a LIB operation [1]. The SEI has a tremendous importance, since it controls the safety and the performance of the overall battery cell [1]. Being electromobility the next challenge for LIBs, research has recently been directed towards the development of a new class of cathodic materials, operating at higher oxidative potentials in order to increase the voltage of the overall battery cell. At such high anodic potentials the electrolyte undergoes an irreversible decomposition, this time oxidative in nature, and a surface layer is deposited onto the positive electrode surface as well [2].

However, the physicochemical characteristics of the surface layer formed at the high voltage operating positive electrodes remain still unclear, and its role in the overall performance of a high energy density LIB is not yet understood. Thus, the following question remains: *is this surface layer electronically insulating, and thus effectively protective against any further irreversible oxidation of the electrolyte*?

Considering that all the established *ex-situ* and *in-situ* analytical tools (i.e. X-ray photoelectron spectroscopy, Fourier transfer infrared spectroscopy, etc.) fail to provide a *direct* experimental evidence of the insulating character of the SEI, scanning electrochemical microscopy (SECM) has been employed to investigate the electronic character of the surface layer formed onto high-voltage operating LIBs positive electrodes. Such non-conventional local electroanalytical tool offers the unique possibility to *directly* probe the electronic character of the SEI *in-situ* and *in-operando* within its native environment [3].

The electronic character of the surface layer formed on both the active materials (such as $LiNi_{0.5}Mn_{1.5}O_4$, and $Li_{1+x}(Ni_{1/3}Mn_{1/3}Co_{1/3})_{1-x}O_2$), and the inactive components (carbon additive, polymeric binder, and metallic current collector) of a high energy density LIB electrode has been investigated. The experimental results have shown that the surface layer formed in a solution containing 1 M $LiPF_6$ EC:DEC (1:1) onto the active materials, the conductive additive, and the polymeric binder has an electronically conductive nature, and thus it is not effective for hindering the further irreversible oxidation of the electrolyte. On the other hand, it has been shown that the surface layer formed onto the aluminium current collector has an insulating character, which is dependent on the lithium salt present in the electrolyte.

Implications and outlooks for an effective surface layer formation onto the high voltage positive electrodes for the next generation of high energy density LIBs will be discussed.

[1] M. Winter, *Z. Phys. Chemie* 2009, **223**, 1395-1406.
[2] K. Xu, *Chem. Rev.* 2014, **114**, 11503-11618.
[3] G. Zampardi, E. Ventosa, F. La Mantia, W. Schuhmann, *Chem.Commun.* 2013, **49**, 4397.

# Separators for the next generation batteries

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To face the ever-increasing energy demand, the use of renewable energy sources needs to be implemented. The development of more efficient energy storage systems plays a crucial role also to foster the mass-market of electric vehicles. In this scenario, many research efforts are devoted to developing next generation batteries, i.e. Li/S, Li metal, metal/air and Na-ion batteries. However, such systems are still far from commercialization due to some operational problems such as the polysulphide shuttle in lithium sulfur systems, the oxygen crossover and the presence of moisture in the air metal batteries and the formation of dendrites for the Li metal batteries [1].

The separator is one of the key components that affects the performance of a battery. Its main purpose is the physical separation of the electrodes to avoid short circuits but allowing the passage of ions. Therefore, the chemico-physical properties, i.e. chemical and mechanical resistance, porosity and thermal stability play a fundamental role in the correct sizing of the separator and for the safety of the battery over cycling [2].

One of the approaches to solve these problems is to modify and functionalize the separators by introducing nanofillers, ionomers and polymers to make them chemically or physically active in contrasting the processes that adversely affect the battery performance and life [3].

Several techniques for the modification and functionalization of commercial polyolefin separators, including electrospinning, are here proposed for the application in lithium metal batteries. Specifically, with the aim to ameliorate the interface properties of lithium and the lamination properties in presence of cathode containing water-processable binders, the chemico-physical properties and electrochemical performance of separators with electrospun polyvinylidenedifluoride layers and separators with dry-cast lithiated Nafion films are investigated and discussed.

Acknowledgments
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[1] J. W. Choi, D. Aurbach, Nature Reviews Materials 1 (2016) 16013.
[2] S. S. Zhang, J. Power Sources 164 (2007) 351–364.
[3] P. T. Dirlam, R. S. Glass, K. Char, J. Pyun, J. Pol. Sci. Part A: Polymer Chemistry, 55 (2017) 1635–1668.

# Simply double layer approach for enhancing Li-S battery performances

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Beyond Li-ion batteries, one of the most promising technology is Lithium-Sulphur (Li-S) not only for its higher theoretical energy density (about 2600 Wh/kg) but also because sulphur is relatively inexpensive and non-toxic. Typically, in a Lithium-Sulphur battery, lithium ions reduce sulphur to produce lithium polysulphides (PSs), which can be directly reduced on metallic Li anode, resulting in capacity fading and battery degradation.

Many strategies have been proposed to prevent the *polysulfide shuttling* [1]. Here, the use of a thin and selective interlayer, directly coated on the sulfur cathode surface, is presented, in order to limit PSs shuttling [2].

Preliminary DFT calculations show that carbon nitride ($C_3N_4$) exhibits a strong interaction with $Li_2S$ (> graphene-like carbon), related to the chemical bond formed between the lithium atom and the undercoordinated nitrogen atom of the interlayer [3].

In this work, $C_3N_4$ is prepared from three different precursors: urea ($CO(NH_2)_2$), dicyandiamide ($NH_2(NH)CNHCN$) and melamine ($C_3N_3(NH_2)_3$) and spread on a sulfur/carbon composite cathode.

It is observed that carbon nitride obtained from urea remarkably improved the performance of the cathode of S, increasing the specific capacity of the cell by 25% and improving its useful life over 150 cycles. According to the electrochemical response and the XPS characterization $C_3N_4$ obtained from urea is the material that shows the highest proportion of $-NH_2$ species on the surface, which favors the interaction with the polysulfide.

[1] L. Borchardt, M. Oschatz, S. Kaskel, *Chem. Eur. J*, 2016, **22**, 7324-7351.
[2] Y. Fan, Z. Yang, W. Hua, D. Liu, T. Tao, M. M. Rahman, W. Lei, S. Huang, Y. Chen, *Adv. Energy Mater*, 2017, ***7***, 1602380.
[3] C. Y. Fan, H. Y. Yuan, H. H. Li, H. F. Wang, W. L. Li, W, H. Z. Sun, X. L. Wu, J. P. Zhang, *ACS appl. Mater. interfaces*, 2016, ***8***, 16108-16115.

# Ionic liquids based on bis(oxalato)borate or difluoro(oxalato)borate anion as electrolyte components in high voltage lithium batteries

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The critical issue for a stable cycling of high-energy lithium batteries is the optimization of the electrode-electrolyte interface at high voltage. Recently, lithium borate salts were used with high voltage $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) cathodes thanks to the formation of a cathode-electrolyte interface (CEI) [1].
Here we propose the combination of N-methoxyethyl-N-methylpiperidinium organic cation [2] and borate based anions to form novel ionic liquids (ILs), aimed at improving the safety of the battery and the stability of the electrode/electrolyte interface with LNMO positive electrodes. The use of organic cations, proposed in this study, permits to improve the low solubility of conventional lithium borate salts in carbonate solutions.
Two ionic liquids (ILs), which contain bis(oxalato)borate (BOB) or difluoro(oxalato)borate (DFOB) as the anion, have been synthesized and applied as additives in a commercial LP71 electrolyte. The high voltage Li|LNMO cell, employing these electrolyte mixtures, exhibited a discharge capacity around 120 mAh $g^{-1}$. The retention of discharge capacity was found to be 99.2% and 98.1% after 100 cycles for 0.3M BOB-IL and DFOB-IL respectively, Figure 1. Impedance analysis, performed during the galvanostatic cycling and the infrared spectra of cycled LNMO electrodes revealed that BOB-IL possesses the ability to form more durable and effective layers on the cathode surface, allowing prolonged cyclability of high voltage lithium cells.

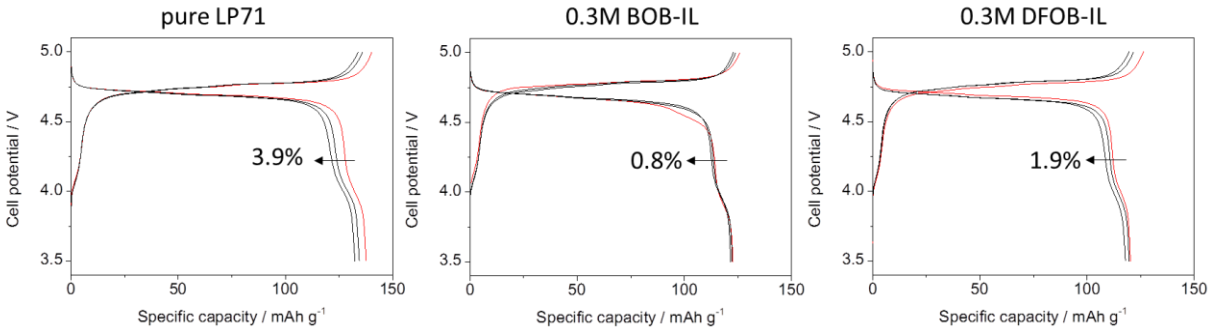


**Figure 1**: Galvanostatic profiles at 1st (red lines), 50th and 100th cycle (black lines)

[1] I. A. Shkrob, Y. Zhu, T.W. Marin, and D.P. Abraham, *J. Phys. Chem. C* 2013, **117**, 23750−23756.
[2] M.A. Navarra, K. Fujimura, M. Sgambetterra, A. Tsurumaki, S. Panero, N. Nakamura, H. Ohno and B. Scrosati, *Chem.Sus.Chem* 2017, **10**, 2496 – 2504.

# Polymer-based artificial solid electrolyte interphases for stable Li metal batteries

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Lithium metal is the optimal anode for high-energy-density batteries. During charge/discharge cycles, the contact between highly reactive Li and organic electrolytes leads to the formation of a solid electrolyte interphase (SEI). The volumetric changes occurring during Li plating/stripping cause continuous breaking and regeneration of a relatively fragile and inhomogeneous SEI, leading to electrolyte depletion and dendrites growth. Conversely, the ex situ creation of an artificial SEI with desirable properties (homogeneity, ionic conductivity, mechanical strength, flexibility) can provide electrochemically and chemically stable Li metal anodes [1],[2].

Herein, we present three different categories of polymer-based artificial SEIs (Fig. 1): i) a single-ion conducting polymer based on a poly(ethylene oxide) (PEO) backbone and dangling anionic groups; ii) hybrid materials composed of poly(styrene-co-acrylonitrile) (PSAN) and poly(ethylene glycol) methacrylate chains grafted onto silica nanoparticles; iii) block copolymers composed of poly(acrylic acid) (PAA) and semi-fluorinated polyacrylates.

The polymers were prepared by atom transfer radical polymerization or anionic polymerization combined to click chemistry, to obtain precise architectures. Li chips were coated by simple drop-casting with polymer (+ Li salt) solutions. Coin cells were assembled and their performances were evaluated by symmetric cycling and impedance spectroscopy. The cycling stability will be discussed in relation to the mechanical properties, conductivity, composition and thickness of the various SEIs.

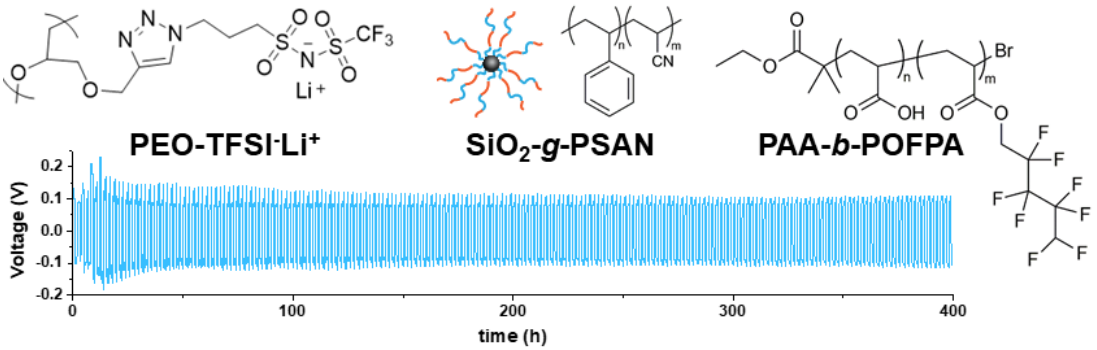


**Figure 1.** Structures of some tested polymer-based SEIs (OFPA = 2,2,3,3,4,4,5,5-octafluoropentyl acrylate), and simmetric cycling performance of Li coated with $SiO_2$-*g*-PSAN, 1 M $LiPF_6$ in EC:DMC 1:1 vol%, current density 1 mA $cm^{-2}$, 1 h charge/discharge.

[1] M. D. Tikekar, S. Choudhury, Z. Tu, L. A. Archer, *Nat. Energy*, 2016, **1**, 16114.
[2] J. Lopez, D. G. Mackanic, Y. Cui, Z. Bao, *Nat. Rev. Mater.* 2019. DOI: 10.1038/s41578-019-0103-6

# Lead-Acid batteries for automotive

## Future perspectives and objects of research: The micro-hybrid application and the EFB technology

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The group of lead-acid batteries represents one of the most important energy resources for several applications, which involves not only the most conventional *SLI* (*Starting-Lightning-Ignition*) utilization, but also stationary, as "*reservoir*" for accumulation stations (*e.g.* UPS) and deep-cycle requests.

Since the discovery of the scientist Gaston Plantè in 1859-60 [1, 2], who highlighted the properties of lead electrodes immerged in a sulfuric acid solution, the technology has been developed over all the following centuries [3] until today, despite the basic principles and the deep knowledge of the electrochemical reaction involved.

SIA is a historical company and represents one of the long-lived societies in Italy in the field of lead-acid batteries for automotive application, developing also an important line for trucks and heavy vehicles. The automotive branch is the core-business of the society, and the increasing level of energy demand and technology of the commercial vehicles, lead the lead-acid batteries toward a continuous process of development. In fact, just think of the modern cars equipped with Start&Stop device (micro-hybrid application) and with energy recovery during braking, and how they need a flexible and fast-responsive system to the electrochemical and physical transformations involved.

The first devices resistant to such strong application were the so-called AGM batteries [4], very high-efficiency batteries but not so easy to manufacture and manage. While Exide, the first, developed EFBs (*Enhanced Flooded Batteries*) in 2008, characterized by lower performances, but their production does not require any modifications to the industrial equipment with respect to standard SLI technology.

The technical norms [5] and the technical specifications imposed by the vehicle's manufacturers for OE (Original Equipment, *e.g.* Volkswagen [6]), give the general guidelines for several properties that the batteries need to have. For example, capacity in 20 hours, cold cranking amperes, water consumption, service life *etc*. and the industrial research is concentrated in each part of the process for controlling each of these properties.

A systematic study of the aspects of design starting from the composition of the active masses to the influence of the separator and of the acid recirculation was carried out by SIA during the last years, in order to produce a product aligned with the request of the market scenario. One of the main focuses of the project was associated to the cyclability of SIA EFB in the so-called high-rate partial state of charge (*HRPSoC*), which is known for being one of the most critical points of the lead-acid technology [7].

[1] G. Plantè, *C.R. Acad. Sci. XLIX*, 1859, **402**
[2] G. Plantè, *C.R. Acad. Sci. L*, 1860, **640**
[3] H. Budde-Meiwes et al., *Journal of Automobile Engineering*, 2013, **227(5)**, 761-776
[4] J. Devitt, *Journal of Power Sources*, 1997, **64**, 153-156
[5] EN 50342 1-6, 2016, **11**
[6] Volkswagen, *VW 75073*, 2017, **08**
[7] P.T. Moseley, D.A.J. Rand, *ECS Transactions*, 2012, **41**, 3-16

# High-voltage cathodic materials for sodium ion batteries

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Despite being more equally distributed and abundant than lithium (making it a potentially cheaper substitute) the use of sodium in alkali-ion rechargeable batteries still presents several issues. One of the most important problem is that the standard reduction potential of the $Na^+/Na$ redox couple is 0.3V higher than the one of $Li^+/Li$, making the overall potential difference of a full cell lower. Moreover, several materials for the positive electrode show a cathodic potential much lower compared to the lithium-based counterparts, reducing the cell energy density. To bypass this issue a deep study on cathodic materials is still necessary. In this frame, an important parameter that needs to be accounted is the mean voltage which can be calculated without uncertainties as the ratio between the stored energy and the achieved capacity of the material in half cells vs. metallic sodium.

In this contribute, we concentrated our studies on $Na_3V_2(PO_4)_2F_3$, a NASICON-like material capable of reversibly oxidating its $V^{3+}$ to $V^{4+}$, freeing two $Na^+$ ions. Characteristic of this material is the strong ionicity of the V-F (guaranteed by the electronegativity of fluoride) and of V-$PO_4$ (related to the strong negative charge of the anion) bonds, which can increase the reduction potential at which the $V^{4+}/V^{3+}$ couple operates [1]. Beside the growth in the mean voltage (up to 3.8V vs $Na^+/Na$) the inductive effect of the anions reduces the electronic conductivity of the material as a drawback. The conductivity can be improved utilising carbon (such as graphite) as coating agent. The effect of the cut-off voltage, the electrolyte composition, the carbon content, and the active material load on the mean cathodic voltage, the Coulomb efficiency, and on the specific capacity are investigated and discussed.

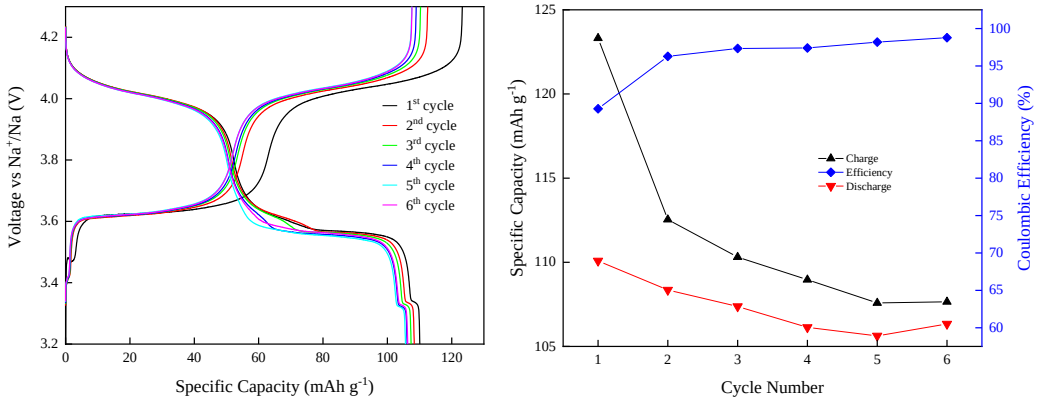


**Figure 1**: On the left, a Voltage vs Specific capacity of the first 6 cycles of $Na3V_2(PO_4)_2F_3$ (80% of active material) at 0.1C. On the right Specific capacity and Coulombic efficiency of the same cycles.

[1] W. Song, X. Ji, Z. Wu, Y. Yang, Z. Zhou, F. Li, Q. Chen and C. E. Banks, *J. Power Sources*, 2014, **256**, 258–263.

# Origin of the irreversible capacity in hard carbon electrodes for sodium-ion batteries

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Sodium-ion battery chemistry is considered a valuable alternative to Li-ion technology for stationary energy storage from renewable energy sources. The current research activities concerning sodium-ion battery chemistry tackle all aspects of the cell formulation, i.e. the positive and the negative electrode active materials, binders, separators and electrolytes. Focusing on negative electrode compounds, the most promising available options studied worldwide are hard carbons (HCs), titanates and conversion materials. HCs derived from waste biomasses or natural products are very promising; thanks to the easily scalable synthesis procedures, large reversible capacities and low operating voltages. The most relevant drawbacks of HC negative electrodes in sodium-ion batteries are the irreversible capacity in the first electrochemical Na incorporation/de-incorporation (see figure 1) and the unsatisfactory Coulombic efficiencies upon cycling at low current densities. These negative performance features originate from the parasitic chemistry due to the degradation of the typical carbonate-based electrolytes at low electrode potentials.

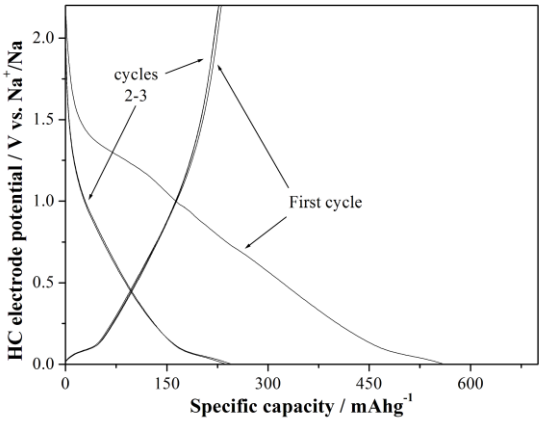


**Figure 1**: Electrochemical Na-loading curve in C electrodes.

Here the origin of the irreversible capacity losses suffered by C electrodes in the first galvanostatic cycle in a Na cell are illustrated. We exploited a combination of various techniques (X-ray diffraction, X-ray photoelectron spectroscopy, infrared spectroscopy, transmission electron microscopy and electrochemical methods) to characterize ex situ and in situ the formation of the solid electrolyte interphase (SEI) and irreversible trapping of sodium ions within the carbonaceous matrix upon cycling.

In summary the large irreversible capacity observed in the first galvanostatic cycle of HC originates from the irreversible trapping of $Na^+$ ions in $Na_xC$ compounds and the precipitation of a porous, organic-inorganic hybrid SEI. This surface layer precipitates over the HC particles in the first galvanostatic cycle and further evolves in morphology and composition in the following cycles. It is mainly constituted of organic carbonates, $Na_2CO_3$ and NaF. The SEI layer physico-chemical features stabilize after approximately 5- 10 galvanostatic cycles at low current rates thanks to the enrichment in inert inorganic components.

# Novel «chemistry» based on aqueous bromate solutions for stationary energy storage, fully electric vehicles and direct solar-to-chemical energy conversion

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We propose a flow battery employing H2 as the fuel and one or more of highly soluble halate salts (such as 50% w/w aqueous solution of LiBrO3) as the oxidant achieving the energy density > 400 W*hr/kg at the system level, which is sufficient for fully electric vehicles with a driving range of 500 km on a single refill [1]. Moreover, such a battery can reach very high areal power density (> 1 W/cm2) when the rate limiting steps (halate-halide comproportionation (1) on discharge and halogen disproportionation (4) on charge) are performed in a 3D solution phase within a porous carbon electrode rather than on a 2D electrode surface [1-3]:

$$LiXO_3 + 5\ LiX + 6\ H^+ = 3\ X_2 + 3\ H_2O + 6\ Li^+ \quad (1)$$

$$3\ X_2 + 6\ e^- = 6\ X^- \quad (2)$$

$$2\ LiX + 2\ HA = X_2 + 2\ LiA + H_2 \quad (3)$$

$$X_2 + 2\ LiA + H_2O = 1/3\ LiXO_3 + 5/3\ LiX + 2\ HA \quad (4)$$

The pH manipulation required for switching between the charge and discharge modes is conveniently accomplished using reagent-free small-size and low-cost Reactor akin to the ion suppression reactor of ion chromatography. Photoelectrochemical splitting process (3) of LiBr, which can be done using low cost silicon photopanels or microparticles, when coupled to the disclosed disproportionation process (4), may finally enable the human civilization to use sunlight (with its average power striking the planet exceeding the 13 TW need of our civilization by a factor of over 10,000) as the primary energy source at a cost competitive with the more traditional methods such as coal combustion and uranium fission.

Acknowledgement: this research was supported by the Russian Ministry of Education and Research (Grant № 14.574.21.0150, UIN RFMEFI57417X0150).

[1] Y. V. Tolmachev, A. Piatkivskyi, V. V. Ryzhov, D. V. Konev, M. A. Vorotyntsev, *J. Solid State Electrochem.,* 2015, **15**, 2711-2722.
[2] M. A. Vorotyntsev, D. V. Konev, Y. V. Tolmachev, *Electrochim. Acta*, 2015, **173**, 779-795.
[3] M. A. Vorotyntsev, A. E. Antipov, Y. V. Tolmachev, *Electrochim. Acta*, 2016, **222**, 1555–1561.

# Recent progresses in ionic liquid-based electrolytes for hybrid multivalent metals secondary batteries

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The finding of stable and high-performing electrolytes is the major bottleneck to the development of future secondary batteries belonging to the so called beyond Li-ion technology. In particular, electrolytes able to reversibly deposit multivalent metals seem to be the answer to the growing energy demand requested by the Electric Vehicles market. Indeed, the multi-electron chemistry could ensure a higher energy value *per* moles of active material.

In this concern, Ionic Liquids (ILs) are considered attractive materials thanks to their low volatility, negligible flammability and good electrochemical performance in the metal reversible deposition process [1-3]. Indeed, it was recently demonstrated how these electrolytes are able to deposit and strip a magnesium/metal alloys with Coulombic efficiencies higher than 99 %, overpotentials lower than 50 mV *vs*. $Mg/Mg^{2+}$ and remarkable current densities (Fig. 1).

In this talk, an overview on the most recent progresses in IL-based electrolytes for hybrid multivalent metals secondary batteries will be given. A detailed description on the interplay between structure and conductivity of ionic species will be presented. Thus, the relationships among metal ion speciation, long-range charge migration processes and electrochemical performances of these materials will be analyzed.

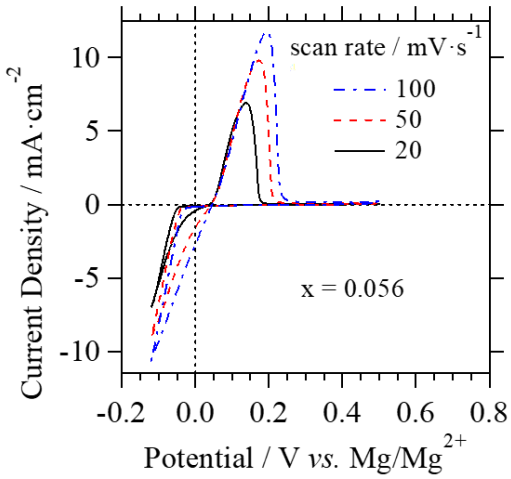


**Figure 1**: Al/Mg deposition and stripping at room-temperature obtained by means of CV.

**References**:

[1] G. Pagot, F. Bertasi, K. Vezzù, E. Negro, S. Greenbaum and V. Di Noto, under submission.
[2] G. Pagot, F. Bertasi, K. Vezzù, F. Sepehr, X. Luo, G. Nawn, E. Negro, S.J. Paddison and V. Di Noto, *Electrochim. Acta* 2017, **246**, 914-923.
[3] F. Bertasi, C. Hettige, F. Sepehr, X. Bogle, G. Pagot, K. Vezzù, E. Negro, S.J. Paddison, S.G. Greenbaum, M. Vittadello and V. Di Noto *ChemSusChem* 2015, **8**, 3069-3076.

# Electrodeposition and applied electrochemistry

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The interest in scientific research within the metal finishing sector is growing. The demand for durable metals and adaptable manufacturing processes are increasing across a wide range of applications, from aerospace and automotive to machinery and jewelry. An essential step in the production line is the surface engineering of metals, as this determines the final appearance and functionality of a product. Therein electroplating is recognized as a mature technology allowing the low cost fabrication of defined surfaces with extensive property profile. Galvanic electrodeposition accounts today for almost 40% of the global market value share with North America and Western Europe leading the scenery. Although technological and processing advancements occurred in the past forty years, industrial firms are still struggling to provide solutions to corrosion protection as well as reduction of toxic wastes. Specifically, large-scale industrialization of electroplating techniques will continue to be limited by strict environmental regulations. Due to adverse ecological impacts, the adoption of plating processes involving toxic metals such as lead or cadmium is prohibited. Moreover, price volatility of the highly demanding electroplated materials gold, copper and nickel is expected to impact the market share for more than 60% by 2026.

In that respect, alloy plating offers better answers in terms of economic growth and environmental sustainability due to fine tuning composition, morphology and crystallinity [1]. Here, current trends on alloy electrodeposition research are reviewed highlighting open challenges and process innovations from an industrial perspective. The main categories of alloy compounds are presented and the most important properties for the manufacturing process discussed. Particular attention is devoted to advances in industrial quality control and viable solutions for the reduction of precious metal content in electroplated accessories as well as replacement of cyanide and nickel baths with non-toxic compounds.

[1] W. Giurlani, M. Innocenti et all. , Review, Coatings 2018, 8(8), 260.

# Role of correlation on nucleation and island growth in potentiostatic transients

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Electrodeposition is a well-known technique suitable for modifying the surface properties of a wide variety of materials. For years it has been used in the field of plating to produce mainly metal or alloy coatings for decorative or protective applications. Nowadays, electrodeposition is an accepted versatile technological procedure for the preparation of nanomaterials made up of metals, oxides and polymers. In this context, it is relevant to advance the comprehension of deposition mechanisms and the kinetics of growth of the deposit since it determines, in large part, the structure and properties of the materials [1]. The initial stage of deposition process can be studied by potentiostatic transient performed by chronoamperometry.

The theoretical description of the potentiostatic transient is based on the knowledge of the processes which rule the electrodeposition in dependence of the overpotential.

When diffusion is rate determining, island growth is controlled by mass transport of the depositing ions to the island surface. Theoretical models have been proposed for describing the current density in terms of simultaneous and progressive nucleation along with two-dimensional (2-D) and three-dimensional (3-D) growth processes which have been profitably employing to interpret experimental chronoamperometric curves. Modeling island growth is an involved problem owing to the interference of diffusional fields of growing nuclei, namely of correlation effects on nucleus growth.

The present research focuses on island growth in electrodeposition, in the framework of “planar diffusion zones” and “3D nucleation and growth” approaches. In the case of simultaneous nucleation, where the distribution of nuclei can be assumed random, we investigate correlation effects on nucleus growth law. In particular, the combination of both approaches allows us to study the kinetics of nucleus growth, mean film thickness and surface coverage of the electrode [2].

In the case of progressive nucleation, we focus on the effect of spatial correlation of nuclei on current density due to non-random distribution of nuclei. We employ a stochastic approach based on a series expansion in terms of correlation functions (CF). Potentiostatic transients with correlated nucleation have been modeled in the framework of time-dependent hard-disk CF. Truncation of the series up to second order terms in CF provides a good approximation of the kinetics of both deposited material and electrode coverage [3].

The analysis of experimental data supports the proposed models which allow to investigate the impact of correlation on chronoamperometric curves. In conclusion the development of theoretical models that take into account correlation effects during electrodeposition can be a valuable support to the controlled production of nanomaterials with efficient functionalities.

[1]L. Guo, G. Oskam, A. Radisic, P. M. Hoffmann and P.C. Searson, *J. Phys. D: Appl. Phys*.,2011, 44(44), 443001.
[2]S.Politi, M.Tomellini, *J.Solid State Eletrochem*., 2018, 22(10), 3085-3098.
[3]M. Tomellini and S. Politi, *Physica A*, 2019, *513*, 175-188.

# Electrochemical conversion of carbon dioxide in pressurized electrochemical cells

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To limit the negative effect of carbon dioxide as a greenhouse gas, an interesting approach is the utilization of Carbon Capture and Conversion (CCC) methodology, 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 framework, an increasing attention has been devoted to the electrochemical conversion of carbon dioxide to formic acid in water [2-3] or CO [1]. Since the main hurdle of the CO2 reduction from aqueous solution is the low $CO_2$ solubility in water, in this work, the utilization of pressurized electrochemical cells is evaluated. The effect of various operating parameters, including pressure, current density, and flow rate, on the conversion of $CO_2$ at tin flat cathodes is also presented and discussed.

[1] G. Wu and P. Zelenay, *Accounts Chem. Res.*, 2013, **46**, 1878–1889.
[2] L. Monico, K. Janssens, E. Hendriks, F. Vanmeert, G. Van der Snickt, M. Cotte, G. Falkenberg, B. G. Brunetti, and C. Milani, *Angew. Chem. Int. Ed.* 2015, **54**, 13293-13297.
[1] S. Ma, P. J. Kenis, *Current Opinion in Chemical Engineering*, 2013, **2**, 191-199.
[2] A. Del Castillo, M. Alvarez-Guerra, J. Solla-Gullòn, A. Sàez, V. Montiel, A. Irabien, J. CO2 Util.. 2017, **18**, 222–228.
[4] O. Scialdone, A. Galia, G., Lo Nero, F. Proietto, S. Sabatino, B. Schiavo, Electrochimica Acta, 2016, **199**, 332-341.

# Gravure printing for printed batteries manufacturing

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Printed batteries, resulting from the combination of conventional battery and printing technologies, are more and more involved in the growing area of small, wearable and portable electronic devices needing on-board power supply. Typically the printed batteries have capacities of 5-10 mAh $cm^{-2}$ and overall dimension below $10mm^3$ [1]. Printing technologies offer the possibilities to decrease the production costs, producing thin flexible and arbitrary shapes of different function layers even in case of multifunctional layered structures. Among the printing technique, the widespread industrial gravure printing (see Fig.1) is considered one of the most promising since its ability to couple high throughput and high quality. In our laboratories such technique was already demonstrated suitable in the production of polymeric and ceramic functional layer for different proposes [2,3], showing a high versatility and a high level of control of the printed layer morphology. Despite to its potential advantages, to date, the gravure printing is few investigated in the field of printed batteries, due to its necessity of highly diluted inks (1-100 mPa s) which makes difficult the proper formation of a functional layer having a thickness able to achieve a certain mass loading, especially in the case of electrodes. The aim of our research is to demonstrate the possibility to involve the gravure printing in the batteries manufacturing through the electrodes realization for lithium-ion batteries. The electrodes are typically highly homogeneous composites layer forming a structure able to realize electrical and ionic conductivity. Thanks to the preparation of suitable inks and to a multilayer approach the gravure printing will be demonstrated the appropriate technology to realize such structures. Moreover this technique allow to skip the calendering step simplifying the overall manufacturing and making easy its industrial scaling. This work may open the way to the possibility of layer by layer devices manufacturing using the only gravure printing bringing large potential advantages in the future fast, easy and low cost printed batteries production.

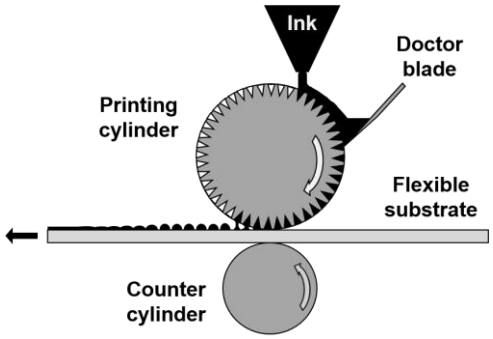


**Figure 1**: Schematic gravure printing process.

[1] J. Oliveira, C.M. Costa, S. Lanceros-Méndez, Printed Batteries Materials, Technologies and Applications; Lanceros-Méndez, S., Costa, C.M.; John Wiley & Sons, 2018, 1-14.
[2] M. Montanino, G. Sico, C.T. Prontera, A. De Girolamo Del Mauro, S. Aprano, M.G. Maglione, C. Minarini, eXPRESS Polym. Lett. 2017, **11**, 518-523
[3] G. Sico, M. Montanino, M. Ventre, V. Mollo, C.T. Prontera, C. Minarini, G. Magnani Scr. Mater. 2019, **164**, 48-51.

# Development of an efficient and green bronze alloy electrodeposition bath

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The electrodeposition of Cu-Zn-Sn alloys (White Bronze), is a well-known procedure in galvanic industry. This process has earned new technological and scientific interest because the obtainment of a Bronze alloy from an efficient and green deposition bath can be advantageous in various sectors, from electronic industry to fashion industry.

Traditional Bronze electrodeposition baths contain cyanides in solution and Sn(IV)-based compounds as Tin precursors. Within this work we've developed a cyanide-free formulation, based on an ecofriendly electrolyte and a Tin precursor containing Sn(II) ions, from which is possible to electrodeposit alloys up to 2:1 Cu-Sn molar ratio. Starting from Methanesulphonic Acid (MSA) as an ecofriendly electrolyte we've studied different formulations in terms of metal precursors, organic additives and their concentrations. As Copper metal precursors has been tested Copper Sulphate and Copper(II) Methanesulphonate and as Tin precursor has been tested Tin(II) Methanesulphonate. To prevent the precipitation of Tin Oxide and Hydroxide has been tested Hydroquinone (a well-known antioxidant) [1] and as metal ions complexing agents has been studied Nitrilotriacetic Acid (NTA) [2] and 2-Picolinic Acid [3]. The study of two different complexing agents has also given us the possibility to observe two different reduction mechanisms for Copper divalent ions.

Each formulation has been tested with Cyclic Voltammetry technique and the electrodeposited samples has been investigated with SEM-EDX and XRD to obtain a morphological, compositional and structural characterization.

Future developments will concern the addition of Zinc in the alloy and the design of a thermal annealing process to reduce grain defects and to homogenize the composition.

[1] C. T. J. Low and F. C. Walsh, *Electrochim. Acta*, Jun. 2008, vol. 53, no. 16, pp. 5280–5286.
[2] R. M. Krishnan and V. S. Muralidharan, *Proc. Indian Acad. Sci. - Chem. Sci.*, 1991, vol. 103, no. 2, pp. 107–118.
[3] A. L. Portela, M. L. Teijelo, and G. I. Lacconi, *Electrochim. Acta*, Apr. 2006, vol. 51, no.16, pp. 3261–3268.


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# Corrosion resistance of different stainless steel grades in cleaning industrial environments

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Nowadays stainless steels are the most employed materials in a large number of applications due to their mechanically and corrosion resistance, mostly in the case of food and pharmaceutical industries, where more severe regulations relating to contamination of processed fluids and a highly awareness regarding health and safety of consumers are required. In fact, in order to avoid contaminations due to the occurrence of corrosion phenomena and to eliminate bacteria, viruses and spoilage microorganisms from surfaces and equipment, *Cleaning*, *Disinfection* and *Sanitization* operations are usually employed thanks to the physical action of high velocity flow jet spray, agitation and chemical action of cleaning agents enhanced by heat [1]. Typical aggressive and corrosion environments in the food and beverage industry involves inorganic acidic and hot alkaline solutions and moderately to highly concentrated chlorides, often mixed with significant concentrations of organic acids [2]. Moreover, composition, surface roughness and passivation steps of materials are crucial, as they actively influence mechanical and corrosion properties of stainless steels.

For this reason, this experimental work is focused on the investigation and monitoring of corrosion resistance of passive film grown on different SS grades after long exposure time in different selected aggressive environment typical of food and pharmaceutical industries. Passive films were grown on austenitic 304L / EN 1.4307, 316L / EN 1.4404 and duplex 2507 / EN 1.4410 by immersion at open circuit potential in aqueous solutions mimiking typical cleaning environments employed in food and beverage industries. In particular, Hot Purified Water at 60°C, 0.25 M NaOH at 82°C and NaClO containing solutions at different concentrantions and temperature were used according to the prescriptions necessary to maintain an acceptable hygiene level in the plant. Finally, SSs with different surface finishing were also passivated in the same simulating solutions in order to understand how surface roughness could affect growth kinetic of passive films and therefore their corrosion resistance.

The experimental investigation was mainly based on electrochemical, photoelectrochemical and impedance measurements in the attempt to correlate the electronic properties of the passive films (band gap and conductivity type) to their corrosion resistance and to make a rank of the stainless steels depending on composition and surface roughness of samples, and on pH and temperature of electrolytes under investigation.

# In situ spectroscopic ptychography during the electrodeposition of Mn-Co/polypyrrole nanocomposites

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This talk will report novel soft X-ray Fresnel Coherent Diffractive Imaging ptychography results, demonstrating the potential of this method for dynamic in situ studies of the fabrication of coatings [1,2]. Specifically, in situ ptychography experiments explored the electrochemical growth of Co-doped Mn-oxide/polypyrrole nanocomposites for sustainable and cost-effective fuel-cell air-electrodes [3]. Oxygen-reduction catalysts based on Mn-oxides exhibit relatively high activity, but poor durability: doping with Co has been shown to improve both reduction rate and stability.

In this study, we examine the chemical state distribution of the catalytically crucial elements to elucidate details of the metal incorporation into the polymer matrix (Figure 1). The measurements were performed using a custom-made three-electrode thin-layer microcell, developed at the TwinMic beamline of Elettra Synchrotron during a series of experiments that were continued at the SXRI beamline of the Australian Synchrotron. Our time-resolved ptychography-based investigation was carried out in situ after two representative growth steps, controlled by electrochemical bias.

In addition to the observation of morphological changes, we retrieved the spectroscopic information, provided by multiple ptychographic energy scans across the Mn and Co L-edges, shedding light on the doping mechanism and demonstrating a general approach for the molecular-level investigation complex multimaterial electrodeposition processes.

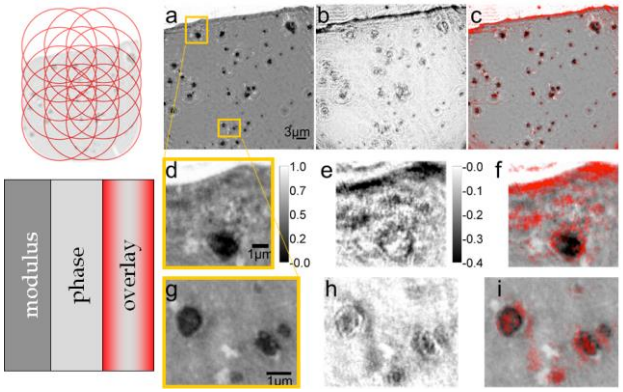


**Figure 1**: *In situ* ptychography during Mn-Co/PPy electrodeposition: emphasizing space resolution with single-state capability.

[1] B. Bozzini, G. Kourousias and A. Gianoncelli, *J. Phys. D* 2017, **50**, 124001 (8 pp.)
[2] B. Bozzini, G. Kourousias, A. Gianoncelli, M. Jones, G. Van Riessen and M. Kiskinova *J. Electron Spectrosc. Relat. Phenom.* 2017, **220**, 147–155.
[3] B. Bozzini, P.Bocchetta, B. Alemán, M. Amati, A. Gianoncelli, L. Gregoratti, H. Sezen, A. Taurino and M. Kiskinova, *J. Mater. Chem. A* 2015, **3**, 19155–19167.

# Correlations between synthesis step and performance of Fe-based PGM-free catalysts in entire pH spectrum

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The reduction of oxygen is one of the most studied electrochemical processes and often the bottleneck for electrochemical systems. Oxygen reduction reaction (ORR) is valuable not just for electrolytic and power generation technologies but also for living organisms. The ORR is of particular importance to fuel cell technology, where it is used across a wide range of temperatures and in extreme pH regions: acidic and alkaline. ORR is also capturing the attention of scientists operating with bioelectrochemical systems (e.g. microbial fuel cells (MFCs)) in which (circum)neutral media has to be maintained for preserving the microorganism life and operation.

At acidic pH, platinum is the most active catalyst while palladium is the best performing in alkaline media. In neutral media, enzymes belonging to the group of the multicopper oxidases showed the highest electrocatalytic activity towards ORR. All these three catalysts are extremely expensive and therefore limit the technologies to the large-scale commercialization. In the past 15-20 years, platinum group metal-free (PGM-free) catalysts containing a transition metal (e.g. Fe, Co, Mn, Ni) for substituting PGM catalysts have been captured the attention of the scientists' worldwide and have been used along the entire pH spectrum.

PGM-free catalysts family fabricated and studied at the University of New Mexico are mainly synthesized through pyrolysis (high temperature) processes. Sacrificial Support Method (SSM) is the technique in which silica is used as templating agent during the pyrolysis and then removed. SSM consists in 6 different steps: 1) organic nitrogen rich precursor, metal salt, and silica template mixing; 2) first pyrolysis in reducing atmosphere (containing $H_2$); 3) ball milling; 4) silica etching using HF; 5) second pyrolysis in ammonia rich atmosphere; 6) final ball milling [1,2].

In this work, the surface chemistry and morphology of each synthesis step was identified through spectroscopy and microscopy analysis. Each pyrolysis step involved chemical and/or thermal and/or mechanical treatment and therefore the catalyst was subject of significant changes in surface chemistry and morphology. The electrocatalytic activity of the catalysts from each synthesis step was tested using rotating ring disk electrode (RRDE) technique in acidic, neutral and alkaline electrolyte. The increase in catalytic activity due to each synthesis step was determined and differs in function of the operating electrolyte. The surface properties and the electrochemical parameters were correlated through statistical tools and surface to property analysis was conducted.

[1] S. Rojas-Carbonell, K. Artyushkova, A. Serov, C. Santoro, I. Matanovic, P. Atanassov. *ACS Catalysis*, 2018, **8**, 3041-3053
[2] C. Santoro, S. Rojas-Carbonell, R. Awais, R. Gokhale, M. Kodali, A. Serov, K. Artyushkova, P. Atanassov. J. Power Sources, 2018, **375**, 11-20.

# Effect of pyrolysis atmosphere and electrolyte pH on the oxygen reduction activity, stability and spectroscopic signature of $FeN_x$ moieties in Fe-N-C catalysts

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Proton Exchange Membrane Fuel Cells (PEMFCs) have achieved impressive power density, but the sluggish Oxygen Reduction Reaction kinetics today requires cathodes based on platinum, a rare and expensive metal, which threatens its large-scale commercialization. As an alternative to platinum, Fe-N-C catalysts prepared via pyrolysis in $NH_3$ have shown promising initial activity, assigned to atomically dispersed $FeN_4$-moieties in N-doped carbon matrix [1] but their poor *in operando* stability is a major drawback, with a lack of clear understanding of the degradation mechanism(s), impeding the identification of rational approaches to solve the issue.

Here, we will report studies on the activity and stability in high and low pH of two Fe-N-C catalysts, one treated in Argon (Fe-Ar) and the second further treated in ammonia (Fe-$NH_3$). Rotating disk electrode and a flow cell connected to an inductively-coupled plasma mass spectroscopy were used to evaluate changes in the activity, stability and iron leaching as a function of the applied electrochemical potential. To identify dissimilarities in $FeN_x$-sites between Ar- and ammonia-pyrolyzed Fe-N-C catalysts, we resorted to operando X-ray absorption spectroscopy, at pH 1 and 13.

It will be evidenced that, in alkaline electrolyte, both Fe-N-C catalysts are stable during the accelerate stress test (AST), with minimized Fe leaching during electrochemical cycles, but Fe-$NH_3$ is significantly more active. In contrast, in acid electrolyte, Fe-$NH_3$ results in 10 times enhanced iron leaching rate compared to Fe-Ar, explaining the higher activity but also reduced stability of ammonia-treated Fe-N-C catalysts in operating PEMFC. This results identifies a specific demetallation for $NH_3$-treated catalysts, in line with a recent report from Dodelet's group [2]. Fe-$NH_3$ was then investigated in anion-exchange membrane fuel cell (AEMFC), reaching a current density up to 100 mA $cm^{-2}$ at 0.9 V, beyond state-of-the-art result for PGM-free catalysts, and a peak power density of 1 W $cm^{-2}$.

[1] Zitolo, A., Goellner, V., Armel, V., Sougrati, M.T., Mineva, T., Stievano, L., Fonda, E., Jaouen, F. Identification of catalytic sites for oxygen reduction in iron- and nitrogen-doped graphene materials. Nat. Mater. **14,** 937–42 (2015).
[2] Chenitz, R., Kramm, U.I., Lefevre, M., Glibin, V., Zhang, G., Sun, S., Dodelet, J.P., A specific demetalation of Fe–$N_4$ catalytic sites in the micropores of NC_Ar + $NH_3$ is at the origin of the initial activity loss of the highly active Fe/N/C catalyst used for the reduction of oxygen in PEM fuel cells Energy Environ. Sci. **11**, 365-382 (2018).

# Synergistic effects of active sites nature and hydrophilicity on oxygen reduction reaction activity of Pt-free catalysts

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Oxygen reduction reaction (ORR) is a fundamental reaction in many electrochemical processes, but, being kinetically hindered, it requires efficient catalysts. Typically, they are based on platinum-group metals that, though very efficient, present some drawbacks such as costs, availability and technological problems. Finding cheaper substitutes with similar or better electrocatalytic properties and stability is a challenge for the scientific community. Effective candidates are based on metal-nitrogen-carbon catalysts, in which the metal is usually iron or cobalt.

In this work, we highlight the importance of the hydrophilicity of the catalyst active sites on ORR through an electrochemical and physicochemical study on catalysts based on nitrogen-modified carbon doped with different metals (Fe, Cu, and a mixture of them). BET, XRPD, micro-Raman, XPS, SEM, STEM and hydrophilicity measurements were performed. All synthesized catalysts are characterized by a porous structure, with porosity distribution centered in the mesoporosity range, and by the presence of carbon nanostructures. In iron-doped materials, these nanostructures exhibit a bamboo-like morphology, typical of nitrogen-doped carbon nanotubes, and are better organized, in larger amount and longer than in the copper-doped material. Electrochemical ORR results show that the co-presence of iron and nitrogen-doped carbon nanotubes is beneficial to the electroactivity of these materials and demonstrate that also hydrophilicity of the active site is an important parameter affecting electrocatalytic properties. The catalyst containing the mixture of Fe and Cu is the most active one.

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# Graphene based electrocatalyst for oxygen reduction reaction

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The Oxygen Reduction Reaction (ORR) is a fundamental process for sustaining life and is an important process utilized in the field of energy conversion and biosensing analysis. The process is exploited in artificial energy devices such as fuel cells and metal-air based batteries. The reaction proceeds at a very slow kinetic rate requiring a catalyst to reduce the activation barrier. Platinum is an ideal catalyst but it is neither cheap nor environmentally friendly[1]. The prospect of a cheap and green alternative is intriguing and has yielded considerable research in the past decade. Amongst the most promising materials as catalysts carbon-based systems, such as carbon nanotubes (CNT) and graphene derivatives, are particularly intriguing. New synthetic strategies [2] allow to produce tunable graphene-based materials, starting from graphene oxide (GO). These are based on the reduction of the oxidized groups of GO in the presence of compounds capable of adding functional groups or heteroatoms to the carbon lattice. We were particularly interested in the material obtained by doping GO with nitrogen and boron through its reduction in presence of idrazine and borazine. Such reduced graphene oxides (rGO) show almost the same electronic properties as graphene, with some X-C (X= N or B) regions within the graphene lattice that have a useful dipole moment which helps the interaction between the oxygen molecule and the catalytic substrate; thus, such sites represent those active for the ORR catalysis. We have investigated the electrochemical behavior of a selection of such material and their electrocatalytic activity for the ORR.

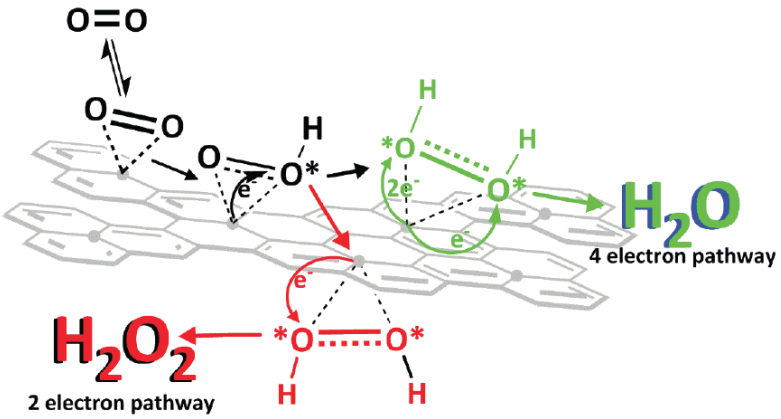


**Figure 1**: ORR 2 electron and the most efficient 4 electron processes

[1] C. Sealy., *Materialstoday*, 2008, **11**, 65-68
[2] C. K. Chua, M. Pumera, *Chem. Soc. Rev.* 2014, **43**, 291

# Experimental and physically based modelling analysis of electrochemical impedance to interpret limiting phenomena during PEMFC operation and ageing

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The required targets for Low-Pt and PGM-free PEMFC in automotive application are not fully achieved, because of a severe performance decay, determined by the interaction of several degradation mechanisms. Electrochemical impedance spectroscopy is a promising in-situ technique to distinguish the contributions of different degradation phenomena, but nowadays data analysis is widely performed by simplified electrical circuits that do not permit to achieve a solid physical interpretation. A physically based modelling approach can cover this gap, however it is not fully consolidated yet.

The present work aims at presenting the effectiveness of an approach that combines experimental and physically based modelling analysis of electrochemical impedance in investigating the limiting phenomena during operation of Low-Pt PEMFC and PGM-free PEMFC. The general methodology is presented, highlighting the possible onset of different regimes. Subsequently some relevant cases are discussed in details.

# Performances of direct methanol fuel cells with chitosan membranes as proton conductors

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Direct methanol fuel cells (DMFCs) have attracted much attention due to several advantages, like a quick start-up at low temperature, a high energy density, rich sources, and easy transportation and storage of fuel [1]. Nafion® membranes are commonly used due to their high proton conductivity and to their chemical, mechanical and thermal stability. However, two major obstacles that currently prevent the widespread commercial applications of DMFCs are low activity of reported methanol electro-oxidation catalysts to date and crossover of methanol through the polymer electrolyte membrane. In order to overcome these problems, much attention has been paid to study the methanol electro-oxidation mechanism on different catalysts, and to develop alternative commercial polymer electrolyte membranes matching a high conductivity with a low methanol permeability and low cost [2]. Chitosan (CS), as abundant and low cost natural biopolymer with low methanol permeability, has been investigated as promising proton exchange membrane (PEM) for DMFCs. However, the proton conductivity of chitosan is too low for possible application in DMFCs, therefore a commonly exploited strategy to enhance its proton conductivity is the introduction inside CS chains of heteropolyacids (HPA) [3]. In refs. [4-5] we proposed an efficient procedure to obtain CS-HPA composite membranes successfully tested as proton conductor in low temperature $H_2$ fed fuel cells. CS is dissolved in an aqueous acetic acid solution, where it is protonated and behaves like a cationic polyelectrolyte and can be ionically cross-linked by anionic species. Therefore, using a porous medium previously embedded with HPA, the slow release of Keggin anions induces the crosslinking with protonated chitosan to occur on its surface allowing to prepare flat, homogenous and freestanding membranes, whose thickness can be finely tuned by tuning the contact (i.e. reticulation) time. According to the scanning electron microscopy images, the membranes are compact without microvoids, thus being very promising as efficient barrier toward methanol crossover.

In this work we prepared chitosan – phosphotungstic acid composite membranes of different thickness to be tested as polymer electrolyte for DMFC. The membranes were tested in a single module Methanol/$O_2$ fuel cell to study the performance of a direct methanol fuel cell using CS/HPA as proton conductor, to study the kinetic of methanol oxidation reaction (MOR) and to study the methanol crossover in operating conditions. Electrochemical Impedance Spectroscopy (EIS) was used to get information about the conductivity of the membrane as well as to model the kinetic of the MOR in the DMFC.

[1] B.G. Choi et al, Carbon 50 (2012) 5395-5402.
[2] F. Lufrano et al., Journal of Power Sources 243 (2013) 519-534.
[3] Journal of Membrane Science 500 (2016) 203-210.
[4] M. Santamaria et al., Journal of Power Sources, 276 (2015) 189-194.
[5] M. Santamaria et al., Int. J. Hydr. Energ. 41 (2016) 5389-5395.

# Towards methanol tolerant and low-cost ORR catalysts based on metal-nitrogen-carbon (M-N-C) for direct methanol fuel cells

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Direct methanol fuel cells (DMFCs) are promising power supply systems because of their good efficiency and the high energy density of the fuel (6100 mWh $g^{-1}$), which allows for prolonged operation [1]. A critical factor is the cost of the anode and cathode catalysts, which are usually based on expensive platinum-group metals (PGMs), and methanol crossover through the polymeric membrane, which creates a mixed potential at the cathode and decreases the overall efficiency [2]. Although Pt is very active for the ORR, it also promotes MOR, which means that if methanol and oxygen are present at the cathode, the selectivity toward ORR is lower than 100%. The development of methanol-tolerant cathode catalysts that are cheaper than Pt for DMFCs has recently received much attention [3]. In this regard, Metal-Nitrogen-Carbon (M-N-C) based electrocatalysts have attracted a special interest due to their promising characteristics in terms of extraordinary methanol tolerance and suitable performance when deposited at the cathode of a DMFC.

In particular, this presentation summarizes the recent advancements achieved by our group in DMFCs using M–N–C catalysts. A comparison with the current literature is also presented.

[1] A. S. Aricò, V. Baglio, V. Antonucci, Direct Methanol Fuel Cells, Nova Publishers, New York, 2010.
[2] D. Sebastián, A. Serov, I. Matanovic, K. Artyushkova, P. Atanassov, A.S. Aricò, V. Baglio, *Nano Energy*, 2017, **34**, 195–204.
[3] C. Lo Vecchio, D. Sebastián, M.J. Lazaro, A.S. Aricò, V. Baglio, *Catalysts*, 2018, **8**, 650.

# Electrochemical behaviour of $La_{0.8}Sr_{0.2}MnO_{3-\delta}$-infiltrated $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ under anodic overpotential

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Solid oxide fuel cells (SOFCs) and electrolysers (SOECs) are currently considered as promising devices to be used in distribution and storage electrical net where renewables operate, because of their high efficiency and flexibility in terms of energy fluctuations. Our research group has recently studied the $La_{0.8}Sr_{0.2}MnO_{3-\delta}$-infiltrated $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ system on $Sm_{0.2}Ce_{0.8}O_{2-\delta}$ supporting electrolyte (LSM-BSCF/SDC), as electrode for SOFCs, under cathodic overpotentials. It was demonstrated a positive effect of LSM both on performance (polarisation resistance) and long-term stability.

However, both pristine BSCF and infiltrated LSM-BSCF electrodes showed unexpected increasing of polarization resistance with increasing cathodic overpotential, namely when a net cathodic current flowed through them [1].

In view of these results, a similar BSCF and LSM-BSCF system on SDC-supporting electrolyte was studied under anodic electrochemical conditions, to explore the behaviour of this electrode as anode in SOEC mode. Due to gas evolution from reaction sites, electrolysis systems usually exhibit huge delamination [2], so the electrode porosity was accurately optimised using a graphite-based pore former.

The results of this investigation will be presented.

[1] A. Giuliano, M. P. Carpanese, D. Clematis, M. Boaro, A. Pappacena, F. Deganello, L. F. Liotta and A. Barbucci, *J. Electrochem. Soc.* 2017, **164** (10) F3114-F3122.
[2] S. Zhang, H. Wang, M.Y. Lu, C-X Li, C.-J Li, S. A. Barnett, *J. Power Sources.* 2019, **426**, 233-241.

# Insights into oxygen reducing activity and poisoning tolerance of platinum-group-metal-free catalysts

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Our century will very likely be remembered as the fossil fuel alternatives development era. Indeed, great efforts in the past decades have been dedicated to the improvement of new and more environment-friendly devices. Among them, the technology of fuel cells (FC), with its high conversion efficiency, has the best chances to be candidate for combustion engines replacement if a suitable and economic platinum substitute for the oxygen reduction reaction (ORR) will be developed. With that purpose, the route of carbonaceous materials containing nitrogen and non-platinum group transition metals (PGM-free) is the most followed to enhance ORR kinetics at all pH values [1,2]. Nevertheless, further improvements are required to solve all the problems of the platinum, especially in terms of stability over time and poisoning of the catalytic activity in presence of contaminated working environments.

Herein, a study on the poisoning tolerance of iron-based catalysts to the most common contaminants is presented. The catalyst selected is obtained by sacrificial support method (SSM) of pyrolyzed precursors containing benzimidazole and iron salts (Fe-BZIM) [3]. Using the rotating disk electrode (RDE) and the rotating ring-disk electrode (RRDE) techniques, the effect of increasing concentrations of chlorides, perchlorates, nitrites, nitrates, sulfides, and sulfates on the ORR mechanism is studied in terms of variation of Onset Potential ($E_{on}$), Halfwave potential ($E_{1/2}$), Limiting Current Density ($J_{lim}$), Hydrogen Peroxide Production ($\%H_2O_2$), and Number of Transferred Electrons ($\#e^-$). The study, conducted at three different pH values (1-7-13), allows to get insights into specific trends for PGM-free catalysts that can be compared with platinum and metal-free catalysts.

[1] B. Mecheri, V.C.A. Ficca, M.A. Costa de Oliveira, A. D'Epifanio, E. Placidi, F. Arciprete, S. Licoccia. Appl. Catal. B Environ. 237 (2018) 699–707.
[2] S. Rojas-Carbonell, K. Artyushkova, A. Serov, C. Santoro, I. Matanovic, P. Atanassov ACS Catalysis 8(4) (2018) 3041-3053.
[3] B. Mecheri, R. Gokhale, C. Santoro, M.A. Costa de Oliveira, A. D'Epifanio, S. Licoccia, A. Serov, K. Artyushkova, P. Atanassov. ACS Appl. Energy Mater. 1(10) (2018) 5755–5765.

# A study on cathodic reactivity of caffeine: A biobased starting material for the development of new products

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Caffeine (1,3,7-trimethylxanthine) is the more thoroughly studied natural xanthine alkaloid to date. It acts as a stimulant in humans and occurs naturally in beans, leaves, and fruit of more than 60 plants. [1] It acts as a natural pesticide. It acts as central nervous system stimulator and plays important role in restoring mental alertness. It is a xanthine and thus its structure can be seen as the fusion of an uracil ring with an imidazole one; it is a bio-based and renewable reagent, quite cheap and convenient as starting material in organic synthesis.

Despite the large number of papers present in the literature on the electrochemical oxidation of caffeine, its electrochemical reduction was never reported. For this reason we decided to study the electrochemical reduction of caffeine. The cathodic reduction in DMF-$Bu_4NBF_4$, yielded N-formyl-N,1-dimethyl-4-(methylamino)-1H-imidazole-5-carboxamide, a highly functionalized imidazole product derived from the opening of the uracil ring. This reactivity is opposite to the cathodic one of the methylated salt of caffeine, which yields the opening of the imidazole ring with the formation of a substituted uracil (hymeniacidin) derived from the hydrolysis of the corresponding electrogenerated N-heterocyclic carbene. [2] Moreover, the products obtained by cathodic reduction of caffeine, or its salt, are different from what can be obtained by classical organic synthesis. (Figure 1)

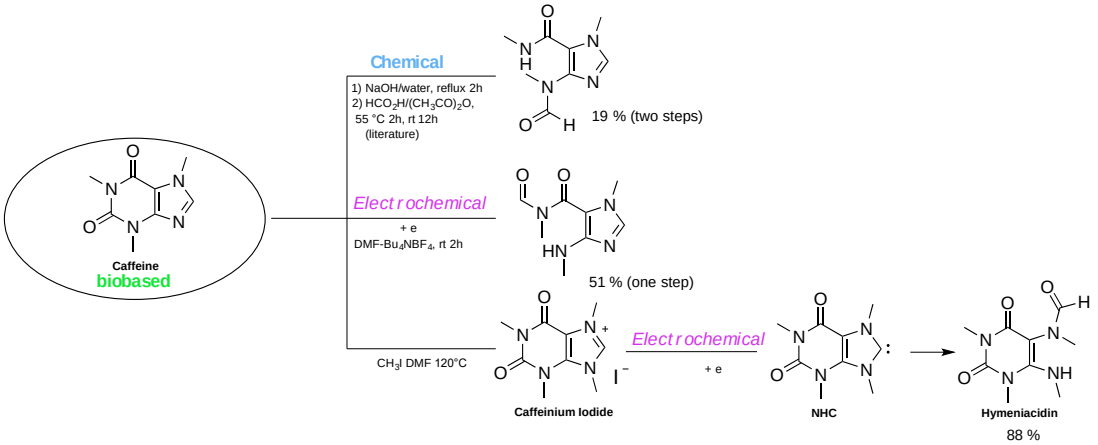


**Figure 1:** Different synthetic strategies

The electrochemical methodology proved to be a valuable ally for organic synthesis, allowing to obtain different products, which were not obtainable (or with difficulty) using classical chemical reactions. [3] Furthermore, the nature of the starting material (caffeine, bio-based and thus renewable) renders this work interesting in the contest of sustainable organic synthesis.

[1] Fredholm, B. B. *Methylxanthines*, Springer-Verlag Berlin Heidelberg, **2011.**
[2] Pandolfi, F.; Mattiello, L.; Zane, D.; Feroci, M. *Electrochim. Acta* **2018**, *280*, 71.
[3] Pandolfi, F; Chiarotto, I.; Mattiello, L.; Rocco, D.; Feroci, M. Synlett **2019**, DOI: 10.1055/s-0037-1611483.

# Performances of compact and porous Pd-Ni electrodes in the oxidation of ethanol in alkali

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Pd is an interesting anode material for alkaline Direct Alcohol Fuel Cells due to its high activity, good stability, relative abundance and lower cost compared to Pt. Accordingly, the preparation of Pd-based electrodes is much investigated [1]. The prevalent approach consists in the chemical preparation of finely dispersed Pd or Pd alloys, deposited on a support of nanostructured carbonaceous materials. A few recent papers have considered the use of anodes obtained by electrodeposition of porous Pd-Ni alloys [2], but the relation between composition and performances has received a limited investigation.

We present here the preparation of homogeneous (compact or porous) and heterogeneous (bilayer) Pd-Ni electrodes. The latter are obtained by deposition of a substrate layer of porous Ni or Pd-Ni, and an overlayer of compact or porous Pd. Cyclic voltammetries of $C_2H_5OH$ oxidation in 1 M KOH show peak current densities $j_p$ varying over two orders of magnitude. The effective Pd surface is estimated by the charges of PdO reduction and expressed with the dimensionless parameter $f_{r,Pd}$, namely the equivalent Pd surface per unit area, reducing to a traditional roughness factor $f_r$ for pure Pd samples.

The log-log plot in Fig. 1 (right) shows that, neglecting some dispersion attributable to peculiar sample properties [3], $j_p$ is basically proportional to $f_{r,Pd}$ for the entire set of samples. This relation indicates that the electrode activity in ethanol oxidation depends, in a first approximation, only on the Pd surface area exposed to the electrolyte, with no evidence of synergistic effects of Ni admixtures.

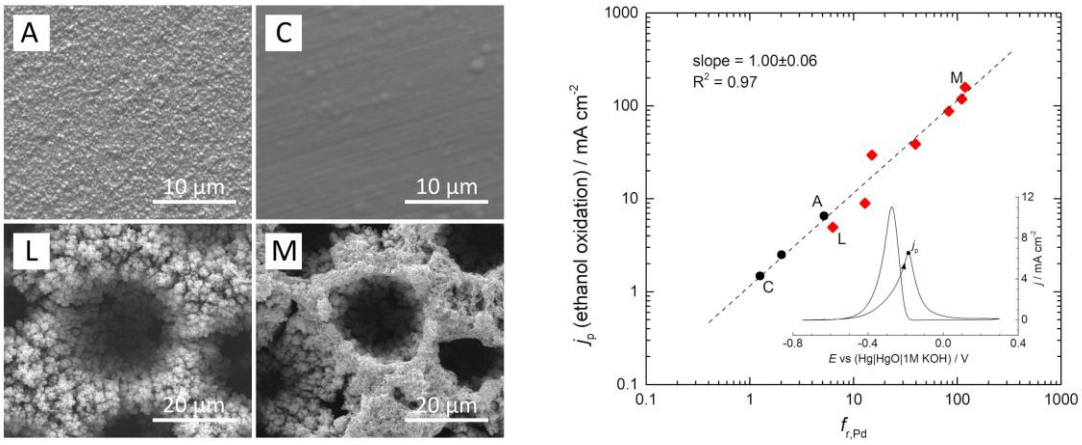


**Figure 1**: left) SEM images of homogeneous (A, C, L) and heterogeneous (M) samples; right) log-log plot of the peak current density $j_p$ as a function of $f_{r,Pd}$ for all samples, compact (black dots) and porous (red diamonds).

[1] C. Bianchini, P.K. Shen, *Chem. Rev.* 2009, **109**, 4183-4206.
[2] R. Li, H. Mao, J. Zhang, T. Huang, A. Yu, *J. Power Sources* 2013, **241**, 660-667.
[3] L. Mattarozzi, S. Cattarin, N. Comisso, R. Gerbasi, P. Guerriero, M. Musiani, L. Vázquez-Gómez, *Electrochim. Acta* 2019, **307**, 503-511.

# Electrochemical reduction of $CO_2$ by Mn and Re bipyiridine complexes: homogeneous and hetereogeneous approaches

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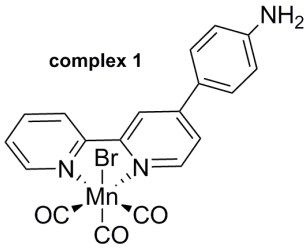
Electrochemical reduction of $CO_2$ mediated by transition metal complexes is appealing because it could reduce the amount of this greenhouse gas that is accumulating in the atmosphere and at the same time yield valuable chemicals. We herein present our recent findings employing Re and Mn bipyridines complexes following two orthogonal approaches: homogeneous and heterogeneous electrochemical reduction, with the aim of take advantage from both worlds. For the heterogeneous approach we attached an intact (*fac*-Mn(apbpy)$(CO)_3$Br) (apbpy = 4-(4-aminophenyl)-2,2'-bipyridine) complex **1** on Carbon Cloth (CC) electrode surfaces via the electrochemical reduction of the corresponding diazonium salt, leading to the formation of strong covalent C–C bonds. The same approach was previously followed by us on a different support (glassy carbon electrode) and solvent (acetonitrile) [1]. The functionalized CC electrode is tested in water (where normally organometallic catalysts are insoluble), resulting in a surprisingly high TON (up to 33200 during 10 hours of operation) [2].




For the homogeneous counterpart we carried out a systematic study of the electrochemical properties of new Mn and Re complexes issued by different substitution on the bipyridine ligand. Substituents with electron withdrawing groups like -$CF_3$ and -CN and with electron donating groups, like -$N(Me)_2$, -Ph and -PhOH, were placed in the 4,4', 4,6 and 5,5' positions of the bipyridine ligand coordinated to the metals, as depicted in the following scheme. Electron-withdrawing substituents shift the reduction potentials to more positive values, and eventually inhibit the catalytic activities of the corresponding Mn and Re complexes toward $CO_2$ reduction. In the case of electron-donating substituents the opposite trend is observed. These observations are in agreement with the induced electron density localized on the metal, strongly influencing the change in the reactivity with the weak electrophile $CO_2$ [3].

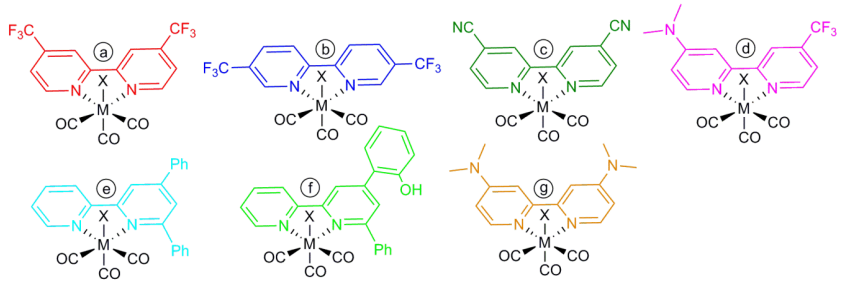



**Figure 1**: Studied complexes in homogeneous solution (M=Re, Mn).

**References**

[1] C. Sun, L. Rotundo, C. Garino, L. Nencini, S. S. Yoon, R. Gobetto and C. Nervi, *ChemPhysChem*, 18, 2017, 3219–3229.
[2] L. Rotundo, J. Filippi, R. Gobetto, H. A. Miller, R. Rocca, C. Nervi and F. Vizza, *Chem. Commun.*, 55, 2019, 775–777.
[3] L. Rotundo, E. Azzi, A. Deagostino, C. Garino, E. Priola, P. Quagliotto, R. Rocca, L. Nencini, R. Gobetto, C. Nervi, *Frontiers in Chemistry*, 2019, submitted.

# Copper-based electrodes for electrochemical $CO_2$ conversion

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Electrochemical conversion of $CO_2$ to value-added products are being intensively investigated, in order to address the issues regarding the excess $CO_2$ emissions, the increasing energy demands and the storage of intermittent electricity from renewable sources. However, the $CO_2$ reduction reaction ($CO_2$RR) involves various pathways with similar standard potentials, leading to poor selectivity for a specific product. Moreover, the reactions inherently demand large overpotentials to overcome the activation energy barriers. To improve the selectivity and overcome sluggish kinetics, appropriate electrocatalysts should be applied. Therefore, the development of efficient catalysts has attracted most interest within the $CO_2$ utilization community. Among many studied elements, copper (Cu) shows unique features of electrochemically converting $CO_2$ to a range of chemicals including hydrocarbons. Its selectivity for a specific product can be tuned by modifying the morphology and the surface composition of the catalysts [1, 2].

Our previous work demonstrates that excellent selectivity for CO can be achieved with an optimal surface CuSn composition and dendritic morphology [3]. The ongoing work studies $Cu/CuO_x$ for converting $CO_2$ to tunable syngas, as shown in Figure 1. We are also exploring other bimetallic materials such as CuZn and CuSb for the $CO_2$RR.

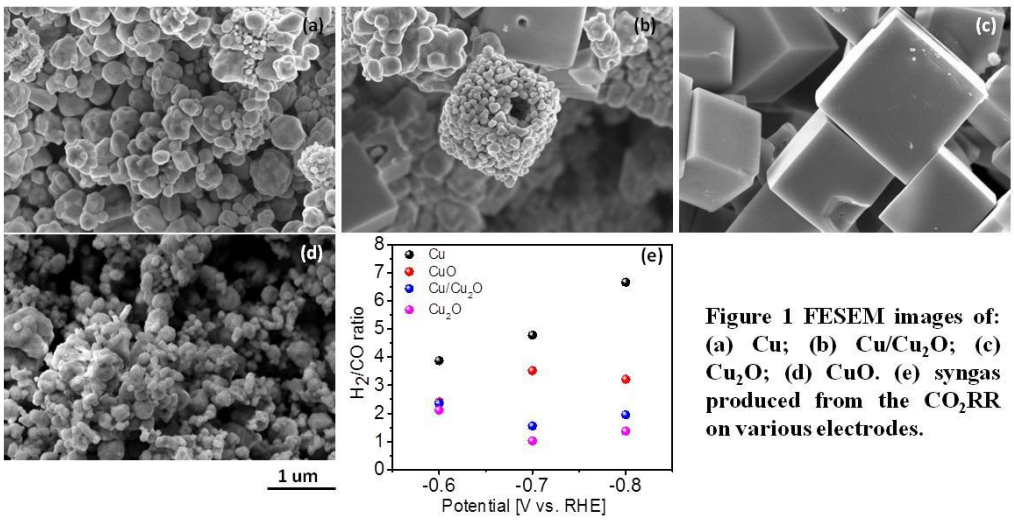


**Figure 1 FESEM images of: (a) Cu; (b) $Cu/Cu_2O$; (c) $Cu_2O$; (d) CuO. (e) syngas produced from the $CO_2$RR on various electrodes.**

**References:**

[1] G. O. Larrazábal, A. J. Martín, F. Krumeich, R. Hauert, J. Pérez-Ramírez, ChemSusChem 10 (2017) 1255-1265.

[2] R. Kas, R. Kortlever, H. Yilmaz, M.T.M. Koper, G. Mul, Chemelectrochem 2 (2015) 354-358.

[3] J. Zeng, K. Bejtka, W. Ju, M. Castellino, A. Chiodoni, A. Sacco, M.Amin Farkhondehfal, S. Hernández, D. Rentsch, C. Battaglia, C. F. Pirri, Appl. Catal. B: Environ. 236 (2018) 475-482.

# n-Type semiconductors for photoelectrochemical environmental remediation

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Nanocrystalline $WO_3$ and n-n $WO_3/BiVO_4$ were successfully applied to the photoelectrochemical degradation of contaminants of emerging concern (CEC) under visible light: atenolol, levfloxacine, ketoprofen and carbamazepine represent examples of widely used pharmaceuticals impervious to conventional potabilization treatments found in increasing concentrations in natural waters.

With respect to open circuit photocatalysis the photoelectrochemical treatment, even in diluted supporting electrolyte conditions, representing the average salinity of natural freshwater, allows for a ×5 acceleration of the contaminant degradation kinetics, leading, with sufficient time to mineralization of the target molecules (Fig. 1) [1,2].

Compared to $WO_3$, the n-n $WO_3/BiVO_4$ junction, with a gap of ca. 2.4 eV, harvests a larger portion of the visible spectrum, and more than doubles its photoanodic current. Nevertheless this junction was found unable to produce OH radicals by monoelectronic water oxidation [3], resulting less universal than wider band gap metal oxides as a photoresponsive substrate for environmental applications relying on oxidative degradation pathways.

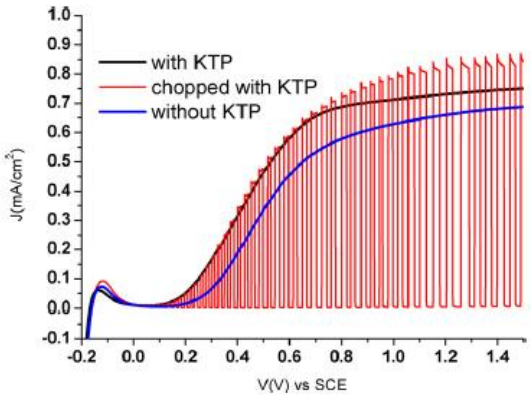


**Figure 1**. J/V characteristics of $WO_3$ in the presence and in the absence of Ketoprofene (KTP)

[1] G. Longobucco et al. *Applied Catalysis B: Environmental* 2017, **204,** 273–282
[2] V. Cristino et al. *Catalysis Today*, **2018** https://doi.org/10.1016/j.cattod.2018.09.020
[3] V. Cristino et al. *Photochem. Photobiol.Sci.,* **2019,** DOI: 10.1039/c9pp00043g

# Thermally decomposed $RuO_2$-$CoO_x$ coated titanium anodes: durability and application in environmental electrochemical processes

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Transition metal oxide electrodes (TMOs) are interesting materials for electrochemical applications in environmental remediation due to different oxidation states, morphologies, amorphous/crystalline nature, moderate conductivity, hydrophilic and mixed capacitive behavior with good stability and low electrochemical series resistance. Some papers report [1] that the binary oxides, especially those which are cobalt-based, such as Co-Mn, Co-Zn, and Co-Fe oxides, are more active and perform better than the pure oxide, due to their peculiar electrocatalytic properties, high ion transportation kinetics, and electrical conductivity. Most of their properties can be attributed to the fact that these elements exhibit multiple oxidation states.

In recent years [2], we have focused our research on the development of TMOs. For the preparation of oxide thin films, chemical deposition via spin-coater is preferred among other techniques. It allows the deposition of well-controlled films in order to have higher reproducibility. Moreover, it requires no sophisticated instruments such as vacuum system, and the starting chemicals are commonly available and cheap.

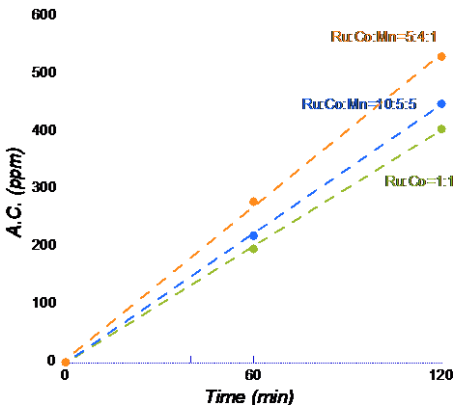


**Fig. 1**. *Active chlorine production of different electrodes in aqueous solution and $H_2SO_4$ and HCl*

The purpose of this work has been to prepare chemically deposited TMOs thin films containing ruthenium and cobalt oxide and to evaluate their durability and electrochemical performances. The films were prepared by thermal decomposition on titanium substrate from alcoholic solutions by using either a RuOx interlayer or directly mixing the precursors of the two oxides. Furthermore, the films were doped with varying amounts of manganese oxide.

Surface morphology (studied by SEM) and chemical composition (by EDX) were analyzed and related with the electrochemical responses, evaluated by potentiodynamic polarization, cyclic voltammetry and impedance spectroscopy (EIS). The durability was assessed by accelerated life tests. The electrodes were then used in the anodic process and the ability to electrogenerate dangerous by-products in the presence of chlorides has been investigated. The effect of the composition of the mixture on the characteristics of the electrode has been finally discussed.

[1] Z. Y. Tian, H. Vieker, P. Mountapmbeme Kouotou and A. Beyer, *Faraday Discuss*., 2015, **177**, 249-262.
[2] E. Petrucci, D. Montanaro, M. Orsini, G. Sotgiu, *J. Electroanal. Chem.,* 2018, **808**, 380-386.

# Bipolar anodic spark deposition to enhance the corrosion resistance of titanium: effect on morphology and structure

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Anodic spark deposition (ASD) is a well-known technique used to enhance the corrosion resistance of titanium in harsh environments inducing localized corrosion [1-2]. However, ASD in direct current leads to a high-energy consumption and to the formation of a high level of porosity and crystallinity. All those effects are strongly related to the sparks' formation, in turns caused by the ionization of the valence electrons of the titanium-oxygen bond, leading to an avalanche reaction generating porosity but also crystalline phases due to local heating. The use of a programmable power supply provides the possibility of controlling process parameters like duty cycle, frequency and voltage offering the opportunity to perform ASD with a monopolar pulsed regime (Fig.1). The technique may be used to obtain desired morphological and structural modifications of the oxide layer, including the variation of shape and area covered by pores, the amount and type of crystalline phase, while maintaining a good corrosion resistance and an interesting level of energy saving with respect to the DC approach. However, SEM images, performed with a Cambridge Stereoscan 360, still demonstrated the presence of a high degree of porosity distributed all over the anodized surface, increasing with the forming voltage. The use of a bipolar pulsed ASD (Fig.1) has been investigated in order to modify the morphological and structural features of the titanium dioxide layer. The percentage of the cathodic peak (2-10% with respect to the anodic peak voltage), the duty cycles ratio (90%anodic-10%cathodic to 10%anodic-90%cathodic) and the frequency (20 - 1000 Hz) have been varied limiting as much as possible the amount of hydrogen introduced during the cathodic polarization. The fraction in cathodic regime has been optimized for corrosion resistance purposes: the anodized samples were characterized by potentiodynamic tests in bromides rich environment (ASTM G5) for localized corrosion and by immersion tests in acidic media (ASTM G31) for uniform corrosion.

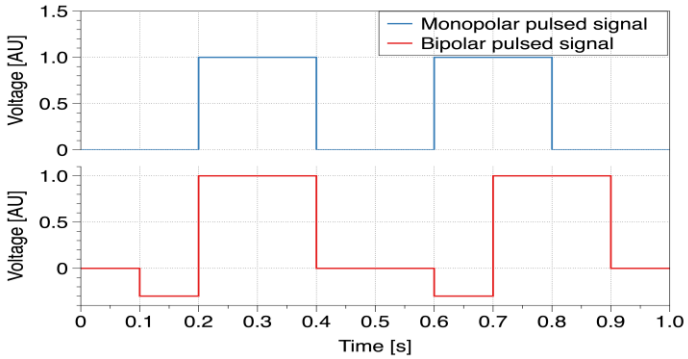


*Figure 2**: Monopolar (blue waveform) and bipolar (red waveform) voltage pulse.***

[1] D. Prando, A. Brenna, M.V. Diamanti, S. Beretta, F. Bolzoni, M. Ormellese, M. Pedeferri, *J Appl Biomater Funct Mater*, 2018, **15**, e3–e13.
[2] D. Prando, A. Brenna, M. Pedeferri, M. Ormellese, *Materials and Corrosion*, 2018, **69**, 503-509.

# On the impact of the oxidation potential on the conversion of D-glucose to D-glucaric acid in alkaline medium

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With the ever-increasing need for green and sustainable chemical processes, electrochemical methods, involving electron transfer in the absence of any kind of oxidizing or reducing agents while working under mild operating conditions, have been recognized as promising green methods in organic synthesis [1-2]. Even more so, they allow control over the reaction outcome by adjusting the operating potential or current density. One such reaction, where electrosynthesis has an answer to the existing drawbacks of current synthesis methods, is glucose oxidation: an important and useful reaction that transforms biomass into useful chemicals, i.e. glucaric acid, which has several potential uses in fine chemistry. Indeed, the carboxylic group is able to react selectively with different amines, alcohols and vinyl derivatives, forming products with new application profiles (e.g. gluconolactones, a number of polymers, including new nylons, hyperbranched polyesters and polyhydroxypolyamides). Unfortunately, several possible oxidation pathways exist, like the oxidation of either one of the two terminal functional groups, or the cleavage of the C-C bonds, making it difficult to promote the selectivity to the desired product, utilizing traditional chemical processes.

In this work, the role of the potential on the selectivity of the glucose electrooxidation process will be elucidated in an attempt to unravel the difference in reactivity of the functional groups available in the glucose molecule, and as such open up possibilities to tune the selectivity towards a desired product. For this purpose, four different solutions of, respectively, glucose, gluconic acid, glucuronic acid and glucaric acid in alkaline medium were studied by cyclic voltammetry with three different metal electrodes (copper, platinum and gold). The potential-selectivity relationship was verified by analyzing the products of long-term electrolysis experiments by HPLC analysis. The highest yield to D-gluconic and D-glucaric acids was obtained on platinum and on gold electrodes (Fig.1), with gold being the most active.

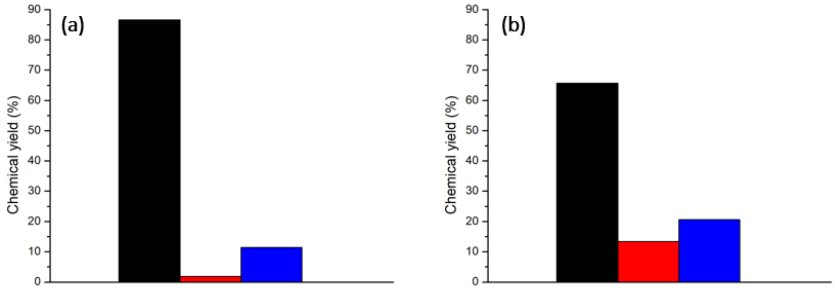


**Figure 1**: Chemical yields of the products of electrolysis on gold after 65h in alkaline media (0.1M NaOH) at 5°C, at (a) 0.55 V and (b) 1.34 V vs. RHE: D-gluconic acid (black), D-glucaric acid (red), and lower molar mass carboxylic acids (blue).

[1] J. Yoshida, K. Kataoka, R. Horcajada, A. Nagaki, Chemical Reviews **108** (2008) 2265.
[2] B.A. Frontana-Uribe, R.D. Little, J.G. Ibanez, A. Palma, R. Vasquez-Medrano, Green Chemistry **12** (2010) 2099.

# Mathematical modelling of TiO2 nanotubes behaviour under solar light irradiation

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In recent years, titania nanotubes (NT) have attracted increasing interests for technological applications due to their unique architecture, consisting of vertically oriented, highly ordered nanotubes which allow to high surface-area-to-volume ratio, enhanced electron transport velocity and charge separation efficiency, so making these materials ideal for solar or UV light photoelectrocatalytic applications. A very important parameter when nanotubular TiO2 structures are adopted, is the morphology of the tubes which in turn influence the specific surface and its exploitation, in terms of surface available for both oxidation and photoelectric effect.

To evaluate the optimal geometry of the nanotubular structure for the different applications, a 2-D mathematical model of the photoelectrochemical processes occurring during irradiation of Titania nanotubes with solar light has been implemented. The model considers phenomena in the solid phase, such as formation and recombination of electron-hole pairs, and chemical and electrochemical reactions in the liquid phase. Moreover, the transport of species in liquid and solid phase are also considered. The solar irradiation has been discretised in the UV and visible range, and the adsorption coefficients have been defined as a function of the wavelength. The model was solved for oxidation of water, as well as for oxidation of organic compounds with different reactivity. The effect of such variables as light intensity, electric potential and organic reactivity, were quantified.

Space distribution of charge carriers in solid phase, and oxygenated radicals and organic compounds in liquid phase have been obtained. The results of the model indicate that, depending on reactivity and concentration of the compounds, the optimal length of nanotubes is different: tubes of 10 micro meters are effective with high concentrations, while shorter tubes can be used where low-concentrated organic compounds must be removed. Moreover, tubes with high length and wall thickness should be used to maximise the current generation, although the feasibility of such structures should be verified. The model provides a versatile tool to assess the performances of nanotubular electrodes at microscale and makes possible the optimal design of the nanostructure.

# POSTER CONTRIBUTIONS

# Insights into the effect of water in electrochemically-mediated ATRP in nonaqueous solvents

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Atom Transfer Radical Polymerization (ATRP) is a powerful and versatile polymerization technique for the synthesis of well-defined polymers and copolymers. The polymerization exploits a reversible transfer of a halogen atom from a dormant species $P_n$-X to a metal catalyst $Mt^zL_m$ in a low oxidation state to produce the propagating radical $P_n^{\bullet}$ and the oxidized metal complex X-$Mt^{z+1}L_m$. Copper-amine complexes involving the $Cu^{II}/Cu^{I}$ redox couple are often used as catalysts. The reaction is conducted under equilibrium conditions strongly favoring the dormant state ($K_{ATRP}$ << 1), so that bimolecular radical terminations are kinetically hampered [1].

In electrochemically mediated ATRP (*e*ATRP), polymerization is triggered and sustained by fast (re)generation of $Cu^{I}$ from $Cu^{II}$. *e*ATRP allows modulation of reaction rate through easy control of the distribution of $Cu^{I}$ and $Cu^{II}$ species in solution and the possibility of switching the process from active to dormant state and vice versa, by varying the electrochemical parameters applied to the system [2].

It has been reported that ATRP in mixtures of traditional solvents and water is faster than the same reaction in pure organic solvents. We investigated the role of small amounts of water (up to 10%) in *e*ATRP of methyl acrylate using $[Cu^{II}TPMA]^{2+}$ as catalyst. Experimentally, we observed an increase of the overall polymerization rate constant, $k_p^{app}$, when the reactions were performed in mixtures of MeCN, DMSO, DMF and [BMIm][OTf] with $H_2O$. The increase of $k_p^{app}$ correlates with the amount of $H_2O$ and is consistent with an enhancement of the activation rate of the dormant alkyl halide. Indeed, the rate of activation of the C-X bond is usually much higher in water than in ionic liquids or organic solvents. Addition of water had a significant effect on the redox properties of the catalyst (Figure 1), as well as its activity.

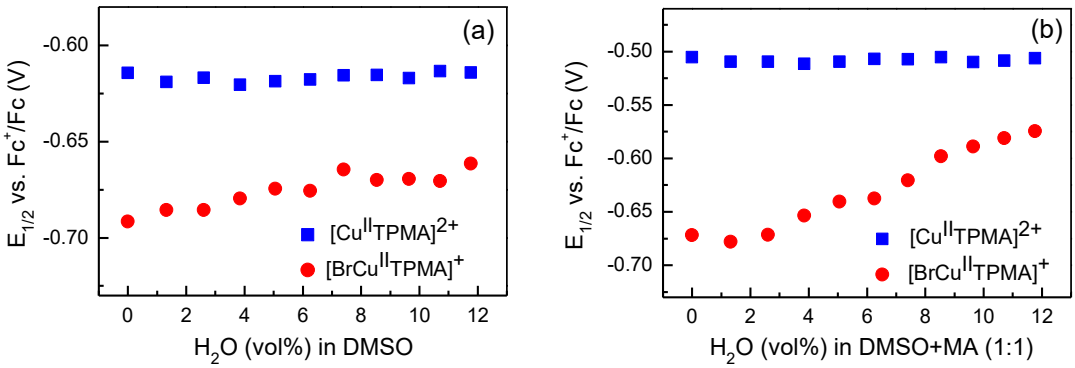


**Figure 1.** Dependence of $E_{1/2}$ of $[Cu^{II}TPMA]^{2+}$ and $[BrCu^{II}TPMA]^{+}$ on water concentration in (a) pure DMSO or (b) DMSO + 50 vol% methyl acrylate.

[1] K. Matyjaszewski, Macromolecules **45** (2012) 4015–4039.
[2] P. Chmielarz, M. Fantin, S. Park, A. A. Isse, A. Gennaro, A. J. D. Magenau, A. Sobkowiak and K. Matyjaszewski, *Prog. Polym. Sci.* **69** (2017) 47–78.

# Dynamic Impedance. What shall we do with all these data?

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A single measurement of dynamic electrochemical impedance provides thousands and even millions of spectra. This poses several challenges in the signal processing. There are several ways to recover the dynamic impedance from the raw data [1] [2]. In this contribution a direct fitting of the dataset is proposed as shown in Figure 1. The goal is to release the restrictions on the choice of the multisine frequencies and to be able to recover also secondary signals, like higher harmonics and intermodulations, and to decrease the interference of the noise.

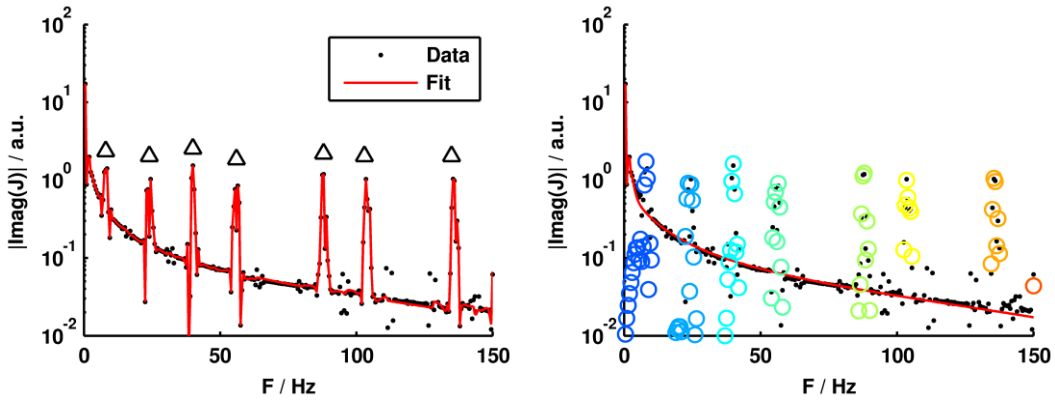


**Figure 1**: Fitting of the current for a multisine superimposed on top of a potential scan. **Left:** total fitting, the triangles represent the perturbed frequencies (8, 24, 40, 56, 88, 104, and 132 Hz); **Right:** components of the fitting: *dc* and multisine frequencies taken singularly. This dataset corresponds to 500 thousands impedance spectra.

Moreover, a large amount of impedance spectra needs to be fitted to a proposed model. Here the procedure to correlate the spectra is revised. This procedure takes advantage of the large number of spectra and quickly provides fitting for thousands of spectra.

Also a vast statistical analysis based on the large number of spectra becomes available. This encircles noise analysis, errors and biases derivation, and ascertains reliability of the fitting parameters.

This contribution provides an overview and a guide through the analysis of dynamic impedance from the computation of the spectra to the elaboration of the results.

[1] A. Battistel, F. La Mantia, *Electrochim. Acta*, 2019, **304**, 513–520.
[2] T. Breugelmans, J. Lataire, T. Muselle, E. Tourwé, R. Pintelon, A. Hubin, Electrochim. Acta, 2012, **76**, 375–382.

# Electrochemical activity of the polycrystalline cerium oxide films for hydrogen peroxide detection

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Hydrogen peroxide ($H_2O_2$) has significant importance in the key processes in medicine, biology, food industry and can be a source of hazardous free radicals which are the reason of oxidative stress in the living cells [1]. Therefore, there is a necessity in development of the reliable and sensitive methods and materials for $H_2O_2$ detection in different biological environments. Electrochemistry is one of the most promising for this purpose technique due to its simplicity, short time response and good sensitivity. Nanomaterials, such as cerium oxide ($CeO_2$) are well known to exhibit specific enzyme-like activities that can be used for $H_2O_2$ detection [2]. In this work, we propose polycrystalline cerium oxide thin film deposited on glassy carbon substrate as a new enzyme-free electrode for hydrogen peroxide detection. $CeO_2$ film was prepared by means of RF magnetron sputtering from cerium oxide target in argon atmosphere with total thickness of the film about 20 nm. The electrode revealed ability for $H_2O_2$ detection in micromolar range in phosphate buffer solution (pH = 6.9) even without using a mediator. Electrochemical measurements show a current plateau, that represent the maximum rate achieved by the system, at saturating $H_2O_2$ concentrations which is typical behaviour for enzymes. Stability in different pH was examined. Surface characterization performed by Scanning Electron Microscopy (SEM) and Atomic Force microscopy (AFM) before and after the electrochemical measurements demonstrate no significant changes of the electrode surface. Stability of the system was also investigated by highly surface sensitive synchrotron radiation photoelectron spectroscopy (SRPES).

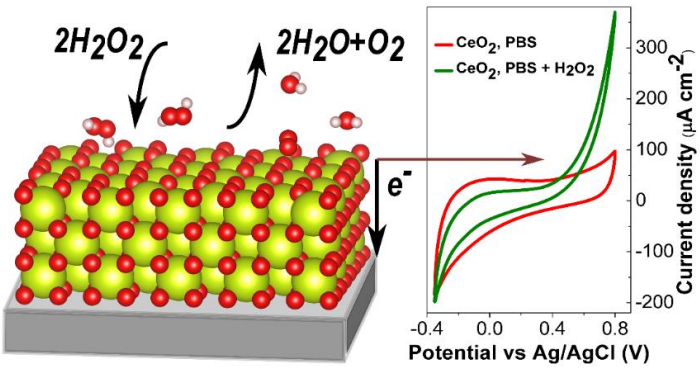


**Figure 1**: Schematic illustration of the electrochemical reaction of $H_2O_2$ on the $CeO_2$/GC electrode surface.

[1] K. B. Beckman,B. N. Ames, *Physiol. Rev*., 1998, **78**, 547–581.
[2] F. Charbgoo, M. Ramezania, M. Darroudic, *Biosensors and Bioelectronics, 2017, **96**, 33-43*1.

# Substituent effect on metal-porphyrins adsorbed on HOPG and its implications towards oxygen reduction reaction

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Metal-phthalocyanines and metal-porphyrins are regarded as very versatile molecules and are currently employed both in inorganic and biological applications [1]. The metal centre is often a transition metal atom, which can easily access different oxidation states, enabling the so-called “redox catalysis”, where upon metal reduction or oxidation a certain chemical species in proximity can be oxidized or reduced.

In this paper, two metal-porphyrins were probed by Electrochemical Scanning Tunnelling Microscopy in their ability to physisorb on a solid substrate and to catalyze the oxygen reduction reaction (ORR). Both aspects are in fact strictly correlated to the ligand chemical structure. Physisorption at the solid/liquid interface is governed by electrostatic interactions, π-π stacking, hydrophobic interactions, dispersion forces, etc., and if the *meso* and/or the *β-pyrrole* substituents are varied, a different behavior at the solid/liquid interface is expected. On the other hand, donor-accepter molecular hardness of the M-$O_2$ complex is regarded as one of the factors governing the ORR electrocatalysis mediated by $MN_4$ chelates. Molecular hardness is a balance between the donor (metal) ionization potential and the acceptor (oxygen) electron affinity, but it can be expressed as the difference between the energy of the LUMO of the acceptor and the energy of the HOMO of the donor [2]. The larger the HOMO-LUMO gap, the stronger the bond between donor and acceptor and the lower the activity. The concept of molecular hardness suggests that if there is the possibility of tuning the HOMO and LUMO energy levels, then the reactivity could be modified as desired. The two molecular systems herein investigated are iron(III) tetraphenyl porphyrin chloride (FeTPP) and iron(III) octaethyl porphyrin chloride (FeOEP). Cyclic voltammetry allowed to compare the ORR activity of the FeOEP and FeTPP adlayers with respect to bare HOPG, while EC-STM visualized the catalytic sites. In Ar saturated 0.1 M $HClO_4$, (fig. 1.a and b), the two molecules were visualized as crosses connected at each vertex with each other. In $O_2$ saturated electrolyte, Fig. 1.c, FeOEP acquired a brighter spot in a shifted position from the centre of each cross, indicating the presence of an $O_2$ molecule adsorbed onto the catalytic site.

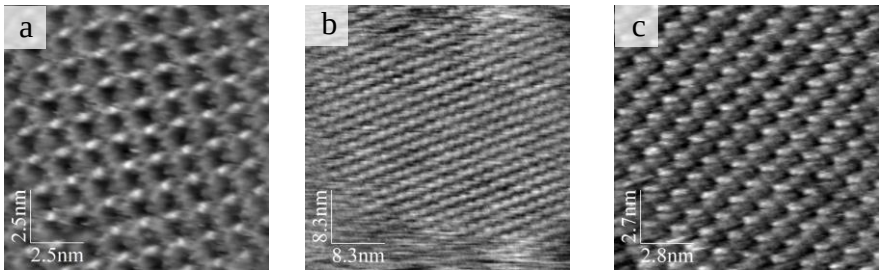


Fig. 1. EC-STM image in Ar purged 0.1 M $HClO_4$ of a) FeOEP adlayer; b) FeTPP adlayer and c) EC-STM image of FeOEP adlayer in $O_2$ saturated 0.1 M $HClO_4$.

[1] J.H. Zagal, S. Griveau, J.F. Silva, T. Nyokong, F. Bedioui, Metallophthalocyanine-based molecular materials as catalysts for electrochemical reactions, Coord. Chem. Rev. 254 (2010) 2755–2791. doi:10.1016/j.ccr.2010.05.001.
[2] J.H. Zagal, F. Bedioui, J.P. Dodelet, N4-Macrocyclic Metal Complexes, Springer, 2006.

# Friedel-Crafts reactions of electrochemically generated carbenium ions

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Electrochemical methods are useful tools in organic synthesis to access valuable compounds with electric current as the principal “reactant” [1]. A notable example is the electrochemical generation of carbenium ions avoiding the use of acidic conditions. This holds a potential to wider the scope of reactions involving the carbenium ion intermediates.

In this study, we investigated an electrochemical generation of stabilized carbenium ions **4** from alcohols **1** derivatized with stannylmethyl group as an electroauxiliary [2] (Fig. 1). Electrochemical activation of the electroauxiliary generates an oxonium ion **3** which undergoes fragmentation to carbenium ion **4**. The reactive intermediate **4** is attacked by an arene providing the Friedel-Crafts alkylation product **6**.

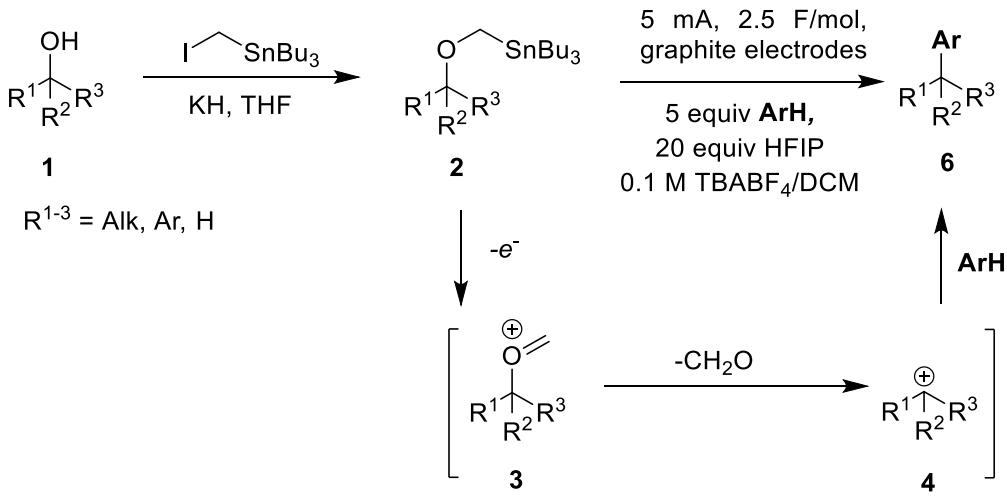


**Figure 1**: Electrochemically induced Friedel-Crafts reaction

The electrolysis of stannylmethylethers **2** has been performed using electron rich aromatic compounds (17 examples, 20-69% yield) as nucleophiles in a single cell under constant current conditions. HFIP was found to be a suitable proton donor for the cathode reaction. $NaHCO_3$ as an additive allows the use of substrates containing acid-labile functional groups, such as Boc, TBDMS, THP, MOM, and even Tr group.

[1] Yoshida, J. *Chem. Rev.* 2008, **108**, 2265.
[2] Yoshida, J.; Ishichi, Y.; Isoe, S. *J. Am. Chem. Soc.* 1992, **114**, 7594-7595.

# Study of the intercalation process and surface optimization of cathode materials for Na-ion batteries

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The inherently low potential of the redox couple $Na^+/Na$, the high abundance and the low cost of sodium make Sodium Ion Batteries (SIBs) a suitable technology for large-scale stationary applications. However, SIBs are still characterized by a low specific energy and power and short cycle life. The cathode materials are key components to address such issues and to foster the SIBs mass-marketing production [1-3].

Among the cathode materials reported to date for SIBs, Li-substituted layered P2-$Na_{1.0}Li_{0.2}Ni_{0.25}Mn_{0.75}O_{\delta}$ (NLMNO) and $Na_2Fe[Fe(CN)_6]$ (NFCN), prussian blue with a cubic framework, are attracting great interest. In the present contribution, the syntheses of NLMNO and NFCN from the respective acetates is described. The cathode materials and the electrodes were characterized and the $Na^+$ deintercalation/intercalation processes analyzed in NLMNO by X-ray diffraction. In order to improve the electrode/electrolyte interface, four different electrolytes were tested, consisting of mixtures of ethylene carbonate (EC), propylene carbonate (PC), 1-fluoroethylenecarbonate (FEC) and dimethylcarbonate (DMC) as solvents and $NaPF_6$ as sodium salt. The electrochemical impedance spectroscopy data were also reported and discussed to evaluate the electrode/electrolyte interface properties of the electrodes after a thin poly-o-aminophenol polymer film was electro-deposited on the cathode surface.

Acknowledgments
Research funded by Ministry of Economic Development – ENEA for the Project Energy storage for electrical systems – PAR 2018.

References

[1] K. Chayambuka, G. Mulder, D. L. Danilov, P. H. L. Notten, *Adv. Energy Mater.* 2018, **8** 1800079.
[2] A. Eftekhari, D.-W. Kim, *J. Power Sources* 2018, **395**, 336–348.
[3] L. Wang, Y. Lu, J. Liu, M. Xu, J. Cheng, D. Zhang, J. B. Goodenough, *Angew. Chem. Int. Ed.* 2013, **52**, 1964 –1967.

# Finite elements models of galvanic cells to even the metal deposition on a cathodic bidimensional array of jewel rings

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A Finite Elements model has been developed, in order to optimize the performances of an electrodeposition process of a precious metal layer on jewels placed into an electrolytic solution. In particular, given a series of identical cathodic elements distributed into an electrolytic cell, the aim is to fix the optimal geometric distribution of the same elements, in order to reduce the odds of total current that flows on the different elements. Given the macroscopic scale of the problem, the density current is calculated in stationary conditions, according to a first species model: a linear relation between current and applied tension is assumed, and overpotential effects due to electrodic cynetics and mass transport are neglected.

A cell system of simple geometry is considered, corresponding to a parallelepiped with a square base. Anodic surfaces are located on the two in front square faces. The cathodes are constituted by a bidimensional square array of rings, each one exemplified by a structure of thoroidal geometry. Different arrays of cathodic elements are considered, with the number of rings in the array that changes from 3x3 to 9x9. Optimization protocols are performed, modulating the distance between the rings in the array according to the Nelder-Mead method [1], in order to minimize the odds of current on the rings. Moreover, on each face a double anode model is designed: the first anode corresponds to an internal square, centered in the face center, while the remaining surface of the face corresponds to the second anode. This allows to apply a tension between the internal and external anode, in order to even the current distribution on the cathodic elements. Hence, the suitability of adopting the inter-anodic tension, as a second adjustable parameter to optimize the uniformity of deposition of metal layer on the cathodes, is evaluated.

In general, for a given cathodic array, various configurations of ring-to-ring distance and inter-anodic tension have been observed to even the distribution of the deposition process. Nevertheless, less-large arrays present a more dispersed distribution of minima; indeed, the higher potential of the internal anode reduces the ring-to-ring distance and evens the metal deposition on the rings. This effect declines for more numerous arrays, for which the low ring-to-ring distance cannot be further reduced, and the minima are located at low inter-anodic tensions. This research was funded by Regione Toscana POR CreO FESR 2014-2020—azione 1.1.5 sub-azione a1 Bando 2 “Progetti di ricerca e sviluppo delle MPMI,” which made possible the project “Gioielli in ArgentoDa Galvanica Ecologica e Tecnologica” (GADGET) and “Tecnologia al plasma per l’industria del lusso: una manifattura innovativa nel comparto accessori in ottica 4.0” (THIN FASHION).

[1] J.A. Nelder and R. Mead, *Computer Journal*, 1965, **7(4)**, 308–313.

# Design of nitrogen containing mesoporous carbon materials for $CO_2$ up-take and sustainable electrochemistry

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The increase of global $CO_2$ concentration, mainly due to anthropogenic emissions from combustion of fossil fuels, is responsible for severe environmental issues, in particular global warming. Limitation in the use of polluting energy sources and development of strategies to reduce $CO_2$ emissions are therefore strictly urgent [1].

Activated carbons can be employed for several applications: separation processes (e.g., biogas purification to biomethane) or as catalyst supports (e.g., bio-oil hydrotreating) as well as electrode/electrolyte components in electrochemical energy storage/conversion devices [2]. Among these, nitrogen-containing ordered mesoporous carbons (OMC) are proposed for $CO_2$ up-take. At present, amine-based technologies are the most promising for $CO_2$ capture, thanks to the possibility to realize a reversible adsorption [1].

OMCs can be synthesized with different pore architectures as nano-replications of a silica hard template, using a three-step procedure: i) infiltration of the sucrose inside the pore channels of the silica materials (see Fig. 1a), ii) pyrolysis and iii) template removal. For example, this approach has been used to prepare the well-known CMK-type materials, CMK-1, CMK-3 and CMK-6, which have been made using MCM-48, SBA-15 and SBA-16 silica templates, respectively. In this work, it is proposed to synthesize nitrogen-containing ordered mesoporous carbon (NOMC) materials for $CO_2$ up-take and sustainable electrochemical applications. NOMC materials can be obtained by the same approach for OCMs but using nitrogen-containing carbon precursors (e.g., chitosan and polyethylenimine - PEI) instead of sucrose. The as-prepared NOMC materials can be applied for $CO_2$ adsorption or can be decorated (see Fig. 1b) with specifically selected nanosized metal oxides (e.g., $TiO_2$, CuO, $FeO_x$, or mixtures thereof) in order to extend their application in energy storage and conversion devices (lithium or sodium based batteries for instance), photocatalysis or electrocatalytic reduction of $CO_2$.

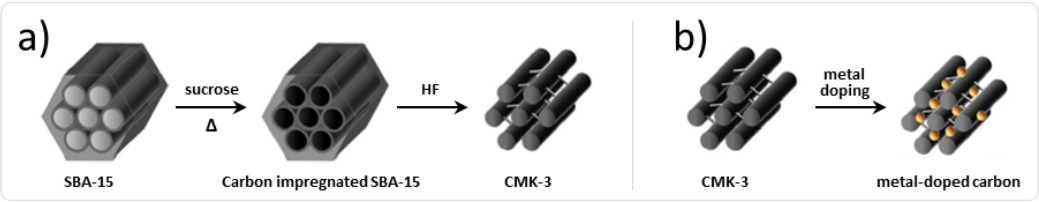


**Figure 1**: (a) Synthesis of CMK-3 from SBA-15 template infiltration with sucrose; (b) decoration of CMK-3 with metal oxide particles. Adapted from [3].

[1] B. Dutcher, M. Fan, and A. G. Russel, *Appl. Mater. Interf.,* 2015, **7**, 2137-2148.
[2] M. A. Tadda, A. Ahsan, A. Shitu, M. ElSergany, T. Arunkumar, B. Jose, M. A. Razzaque, and N. N. N. Daud, *J. Adv. Civil Eng. Pract. Res.*, 2016, **2**, 7-13.
[3] D. Nettelroth, H. C. Schwarz, N. Burblies, N. Guschanski, and P. Behrens, *Phys. Status Solidi A*, 2016, **213**, 1395-1402.

# Exploiting plasma electrolytic oxidation to synthesize $TiO_2$ films with enhanced photoelectrocatalytic activity

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Despite several alternative materials have been described in literature, titanium dioxide-based films and powders are still considered the most practical photocatalytic materials for applications in self-cleaning of surfaces, light-assisted hydrogen generation and environmental remediation [1].

Photoactive $TiO_2$ films can be obtained by a wide range of techniques, including wet chemical methods, vacuum deposition technologies, and electrochemical oxidation. In recent years, Plasma Electrolytic Oxidation (PEO) has attracted attention, due to the high crystallinity, excellent interfacial bonding and electrical contact of $TiO_2$ films with titanium substrate [2,3].

PEO already found industrial applications mainly to produce oxide coatings on Aluminum and Magnesium alloys for corrosion protection applications.

This work aims at demonstrating that PEO is also a promising technique to synthesize $TiO_2$ films having excellent photoelectrocatalytic activity, showing that the crystallographic and photoelectrocatalytic properties of the films can be finely tuned by controlling the PEO processing parameters.

Additionally, this work describes how PEO can be exploited to obtain doped $TiO_2$ films having good photoelectrocatalytic activity in the VIS region.

PEO was carried out in DC mode in 0.5-1.5 M $H_2SO_4$ solutions at voltages in the range 100÷180 V. Processing times ranged from 0.5 to 15 min. Doping of the $TiO_2$ films was obtained either by addition of dopant-containing salts in the electrolyte and/or by anodizing Ti alloys of suitable composition. The effect of processing parameters, mainly PEO cell voltage, processing time, electrolyte temperature and composition on surface morphology, crystallographic structure, Incident Photon-to-Current Efficiency (IPCE) and electrochemical surface area (ECSA) of $TiO_2$ catalysts were investigated [4]. SEM micrographs show that the oxide layers are porous and homogenous, with an increasingly pronounced sponge-like morphology when anodization voltage is increased. Depending on the processing conditions, either pure anatase, a mixture of anatase and rutile, or pure rutile were obtained in a single-step anodization of 1-5 minutes. No pre- and post-annealing treatments were required. The maximum IPCE of $TiO_2$ films was 93% at 310 nm and 65% at 380 nm under applied voltage of 0.6 V vs. SCE.

The photoelectrocatalytic activity of the $TiO_2$-based films was assessed by measuring the separate hydrogen and oxygen production and by studying the decolourization of textile dyes solutions under simulated solar light and electrical polarization.

***References***

[1] S. Franz, D. Perego, O. Marchese, M. Bestetti, *J. Water Chem. Technol*. 37 (2015) 108-115.
[2] M. Bestetti, M. Cuzzolin, S. Franz, P. Arosio, P. L. Cavallotti, *Thin Solid Films* 515 (2007) 5253-5258.
[3] S. Franz, D. Perego, O. Marchese, A. Lucotti, M. Bestetti, *Appl. Surf. Sci.* 385 (2016) 498-505.
[4] G. L. Chiarello, A. Zuliani, D. Ceresoli, R. Martinazzo, E. Selli, *ACS Catal.* 6 (2016) 1345−1353.

# 3D Electrocatalysts for the reduction of biomass-derived compounds

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The electrocatalytic reduction of biomass-derived compounds is a promising way for the sustainable production of fuels and chemicals, operating at milder reaction conditions than those required in conventional thermo-catalytic processes, i.e. room temperature and avoiding high $H_2$ pressures. The electrochemical conversion of 5-hydroxymethylfurfural (HMF), a biomass derived platform molecule, is an important route to obtain value-added products, such as 2,5-bis-(hydroxymethyl)furan (BHMF), a monomer for the manufacture of polyurethane foams or polyesters. In an alkaline media and with a 2D electrocatalyst made by Ag particles on a Cu support, prepared by galvanic displacement, Roylance et al. have achieved the selective reduction of a 0.02 M HMF solution with 100% Faradic Efficiency (FE) [1].

In this work we proposed the use of 3D electrocatalysts, obtained by electrodeposition of Ag particles on Cu open-cell foams, to replace conventional 2D electrodes in the electrochemical reduction of HMF at higher concentrations, closer to industrial ones. The resulting catalysts merge the high performance of Ag particles homogeneously coated on the surface (Fig. 1) with the large geometrical surface area, enhanced mass and electron transfer and high mechanical stability of Cu open-cell foams.

Electrochemical measurements were performed in a three-compartment cell with 25 ml of HMF 0.05M in borate buffer as electrolyte, by applying a constant potential (-1.3V vs SCE) or current (from 5 to 50 mA/cm$^2$).

The catalytic tests at -1.3V vs SCE were conducted collecting different amount of charge to follow the progress of the reaction. BHMF selectivity and FE increased with the HMF conversion, reaching values of ca. 89% at full HMF conversion, higher than those reported in literature for 2D catalysts at high HMF concentrations [1]. While, varying the current from 5 to 50 mA/cm$^2$ the conversion decreased from 99% to 80% and selectivity increased from 70 to 85% with FE of around 70-75%.

The formation of side-products was investigated to understand the reaction mechanism.

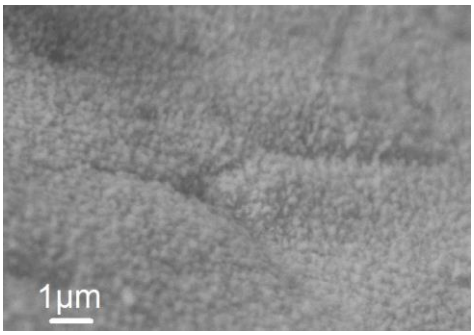


**Figure 1**: SEM image of a Cu foam coated by Ag

[1] J. J. Roylance, T. W. Kim, K.-S. Choi, *ACS Catal.*, 2016, **6**, 1840−1847.

# Effect of N- and S-doping and texture properties of carbon support on Fe-N-C catalysts performances for ORR

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Iron-nitrogen-doped carbon materials (Fe-N-C) have emerged as the most promising non-precious alternative to Pt/C catalysts for the electrochemical reduction of oxygen (ORR).Two kinds of active sites, Fe-$N_x$ and N-functional groups, are supposed to be responsible for the ORR activity [1]. Specific surface area and microporous structure, which determine the accessibility of active sites and the transport of reagents and products, play important roles in enhancing the catalyst activity and stability [2]. Furthermore, doping Fe-N-C with other heteroatoms, especially sulfur, has been discovered to show great potential in boosting ORR activity [3]. In fact, sulfur seems beneficial for anchoring Fe and N species thanks to its large size, electronegativity and polarizability [3].

In this work different carbon materials (commercial and homemade), presenting different N- and S-doping and porous structure, were tested as a support for Fe-N-C catalysts. The aim is to determine what physical and chemical properties of the carbon support allow an effective coordination of Fe atoms, increasing the Fe-$N_x$ active site density. A precise XPS evaluation of the Fe-$N_x$, nitrogen and sulfur functional groups was accomplished and correlated to the catalytic performances. RDE technique (Fig 1) showed that the best catalyst in terms of $E_{onset}$ is obtained from a support containing the highest amount of sulfur 0.65 %. Moreover, the ratio between the mesoporous and the total pore volume can be correlated to the catalytic activity and the limiting current density.

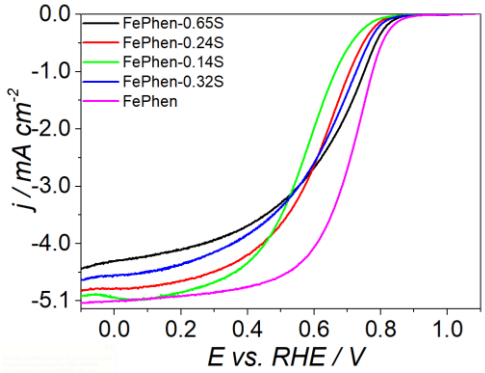


Fig 1: LSV at RDE in $O_2$-saturated 0.5 M $H_2SO_4$ of catalysts recorded at $v$ = 2 mV $s^{-1}$ and ω = 1600 rpm.

**Acknowledgments**
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[1] R. Ma, Y. Zhou, C. Hu, M. Yang, F. Wang, K. Yan, Q. Liu, J. Wang, Energy Storage Mater., 2018, **13,** 142–150.
[2] J. Shi, X. Zhou, P. Xu, J. Qiao, Z. Chen, Y. Liu, Electrochim. Acta., 2014, **145,** 259–269.
[3] M. Guo, L. Wang, Y. Gao, G. Li, Int. J. Hydrogen Energy., 2019, **44**, 3625–3635.

# Water-mediated electro-hydrogenation of $CO_2$ at near-equilibrium potential by undoped nanocarbon@$CeO_2$

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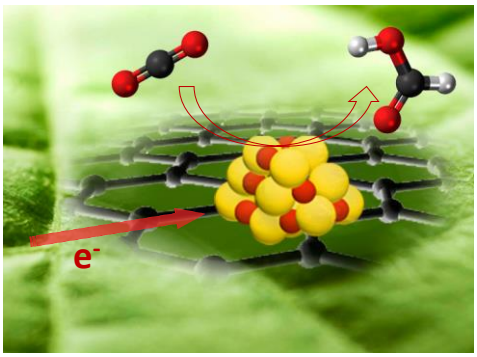
$CO_2$ concentration in the atmosphere increased from 320 ppm in the early 60's, to more than 400 ppm in 2014, with an exponential trend never observed before. It is thus not surprisingly that recently a lot of efforts were focused in the research and improvement of new/existing materials, catalysts, methods, and technologies, able to capture and to convert CO2 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.

Here 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 nanomaterials (such as carbon nanotubes and carbon nanohorns) 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 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] In the nanocomposite, where the nanomaterials are covered by nanoparticles of $CeO_2$, 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. [3]

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.




[1] N. Armaroli, V. Balzani, *Angew. Chem. Int. Ed.* 2007, **46**, 52-66.
[2] T. Montini, M. Melchionna, M. Monai, P. Fornasiero, *Chem. Rev.* 2016, **116**, 5987–6041 [3] G. Valenti, A. Boni, M. Melchionna, M. Cargnello, L. Nasi, G. Bertoni, R. J. Gorte, M. Marcaccio, S. Rapino, M. Bonchio, et al., *Nat. Commun*. 2016, **7**, 13549.

# ZnO nanoestructures anodized under hydrodynamic conditions for hydrogen production

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The increase in energy consumption and high $CO_2$ emissions lead to the development of sustainable and clean methods to energy production using renewable sources such as solar light. Zinc oxide is a promising semiconductor material with numerous applications in photocatalysis due to its abundance, non-toxicity, versatility and unique photoelectrical properties.

In this work, ZnO nanostructures were obtained by Zn anodization applying 10 V for 10 minutes in 50 mM $NaHCO_3$ aqueous electrolyte stirring the electrode at 3000 rpm by using a Rotating Disk Electrode (RDE). A posterior annealing at 300ºC for 1 hour was also carried out. Water splitting was performed by measuring photocurrent density transients of the ZnO nanostructures in two different media: 0.24 M $Na_2S$ + 0.35 M $Na_2SO_3$ aqueous solution and 0.1 M NaOH aqueous solution under simulated AM 1.5 illumination as a function of applied potential.

According to the first results, Fig.1) shows that the ZnO nanostructures might be interesting in order to be used as a photocatalyst for photoelectrochemical water splitting, especially, working in $Na_2S/Na_2SO_3$ electrolyte in the potential range of 0.2-0.8 $V_{Ag/AgCl}$, where samples were stable and a good photoelectrochemical response is obtained.

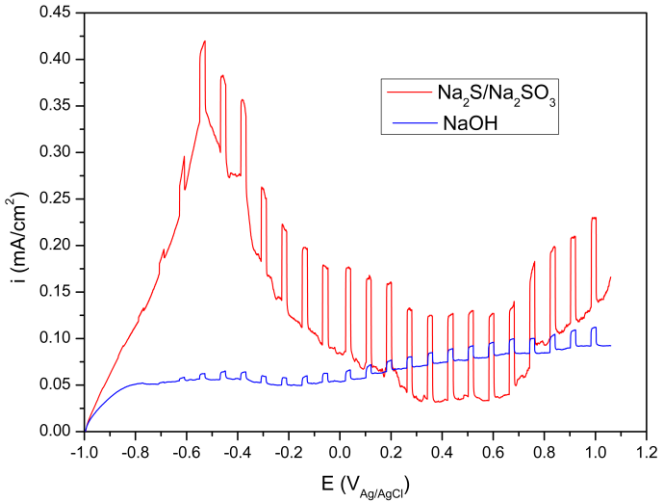


**Figure 1**: Photocurrent density vs potential plot of the anodized ZnO nanostructures measured in a 0.24 M $Na_2S$ + 0.35 M $Na_2SO_3$ solution and 0.1 M NaOH solution under simulated AM 1.5 illumination.

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# $WO_3$ nanostructures optimization for the photoelectrocatalytic mineralization of organic pollutants

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The use of tungsten oxide as a photoanode in photoelectrochemical processes, is increasing due to its excellent properties. These include its high stability in aqueous solutions and its ideal band-gap energy (<3 eV) [1]. However, tungsten oxide is still been studied and optimized under illumination conditions. In this study, $WO_3$ nanostructures have been synthesized using the technique known as electrochemical anodization. This technique is widely used in nanostructures production, since they are obtained in an orderly and closely interconnected manner with each other and with the metallic substrate. In addition, the nanostructures characteristics can be easily controlled with this technique.

In this work, nanostructures with different surface morphologies, thicknesses and photoelectrochemical properties have been obtained by varying process conditions such as the voltage used in the anodization (varying between 10V and 40V) and the heating conditions in a postanodization phase (varying the temperature and the heating atmosphere).

These nanostructures have been characterized by different techniques to analyze their morphology and their photoelectrochemical properties. Raman spectroscopy technique has been used to verify the composition and crystallinity of the nanostructures whereas field emission scanning electron microscopy (FE-SEM) has been used to analyze its morphology. Finally, impedance measurements have been used to study the electrochemical and photoelectrochemical properties. In the last part of this study, these nanostructures have been applied for pesticides degradation, such as organophosphorus pesticides due to their recalcitrant nature and high acute toxicity, by the technique known as photoelectrocatalysis using visible light. This combines electrolytic and photocatalytic processes and has received considerable attention due to the ability to delay the recombination of electron-holes pairs, increasing the useful life of the holes [2]. UV-Vis spectroscopy has been used to observe the pesticide degradation evolution and high performance liquid chromatography with mass spectrometry (HPLC-MS) has also been used to follow the degree of pollutants degradation, as well as the mechanism of formation and subsequent destruction of the intermediate products.

[1] Ruiling Wang, Tian Xie, Tong Zhang, Taofei Pu, Yuyu Bu and Jin-Ping Ao, J. Mater. Chem. A, 2018, **6**, 12956–12961.
[2] Sergi Garcia-Segura and Enric Brillas, Journal of photochemistry and photobiology, 2017, **31**, 1–35.

**Acknowledgements.** Authors thank for the financial support to the Ministerio de Economía y Competitividad (Project Code: CTQ2016-79203-R) and for the co-finance by the European Social Fund. Ramón M. Fernández Domene also thanks the UPV for the concession of a post-doctoral grant (PAID-10-17) and Gemma Roselló Márquez also thanks the Generalitat Valenciana for the concession of a pre-doctoral grant (ACIF/2018/159).

# Emerging strategies towards ambient condition fabrication of perovskite solar cells

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The power conversion efficiency of perovskite solar cells (PSCs) has remarkably increased, in just a few years, from 3.8 to 22.7%, due to the excellent properties of organometal-halide perovskite, such as strong and broad optical absorption from visible to near infrared, high electron and hole diffusion length and a low surface recombination velocity [1]. Nevertheless, PSCs are susceptible to oxygen and water, because of a degradation pathway leading to the formation of lead iodide, methylammonium and hydrogen iodide. For this reason, perovskite materials require high temperature and glove-box synthetic conditions, thus hindering large-scale applications.

During last year, a few efforts have been made in the development of ambient condition fabrication strategies, such as thermal engineering [2] and the use of anti-solvents [3]. In the first case, the substrate $TiO_2$ is pre-heated at low temperature before spin-coating deposition of perovskite precursors. This ensures phase purity and a pinhole-free morphology, with a PCE reaching 12%. In the second case, the use of anti-solvents reduces the solubility of perovskite precursors, thereby promoting fast nucleation and rapid crystallization. In this way, the effect of air-moisture is less relevant.

In conclusion, the fabrication of PSCs in open air atmospheric conditions is challenging, but necessary for photovoltaic application of perovskite materials.

[1] E. Calabrò, F. Matteocci, A. L. Palma, L. Vesce, B. Taheri, L. Carlini, I. Pis, S. Nappini, J. Dagar, C. Battocchio, T. M. Brown, and A. Di Carlo, *Sol. Energy Mater. Sol. Cells*, 2018, **185**, 136-144.
[2] S. A. Moyez and S. Roy, *Sol. Energy Mater. Sol. Cells*, 2018, **185**, 145-152.
[3] A. A. Nurunnzar, R. Hydayat, *J. Phys. Conf. Ser.*, 2018, **1057**, art. no. 012007.

# Electrochemical strategy coupled with spectroscopic techniques for trace lead analysis in olive oil/RTIL mixtures

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Trace heavy metals dangerous to human health can be present in olive oil because of contamination from soil and fertilizers, production or storage procedures, or exposition of the olive plants to vehicular and industrial emissions [1]. The detection of metal ions in such highly viscous organic matrix by using conventional analytical methods is rather challenging, since it requires the application of series of strong and time-consuming pretreatment steps which can be a source of contamination of the sample, possibly reflecting in scarce accuracy and precision.

With the goal of developing a fast and reliable method specifically suitable to monitor trace levels of heavy metals directly in edible oils, in this work we investigated and optimized a strategy which combines electrochemical preconcentration with spectroscopic detection, focusing on the determination of lead in olive oil as a case study. To this aim, we explored the use of a platinum spiral electrode and the adoption of an electrochemical deposition of the metal followed by a reoxidation procedure, after transfer of the electrode to a "clean" aqueous solution, suitable for ICP-MS or GF-AAS analysis. In order to perform electrochemical experiments in such complex and low-conductive food matrix, the room temperature ionic liquid (RTIL) $[P_{14,6,6,6}]^+[NTf_2]^-$, which is soluble in vegetable oils, was used as supporting electrolyte [2].

The detailed procedure proposed here includes the following steps: mixing of the oil sample with the RTIL; potentiostatic electrochemical deposition of the analyte onto a Pt coil directly from the tested real sample; potentiostatic anodic re-oxidation of the metal deposit after transfer to acid aqueous solution; ICP-MS or GF-AAS analysis of the acid solution collected. The feasibility and performance of this analytical protocol were tested both in standard solutions of $Pb^{(II)}$ in RTIL, which were produced by galvanostatic anodic dissolution of high-purity Pb in the RTIL according to the electrochemical procedure recently proposed in our previous paper [3] and in olive oil/ 0.5M RTIL mixtures spiked with Pb.

The optimization of the electrochemical deposition and re-oxidation parameters was achieved by applying an advanced D-Experimental Design model, properly set up to get optimal conditions in terms of efficiency of deposition/re-oxidation steps, quantitative recovery and measurement time. In particular, the experimental model and data matrix were built by considering four factors and twenty-six experiments, respectively.

[1] L. La Pera, S. Lo Curto, A. Visco, L. La Torre and G. Dugo, *J. Agricolt. Food Chem.,* 2002, **50**, 3090-3093.
[2] M.A. Baldo**,** P. Oliveri, R. Simonetti and S. Daniele, *J. Electroanal. Chem.,*2014, **731**, 43-48.
[3] M.A. Baldo, A.M. Stortini, L.M. Moretto, M. Ongaro, M. Roman and P. Ugo, *Talanta*, **2017**, 172, 133-138.

# Influence of process parameters of simultaneous anodization/anaphoretic electrodeposition synthesis of hydroxyapatite/titanium oxide composite coatings on adhesion

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*In-situ* synthesis of hydroxyapatite/titanium oxide ($HAp/TiO_2$) coating on titanium was performed via anaphoretic deposition of hydroxyapatite (HAp) and simultaneous anodization of Ti to produce highly adherent and strengthened composite coating. The influence of electric potential, time, electrolyte concentration and pH value of the anodization process on titanium surface roughness and anodization of titanium was examined, as well as influence of same process parameters on adhesion strength and compactness of composite $HAp/TiO_2$ coatings was investigated. Prior to novel *in situ* method of synthesis of hydroxyapatite/titanium oxide composite coatings by simultaneous anodization/anaphoretic electrodeposition described in this manuscript, optimization of anodization process of titanium was performed. Anodization was executed under different electric potentials and different distances of counter electrodes from working electrodes, but all anodization processes had constant quantity of electric charge. Characterization of titanium samples, prepared from grade 6 Ti, and having rectangular contact surfaces of 10×10×0.89 mm included SEM/EDS analyses, X-ray diffraction analyses, AFM surface topography, morphology and roughness analyses and linear measurements of roughness.

A chemical precipitation method was used to prepare hydroxyapatite powder by the reaction of calcium oxide (obtained by calcination of $CaCO_3$ for 5 h at 1000 °C in air) and phosphoric acid. A stoichiometric amount of the calcium oxide was stirred in distilled water and phosphoric acid was added drop wise to the suspension in order to obtain hydroxyapatite powder, $Ca_{10}(PO_4)_6(OH)_2$.

Two types of HAp coatings were prepared, in order to compare the adhesion, morphology and consistency of the HAp and composite $HAp/TiO_2$ on Ti, namely cathaphoretic and anaphoretic coatings, respectively [1,2]. The prepared coatings were characterized by field emission scanning electron microscopy, X-ray diffraction and electron dispersive spectroscopy. Adhesion was investigated by *ASTM D 3359 – 97 Test method B*. Uniform and adherent $HAp/TiO_2$ composite coating on Ti was obtained. Since smaller size of HAp crystals within highly porous coating structures is of improved binding ability to various biomolecules, our coating is expected to be of excellent coverage and compactness. The obtained coating can be good candidate for bone implants due to improved adhesion.

[1] S. Eraković, A. Janković, I.Z. Matić, Z.D. Juranić, M. Vukašinović-Sekulić, T. Stevanović and V. Mišković-Stanković, *Mater. Chem. Phys.*, 2013, **142**, 521–530.
[2] M.R. Pantović Pavlović, S.G. Eraković, M.M. Pavlović, J.S. Stevanović, V. V Panić and N.L. Ignjatović, *Surf. Coatings Technol.*, 2019, **358**, 688–694.

# Versatile decoration of carbon composites with metal nanoparticles for electrocatalytic application

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The synthesis of novel catalysts is crucial for achieving a shift from fossil-based energy vectors to renewable alternatives, such as hydrogen technology [1]. Generally, price, stability and activity are major issues for existing catalysts, which hamper widespread mass market application.

Metal oxide nanoparticles/graphene composites have been shown to exhibit high catalytic activity due to the synergy between particles and carbon framework [2]. Synthesis of those composites mainly relies on reduction of metal salts by graphene oxide or surfactant stabilized few-layer graphene through wet chemical approaches. However, specific reaction conditions need to be carefully adjusted for each type of nanoparticle. Furthermore, synthetic protocols yielding specific size distribution of nanoparticles are rare.

Here we present a novel approach for combining graphene flakes and metal oxide nanoparticles [3]. The reduced carbon layers were exploited as reduction agents for different metal salts, resulting in decoration of nanoparticles on carbon framework, such as Rh(nP)/nC, Pt(nP)/nC and Fe(nP)/nC. In addition, different carbon starting materials determined not only the size of carbon flakes but also tailored the size of nanoparticles (Fig. 1). This is a novel concept to alter particle size distribution. These composite materials, free of stabilization or capping agents, showed remarkable electrocatalytic activity in the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER).

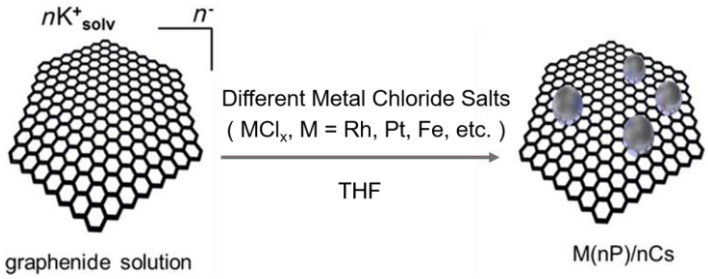


**Figure 1**: Reaction scheme for the synthesis of M(nP)/nCs.

[1] G. Valenti, A. Boni, M. Melchionna, M. Cargnello, L. Nasi, G. Bertoni, R. J. Gorte, M. Marcaccio, S. Rapino, M. Bonchio, P. Fornasiero, M. Prato and F. Paolucci, *Nat. Commun.* 2016, **7**, 13549.
[2] D. Voiry, H. S. Shin, K. P. Loh and M. Chhowalla, *Nat. Rev. Chem.* 2018, **2**, 105.
[3] F. Hof, A. Boni, G. Valenti, K. Huang, F. Paolucci and A. Penicaud, *Chem. Eur. J.* 2017, **23**, 15283-15288.

# Synthesis and electrochemical performance of multicomponent oxide materials toward oxygen reduction reaction

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Low cost and highly active electrocatalysts for the oxygen reduction reaction (ORR) are necessary for the development of fuel cells and metal air batteries. Currently, Pt based electrodes have the best catalytic performance but due to its high cost its employment on a significant scale is limited [1]. Perovskite materials would be a good alternative because of its abundant supply, environmental benignity, electronic structure, ionic conductivity and redox behavior [2]. Therefore, the aim of this work is synthesis and characterization of Lanthanum cobalt oxide ($LaCoO_3$) powders doped with Manganese (Mn) - LMCO or Strontium (Sr)- LSCO, as promising candidates for energy storage and conversion devices. Ultrasonic spray pyrolysis (USP) was used to successfully synthesize spherical sub-µm-sized of $La_{0.6}Sr_{0.4}CoO_3$ and $La_{0.6}Mn_{0.4}CoO_3$ perovskite type materials. Detailed microscopic analysis (SEM-EDX, TEM, XRD) as well as electrochemical characterization by CV, LSV and EIS technique has been conducted.

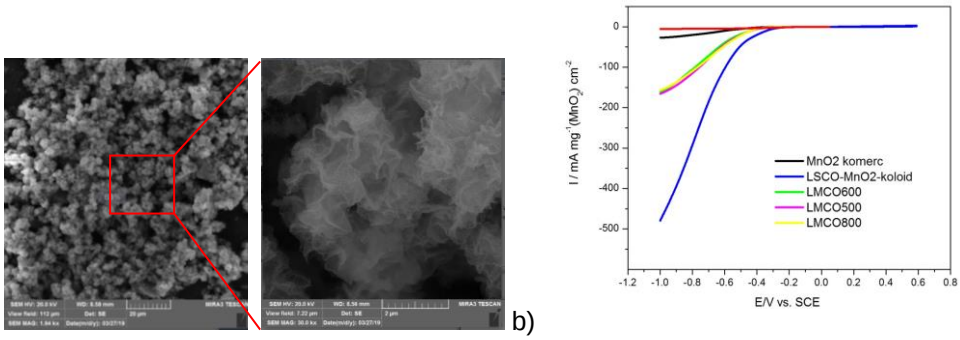


**Figure 1**: a) SEM images of LMCO prepared materials at 600° b) LSV performance and comparison of LMCO, LSCO and $MnO_2$ electrodes for oxygen reduction

The investigation of different perovskite-based electrodes showed excellent catalytic activity toward oxygen reduction in alkaline medium. Our work indicates that synthesized perovskite materials especially doped with Mn show potential application in the field of catalysis and are worthy of further investigation.

[1] I Roche et al. *J. Phys. Chem. C.*, 2007, **111**, 1434–1443.
[2] H. Zhu, P. Zhang, S. Dai, *ACS Catal.*, 2015, **5**, 6370–6385.

# Electrochemical impedance spectroscopy techniques for quality control on electroplated metals

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Corrosion testing is a very important step in quality control for metal industrial processes. Especially for electroplated goods, corrosion resistance is a primary indicator of surface quality. Electrochemical Impedance Spectroscopy (EIS) is a versatile procedure for the accelerated evaluation of the anti-corrosion performance of coatings: unlike other standard procedures is generally a non destructive method. EIS works applying an electrical sinusoidal perturbation (AC current) of fixed frequency and measuring electrical impedance Z of the sample (opposition that a circuit presents to a current when the sinusoidal wave is applied): measures are repeated at different frequencies and data are stored and properly plotted. In circuity theory impedance Z is a complex number that accounts for resistive and reactive components of the circuit. Measuring impedance at different frequencies and analyzing the data we can postulate the structure of an equivalent circuit and extract corrosion resistance data. One of the objectives is to develop several methods (combining EIS and other electrochemical techniques) to determine corrosion resistance for electroplated goods that can give results as reliable as other more diffuse and traditional destructive corrosiong testing techinques with a non destructive process and in a fair less amount of time.

# $^{17}$O NMR and electrochemical characterization of super-concentrated solutions

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The combination of electrochemical techniques with bulk and advanced spectroscopic ones is a powerful tool to investigate the processes occurring in the novel electrochemical energy storage systems based on lithium metal anode. NMR exploits the magnetic properties of atoms nuclei to find out information on the chemical environment in molecules and solids, as well as on its changes over time. The combination of $^{7}$Li and $^{17}$O (at natural abundance) nuclear magnetic resonance (NMR) [1] and electrochemical characterization is here proposed as an effective approach to investigate the $Li^+$ solvation structures and properties of electrolytes featuring tetraethylene glycol dimethyl ether and lithium-bis(trifluoromethane sulfonyl) imide. The NMR results, also supported by physico-chemical characterizations such as thermal gravimetric analyses, differential scanning calorimetry, specific conductivity and viscosity, provide information about the association of $Li^+$ ions with anion and solvent molecules, so allowing a deeper knowledge on the relationships among structure and functional properties of super-concentrated solutions. The increase of the electrolyte concentration is, indeed, a multi-effective strategy to improve the performance of high energy batteries featuring Li metal anode [2, 3].

**Acknowledgments**
The authors thank for financial support MIUR-DAAD Joint Mobility Program "Interface properties of electrode materials".

[1] J. Peng, L. Carbone, M. Gobet, J. Hassoun, M. Devanye, and S. Greenbaum, *Electrochim. Acta* 2016, **213**, 606–612.
[2] L. Suo, Y.-S. Hu, H. Li, M. Armand, and L. Chen, *Nat. Commun.* 2013, **4**, 1481
[3] F. Messaggi, I. Ruggeri, D. Genovese, N. Zaccheroni, C. Arbizzani, and F. Soavi, *Electrochim. Acta* 2017, **245**, 296–302.

# Mesoporous carbon characterized by different carbon structures and modulable density of thiophenic groups: effect on platinum NPs activity for oxygen reduction

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Several strategies are oriented to improve the Pt catalyst performance for Oxygen Reduction Reaction (ORR), so that to reduce its loading. One way is to trigger an interaction between the Pt metal NPs and the support, which can, generally, affect the catalytic activity by influencing the NP morphology and dimension, inducing strain on the NP due to lattice mismatch and changing the electronic structure via charge transfer processes.

Sulphur doped mesoporous carbons (SMC) showed to exert a great metal-support interaction on Pt NPs [1]. In this contribution, SMC with different amounts of S (1 $\%_w$ to 14 $\%_w$), were synthetized by pyrolysis, following a hard template method employing mesoporous silica as a template. The graphitization degree and the surface area were tuned by a subsequent steam treatment at high temperature for different exposure time. During the steam treatment, the sulphur content gradually decreased while the surface area increased to 1750 $m^2\ g^{-1}$ (Fig. 1). Pt NPs were allowed to grow over the carbon supports by thermal treatment of $Pt(acac)_2$ under $H_2$ flow. TEM images showed NPs with average dimension of 2.3 nm and a good distribution all over the carbon support.

The catalysts were characterized and tested for ORR in 0.1 M $HClO_4$. Mass activity and $E_{1/2}$ sensitively showed to depend on both sulphur content and specific surface area, though in opposite directions so that the best performance was observed at intermediate values of the two parameters (Fig. 1). The results were rationalized on the basis of a metal-support interaction, mass transport and conduction properties of the synthetized materials.

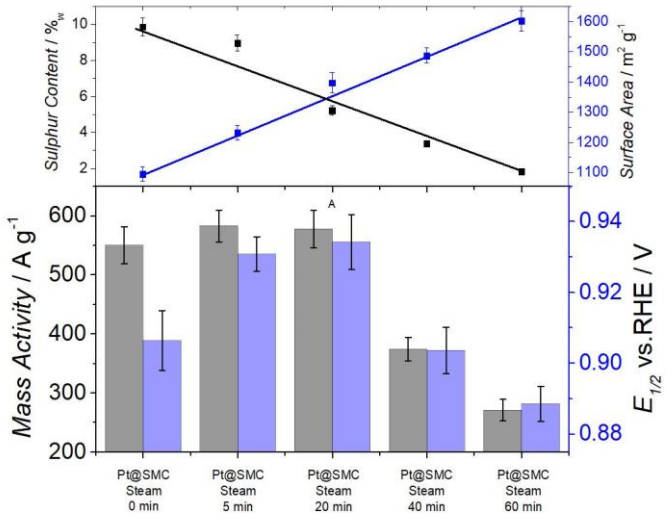


Figure 1: Sulphur content, surface area, mass activity and $E_{1/2}$ variation after steam treatment

[1] V. Perazzolo, R. Brandiele, C. Durante, M. Zerbetto, V. Causin, G. A. Rizzi, I. Cerri, G. Granozzi, A. Gennaro, *ACS Catal.* **2018**, *8*, 1122–1137.
[2] V. Perazzolo, C. Durante, R. Pilot, A. Paduano, J. Zheng, G. A. Rizzi, A. Martucci, G. Granozzi, A. Gennaro, *Carbon* **2015**, *95*, 949–963.

# Study of theophylline anodic oxidation products in organic solvents by µHPLC-PDA-ESI-MS/MS analysis

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Theophylline (1,3-dimethylxanthine, TPh) is widely distributed in nature, and generally assumed in the human diet because widespread in many products highly consumed all over the world, with tea as the major natural source. Metabolite of caffeine and other naturally occurring alkaloids, TPh is also an extensively used drug for the therapy of different respiratory diseases, being moderately toxic to mammals. The relevant biological effects combined with a relatively low toxicity makes TPh, a pharmacological tool with increasing therapeutic potentialities [1]. But if many systemic effects in humans are well known, the mechanism underlying these biological effects is not yet well understood.

Few studies on the chemically induced oxidation of TPh have been reported in literature [2], and also the electrochemical oxidation has been sparingly studied, all studies mainly carried out in water at different pH. A recent study on the oxidative mechanism of caffeine and TPh in aprotic medium by cyclic voltammetry and electrolysis in UV-vis cell [3] has been carried out by our group and a reaction pattern following the primary mono-electronic anodic oxidation has been proposed.

In the present work a preliminary study on the anodic oxidation of TPh in different organic solvents was carried out by cyclic voltammetry and controlled potential electrolysis and the electrolyzed solutions were analyzed by UV-vis spectrophotometry and mass spectrometry after chromatographic separation by a µHPLC-PDA-ESI-MS/MS system. As a useful comparison, the same study was carried out in water.

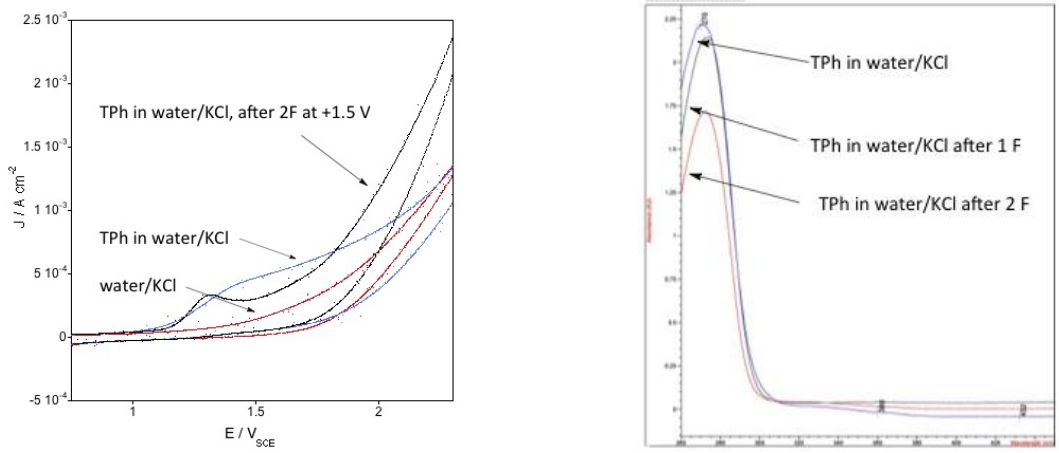


**Figure 1**. Left: CV of TPh in $H_2O$/KCl at GC electrode (vs SCE); scan rate 0.2 V $s^{-1}$. Right: UV-vis spectral changes relative to the anodic oxidation of TPh.

[1] J. Monteiro, M.G. Alves, P.F.Oliveira, B.M. Silva, *Crit. Rev. Food Sci. Nutr.,* 2018, **6**, 1–29
[2] M.M. Sunil Paul, U.K. Aravinad, G. Pramod, A. Saha, C.T. Aravindakumar, *Org.Biomol. Chem.,* 2014, **12**, 5611-5620
[3] R. Petrucci, G. Zollo, A. Curulli, G. Marrosu, *BBA-General Subjects,* 2018, **1862**, 1781-1789

# Investigation on the cathode capacity gain in high voltage spinel structures

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As energy storage materials, Lithiuim-Ion Batteries (LIBs) represent the future of electric vehicles locomotion due to the high volumetric and gravimetric energy density of the cells. Research in this field is focused on the enhancement of the electrochemical performances and on the extended cycle life of LIBs coupled with low cost and environmental friendliness of the employed materials and production processes.

Innovative LIBs cathode materials are designed to achieve raised capacity and high working voltage of the cell to increase supplied power of the device. One of the most promosing cathode active materials is the Ni-substituted spinel $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO), featuring a theoretical capacity of around 147 mAh $g^{-1}$ and a working voltage of 4.7 V, corresponding to the redox couple Ni $4^+/2^+$. The usual working range of cathode half cell is between 5 and 3.5 V vs $Li^+/Li$, exploiting Nickel participation and avoiding Mn involvement in the insertion mechanism.

The first aim of this study is the evaluation of the capacity gain due to the action of Mn $4^+/3^+$, at potentials around 3 V vs $Li^+/Li$, when widening the electrochemical working range of the cell down to 2.3 V. To achieve the capacity gain it is necessary to increase the stability of the LNMO structure doping with transition metals, like Fe or Cr. In this work, the Fe(Cr)-doped active material has been obtained with a simple solid-state synthesis [1,2], employing a high energy ball milling for the blending and grinding of reactive precursors; the mixed powder is then annealed in air at high temperature.

Another strategy of this work is the load of extra lithium in the spinel structure to achieve a Li-rich $Li_{1+x}Ni_{0.5}Mn_{1.5}O_4$ active material with a higher content of Mn having a $3^+$ valence state [3]. The enrichment has been obtained in our laboratory with different methods, both electrochemically or from chemical synthesis.

The properties of synthesized materials, in terms of structures and electrochemical performances in both lithium-metal and lithium-ion cells, adopting a graphite anode, will be presented.

[1] M. Agostini, A. Matic, S. Panero, F. Croce, R. Gunnella, P. Reale, and S. Brutti, *Electrochim. Acta*, 2017, **235**, 262-269.
[2] M. Agostini, S. Brutti, M.A. Navarra, S. Panero, P. Reale, A. Matic, B. Scrosati, *Scientific Reports*, 2017, **7**, 1104.
[3] M. Mancini, P. Axmann, G. Gabrielli, M. Kinyanjui, U. Kaiser, and M. Wohlfahrt-Mehrens, *ChemSusChem* 2016, **9**, 1843-1849.

# Electrochemiluminescence meets nanotechnology: nanomaterials for enhance the signals

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Electrochemiluminescence is a luminescence induced by an electrochemical stimulus. 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. In the last decades, ECL became a very promising analytical technique for clinical applications. In order to generate electrochemically the excited state, two different precursors, i.e. luminophore and co-reactant, are required. In the quest for ever-increasing sensitivities, ECL can ideally be coupled to nanotechnology to develop new systems and strategies for analyte determination even in very complex matrices [1]. In this context, two alternatives are investigated in order to increase the ECL efficiency such as dye doped silica nanoparticles and Bodipy Carbon Nanodots (BCNDs) [2].

BCNDs are Carbon Nanodots functionalized with boron-dipyrromethene (Bodipy). BCNDs are investigated as an alternative to $Ru(bpy)_3^{2+}$ luminophores in co-reactant ECL mechanism thanks to their excellent features, like nontoxicity, chemical inertness, high resistance to photobleaching and excellent ECL properties [3]. Results obtained with ECL are also compared to photoluminescence (PL) in order to better understand the behaviour of the excited state obtained with the two techniques. Alternatively, silica nanoparticles synthesized by "inverse microemulsion" represent a very useful tool thanks to the possibility to immobilize biomolecules or enzymes on their silica surface. Nanoparticles are doped with different amount of $Ru(bpy)_3^{2+}$ in order to investigate on the different ECL response. In this communication, we will present two different strategies with the final goal of development of an efficient ECL nanomaterial with higher ECL intensity, different ECL emission and simple bioconjugation.

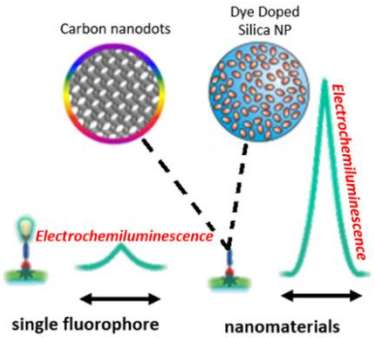


**Figure 1:** Nanomaterials enhance the ECL signal compared to single fluorophore

[1] S. Kesarkar, E. Rampazzo, A. Zanut, F. Palomba, M. Marcaccio, G. Valenti, L. Prodi, F. Paolucci, *Curr. Opin. Electrochem.,* 2018, **7**, 130–137.
[2] G. Valenti, E. Rampazzo, S. Bonacchi, L. Petrizza, M. Marcaccio, M. Montalti, L. Prodi, F. Paolucci, *J. Am. Chem. Soc.*, 2016, **138**, 15935–15942.
[3] S. Carrara, F. Arcudi, M. Prato, L. De Cola, *Angew. Chemie Int. Ed.* 2017, **56**, 4757–4761.

# Syngas production by electrocatalytic reduction of $CO_2$ by using Ag-decorated $TiO_2$ nanotubes

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Carbon dioxide is recognized to be one of the main contributions to global warming and its reuse is currently considered a key challenge to the current society. The $CO_2$ electrochemical (EC) reduction is considered a promising technology for the storage and reutilization of $CO_2$ from both economic and environmental points of view. The competitive $H_2$ evolution side-reaction in all aqueous-electrolyte-based $CO_2$ EC reduction, can be exploited in a competitive approach for the production of syngas with different $CO/H_2$ ratios, a mixture for which there are well-established options for further processing to obtain more reduced products, such as alcohols and hydrocarbons (e.g. via heterogeneous Fischer-Tropsch catalysis) [1]. In this work, $TiO_2$ nanotubes (NTs) were grown by anodic oxidation of Ti foils and were then decorated with Ag nanoparticles (NPs) deposited by sputtering with a low loading (<20 wt%) [2]. Due to their quasi 1D structure, the $TiO_2$ NTs provides a higher surface area and better electron transport properties than other Ti-based substrates, like Ti foil and $TiO_2$ NPs. These results were confirmed by electrochemical techniques (CV, EIS, electrochemical active surface area) and chemical-physical analysis (FESEM, TEM, EDS). Additionally, the $TiO_2$ NTs play a role in enhancing the stability of the $CO_2^{\cdot-}$ intermediate thanks to the titania ($Ti^{IV}/Ti^{III}$) redox behaviour, leading to an improvement of the CO production in the $Ag/TiO_2$ NTs electrodes. The best Ag NPs/$TiO_2$ NTs sample outperform Ag-decorated $TiO_2$ NPs (see Fig. 1) [2], achieving a molar ratio of $CO/H_2$ of 1:2 which is suitable as feedstock for methanol production. A noteworthy current density of -65 $mA/cm^2$ was achieved for the EC $CO_2$ reduction at -1.6V vs SHE, which can be considered high with respect to the experiments carried out with bulk noble metal electrodes.

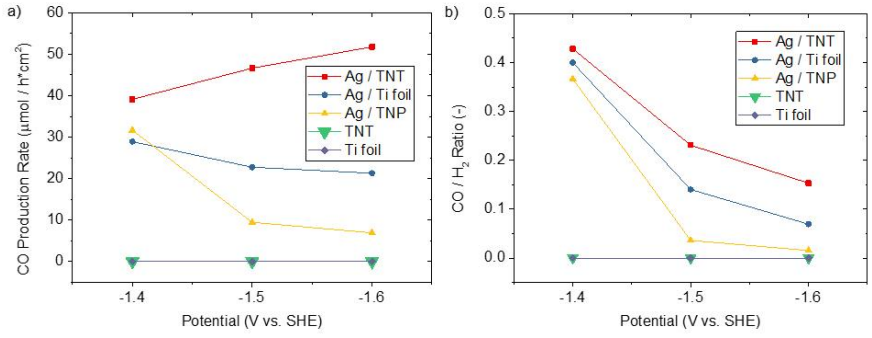


Fig. 1: Comparison of performance of different Ag-based electrodes for the EC $CO_2$ reduction in aqueous $KHCO_3$ electrolyte.

[1] S. Hernandez, M.A. Farkhondehfal, F. Sastre, M. Makkee, G. Saracco, N. Russo, Green Chemistry, 2017, 19, 2326 - 2346.
[2] M. A. Farkhondehfal, S. Hernandez, M. Rattalino, M. Makkee, A. Lamberti, A. Chiodoni, K. Bejtka, A. Sacco, C. F. Pirri, N. Russo, Int. J. Hydrogen Energy, 2019, in press.

# Laser ablation synthesis in solution of AgCo alloy nanoparticles for oxygen reduction reaction

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Laser Ablation Synthesis in Solution (LASiS) is an innovative technique for the realization of metal alloy nanoparticles (NPs). In fact, the major drawbacks associated to Ag-3d alloys are their immiscibility in the bulk phase and the great difference in their reduction potentials, leading to a faster Ag reduction compared to 3d metals and to an unlikely entrapment of 3d metals in Ag substrate [1]. Extreme conditions realized during LASiS technique allow overcoming these issues, leading to the formation of Ag – 3d metal alloys [2].

In this work, AgCo alloy NPs were synthesized through LASiS technique in different liquid solutions in order to realize different Co oxidation states, and eventually check whether they promote different selectivity toward Oxygen Reduction Reaction (ORR). As a reference, ORR was tested also on pure Ag and Co synthesized by the same LASiS procedure, and on their mixture.

Both pure Ag and Co NPs and their alloy were mixed with carbon black (CB) support in a 30:70 weight ratio, homogenized through ultrasound in a proper solution and drop-casted on a mirror-finished Glassy Carbon electrode for the electrochemical characterization. Activity toward ORR was tested by cyclic voltammetry (CV) through a Rotating Ring Disk Electrode (RRDE) configuration in alkaline solution. Preliminary results showed an improved ORR activity on AgCo alloy NPs with respect to both pure metals and their mixture (Figure 1).

Besides electrochemical tests, a full phisico-chemical characterization was conducted through X-ray Photoelectron Spectroscopy (XPS), Transmission Electron Microscopy (TEM) and Inductively Coupled Plasma Mass Spectroscopy (ICP-MS).

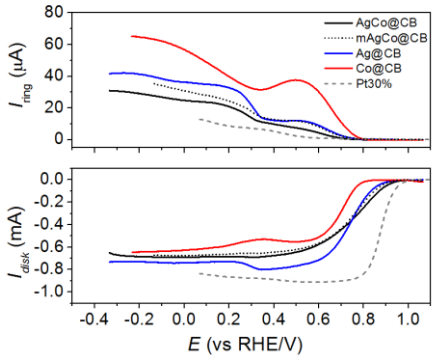


**Figure 1** RRDE characterization toward ORR of AgCo alloy NPs (black), Ag and Co NPs mixture (black dotted), pure Ag NPs (blue), pure Co NPs (red) and Pt NPs (gray dashed) on CB. ORR activity (below) and $H_2O_2$ production (above).

[1] A. Holewinski, J.C. Idrobo, S. Linic, *Nature Chemistry*, 2014, 6, 828 – 834
[2] S. Scaramuzza, M. B.Fernandez van Raap, D. Badocco, P. Pastore, D. F. Coral, V. Amendola, *ChemPhysChem*, 2017, 18,1026 –1034.

# Counter electrodes based on Fe-N-C materials for low cost dye-sensitized solar cells

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Dye-sensitized solar cells (DSSCs) are well known as potentially low-cost photovoltaic devices [1] and are attracting great attention for their capability to provide low cost power.

DSSC components include a photoanode composed of a dye-sensitized wide-bandgap semiconductor, a redox electrolyte (e.g. iodide/triiodide), and a counter electrode (CE) for reducing oxidized species in the electrolyte, generally based on a noble metal thin film. The CE collects the electrons from the external circuit to reduce the redox species used as a mediator in regenerating the sensitizer after electron injection into the photoanode. Platinum is well known as benchmark CE due to its high catalytic activity [2]. Efforts are nowadays directed to decrease the fabrication cost through alternative CE formulations.

Metal-Nitrogen-Carbon (M-N-C) materials represent an attractive alternative to platinum in DSSC counter electrodes to contribute to an efficient conversion of solar energy into electricity. Despite the slower kinetics of these carbon-based materials for the reduction of triiodide compared to platinum, they are characterized by low cost.

Various Fe-N-C catalysts were prepared by the so-called sacrificial support method (SSM) [3], consisting of the use of a templating agent based on silica, which is removed by hydrofluoric acid (HF) after a thermal treatment. The influence of the Fe-precursor, used for the synthesis, on the electrochemical behavior as counter electrodes in DSSC is analysed. The fabricated DSSCs were investigated by polarization experiments and electrochemical impedance spectroscopy, and compared with a cell equipped with a benchmark CE.

[1] B. O'Regan, M. Grätzel, *Nature*, 1991, **353**, 737-740.
[2] S. Thomas, T.G. Deepak, G.S. Anjusree, T.A. Arun, S.V. Nair, A.S. Nair, *Journal of Materials Chemistry A*, 2014, **2**, 4474-4490.
[3] D. Sebastián, A. Serov, I. Matanovic, K. Artyushkova, P. Atanassov, A.S. Aricò, V. Baglio, *Nano Energy*, 2017, 34, 195–204.

# Electro-thermal behaviour of large size Li-Ion batteries from end of life (EOL) EV module

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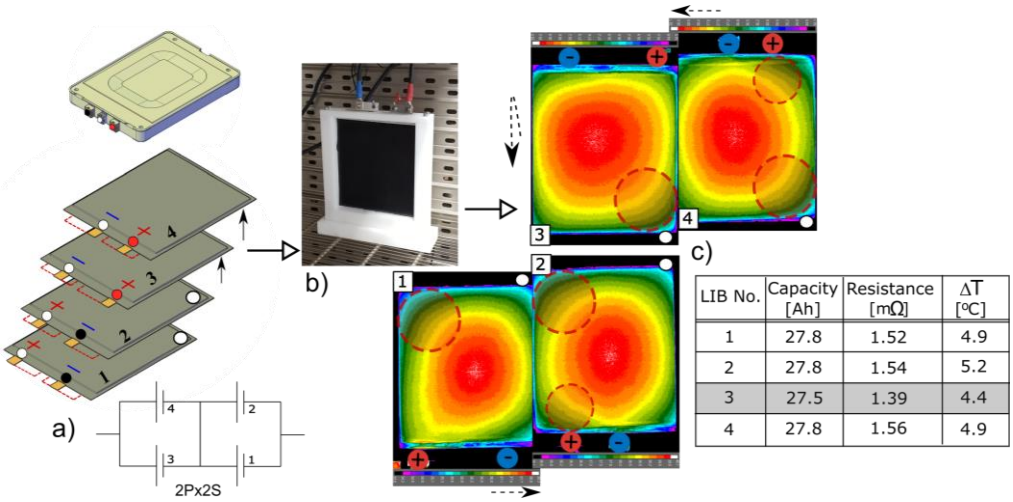
Li-ion batteries (LiBs) reach the end of life (EOL) in electric vehicles (EV) application when their capacity reaches 80% of nominal value. However, there is plenty of energy and power remaining in them, which can be used in second-life applications. The suitability of EOL EV-batteries for second-life applications needs to be carefully investigated. For instance, the state of charge (SOC), state of health (SOH), and thermal behaviour during ageing need to be accurately assessed before implementation in the second-life application, otherwise, the second-life system performance would suffer. Moreover, the variation of voltage and current density during cycling lead to a non-uniform temperature distribution, degradation and imbalanced ageing. A clear understanding of these degradations is also essential to achieve the full potential of EOL EV-batteries in the second-life applications.

In this study, the electro-thermal behaviour of EOL Nissan Leaf battery pack is investigated. Four EOL batteries (LMO chemistry and an initial capacity of 33Ah) from the same Nissan Leaf battery module are used in this study. Batteries arrangement in the module is shown in Fig. 1 (a) and to establish the connection in the module, tabs were cut and their active connection width was 1/4 of full tab width.




| LIB No. | Capacity [Ah] | Resistance [mΩ] | ΔT [°C] |
|---|---|---|---|
| 1 | 27.8 | 1.52 | 4.9 |
| 2 | 27.8 | 1.54 | 5.2 |
| 3 | 27.5 | 1.39 | 4.4 |
| 4 | 27.8 | 1.56 | 4.9 |

**Figure 1**: (a) Batteries arrangement in the module, (b) thermal imaging setup, and (c) a few preliminary results.

LiBs thermal imaging is performed during discharging from 100% SOC (4.2V) to 0% SOC (2.7V) with 50A current in a thermal chamber at 25°C with FLIR A655sc camera as shown in Fig. 1 (b). Thermal images at the end of discharge are shown in Fig. 1 (c). All four batteries have shown increased resistance in the lower corner below the positive tab, while batteries with smaller tabs connection distance (No.2 and No.4) show increased resistance underneath the positive tab. Battery with the most uniform temperature distribution over the surface (No. 3) is the battery with the lowest measured resistance. These results clearly indicate that not all four cells from the same module will perform equally in second-life applications.

# Measurement of exchange current for redox-pair $Br_2/Br^-$ on platinum electrode

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The aim of this work was to measure exchange current ($i_0$) of the bromide-anion oxidation reaction ($Br^-$) with operating concentrations of 0.01; 0.1 and 1 M in a solution of 1M sulfuric acid to molecular bromine ($Br_2$) or to the tribromide anion ($Br^{3-}$), algorithmization of this process and writing a program for data processing. The present variants of the reduction products are explained by the concentrations$Br^-$, since at the maximum value $Br^{3-}$ in the solution they predominate.

A potentiostatic method for studying electrochemical reactions on a rotating disk electrode (VDE) with a working range of 110, 138, 178, 237, 330, 494, 818, 1600, 3460 and 4444 RPM was chosen.

Because of the large volume, the data obtained during the experiment (values I and E at each rotation speed) were tabulated in the program OriginPro 9.1. After that, a script was developed in the high-level language in the Mathcad software environment and the value was calculated by importing the data.

The obtained results ($i_0 = 9{,}178\ mA/cm^2$ for $c(Br^-) = 0{,}01\ M$) coincide with the data from the literature sources ($i_0 = 1\ mA/cm^2$) [1] and confirm the possibility of using $Br^{3-}/Br^-$ as a mediator redox pair in electrochemical power sources.

Acknowledgement: this research was supported by the Russian Ministry of Education and Research (Grant № 14.574.21.0150, UIN RFMEFI57417X0150).

[1] R. E. White, S. E. Lorimer // *J. Electrochem. Sac,*1983, **130**, 1096 – 110.

# Voltammetric characterization of gold-based bimetallic (AuPt; AuPd; AuAg) nanoparticles

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Bimetallic nanoparticles are nowadays some of the most promising materials for catalytic, electrocatalytic and electroanalytical applications thanks to their novel optical, catalytic, magnetic, and sensing properties. Such novel features, often different and enhanced with respect to the monometallic counterparts, make these systems good candidates to be conveniently applied in a wide range of fields. The possibility to obtain different kinds of bimetallic composites (in terms of composition, structure, metal loading, morphology, etc.) goes in parallel with the need of powerful and accurate characterization tools. Among the commonly involved techniques like Optical Spectroscopy and Dynamic Light Scattering (DLS), also the more powerful Transmission Electron Microscopy (HR-TEM) and Extended X-Ray Absorption Fine Structure (EXAFS) are widely used. However, these analytical tools present some drawbacks in terms of high costs and low accessibility. In this context, electrochemistry and particularly Cyclic Voltammetry, is here proposed as an alternative, low cost, easy to use and simple characterization technique.

The possibility to use electrochemical methods to study the final structure of bimetallic nanocomposites was already demonstrated in the Literature [1-2], but there is still lack of information on how such systems change and evolve in time and after aging periods. Therefore, Cyclic Voltammetry is here used as a complementary technique to HR-TEM and EXAFS not only to investigate the structure of alloyed or core-shell gold-based (Au-Pt; Au-Pd; Au-Ag) systems (by studying the quantity and type of metals present in the materials), but also to elucidate the evolution and growth in time of such bimetallic samples. Time evolution characterization allows to control the morphology and to fix it at the desired point.

Finally, the characterized gold-based nanocomposites are used in electrochemical sensing and electrocatalytic applications. A strong improvement in the response of the bimetallic systems with respect to the monometallic counterparts is evidenced, due to the intimate contact between the two metals, which is responsible of synergistic effects. Moreover, the influence of an eventual carbonaceous support on the properties of the metal nanoparticles and also the possible synergistic effects between composites and supports are investigated [3].

[1] K. Tschulik, K. Ngamchuea, C. Ziegler, M.G. Beier, C. Damm, A. Eychmueller, R.G. Compton, *Adv. Funct. Mater.*, 2015, **25**, 5149–5158.
[2] V. Pifferi, C. Chan-Thaw, S. Campisi, A. Testolin, A. Villa, L. Falciola, L. Prati, *Molecules*, 2016, **21**, 261.
[3] A. Testolin, S.Cattaneo, W. Wang, D. Wang, V. Pifferi, L. Prati, L. Falciola, A. Villa, *Surfaces,* 2019, **2**, 205-215.

# Oxidation of water by oxammonium cations

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Oxammonium cations ($OA^+$), produced in situ by oxidation of stable nitroxyl radicals $SNR^{\cdot}$, can react with $OH^-$ ions to regenerate the initial radical. Electron paramagnetic resonance (EPR) experiments and electrochemical methods show that the rate of recovery depends on both the $OH^-$ concentration and the redox potential of the $OA^+/SNR^{\cdot}$ couple.
EPR measurements also performed in $H_2{}^{17}O$, together with analysis of the pH-dependence of the reaction, provide evidence that reversible insertion of an $OH^-$ anion into the $>N^+=O$ bond is a fundamental step.

For a series of nitroxides, electrochemical measurements display a linear correlation between the redox potential and the logarithm of the recovery reaction rate constant. It is shown that $OA^+$, produced by electrochemical or photochemical oxidation of SNR, reacts with $OH^-$ ions to produce molecular oxygen. This could be a new mechanism of water oxidation.

We further propose a plausible reaction scheme for the observed process.

# Safe polymer electrolytes and high performing anode materials for Na-based secondary batteries

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Secondary (rechargeable) Na-based batteries are an attractive alternative to Li-ion batteries for large/scale energy storage technologies, because of high-energy density, sodium abundance, low-cost, simple design, and easiness in maintenance. However, safety concerns related to the use of carbonate-based liquid electrolytes (toxic and volatile) are similar to their Li-based counterpart, mainly due to their flammability and risk of explosion. The most striking solution at present is switching to an all solid-state design exploiting polymer electrolyte materials, ceramics, and hybrids thereof. Moreover, the use of an appropriate and efficient negative electrode material to replace the unpractical graphite-based anodes is fundamental to obtain high energy density batteries.

In the present work, an overview will be provided on both truly solid and quasi-solid polymer electrolytes specifically conceived and developed for Na-ion cells, based on polyethylene oxide (PEO), acrylates/methacrylates and/or mixtures thereof. Eventually, pyranose ring based natural additives and/or low volatile plasticizers are added along with supporting sodium salts to improve specifically defined characteristics. Both standard casting and UV-induced photopolymerization techniques have been explored [1].

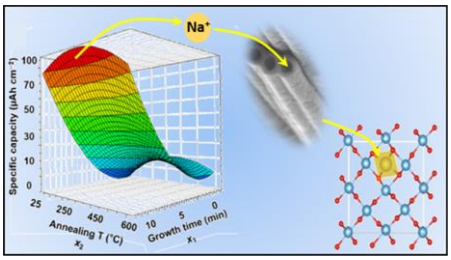


**Figure 1**: Modelling and DoE of advanced nanotubular $TiO_2$ electrodes.

Furthermore, our results regarding nanostructured $TiO_2$ nanotubular electrodes will be presented, including different electrochemical responses of amorphous, rutile and anatase based nanotube arrays, obtained by simple anodic oxidation, when tested as binder- and conducting additive-free electrodes in lab-scale sodium cells [2]. Thorough modelling by ab-initio and DFT calculations of the sodiation processes will be also discussed [3].

**Acknowledgements:** Part of this work was carried out within the activities "Ricerca Sistema Elettrico" funded through contributions to research and development by the Italian Ministry of Economic Development.

[1] F. Colò, F. Bella, J.R. Nair, and C. Gerbaldi, *J. Power Sources* 2017, **365**, 293-302.
[2] F. Bella, A. B. Muñoz-García, F. Colò, G. Meligrana, A. Lamberti, M. Destro, M. Pavone, and C. Gerbaldi, *ACS Omega* 2018, **3**, 8440-8450.
[3] F. Bella, A. B. Muñoz-García, G. Meligrana, A. Lamberti, M. Destro, M. Pavone, and C. Gerbaldi, *Nano Res.* 2017, **10**, 2891-2903.

# Thermally regenerable redox-flow batteries

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A Thermally Regenerable redox-flow Batterie (TRB) is an electrochemical cell which produce electrical current by consuming solutions, with the same composition, but different concentrations. In this kind of device, the two solutions can be regenerated by distillation, exploiting low temperature heat (<100°C) produced in different industrial applications. The produced energy is extracted at the expenses of the mixing free energy of the two solutions. This cell stores energy in form of solutions and it will enable to convert heat from geothermal sources, industrial waste and solar heat collected by low-concentration optics, in a more efficient way then the traditional thermoelectrical converters. The efficiency of the whole device depends by the efficiency of the electrochemical cell and the efficiency of the distillation unit, which can be improved choosing a salt that gives a high boiling point elevation.

An example of TRB is based on LiBr solutions, in which the different electrochemical equilibrium reached at the electrodes (Pt) lead to an efficient production of electrical current, with the passage of $Li^+$ and production/consumption of $Br_2$ and $Br^-$ at the electrodes.

To equilibrate the bromine concentration (to extract the maximum energy possible), the solutions are pumped in a second device called “through liquid exchanger” which is based on the passage of bromine through an organic solvent in which LiBr and water are insoluble.

A cell based on LiBr could provide 38,5 Wh/L starting from two solutions at 26% and 2.5% of molar fraction at room temperature.

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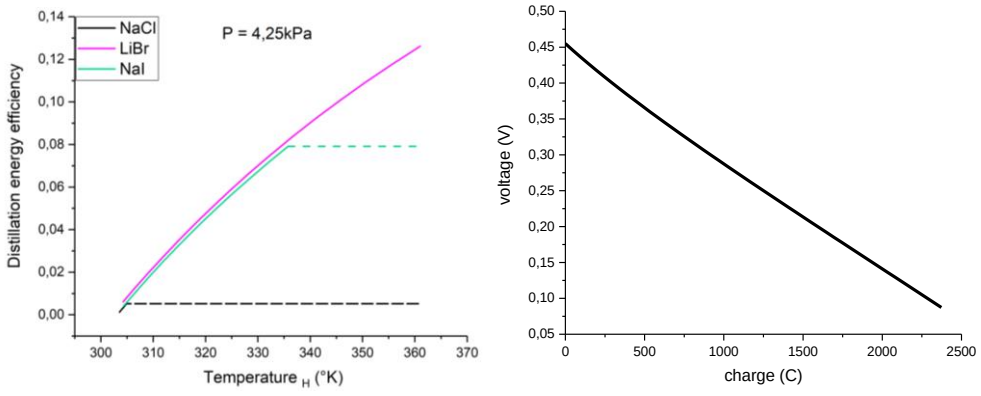


**Figure 1**: On the left, distillation efficiency vs Heat Temperature for different salts. On the right a graph “voltage vs charge” starting from two solution with a molar fraction of 26% and 2,5% respectively. The solutions are separated by a $Li^+$ conducting ceramic membrane with 150µm in thickness.

# Effect of the particle-size distribution on the electrochemical performance of a red phosphorus-carbon composite anode for sodium-ion batteries

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Sodium-ion batteries will have an important role as a complement to lithium-ion in a future where lithium or cobalt, two critical elements for lithium-ion batteries, become scarce or prohibitively expensive. Red phosphorus (RP) is a promising candidate as an anode for sodium-ion batteries because of its low potential and high specific capacity. Its main disadvantage is its 490% volumetric expansion during sodiation. This leads to particle pulverization and substantial reduction of the cycle life. Furthermore, RP has an extremely low electronic conductivity of $10^{-14}$ S cm-1. Both issues have been previously addressed by ball milling RP with a carbon matrix. This decreases the RP particle size and also forms a more electronically conductive composite. However, it is challenging to determine the RP particle size independent of the size of the composite particles. Consequently, little is known about how much the RP particle size must be reduced to improve anode performance.

We quantified the relationship between the RP particle-size distribution and its cycle life for the first time by separating the ball milling process into two steps. An initial wet ball milling is used to control the RP particle-size distribution, which is measured via dynamic light scattering. This is followed by a dry milling step to produce RP-graphite composites. We found that wet milling breaks apart the largest RP particles in the range of 2 to 10 µm decreases the Dv90 from 1.85 to 1.26 µm and significantly increases the cycle life of the RP.

The RP with a Dv90 of 0.79 µm mixed with graphite for 48h delivered 1,354 mA h g-1 with high coulombic efficiency (>99%) and cyclability (88% capacity retention after 100 cycles). Furthermore, we determined that the length of time of the second milling step affects the uniformity of the carbon distribution in the composite. Photoelectron spectroscopy and transmission electron microscopy confirms the successful formation of a carbon coating, thus improving the performance of the resulting material. These results are an important step in the development of cyclable, high-capacity anodes for sodium-ion batteries.

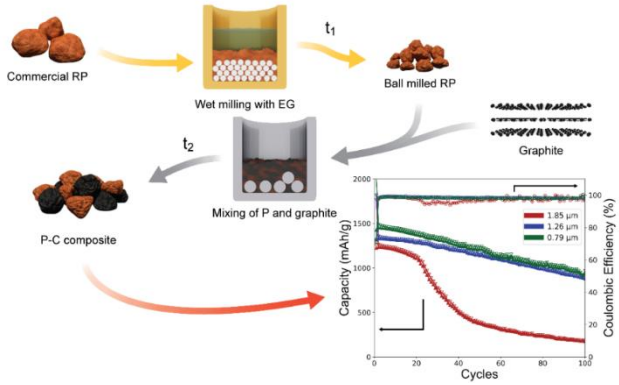


Figure 3) A scalable method for preparing P-C composites for anodes in SIBs. During the first step, the particle size of commercial red phosphorus is controlled using a wet milling technique with ethylene glycol as the solvent (t1). Afterwards, the P-C composite is prepared by mixing phosphorus with a specific particle size distribution and graphite (t2).

# Operando hard and soft X-ray absorption spectroscopy in (photo)-electrochemistry

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Operando X-ray Absorption Spectroscopy (XAS) proved to be an efficient technique to investigate the mechanism of (photo)electrochemical reactions while simulating the real operating conditions of a given process [1]. While operando XAS experiments with hard X-rays (*i.e*. highly energetic X-rays) are quite established, the same cannot be said for operando XAS with soft X-rays (*i.e.* low energetic X-rays), since their low penetration depth and the severe vacuum limitation have somehow hindered a parallel development. Here I present two applications of operando XAS, respectively with hard and soft X-rays.

The potentiality of hard X-rays XAS was exploited for the study of $WO_3$ photoanodes, which are well-known photoactive materials in the photosplitting of water. The experiment was carried out in a properly-designed photoelectrochemical cell [2], while simultaneously irradiating the sample with X-rays and UV/Vis radiation and applying a suitable external potential. The water splitting reaction, and especially the promotion of the electrons from the valence to the conduction band, was studied at different timescales. The results point towards the filling of the $t_{2g}$ orbitals due to the photogenerated electrons, followed by a structural rearrangement to compensate for the accumulation of electrons in the conduction band under open circuit conditions.

As regards operando XAS with soft X-rays, we could successfully perform an experiment to study the interaction of a $SnO_2$-based gas sensor with different gaseous species. This experiment, which represents one of the first examples of operando soft X-rays XAS at ambient pressure, provides interesting insights into the working mechanism of this gas sensor, allowing us to directly observe the reduction of Sn(IV) to Sn(II) at the surface of the sample during the interaction with reducing gases ($H_2$, $CH_4$ and $C_3H_6$).

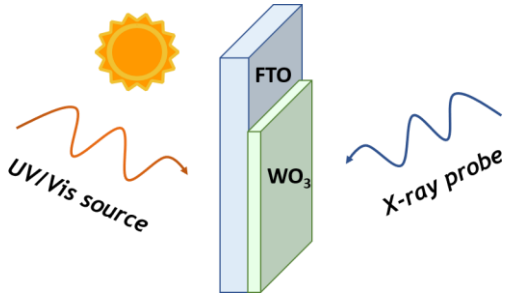


**Figure 1**: Schematic representation of operando hard X-rays XAS on $WO_3$ photoanodes.

[1] M. Fracchia, P. Ghigna, A. Vertova, S. Rondinini and A. Minguzzi, *Surfaces*, 2018, **1**, 138–150.
[2] E. Achilli, A. Minguzzi, A. Visibile, C. Locatelli, A. Vertova, A. Naldoni, S. Rondinini, F. Auricchio, S. Marconi, M. Fracchia and P. Ghigna, *J. Synchrotron Rad.*, 2016, **23**, 622-628.

# Electrochemical impedance spectroscopy: a powerful tool to unveil the charge transport/recombination processes in aqueous dye-sensitized solar cells

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Long term stability of Dye-Sensitized Solar Cells is one of the main issues preventing the large-scale commercialization of this class of device. Indeed, high-efficiency DSSCs are prepared mainly with liquid electrolytes based on organic solvents, such as acetonitrile (ACN) and methoxypropionitrile (MPN). These are often oil derivatives characterized by toxicity and flammability; additionally, they possess high vapor pressure and volatility, which often straightforwardly lead to electrolyte leakage and decrease of photovoltaic performances over time. For this reason, the researchers' efforts move towards alternatives solvents to obtain efficient, safe and low-cost devices. Above all, DSSCs with water-based electrolytes are amongst the best solutions providing reduced costs, non-flammability, better stability and environmental compatibility, all at once. In the last years, scientific literature on this topic has significantly increased [1] and, recently, devices have been reported that achieved 5.5% photoconversion efficiency with an efficiency 100% aqueous electrolyte [2].

Electrochemical Impedance Spectroscopy (EIS) has been proven to be a very powerful tool to investigate the charge transport/recombination phenomena occurring in classical device (i.e., organic-based). Yet, just few studies are reported in which EIS is used to investigate aqueous systems [3]. As a matter of fact, the fastening of the recombination processes occurring at the electrode/electrolyte surface and the slackening of the charge transfer reactions at the counter-electrode could worsen the interpolation of experimental data.

Herein, we report the electrochemical impedance spectroscopy analyses of both liquid and polymeric aqueous-based electrolytes to unveil the charge transport and recombination processes. The latter are compared to those of reference devices assembled with standard organic-based electrolyte. Results obtained confirm that the diffusion processes throughout the electrolyte are slower in aqueous environment with respect to the organic counterpart. Very interestingly, the resistance of the charge recombination reactions at the electrode/electrolyte interface is sensibly higher when an aqueous electrolyte (both liquid and polymeric) is employed. Unfortunately, this evidence does not lead to a better photoconversion efficiency because of the simultaneous worsening of the charge injection (transport) processes into (throughout) the $TiO_2$ electrode. Nevertheless, the results discussed in this work could be considered as a starting point to further enhance the overall efficiency of aqueous-based Dye-Sensitized Solar Cells and demonstrate that EIS might be a very powerful tool in this respect.

[1] F. Bella, C. Gerbaldi, C. Barolo and M. Grätzel, 2015, Chem. Soc. Rev. **44**, 3431–3473.
[2] H. Ellis, R. Jiang, S. Ye, A. Hagfeldt and G. Boschloo, 2016, *Phys. Chem. Chem. Phys.* **18**, 8419–8427.
[3] F. Bella, S. Galliano, M. Falco, G. Viscardi, C. Barolo, M. Grätzel and C. Gerbaldi, 2016, *Chem. Sci.* **7**, 4480–4490.

# High performance vanadium redox flow battery incorporating graphite foil as bipolar plates

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Vanadium redox flow battery (VRFB) plays a key role in the development of novel stationary electrochemical energy storage. Many efforts were made to improve its peak power density and increase energy efficiency. To the best of our knowledge, among the commercially available VRFB and laboratory test cells of VRFB there are no devices that employ graphite foil as a material for bipolar plates.

We propose VRFB employing graphite foil as bipolar plates. The utilization of graphite foil and simplicity of its treatment can significantly reduce the time for the cell production and offers an opportunity to vary factors determining the specific power of the RFB (configuration of flow field, type of electrode material and membrane) with the minimal capital costs that forms a substantial part of leverized cost of storage (LCOS).

We demonstrate the high performance VRFB without any membrane and electrode pretreatment. The performance of VRFB with graphite foil was measured for different types of flow fields and membranes. High performance VRFB with Nafion XL membrane and carbon paper Sigracet as electrodes demonstrated the peak power density as high as 1065 mWt/cm$^2$ at current density 1450 mA/cm$^2$. Energy efficiency for this VRFB reaches 83 % at 75 mA/cm$^2$.

The highest performance was measured for VRFB with Nafion N117 membrane, which displayed energy efficiency 87 % at 50 mA/cm$^2$ with a capacity utilization of 70 %. These numbers are close to record values for the used electrolyte (1 M V 4 M H2SO4), most notably that no additional efforts were made to develop surface of carbon paper or its catalytic activity. We attribute the achieved result to the successful combination of an effective channel system of the flow field and low contact resistance at graphite foil/carbon paper interface.

Acknowledgement: The study was supported financially by the Russian Ministry of Education and Research (grant 14.574.21.0150, UIN RFMEFI60417X0150).

# Electrodeposition of Cadmium Selenide on n-Si (100)

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Monocrystalline silicon has been considered for years among the materials at the base of the macro and micro-electronics industry. At the bulk state silicon is an intrinsic semiconductor whose conductive properties can be easily modulated by using doping agents. This feature combined with high availability and accessible production costs makes it particularly suitable for many applications based on semiconductor technology. With the development of vacuum deposition techniques, it has been possible to create systems that integrate monocrystalline silicon with other materials of technological interest, thus allowing the realization of highly performing devices [1]. However, the use of these techniques is limited by special working conditions and very expensive instruments. An alternative to these techniques is the electrodeposition from aqueous solution. Studies on the deposition of materials of technological interest on gold and silver have been known for several years now [2]. In this work we use the electrodeposition technique, with all the advantages it brings both in terms of costs and deposition quality, on monocrystalline 100 n-type silicon. The study dealt with the co-deposition and alternate deposition of the semiconductor cadmium selenide (CdSe). First of all, we carried out the electrochemical characterization of the precursors on the substrate to find the optimal conditions (pH and concentrations) for the deposition, then the deposition was performed using two different approaches: co-deposition (both the precursors present in the same solution) and charge controlled alternate deposition of the two components. Finally, deposits were characterized spectroscopically and microscopically: we found that, with the electrochemical method, we obtained to the formation of micro-clusters of CdSe on n-Si.

[1] M. J. Lo Faro, A. A. Leonardi, C. D'Andrea, D. Morganti, P. Musumeci, C. Vasi, F. Priolo, B. Fazio, A. Irrera, *J Mater Sci: Mater Electron* 2019, 1-7.
[2] A. Giaccherini, R. Felici, M. Innocenti, Massimo, *X-ray Characterization of Nanostructured Energy Materials by Synchrotron Radiation. IntechOpen*, 2017.

# $Fe_3O_4$ nanoparticles with dual electromagnetic functions for highly efficient catalytic advanced oxidation processes

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Chlorophenols (CPs) belong to a group of ubiquitous contaminants in the environment, which have been listed as environmental priority pollutants by both China and U.S. EPA due to their strong toxicity and even carcinogenic property to human beings. The development of effective remediation strategy for recalcitrant pollutants including CPs is one of the central topics and key issues in the environment field. Here we propose the concept of nano-galvanic cell, with the goal providing a promising alternative strategy, new insight and a guide for highly efficient degradation of water pollutants from contaminated sites. Magnetic $Fe_3O_4$ and its derivative (Pd/$Fe_3O_4$) were chosen and prepared as model nanoparticles because of the excellent recovery property of $Fe_3O_4$ and the high catalytic ability of Pd. These particles exhibit dual functions as galvanic cell and magnet in the electrochemical system (or in electromagnetic field). The spherical $Fe_3O_4$ nanoparticles are polarized to form numerous nano-galvanic cells under the electric field force, with high accumulation of positive charge Fe-based species on one side and concentration of negative charge (electrons) on the other, respectively, which simultaneously facilitates electron transfer for triggering reduction (e.g., $O_2$ reduction to produce $H_2O_2$ and $\bullet O_2^{-}$) and oxidation (e.g., 4-CP and its intermediates activation) reactions. We show that the nano-galvanic cell system exhibits a strong oxidation capacity for the degradation of 4-CP, which was completely removed in 1 h and further efficiently mineralized as revealed by total organic carbon (TOC) removal efficiency of beyond 90% at 8 h. Meanwhile, the charged Fe3O4 nanoparticles induced by current can give rise to magnetic field, which further accelerates the corrosion of Fe-based species and in turn, contributes to producing nanoparticle galvanic cells via facilitating surface $Fe^{2+}/Fe^{3+}$ moving to the high magnetic field direction. The strength of this approach lies in a methodology that overcomes the common problems of heterogeneous electrochemical process, such as limited electrode area, mass transfer limitation and poor current efficiency, and realizes synergistic electromagnetic interaction for effective removal of organic pollutants.

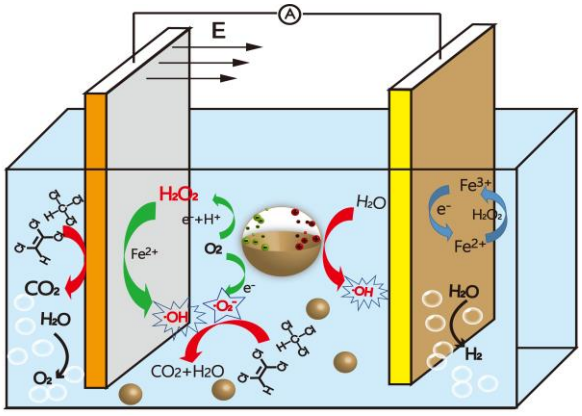


**Figure 1**: Schematic representation of nano-galvanic cell system for effective degradation of 4-CP

[1] B. Huang, C. Qi, Z. Yang, W. Chen, G. Zeng, and C. Lei, *Journal of Catalysis* 2017, 352, 337–350.

# Process scale-up for pilot scale production of lithium-ion electrode materials

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Nowadays a number of manufacturers of lithium iron phosphate (LiFePO4) batteries are emerging and it drives the research for new methods of production and new formulations for electrode manufacturing. The advantages in effectiveness, practicality, and economics of new technologies are indispensable for their widespread application. Similarly, designing a cost-effective production process with controlled quality is critical for the commercialization of $LiFePO_4$ Batteries [1].

In our research center, an efficient $LiFePO_4$ synthetic procedure has been developed and already successfully performed on lab-scale [2]. Moving from this know-how, we designed a process (Fig. 1) aimed to synthesize kilos of $LiFePO_4$ and optimized the production obtaining a material with specific capacity up to 160 mAh $g^{-1}$ in batteries (being 170 mAh $g^{-1}$ its theoretical maximum value).

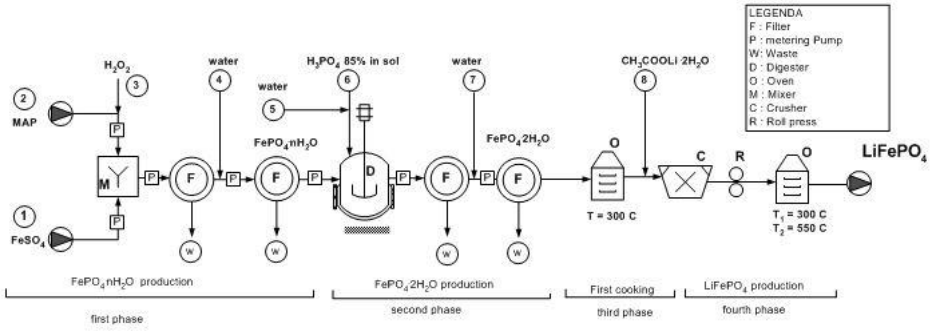


**Figure 1**. Scheme of the process plant for the synthesis of $LiFePO_4$.

The so synthesized material has been used in a semi automatic manufacturing process for the production of water based $LiFePO_4$ cathode electrodes. The experimental processing conditions in water are more restrictive than the use of organic solvents to obtain homogeneous slurries and cracking free electrode coating. So, the an optimized process has been developed in order to obtain electrodes with good structural characteristic and satisfying cycling performance. These electrodes have been then coupled with graphite base anode to build Li-ion batteries and their electrochemical performance evaluated by galvanostatic cycles. Besides the production of semi-industrial amount of materials, our purpose is to promote the technology transfer to small and medium-sized companies, acting as a trait-d'union between academia and business world.

[1] J. Li and Z. -F. Ma, *Chem.,* 2019, **5**, 3-6.
[2] P.P. Prosini, M. Carewska and M. Pasquali, *Solid State Ionics,* 2016, **286**, 66-71.

# Si-NWs grown by Cu-catalysed CVD for lithium-ion batteries

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In the challenge to improve the charge capacity of lithium–ion batteries (LIBs), silicon (Si) is considered a promising material to replace the conventional C-based anode, due to its higher theoretical capacity of 3800 $mAhg^{-1}$ and a low delithiation potential, below 0.5 V vs $Li/Li^{+}$[1]. However, its use has been hindered by the poor capacity retention upon cycling, due to electrode cracking and pulverization related to thehuge volume expansion (up to 400%) upon cycling. In order to overcome the stress due to the volume changes and enhance or maintain the electric contact between silicon and the electrode, nanostructured anodes [2] including, Si nanowires (Si-NWs), porous Si, and Si dispersed in an active/inactive matrix have attracted particular attention.

In particular, Si-NWs offer direct one-dimensional electronic pathways for rapid charge transport and reduce stress relaxation, preventing material fragmentation.

In this context, we have electrochemical characterized Si-NWs grown on highly porous 3D-like carbon paper substrate by Cu-catalysed Chemical Vapour Deposition [3]. In addition, the use of additives such as FluoroEthylene Carbonate (FEC) has been investigated.

[1] J.R. Szczech, S. Jin**,** *Energy Environ Sc*i, (2011), **4**, 56-72
[2] H. Wu, Y. Cui, *Nano Today*, (2012), **7**, 414-429
[3] E. Peled, F. Patolsky, D. Golodnitsky, K. Freedman, G. Davidi, D. Schneier, *Nano Lett.*, (2015), **15**: 3907−3916

# Fabrication and electrochemical characterization of Sm-doped ceria (SDC) electrolyte for IT-SOFC and study of complete cells

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One of the actual global challenges is to find some new clean and efficient way for energy production. The use of hydrogen into fuel cells is one of the solutions. Among the different fuel cells-based technologies, the Solid Oxide Fuel Cell (SOFC) is the most promising in term of yield and volumetric power density [1]. However, this device operates at high temperature (600-900°C) so, to allow a better durability, it is necessary to decrease the working temperature. One way is to use adapted materials for the electrolyte layer. Sm-doped ceria ($Ce_{0.8}Sm_{0.2}O_{1.9}$ noted SDC), which exhibits an ionic conductivity higher than $10^{-2}$ S.cm$^{-1}$ at 600°C, allows to reduce the working temperature in the range of 500-600°C [2].

In this present work, a symmetric cell, composed of SDC as electrolyte and $(La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) as electrodes is studied. The electrolyte has been prepared by uniaxial pressing and electrodes have been deposited on the SDC pellet by screen printing. This cell has been systematically analyzed by Electrochemical Impedance Spectroscopy (EIS) from 200°C to 700°C in air atmosphere. Results showed a total electrolyte ionic conductivity of $1.1*10^{-2}$ S.cm$^{-1}$ at 600°C, which corresponds to the theoretical value [2].

Furthermore, to study SDC material for an application as electrolyte for IT-SOFC (Intermediate Temperature SOFC), complete cells composed of Ni-SDC for anode, SDC and LSCF for cathode has been prepared by co-tape casting and co-sintering. The cells have been characterized by EIS in the 450-650°C range of temperature in both air and hydrogen atmosphere, to obtain preliminary results. One cell, sintered at 1200°C, presented a maximum OCV of 0.72 V at 500°C. Nyquist plots showed high electrolyte resistance (~ 550 Ω.cm$^{-2}$) at the same temperature. Those results can be explained by the poor densification of the electrolyte due to the low sintering temperature. One other cell, sintered at 1300°C, showed a better electrolyte resistance (~ 40 Ω.cm$^{-2}$) at 500°C but a lower OCV (0.50 V) at 550°C. The better densification gives an explanation for the better resistivity and the lower OCV can be justified by a delamination observed by SEM analysis between the cathode and the electrolyte.

[1] Eric D. Wachsman and Kang Taek Le, *Science*, 2011, **334**, 935-939.
[2] G. B. Balazs and R. S. Glass, *Solid State Ionics*, 1995, **76**, 155-162.

# Hierarchical *"Core-Shell"* low-loading Pt electrocatalysts for the oxygen reduction reaction based on a graphene *"core"* and a carbon nitride *"shell"*

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Toward a sustainable energy system at the global level, a pivotal role is expected to be played by electrochemical energy conversion and storage (EECS) such as proton exchange membrane fuel cells (PEMFCs), where chemical energy is converted into electrical energy through oxidation of hydrogen (HOR) and reduction of oxygen (ORR)[1]. To ensure that the PEMFC achieves a sufficient performance level, the ORR must be promoted by suitable electrocatalysts (ECs). Platinum is the most promising material for this application, but to place PEMFCs closer to market, the total amount of noble metal must to be limited.

This work overviews the development of a new family of low-Pt ECs for the ORR, whose active sites are found on the surface of sub-nanometric clusters (SNCs) where Pt is alloyed with a first-row transition metal (*e.g.*, Ni, Cu) that operates as a *"co-catalyst"* and raises the intrinsic performance [2]. The SNCs raise the utilization of Pt atoms by up to *ca.* one order of magnitude with respect to the Pt nanoparticles (NPs) adopted in state-of-the-art ORR ECs, thus raising the specific power yielded by the PEMFC. Values as high as 14 $kW/g_{Pt}$ are achieved, that exceed the target set by the DoE for 2020 (*i.e.*, 8 kW/gPt).

The support of the low-Pt ECs exhibits a *"core-shell"* morphology, including a hierarchical graphene-based (H-GR) *"core"* that is covered by a carbon nitride (CN) *"shell"*. H-GR consists of highly defective graphene nanoplatelets and carbon black NPs [3], to facilitate mass and charge transport. The CN *"shell"* includes less than 5 wt% of N (to prevent the introduction of ohmic drops) and though C- and N-based ligands makes up a *"coordination nest"* that, together with defects of the graphene, stabilize the SNCs resulting in an outstanding durability of the ECs.

This report takes into consideration the various families of low-Pt ECs based on H-GR supports developed so far by our group, and compares the interplay between the preparation parameters (in particular the type of support) and the physicochemical properties with the electrochemical behavior and the performance in a single PEMFC tested under operating conditions.

**References**

[1] B. Dunn, H. Kamath, J.M. Tarascon, *Science*, 2011, **334**, 928-935.
[2] V. Di Noto, E. Negro, K. Vezzù, F. Bertasi, G. Nawn, *Electrochem. Soc. Interface,* 2015, **24**, 59-64.
[3] V. Di Noto, E. Negro, A. Bach Delpeuch, F. Bertasi, G. Pagot, K. Vezzù, *Patent application PCT/EP2017/084801,* 2017.

# Tailoring the conductivity and chemosensing properties of monolayer-protected gold nanoclusters films

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Chemiresistive sensors are devices that measure the variation in the resistance of an active material due to its interaction with the analyte. Metal nanoparticles protected by suitable organic monolayers have recently shown to provide very interesting materials in terms of both sensitivity and selectivity for the detection of volatile organic compounds (VOCs). These "electronic noses" can find important applications, for example, in the detection of hazardous chemical vapors and in the early-stage diagnosis of diseases from exhaled breath [1].

Most of the work carried out in this area is based on the use of nanoparticles with gold cores of 2-10 nm, whereas a very limited amount of work in this field has been done on atomically precise monolayer-protected Au clusters (MPCs), although their tunable properties appear so clearly promising in particular to the scope of increasing selectivity and sensitivity. MPCs with gold cores of diameter <1.6 nm are unique materials in nanoscience because the number of Au atoms is sufficiently small to make them display molecular features. They can be prepared with atomic precision and fully characterized for the structures of the core atoms and surface capping ligands [2,3]. MPC based chemiresistors is easily performed by drop casting and drying MPC solutions onto a two-electrode system followed by application of a bias potential between the electrodes. These films are disordered assembly but this approach represents a simply applicable method to create films with tailored conductive properties. The principle by which these chemiresistors operate is that vapors reversibly partition into the organic monolayer: this induces an increase in the average distance between the metal cores, due to the swelling, and an alteration of the monolayer dielectric constant.

In this communication, the conductivity properties of films of Au MPCs will be illustrated. Most of the work has been carried out on $Au_{25}(SR)_{18}$ nanoclusters for which the effect of the monolayer thickness, the presence of doping metals and the temperature has been analyzed. The effect of core dimension has been considered by carrying out investigation on larger clusters as $Au_{38}(SR)_{24}$ and $Au_{144}(SR)_{60}$. Results on the sensing response of drop casted films on selected organic vapors will be shown.

[1] Potyrailo, R. A. *Chem. Soc. Rev*. **2017**, *46,* 5311.
[2] Antonello, S.; Maran, F.: *Curr. Opinion Electrochem*. **2017**, 2, 18.
[3] Antonello, S.; Dainese, T.; De Nardi, M.; Perotti, L.; Maran, F. *ChemElectroChem* **2016**, *3*, 1237.

# Elucidation of the interplay between vanadium species and charge-discharge processes in VRFBs by raman spectroscopy

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Vanadium Redox Flow Batteries (VRFBs) are believed to be a key technology for large scale electrochemical energy storage. One of the largest obstacles to the implementation of VRFBs is self-discharge, which is believed to be related mainly to vanadium crossover [1]. In addition to crossover, the presence of side reactions might also influence charge/discharge processes and, in terms of performance, coulombic efficiency. For this reason, this work analyzes the different species present in the catholyte at different values of state of charge (SoC) / state of discharge (SoD) through Raman spectroscopy. This analysis allows for the identification of the species present in the catholyte and gives a first quantitative analysis of them. Raman results reveal that the most abundant species in the catholyte are $VO^{2+}$ (V(IV) species formed during discharge) and $VO_2^+$ (V(V) species formed during charge). Both species are coordinated with $HSO_4^-$ and $SO_4^{2-}$ ligands. A non-negligible presence of $HV_2O_5^-$ and $H_3V2O_7^-$ species is also detected, suggesting other unwanted electrochemical reactions that can play a crucial role in the modulation of coulombic efficiency. This work highlights the complexity of the chemical situation at a VRFB cathode, and the great importance of understanding and controlling this chemical situation to improve the performance of VRFBs in the scenario of electrochemical energy storage field.

**References**

[1] C. Sun, A. Zlotorowicz, G. Nawn, E. Negro, F. Bertasi, G. Pagot, K. Vezzù, G. Pace, M. Guarnieri, V. Di Noto, *Solid State Ionics,* 2018*,* **319,** 110-116.

# PEO-polysulfides composite cathodes: towards solid lithium/sulphur batteries

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Lithium sulfur (Li/S) batteries have attracted a lot of interest in the past few years because their high theoretical energy density values. Unfortunately, their performance are hindered by the insulating nature of both redox species (sulphur and lithium sulphide) and the reactivity between lithium and the ether-based electrolyte. To overcome this latter problem the use of a solid polymer electrolyte was suggested to improve the lithium/electrolyte interface[1]. Consequently, a composite cathode containing the same polymer has to be developed.
Among the possible configurations of this composite cathode, the one containing dissolve lithium polysulphides as the sulphur source has showed very promising performance.

The preparation of the composite cathodes has been optimized to obtain a good conductivity and a homogeneous distribution of the active material inside the electrode. The cathode was prepared as depicted in Figure 1, starting from high molecular weight PEO (4MDa) and Ketjen black (KJB) carbon. Thanks to the segmental movement of the oxyethylene chains polyethylene oxide (PEO) shows a good ionic transport properties for lithium at moderate-high temperature. To increase the ionic conductivity at room temperature, tetraethylene glycol-dimethyl ether (TEGDME) was added to the PEO-carbon mixture. The polysulphides have been added and incorporated into the mixture at the end of the process, dissolved in TEGDME. In this way it is possible to limit the polysulfides dispersion in the polymer electrolyte and the consequent parasitic reactions that limit the performance of the batteries themselves. After that, the composite cathode was subjected to pressure and heat to increase its mechanically properties. The composite cathodes were characterized by chemical-physical analyses and electrochemical tested to evaluate their performance in a Li/S battery.

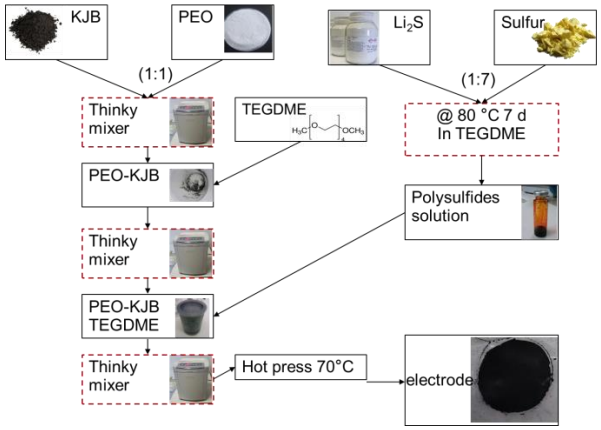


**Figure 1**: Schematic representation of the optimized synthesis procedure.

[1] M. Falco, M. Moreno, M. Di Carli, G. Tarquini, G. Meligrana, P. P. Prosini, C. Gerbaldi - Use of a crosslinked polymer electrolyte in Li/polysulphides cell at room-temperature – Manuscript in preparation.

# Graphene quantum dots@Benzoquinone@β-cyclodextrin systems for a dual mode sensing

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Host-Guest inclusion systems have aroused widespread interest, since they play important roles in molecular recognition, particularly in sensor devices. A class of host molecules that has often been used in sensing applications is that of the cyclodextrins, cyclic oligosaccharides that consist of six (α-cyclodextrin), seven (β-cyclodextrin, β-CD), or eight (γ-cyclodextrin) glucose moieties [1]. Depending on the cavity size, cyclodextrins have shown a selective affinity to a wide variety of molecules. For instance, in a previous work we succeeded to demonstrate the affinity of cyclodextrins for o-toluidine, a toxic water pollutant [2].

Various functional composites based on β-CD have been developed in the Literature. Particularly, Organic-Metal oxides nanocomposites have emerged as an outstanding surface modifier for sensors construction. However, the composite concept can even go beyond this approach by combining electroactive and fluorescent nanomaterials for the creation of a dual-mode sensing device.

Based on this, a novel system based on Graphene Quantum Dots GQDs@Benzoquinone@β-cyclodextrin as a host guest capturing probe was proposed. In this approach, EDC/NHS chemistry was used to covalently immobilize benzoquinone, the electroactive probe, via a cysteamine spacer on graphene quantum dots. Finally, β-cyclodextrin was added via a reductive amination. The optical properties of the synthesized GQDs were studied using UV-vis and PL spectroscopy. Structural and morphological characterizations were examined by the Transmission Electron Microscopy and Fourier-Transform InfraRed spectroscopy. Cyclic voltammetry, differential pulse voltammetry and electrical impedance spectroscopy were performed to investigate the surface modification at each step.

The system was firstly immobilized directly on glassy carbon electrode, then on fluorine tin oxide glass, bare or covered with a thin layer of titania film, to test the possibility of a dual mode sensing. In fact, the capturing of the target molecule will be accompanied by a simultaneous substantial variation in the benzoquinone electrochemical signal and an evident fluorescence quenching of GQDs.

[1] Niu, X., Mo, Z., Yang, X., Sun, M., Zhao, P., Li, Z., Ouyang, M., Liu, Z., Gao, H., Guo, R. and Liu, N., *Microchim. Acta*, 2018, **185**, 328.
[2] Pifferi, V., Cappelletti, G., Di Bari, C., Meroni, D., Spadavecchia, F., & Falciola, L., *Electrochim. Acta*, 2014, **146**, 403-410.

# Plasma activation of copper nanowires arrays for electrocatalytic sensing of nitrate in food and water

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In this research, we present improvements in a previously proposed electrochemical analysis of nitrate in natural water and food, by taking advantage of the detection capabilities of ensembles of copper nanowire electrodes (CuWNEEs). These electrodes are prepared by template potentiostatic deposition of copper within the nanopores of track-etched polycarbonate (PC) membranes [1]. The removal of the template membrane is a critical point to obtain a more active copper nanostructured surface suitable for nitrate determination. To this aim we propose to combine two etching treatments, i.e., a chemical etching with dichloromethane followed by a low-temperature atmospheric plasma under reduction conditions. In this way it is possible to prepare CuWNEEs completely exposed to the analytical solution and with improved electrocatalytic properties (Fig. 1).

Linear Sweep Voltammetry (LSV) was performed to record nitrate reduction (-0.2 to -0.8 V) in solution. In order to determine the correct peak potential value to perform quantitative analyses, the first derivative was calculated for each voltammogram. The proposed CuWNEE sensor was applied for nitrate analyses in river water and leafy vegetable samples. Analytical results obtained compare satisfactorily with those achieved by standard ion-chromatography [3].

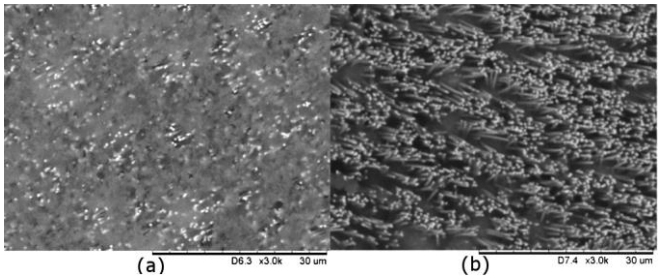


**Figure 1**: SEM images of CuWNEEs: (a) after chemical etching and (b) after chemical etching plus low-temperature atmospheric plasma.

[1] A. M. Stortini, L. M. Moretto, A. Mardegan, M. Ongaro and P. Ugo, Sens. Actuators B Chem., 2015, **207**, 186–192.
[2] A. Patelli, F. Mussano, P. Brun, T. Genova, E. Ambrosi, N. Michieli, G. Mattei, P. Scopece and L. Moroni, ACS Appl. Mater. Interfaces, 2018, **10**, 39512–39523.
[3] A. M. Stortini, S. Fabris, G. Saorin, E. Verga Falzacappa, L. M. Moretto and P. Ugo, Nanomaterials, 2019, **9**, 150-162.

# Volterra Series and the Generalization of the Equivalent Circuits

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Equivalent circuits are widely used in connection with electrochemical impedance spectroscopy. They are powerful tools because they can represent the studied reaction with few visual terms and convey the often much more complicated underlying physico-chemical equations. Also because of their relative simplicity they can be used directly to fit the impedance spectra and recover the value of their components.

An equivalent circuit represents the linearized part of the system which corresponds to the first order kernel ($h_1$) of a Volterra series expansion of the current *i(t)* given by a potential input *v(t)*:

$$i(t) = h_1(t) \otimes v(t) + \sum_{i=2}^{n} \int \mathrm{K} \int h_i(\tau_i, \mathrm{K}, \tau_n) \prod_{j}^{i} v(t-\tau_j) d\tau_j$$

However, this is a general equation and it can be applied to any electrochemical experiment.

As an example, the Figure 1 shows the typical Randles equivalent circuit. In the easiest case of an irreversible reaction, the Faradaic impedance can be replaced by a series combination of a resistor, a diode, a potential source, and a simplified Warburg element. They symbolize the charge transfer resistance, the Tafel law, the formal potential of the reaction, and the mass transport, respectively. This representation can already convey all the information of a Tafel slope.

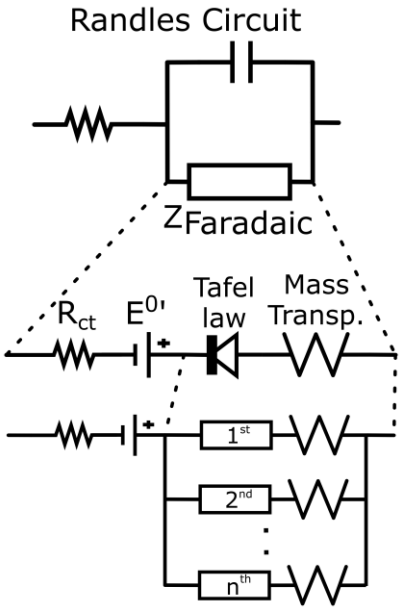


**Figure 1**: Expansion of the Randles circuit.

The only nonlinear term in this example is the diode which embodies the exponential dependence of the current on the potential. By the simple rules of the Volterra series [1] the Faradaic impedance can be expanded into simple terms. These terms represent the $n^{th}$ order expansion of the Tafel law followed by the mass transport element, a simplified Warburg element. Keeping only the first order (*n=1*) one gets the classic Randles circuit. With this representation it is possible to recreate a cyclic voltammetry, a polarization curve, or a more involved square-wave voltammetry. As in the case of the impedance spectroscopy, the “expanded” equivalent circuit can be used directly to fit the experimental results.

In this contribution, the basic idea of Volterra series is explained in terms of electrochemical systems and several example applications are reported.

[1] S. Boyd, L. O. Chua, C. A. Desoer, IMA J. Math. Control Inf., 1984, **1**, 243–282.

# $FeTiO_3$ as anode material for sodium ion batteries: from morphology control to decomposition

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Ilmenite $FeTiO_3$ has been proposed as conversion anode material for sodium ion batteries based on the possible conversion reaction:

$$FeTiO_3 + (2+x)Na^+ + 3e^- \rightarrow Fe + Na_xTiO_2 + Na_2O$$

characterized by high theoretical capacity. At the same time $FeTiO_3$ materials is highly appealing due to the chemical stability, non-toxicity, and huge availability, being one of the most abundant Ti-rich minerals on the Earth crust. Promising electrochemical performances have been reported for ilmenite underwent to hydrothermal process in basic conditions. This treatment with concentrated NaOH at moderate temperature was claimed to be necessary for the modification of the morphology of the ilmenite nanoparticles with the formation of nanoflowers with high surface area. The beneficial effect due to the morphology modification has been demonstrated by comparison of the electrochemical performances of the spherical particles and the nanoflowers particles [1,2]. However, it cannot be disregarded that the hydrothermal treatment in basic conditions can strongly affect not only the morphology but also the structure of the ilmenite. Hydroxide-based hydrothermal treatments have been recently proposed as a cost-effective and sustainable method for the decompositions of ilmenite and subsequent separation of titania at industrial scale [3].

Here we report the multi-technique investigation of the effect of the hydrothermal treatment of the structure, composition and stability of commercial ilmenite powders, finally arriving in the definition of the possible decomposition mechanism. The electrochemical performances of pristine and degraded ilmenite obtained under different experimental conditions are reported and revalued in the perspective of the degradation of the material into different phases.

[1] T. Tao, A. M. Glushenkov, H. Liu, Z. Liu, X. J. Dai, H. Chen, S. P. Ringer, Y. Chen, *Phys. Chem. C*, 2011, **115**, 17297-17302.
[2] T. Tao, A. M. Glushenkov, M. M. Rahman, Y. Chen, *Electrochem. Acta*, 2013, **108**, 127-134.
[3] Y. Liu, T. Qi, J. Chu, Q. Tong, Y. Zhang, *Int. J. Miner. Process.*, 2006, **81**, 79-84.

# EnABLES: European infrastructure powering the internet of things

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Most of the 1 trillion Internet of Things (IoT) devices expected in the world by 2025 will be wireless meaning a portable power source (e.g., battery) is needed. For many applications, it is critical for the battery to outlive the device it powers or, at the very least, significantly extend battery replacement intervals [1]. To do so, development of energy harvesting solutions and/or finding ways to reduce device power consumption are definitely required and developers from academia and industry need to work more together. EnABLES, a €5.2M EU research infrastructure project that started in January 2018, addresses this by building an ecosystem for collaboration to provide access to research infrastructure to allow 'self-sustaining' energy solutions to 'power the internet of things' based on technology pillars of energy harvesting, storage, micro-power management and their system integration. Simulations, data libraries, equipment and expertise access, along with feasibility studies, can all be undertaken in a fast-track manner via a Transnational Access (TA) and Virtual Access (VA) program. It also funds Joint Research Activities (JRAs) between partners that are designed to develop further TA and VA offerings.

The mission of EnABLES is to open up key research infrastructure in powering the IoT to all European researchers, from both academia and industry. Six research institutes together with five knowledge hubs are providing access to researchers to enable them to create 'self-sustaining' energy solutions to 'power the IoT'. This encompasses providing free-of-charge access to external academic and industry stakeholders, as well as fostering collaborations between the project partners to develop standardised and application-optimised materials, devices and systems. The ultimate goal of EnABLES is to create a 'starting community' to foster collaborations to accelerate technology development. This contribution outlines why EnABLES is needed, particularly for enabling researchers address key challenges of modern society, such as extending battery life of wireless IoT edge devices.

**Acknowledgements**
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[1] M. Falco, S. Ferrari, G.B. Appetecchi, and C. Gerbaldi, *Mol. Syst. Des. Eng.* 2019, DOI:10.1039/C9ME00050J.

# Facile synthesis of $SnO_2$/carbon anode material for high performance Li-ion battery

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Tin-based materials, especially tin dioxide, have been widely investigated as potential graphite substitute anodes of Li-ion batteries. In comparison to graphite, the $SnO_2$ anodes shows higher theoretical capacity of 1494 $mAhg^{-1}$ *vs.* 375 $mAhg^{-1}$. Furthermore, $SnO_2$ is also easy to obtain, inexpensive and environmentally friendly. Unfortunately, during the lithiation process (*i.e.* conversion and alloying reaction) tin dioxide suffers of a drastic volumetric expansion that induces surface cracking accompanied by an electrical contact loss with the current collector and subsequent capacity fading [1]. We synthesized $SnO_2$ nanoparticles (~5 nm) finely dispersed on a commercial carbon black matrix (Timcal C-Energy Super C45) by a facile method, since it is well known that the volume expansion during lithium insertion/extraction is reduced by decreasing the particle size of $SnO_2$ [2].

The samples were characterized by multi-technique approach in order to individuate the electrochemical performances (galvanostatic cycling and cyclic voltammetry) in relation with crystal structure, particle size, morphology, surface area and pore size distribution.

During charge/discharge, the $SnO_2$/C composite shows a high specific capacity around 1000 $mAhg^{-1}$ at rates of C/10, and a coulombic efficiency of 99.7% after more than 1000 cycles at 1C with a good capacity retention (Fig. 1). The presence of an intermediate species during lithiation process, and the consequent formation of different Li-Sn-O phases especially during the first cycles is proposed as responsible of this extra-capacity.

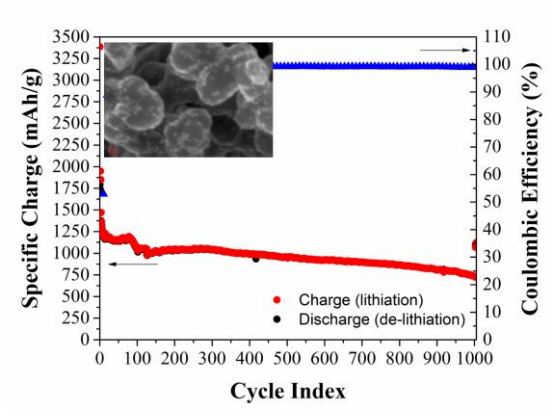


**Figure 1**: Galvanostatic charge and discharge at C/10 and 1C and FESEM micrography (insert).

[1] M. Winter, and J.O. Besenhard, *Electrochimica Acta*, 1999, **45**, 31-50.
[2] H. Song, X. Li, Y. Cui, D. Xiong, Y. Wang, J. Zeng, L. Dong, D. Li, X. Sun, *Int. j. hydrogen energy*, 2015, **40**, 14314-14321.

# Electrochemical conversion of carbon dioxide to formic acid at Sn and BDD cathodes

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Electrochemical reduction of $CO_2$ to useful compounds in the aqueous electrolyte has been actively investigated as alternative technologies to contribute to curbing the rising levels of $CO_2$ in the atmosphere. Many researchers have focused on the $CO_2$ reduction to formic acid, which is considered one of the main target-products owing to its usefulness for agriculture, chemical and pharmaceutical industry, and it is expected to be a good hydrogen storage medium for an upcoming $H_2$-energy-based society [1,2].

In the last few years, an increasing attention was devoted to the utilization of tin electrode for its low cost, low toxicity as well as the high selectivity towards the synthesis of formic acid [2]. Recently, it was shown that boron-doped diamond (BDD) used as working electrode could be a promising material for the production of formic acid by $CO_2$ reduction characterized by high stability and high faradic efficiency at low current density. In this work, the electrochemical conversion of $CO_2$ in water solution using both tin and BDD cathode was systematically investigated to compare the performances achieved at these two electrodes.

[1] M. Tomisaki, K. Natsui, N. Ikemiya, K. Nakata, and Y. Einaga, *ChemistrySelect*, 2018, **3.36**, 10209-10213.
[2] O. Scialdone, A. Galia, G. Lo Nero, F. Proietto, S. Sabatino, and B. Schiavo, *Electrochimica Acta*, 2016, **199**, 332-341.

# High valence transition metals doping of olivine cathode for superior energy and fast cycling lithium batteries

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In state-of-the-art lithium-based secondary batteries, the olivine materials of the type $LiMPO_4$ (M = Fe, Ni, Mn, or Co) and their derivatives are intensively studied as active materials for the cathode due to their high specific capacity, high efficiency, and long lifespan [1]. Nevertheless, these systems are still suffering from low values of working potential, specific energy and electronic conductivity. Further improvements must be undertaken in order to overcome these limitations and to respond to the energy demand in portable electronics, electric automotive, and stationary applications [2].

A method that can be followed to address these issues is to modulate the electrochemical performance of materials by changing their composition. Here, the study of the effects of the modification of the composition of a previously investigated high-performing multi-metal olivine material of the type $LiMPO_4$ (M = Fe, Ni, and Co) [3], is reported. High valence transition metal ions, *i.e.* V(V), Nb(IV), or Ta(IV), are exploited as dopant species.

Five samples are easily obtained by varying the parameters of synthesis. Stoichiometries are evaluated by means of Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Energy Dispersive X-Ray (EDX). A pool of techniques permits to get comphehensive information of samples in terms of morphology and size distribution (Scanning Electron Microscopy – SEM and High-Resolution Transmission Electron Microscopy- HR-TEM), structure (powder X-Ray Diffraction – XRD; FIR and MIR vibrational spectroscopy) and ionic diffusion (Electrochemical Impedance Spectroscopy - EIS).

Electrochemical measurements of samples involving Cyclic Voltammetry (CV), and charge/discharge tests at different current rates are carried out. In single-cell tests, the proposed materials show an enhanced performance in comparison to commercial cathodes. The working potential reaches an average value of 4.5 V *vs*. $Li/Li^+$ and a specific capacity and energy value of 149 $mAh \cdot g^{-1}$ and to 656 $mWh \cdot g^{-1}$, respectively. Finally, the insertion of high valence transition metals results in an improvement of the rate capability of the cathodes.

**References**

[1] B. Scrosati, J. Garche, *J. Power Sources* 2010, **195**, 2419-2430.
[2] B. Dunn, H. Kamath, J. M. Tarascon, *Science* 2011, **334**, 928-935.
[3] G. Pagot, F. Bertasi, G. Nawn, E. Negro, G. Carraro, D. Barreca, C. Maccato, S. Polizzi, V. Di Noto, *Adv. Funct. Mater.* 2015, **25**, 4032-4037.

# Pros and cons of highly active Cu-catalysts for atom transfer radical polymerization

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25 years after the invention of atom transfer radical polymerization (ATRP), efforts are still devoted to synthesizing new polydentate amine ligands (L) to achieve more ATRP active Cu/L complexes. Highly active catalysts will allow for i) performing ATRP of less activated monomers (i.e. monomers lacking radical stabilizing groups on the double bond), ii) using sub-ppm loadings of Cu [1]. However, it is predicted that more active catalysts are involved to a greater extent in side reactions, such as formation of organocopper intermediates and Cu-catalyzed radical termination (CRT) [2].

Cyclic voltammetry (CV) is the most common technique to assess the activity of ATRP catalysts: the more negative the standard reduction potential of $[Cu^{II}Br(L)]^+$ and the higher the ATRP equilibrium constant ($K_{ATRP}$) [3]. Moreover, the activation rate constant ($k_{act}$) of such active catalysts towards alkyl halide ATRP initiators can be measured only by digital simulations of experimental CVs (e.g., Fig. 1, right). Finally, a modification of the latter technique, combined to spectrophotometric analysis, provides kinetic and thermodynamic parameters for the formation of organocopper intermediates and CRT.

These methods have been applied herein to two families of L: i) tris-(2-pyridylmethyl)amine (TPMA) modified with electron-donating groups in para position onto the pyridyl rings (Fig. 1, left); ii) variously bridged tetraaza-macrocycles. The analyzed Cu/L complexes showed $k_{act}$ ≥ billion times higher than for seminal ATRP catalysts. Importantly, no direct correlation has been observed between increased ATRP activity and extent of side reactions. This suggests that some of these compounds can effectively allow for expanding the monomer scope and the sustainability of ATRP.

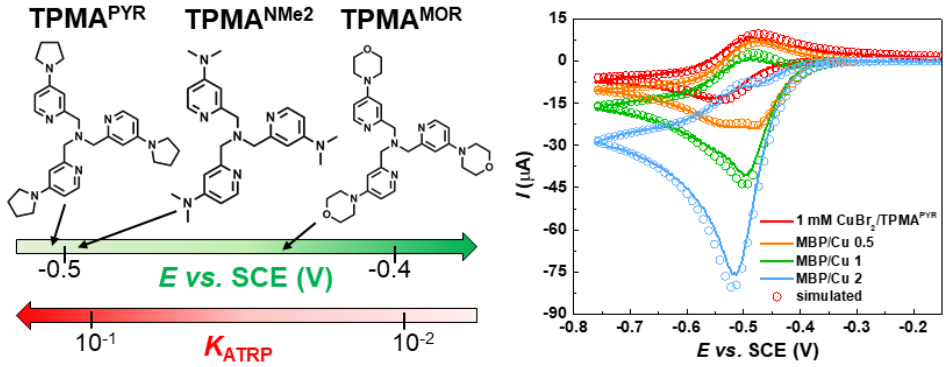


**Figure 1**: (left) measured standard reduction potential of $[Cu^{II}Br(L)]^+$ and predicted $K_{ATRP}$ in DMF, for showed L. (Right) Experimental and simulated CVs of $[Cu^{II}Br(TPMA^{PYR})]^+$ in DMF + 0.1 M $Et_4NBF_4$ + radical scavenger and/or methyl-2-bromopropionate (MBP).

[1] T. G. Ribelli, F. Lorandi, M. Fantin, K. Matyjaszewski *Macromol. Rapid Commun.*, 2019, **40**, 1800616.
[2] T. G. Ribelli, S. M. W. Rahaman, J.-C. Daran, P. Krys, K. Matyjaszewski, R. Poli, *Macromolecules*, 2016, **49**, 7749-7757.
[3] A. A. Isse, F. Lorandi, A. Gennaro, *Curr. Opin. Electrochem.*, 2019, **15**, 50-57.

# Innovative single-ion conducting solid electrolytes for safe, high performing energy storage devices

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The pressing demand for long-lasting, high-power portable electronics and the emerging large-scale diffusion of electric vehicles (EVs) and energy storage from renewable sources require batteries with lower cost and improved energy density, along with enhanced cycle life and safety [1]. State of the art Li-ion batteries (LIBs) currently on the market contain liquid electrolytes, which makes it difficult to design flexible cells, being also hazardous in terms of leakage and flammability. Within this context, a variety of solid-state electrolytes (*viz.*, polymeric, inorganic, composites thereof) have been investigated to date as, in principle, they enable extension of the operating temperature range of a device; this ensures higher safety even in the case of fire, together with high energy and power density, thus favouring the transition to all-solid-state batteries. In the field of polymer electrolytes, the development of innovative single-ion conductors has 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) [1].

Starting from the previous experience in the development of single-ion conducting copolymers based on the specifically designed lithium 1-[3-(methacryloyloxy)propylsulfonyl]-1-(trifluoromethylsulfonyl)imide anionic monomer [2], this work is focused on the challenging synthesis by RAFT of novel ionic monomer with polyethylene glycol (PEG) based side chains and block copolymers comprising polycarbonate units in the backbone chain.

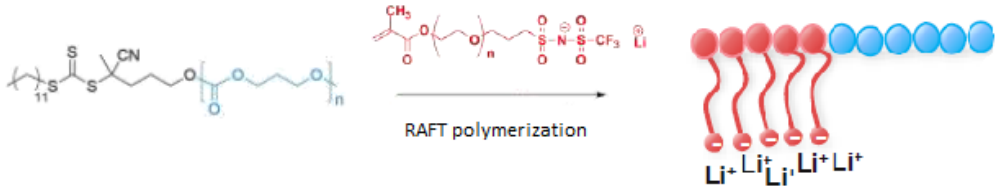


**Figure 4:** Synthesis of block copolymer by means of RAFT polymerization.

The development of new block copolymers with PEG pendant chains should impart high flexibility and enhanced $Li^+$ ion transport, while the introduction of polycarbonate in the main chain concurrently improve the electrochemical stability window (ESW ≥ 5 V) [3]. It would result in solid-state single-ion conducting polymer electrolytes that meet the request of high ionic mobility for ambient temperature practical application, with the chance to exploit their safe use with high voltage cathodes thus enhancing the overall device energy density.

[1] H. Zhang, C. Li, M. Piszcz, E. Coya, T. Rojo, L.M. Rodriguez-Martinez, M. Armand and Z. Zhou, *Chem. Soc. Rev.*, 2017,**46**, 797-815.
[2] L. Porcarelli, A.S. Shaplov, F. Bella, J.R. Nair, D. Mecerreyes, and C. Gerbaldi, *ACS En. Lett.,* 2016, **1**, 678-682.
[3] A.S. Shaplov, R. Marcilla, and D. Mecerreyes, *Electrochim. Acta*, 2015, **175**, 18-34.

# Graphene-modified $LiFePO_4$ cathodes for advanced Li-/Na-ion secondary batteries

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From the first understanding of the critical consequences associated with the uncontrolled rise of human emissions, the scientific community embraced the tough task of developing new and clean solutions to match the energy demand. In particular, the growing interest in electric (EV) and hybrid-electric vehicles (HEV) is one of the driving reasons to claim the importance of the current wide research over electrochemical storage technologies. In this scenario, Li-ion batteries (LIBs) are the reference commercial solution for the smart portable electronic market and the best choice for powering the new-born EV sector, because they combine high energy and power density with lightweight and design compactness, along with good cycling stability [1].

Recently, research over materials for electrochemical storage systems opened towards a new path, which combines the striking features of graphene in terms of ionic/electronic conductivity and mechanical stability [2], with the deep knowledge on insertion compounds that can host $Li^+$ ions, responsible for the electrochemical process between the two electrodes. The attention has been focused so far on materials for the negative electrode and several techniques have been developed to form hybrids of graphene/insertion compounds, which exploit the appealing properties of the two materials. Nevertheless, the cathode is particularly critical in determining the capacity of a Li-ion cell and enhancement of its characteristics can trigger huge profits in the overall performance of the battery.

Thus, it seemed worthy to explore the possible benefits that graphene might bring to a cathode material like lithium iron phosphate ($LiFePO_4$), obtained by mild hydrothermal synthesis [3], in terms of enhancement of $Li^+$ ion diffusion and electronic conductivity, particularly at high current rates. In addition, this work tries to look forward to the future of electrochemical storage beyond LIBs. In this sense, intense research efforts are made on developing sodium-ion batteries (NIBs), which own several similarities with LIBs technology, but rely on a cheaper, more abundant element, namely sodium, Na. Following this environmental sensitivity, $LiFePO_4$ has been used as pristine material to obtain the sodiated equivalent, $NaFePO_4$, that can combine the safety and stability advantages with the raliability and environmental advantages of Na. Two different methodologies, namely an electrochemical and a chemical process, have been used for the purpose and the electrochemical results analysed in details. Furthermore, both the resulting $NaFePO_4$ samples are coupled with commercial hard carbon anodes thus evaluating, for the first time, the practical application of this material in real Na-ion full-cell configuration.

[1] B. Scrosati and J. Garche, J. Power Sources, 2010, **195**, 2419-2430.
[2] A. K. Geim and K. S. Novoselov, *Nat. Mater.*, 2007, **6**, 183-191.
[3] G. Meligrana, C. Gerbaldi, A. Tuel, S. Bodoardo, and N. Penazzi, *J. Power Sources*, 2006, **160**, 516–522.

# Preparation of catalytic anodes for oxygen evolution by oxide-oxide galvanic exchange reactions

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Spinel oxides like $Co_3O_4$ and $NiCo_2O_4$ are known to be active catalysts for the oxygen evolution reaction (OER) in basic media. Our group has studied a new approach, based on oxide-oxide galvanic exchange reactions [1,2], which allows the conformal deposition of layers of the spinel oxides onto substrates with large surface area and high electronic conductivity. The porous substrates, consisting of Pb oxides, have been obtained by gas bubble templated electrodeposition, either directly by anodic oxidation of $Pb^{2+}$ to $PbO_2$, or indirectly via cathodic reduction of $Pb^{2+}$ to Pb and successive oxidation [3]. Both $PbO_2$ and Pb have been deposited by imposing current densities about 10 times higher than the limiting diffusion current of $Pb^{2+}$, thus causing extensive formation of either $O_2$ or $H_2$ bubbles.

The oxide-oxide galvanic exchange reactions have been performed at open circuit, by simple immersion of porous oxide substrates in acetate solutions containing $Co^{2+}$ or $Co^{2+}$ + $Ni^{2+}$ mixtures. In the latter case, we found that the Co/Ni atomic ratio in the deposit was always higher than the $Co^{2+}/Ni^{2+}$ ratio in solution. To obtain the desired Co/Ni ratio of 2, solutions with a $Co^{2+}/Ni^{2+}$ concentration ratio 0.2 were used. The growth rate of mixed oxide layers was intermediate between those of individual oxides.

The most active catalysts for the OER were those grown on substrates prepared via cathodic deposition and oxidation, which had a more favourable morphology. No major differences were observed between $Co_3O_4$ and $NiCo_2O_4$.

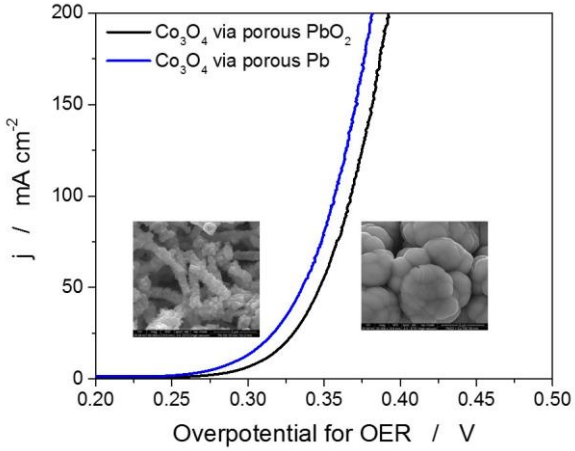


**Figure 1**: Current-overpotential curves for $Co_3O_4$-modified porous Pb oxide layers.

[1] N. Comisso, S. Cattarin, P. Guerriero, L. Mattarozzi, M. Musiani, E. Verlato, *Electrochem. Commun*. 2016, **73**, 59-62.

[2] N. Comisso, L. Armelao, S. Cattarin, P. Guerriero, L. Mattarozzi, M. Musiani, M. Rancan, L. Vázquez-Gómez, E. Verlato, *Electrochim. Acta* 2017, **253**, 11-20.

[3] N. Comisso, L. Armelao, S. Cattarin, P. Guerriero, L. Mattarozzi, M. Musiani, M. Rancan, L. Vázquez-Gómez, E. Verlato, *Electrochimica Acta*, 2018, **273**, 454-461.

# Aluminium anodization from ionic liquid and deep eutectic solvent: alternative routes to traditional surface treatment

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Among the emerging non-aqueous solvents suitable for industrial applications Deep Eutectic Solvents (DESs) [1] and Ionic Liquids (ILs) [2] are gaining tremendous interest in owe to their "green" characteristics, i.e. to be ecologically safe, nontoxic, biodegradable and to be easily prepared from renewable sources [3]. The present study funded by Regione Toscana within POR Creo FESR 2014-2020, "EL4ALL" project, deals with the electrochemical growth of passive layer of aluminum oxide in ILs and DESs media. The obtained passive layers were characterized as a function of the electrochemical media, and operating parameters, via SEM microscopy and XPS spectroscopy. Their efficiency to mitigate corrosion phenomena were assessed by means of electrochemical and free corrosion tests in chloride–bearing aerated solutions, finding similar, if not better performances, respect to the traditional aqueous acidic anodization.

[1] Y. Marcus, *Deep Eutectic Solvents* (e-Book) Springer Nature Switzerland AG 2019
[2] A.I. Siriwardana *Industrial Applications of Ionic Liquids.* In: Torriero A. (eds) *Electrochemistry in Ionic Liquids.* 2015 Springer, Cham.
[3] Q.-P. Liu, X.-D. Hou, N. Li, M.-H. Zong. *Green Chem.* 2012, **14**. 304-307.

# Electrodeposition and characterization of nanosized metallic copper from deep eutectic solvent

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Deep eutectic solvents (DESs) are widely acknowledged as a new class of electrochemical media [1,2]. DESs are non-aqueous solvents formed from an eutectic mixture of Lewis and Brønsted acids and bases, mainly obtained from natural sources, characterized by low cost and low toxicity, high electrical conductivity and low melting point. These characteristics make them potentially suitable as green and sustainable solvents for niche industrial applications such as the electrodeposition of metals free from hydrogen embrittlement [3]. The present study funded by Regione Toscana within POR Creo FESR 2014-2020, “EL4ALL” project, deals with the electrodeposition of copper from Ethaline 200 (Choline Chloride/Ethylene Glycol molar ratio 1:2) under ambient atmosphere. The DES was prepared by mixing stoichiometric amount of ChCl and Ethylene Glycol and adding different amounts of copper chloride to obtain [$Cu^{2+}$] ranging from 0.5 to 20 mM. These mixtures were electrochemically characterized by cyclic voltammetry (Fig 1) and the morphology, and structure of the obtained electrodeposits, were evaluated via SEM microscopy (Fig. 1), XRD and XPS spectroscopy as function of the working parameters.

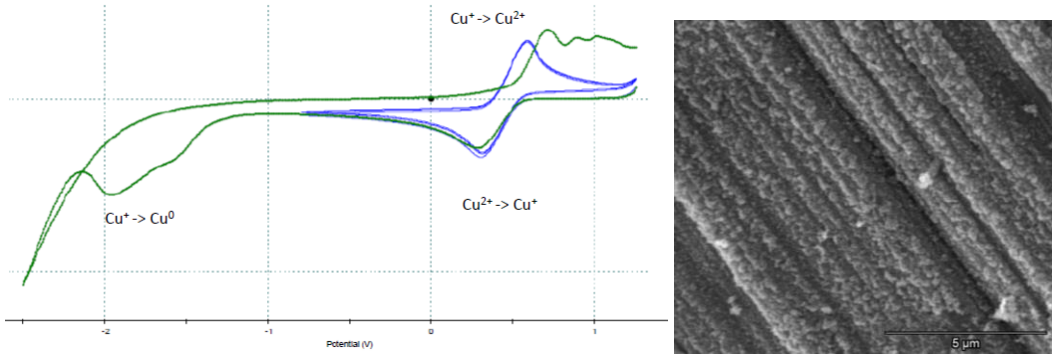


**Figure 1**: (left) CVs obtained in a mixture of Ethaline 200 and CuCl2 $10^{-3}$ M in open air at 60°C and (right) SEM image of the copper deposit on stainless steel wire.

[1] E. L. Smith, A. P. Abbott and K. S. Ryder, *Chem. Rew.*, 2014, **114**, 11060–11082.
[2] P. Valverde, T.A. Green and S. Roy, *ECS Tran.*, 2017, **77**, 859–864.
[3] C.D. Gu, Y.H. You,X.L. Wang and J.P.Tu, *Surf. Coat.Tech* 2012, **209**, 117-123.

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# Electrochemical studies of new donor-acceptor oligothiophenes

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The term “Organic Electronics” is used to indicate the vast field of science regarding the use of organic materials (either “small” molecules, oligomers or polymers) in electronic devices [1]. Thiophene derivatives surely fall in the class of the most studied (and used) organic semiconductor materials, probably because of their excellent charge transport properties and well-established synthetic procedures.

These requisites are fulfilled by oligothiophene derivatives: in many cases they possess better characteristics (physical, optical, electronic and self-assembly properties, possibility to work in solution, ease of purification, low-cost synthetic procedures, and so on) over their polymeric counterparts [2].

In particular, thiophene oligomers possess extended π-electron delocalization along the backbone and are good hole-transporting materials, and they can be synthesized with different Donor-Acceptor architectures in order to fine tuning their optical and electrochemical properties [3].

Electrochemical studies on a series of new conjugated oligothiophene derivatives (Fig. 1) are reported. The molecular architectures (D-π-A and A-π-D-π-A) of these compounds present different donor cores (thiophene, bithiophene) with different numbers of 3-octylthiophenes units (that act as π-bridge and solubilizing components). The acceptor end groups adopted were, in all the cases, ethyl cyanoacrylate units. The results from voltammetric experiments confirm the close relationship between the structure of these oligothiophenes and their electrochemical behaviour.

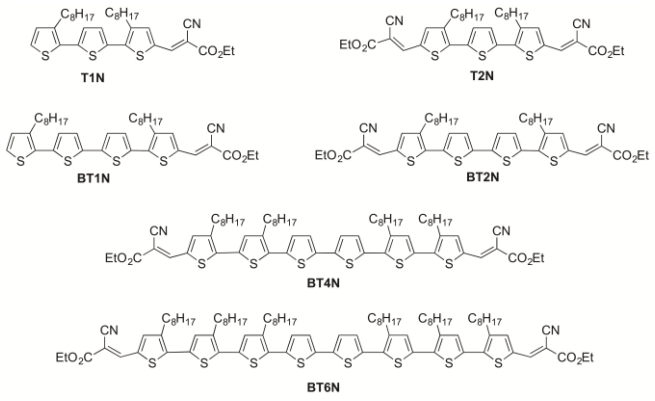


**Figure 1**: Structures of studied oligothiophenes.

[1] *Organic Electronics II: More Materials and Applications* (Ed.: H. Klauk), Wiley-VCH, Weinheim, 2012.
[2] *Electronic Materials: The Oligomer Approach* (Eds.: K. Müllen, G. Wegner), Wiley-VCH, Weinheim, 1998.
[3] F. Pandolfi, D. Rocco and L. Mattiello, *Org. Biomol. Chem.* 2019, **17**, 3018-3025.

# Study of the oxygen reduction reaction in alkaline media of functionalized carbon nanotubes

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Functionalized carbon nanotubes are an important alternative to platinum-based catalysts, which are considered to be the most efficient electrocatalysts on the oxygen reduction reaction (ORR).

In this work, multi-walled carbon nanotubes have been functionalized with an azamacrocycle adsorbed on the surface by π-π interactions. The azamacrocyclic ligand (HL2) consists of a pyrimidine acting as an anchorage site, a spacer group and a terminal macrocycle, which forms complexes with Ni(II) and Pd(II) [1].

For each sample of functionalized carbon nanotubes we determined the onset potential (Eon) of the oxygen reduction reaction and the number of electrons exchanged. The latter allows the evaluation of the reaction mechanism, which can be the reduction to water (4 electrons per molecule of $O_2$) or to hydrogen peroxide (2 electrons). The samples were treated by preparing dispersions (inks) and tested with electroanalytical techniques, such as cyclic voltammetry (CV), Rotating Disk Electrode (RDE) and Rotating Ring and Disk Electrode (RRDE). The number of electrons exchanged was determined using the Koutecky-Levich model and the RRDE method. In the RRDE method the Collection Efficiency Number was determined experimentally using a known redox couple ($Fe^{3+}/Fe^{2+}$) [2].

The study of the catalytic activity of the functionalized carbon nanotubes confirmed that there is a direct correlation between the catalytic efficiency and the concentration of palladium complexed by the macrocycle on the nanotubes surface. Instead, the presence of Nickel complex on carbon nanotubes does not contribute to the catalytic efficiency on ORR. Nanotubes containing a lower quantity of Pd(II) shows a lower catalytic activity. The results are encouraging if we consider the 30% decrease of the amount of the precious metal inside the catalyst. These results provide the basis for further developments in order to improve the efficiency of future low-cost catalysts, which could be used for renewable energy technologies.

[1] M. Savastano, P. Arranz-Mascarós, C. Bazzicalupi, M. P. Clares, M. L. Godino-Salido, M. D. Guitiérrez-Valero, M. Inclán, A. Bianchi, E. García-España, R. López-Garzón, *J. Catal.*, 2017, **353**, 239-249.
[2] M. Passaponti, M. Savastano, M. Paz Clares, M. Inclán, A. Lavacchi, A. Bianchi, E. García-España, and M. Innocenti, *Inorg. Chem.*, 2018, **57**, 14484-14488.

# Chiroptical redox switching of azoniahelicenes

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Condensed aromatic helicenes with quaternary nitrogen atoms have a spiral shape and are called helquats, N-heterohelicenia or azoniahelicenes. Recently, helquats were introduced as a new link between helicenes and viologens [1]. Electrochemical switching of the redox state of a di-cationic helquat [5]HQ can reversibly invert the sign of ECD signal (Fig.1 left). Heterogeneous electron transfer changes electronic structure and hence the interaction with the electric vector of the radiation [2].

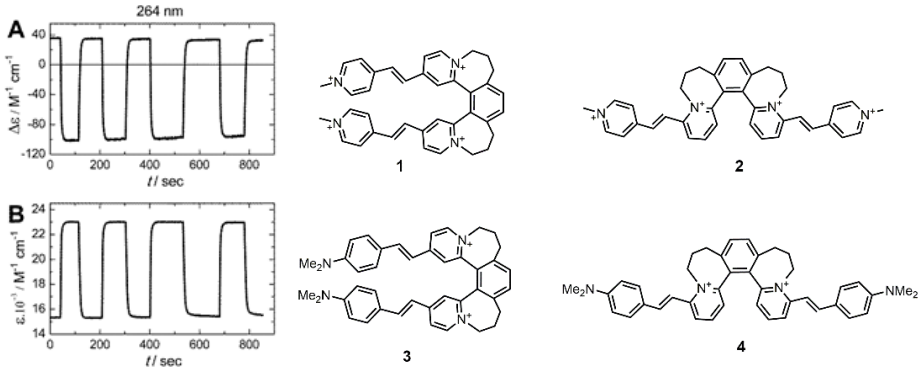


**Figure 1: Left graphs:** Redox switching of **ECD** response (A) and the corresponding changes in UV-vis absorption (B) of [5]HQ. Switching is due to application of potential steps between the oxidation and the full reduction. **Right scheme:** Tetra-cationic (**1,2**) and di-cationic (**3,4**) helquats containing seven-membred rings.

Di-cationic helquats containing two seven-membered rings are irreversibly reduced in two steps. Substitution by redox active ethenylpyridinium in α or γ position with respect to nitrogen atoms of helquat core (**1**, **2**) yields tetra-cationic derivatives with reversible redox steps and communicating redox centers (Fig.1 right). Redox inactive substituents in di-cationic azoniahelicenes(**3**, **4**) retain redox irreversibility. Redox switching of ECD of tetra-cationic enantiomers was observed.

Strong product adsorption slows down the ECD time change of **1** to **4**. Quantum chemical calculations (DFT) indicate that the first electron transfer step of tetra-cationic derivative substituted in γ position yields a folded structure, which favors internal donor-acceptor interaction. Switching of tetra-cationic helquats and electrochemistry will be presented [3].

**Acknowledgement.** This research was supported by the Czech Science Foundation (18-04682S) and by the Czech Academy of Sciences (61388963, 61388955).

[1] L. Adriaenssens, L. Severa, T. Šálová, I. Císařová, R. Pohl, D. Šaman, S. V. Rocha, N. S. Finney, L. Pospíšil, P. Slavíček, F. Teplý *Chem. Eur. J.* 2009, **15**, 1072–1076.

[2] L. Pospíšil, L. Bednárová, P. Štěpánek, P. Slavíček, J. Vávra, M. Hromadová, H. Dlouhá, J. Tarábek, F. Teplý *J. Am. Chem. Soc*. 2014, **136,** 10826–10829.

[3] I. Rončević, L. Severa, P.E. Reyes-Gutierrez, L. Bednárová, M. Hromadová, L. Pospíšil *ChemElectroChem,* 2019, http://dx.doi.org/10.1002/celc.201900204.

# Electrodeposition of compact Ag-Ni alloys from concentrated chloride baths

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Ag-Ni alloys or bimetallic structures are arising much interest in the search for efficient and cheap materials in many applications, from electrical devices to (electro)catalysis [1]. Ag and Ni crystallize both in the fcc structure, but are immiscible in the solid state at equilibrium. Electrodeposition of Ag-Ni is complicated by the large difference in redox potentials ($E^0$ = 0.799 V and $E^0$ = -0.25 V for Ag and Ni, resp.), leading to formation of porous deposits in the absence of suitable additives [2]. Deposition baths should provide a complexation of Ag ions shifting closer the two reduction processes. Cyanide baths work well for the deposition of Ag alloys [3], but pose a severe safety hazard. Fairly good results are obtained using thiourea baths, but the obtained layers include up to 20 at% of sulfur [2].

The use of concentrated chloride baths as an alternative to cyanide for the deposition of Ag-Pt and Ag-Pd alloys is well established [3]. The basis of these approaches is that silver and several other metal ions form complexes in concentrated halide media and may be dissolved in suitable concentrations. To the best of our knowledge, deposition of Ag-Ni alloys from this medium has not been reported. The approach appears promising since chloride complexes with Ag ions are more stable than those with Ni ions, promoting co-deposition.

Linear sweep voltammetries (LSVs) in the concentrated chloride medium (Fig. 1a) show a short diffusion plateau of Ag deposition, and a subsequent plateau of Ag-Ni deposition preceding $H_2$ evolution. Galvanostatic depositions produce compact Ag-Ni layers with globular microscopic morphology (Fig. 1b). Formation of metastable solid solutions is investigated. The achievement of this approach is the deposition of compact, sulfur-free Ag-Ni layers [2], from a "green" aqueous bath devoid of toxic species like thiourea or cyanide.

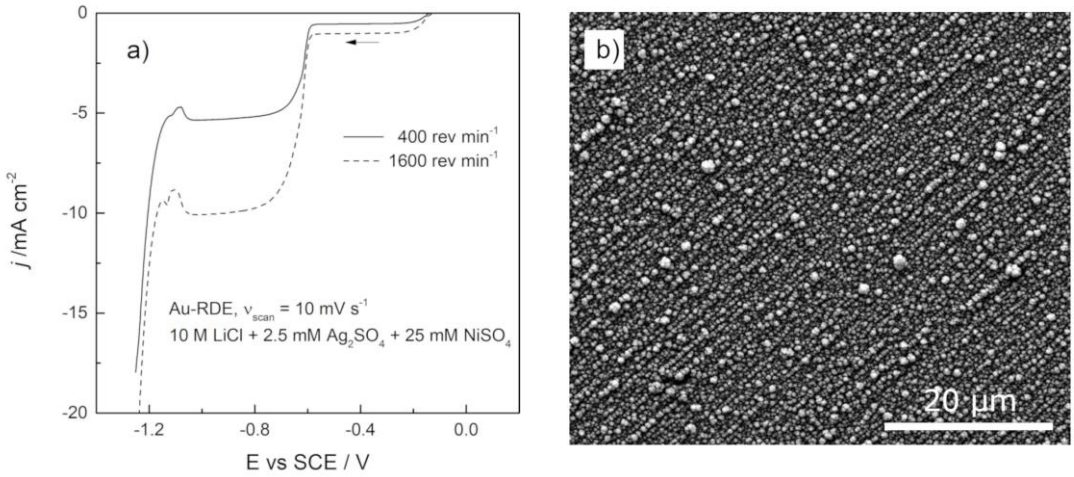


**Fig. 1**: a) LSVs for the deposition of Ag and Ag-Ni alloy from a conc. chloride medium; b) SEM image of a $Ag_{30}Ni_{70}$ deposit obtained by constant current deposition.

[1] B. Vanrenterghem, A. Papaderakis, S. Sotiropoulos, D. Tsiplakides, S. Balomenou, S. Bals, T. Breugelmans, *Electrochim. Acta* 2016, **196**, 756-768.
[2] D. Liang, Z. Liu, R.D. Hilty, G. Zangari, *Electrochim. Acta* 2012, **82**, 82-89.
[3] A. Brenner, Electrodeposition of alloys, Academic Press, New York, 1963, Ch. 19.

# Electrochemically mediated atom transfer radical polymerization of *N,N*-dimethylacrylamide

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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 $P_nX$ ($K_{ATRP}$<<1), thus $[P_n^\bullet]$ is very low during polymerization, drastically reducing the rate of radical-radical terminations [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 stopping and restarting the reaction on demand [2].

Here we report *e*ATRP of *N,N*-dimethylacrylamide (DMAA) in water. The polymerization of this monomer is somewhat challenging due to some side-reactions, yet not fully clarified. The polymerization was triggered by applying a constant electrolysis potential ($E_{app}$, potentiostatic polymerization) or steps of constant current ($i_{app}$, galvanostatic polymerization). The process was studied by changing the temperature, applied potential, degree of polymerization, initiator, and type and concentration of supporting electrolyte (NaBr *vs* NaCl 0.05-0.1 M). It was found that the best conditions for the process are: 1) use of aliphatic alkyl amine ligands ($Me_6$TREN or TREN) that form Cu complexes able to quickly reactivate the dormant C-X bond (X = Br, Cl); 2) low temperature ($T$ = 273 K) to impede undesired side reactions; 3) moderate monomer concentration (10-25% DMAA v/v) to avoid excessive viscosity; 4) relatively fast regeneration of $[Cu^IL]^+$ in solution. With optimized conditions, the reactions proceeded extremely rapidly (>99% conv. in ~30 min) with narrow molecular weight distribution ($M_w/M_n$ = 1.20-1.30). Linear homopolymers of poly(*N,N*-dimethylacrylamide) were obtained with molecular weight up to 240 kDa. Galvanostatic and potentiostatic polymerizations occurred in a very similar manner when $Me_6$TREN was used as ligand.

[1] K. Matyjaszewski, Macromolecules **45** (2012) 4015–4039.
[2] P. Chmielarz, M. Fantin, S. Park, A. A. Isse, A. Gennaro, A. J. D. Magenau, A. Sobkowiak and K. Matyjaszewski, *Prog. Polym. Sci.* **69** (2017) 47–78.

# Anodic titanium dioxide nanotube arrays for electroanalytical purposes

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Titanium dioxide ($TiO_2$) is widely used in the commercial manufacturing of different products (sun-blockers, paints, sensors, photocatalysts, solar cells, electrochromic devices, drug delivery systems) since, among transition metal oxides, it presents a broad range of functional properties: chemical inertness, corrosion-resistance and stability, biocompatibility, electrical and optical features.

More recently, one-dimensional (1D) $TiO_2$ nanostructures, such as arrays of nanowires, nanorods, and particularly nanotubes (NTs), are widely investigated as promising morphologies due to the 1D morphology that combines a relatively high surface area with a directional charge transport, providing high electron mobility rate or quantum confinement effects [1].

In the field of sensors, a lot of efforts has been made for the optimization and production of gas sensors based on titanium dioxide nanotubes [2], but only few examples about the detection of analytes in liquid phase can be found in the literature [3].

Here, a deep study of the electrochemical behavior of electrochemically anodized self-organized titanium dioxide nanotubes is presented with the focus on the possible electroanalytical applications. The calcination procedure and the length of the nanotubes are taken into considerations as key parameters for device performances. Molecular probes with different properties (negatively positively or not charged, different steric hindrance or hydrodynamic radius, organic or inorganic nature) are chosen to characterize the systems. A study of electroanalytical conditions (different pH and ionic strength of the electrolyte solution) is performed for a deep understanding of nanotubes electroanalytical features.

[1] Y. Fu, and A. Mo, *Nanoscale Research Letters*, 2018, **13**, 187.
[2] V. Galstyan, E. Comini, G. Faglia and G. Sberveglieri, *Sensors*, 2013, **13**, 14813-14838.
[3] S.S. Mandal, K.K. Narayan and A.J. Bhattacharyya, *J. Mater. Chem. B*, 2013, **1**, 3051.

# Single molecule conductance of electroactive helquats. Solvent effect

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Charge transfer and charge transport characteristics of a series of helical extended diquats (helquats) that differ in the number of rings n = 5,6 and 7 (see Fig.1 left) are presented. Helquats represent fast electron transfer systems that can be reversibly reduced in two one electron steps [1,2]. Their electrochemical properties were studied by polarography, cyclic voltammetry and by phase-sensitive AC methods. Their single molecule charge transport characteristics were studied in the electrode-molecule-electrode arrangement in two different solvents (water and 1,3,5-trimethylbenzene (TMB)) by scanning tunneling microscopy break junction (STM BJ) technique. Electrochemistry of all three helquats is similar giving two one electron waves (see cyclic voltammogram in Fig.1 middle). Standard redox potential $E^0$ of the first electron transfer step for [5]helquat was found to be –1.248 V, for [6]helquat –1.103 V and for [7]helquat –1.054 V versus ferrocene/ferrocenium internal standard. This trend is preserved for the second electron transfer step as well. Thus it is energetically less demanding to reduce [7]helquat compared to [5]helquat. Charge transfer rate constants are slower for the first reduction step compared to the second step for the entire series. The rate constants of both charge transfer steps increase from [5]helquat to [7]helquat.

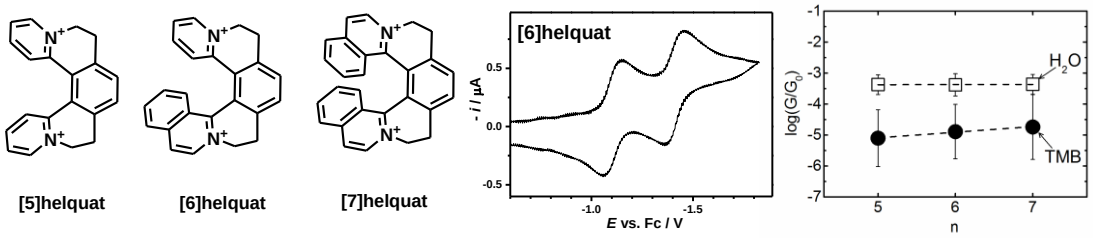


**Figure 1**: Chemical structure of helquats (left), representative cyclic voltammogram (middle) and single molecule conductance on the logarithmic scale in different solvents (right).

Two solvents selected for single molecule conductance measurements represent two extremes in the polarity. Thus the role of the environment on the charge transport in non-covalent molecular junctions can be addressed (Fig. 1 right). Single molecule junctions formed in the aqueous environment are stable and possess defined helquat geometry, but transport is dominated by a through-solvent tunneling. In trimethylbenzene the single molecule conductance is dominated by tunneling through the molecule and theoretical computations suggest LUMO orbital as the charge transporting orbital. Molecule with faster charge transfer rate constants (less negative $E^0$) has higher single molecule conductance and single molecule conductance values correlate with the electrochemical properties.

This research was supported by the Czech Science Foundation GAČR (project 18-04682S).

[1] L. Pospíšil, F. Teplý, M. Gál, L. Adriaenssens, M. Horáček and L. Severa, *Phys. Chem. Chem. Phys.* 2010, **12**, 1550–1556.
[2] L. Adriaenssens, L. Severa, T. Šálová, I. Císařová, R. Pohl, D. Šaman, S. V. Rocha, N. S. Finney, L. Pospíšil, P. Slavíček, and F. Teplý, *Chem. Eur. J.* 2009, **15**, 1072–1076.

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

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

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

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

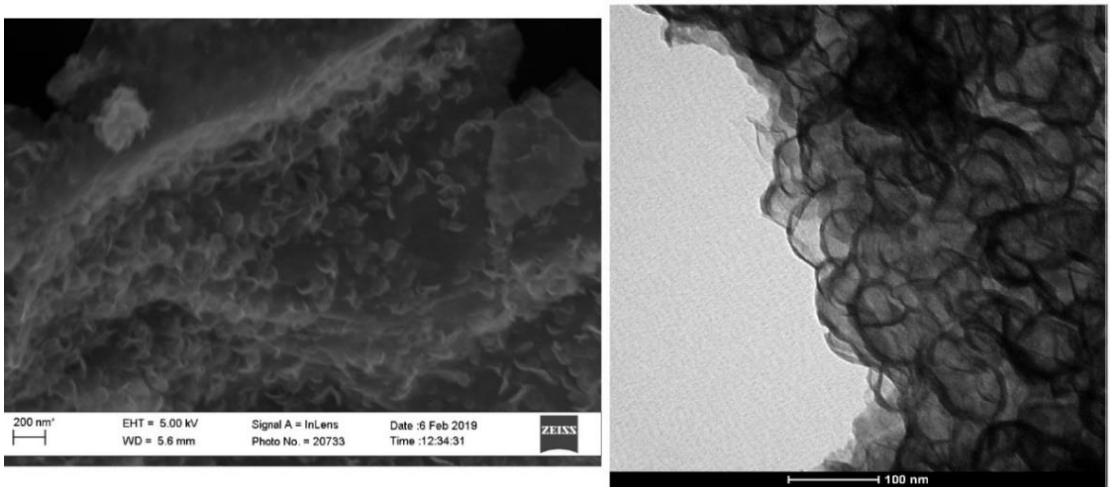


**Figure 5:** Electronic microscopy images of G-$MoS_{0.9}Se_{1.1}$ systems obtained by hydrothermal synthesis: Left, SEM of nano-flowers hybrid; Right, TEM image of inorganic fullerene-like material. Stoichiometry is evaluated by XPS.

[1] Honglin Li, Ke Yu, Zheng Tang, and Ziqiang Zhu, *ACS Appl. Mater. Interfaces,* 2016, **8**, 29442−29451.
[2] Qiufang Gong, Liang Cheng†, Changhai Liu, Mei Zhang, Qingliang Feng, Hualin Ye, Min Zeng, Liming Xie, Zhuang Liu, and Yanguang Li, *ACS Catal*., 2015, **5**, 2213−2219.
[3] Wenting Zhang, Xiaodong Li, Tongtong Jiang, Jiangluqi Song, Yue Lin, Lixin Zhu and Xiaoliang Xu, *Nanoscale*, 2015, **7**, 13554–13560.

# A sub-stoichiometric calcium titanate $CaTiO_{3-\delta}$ additive to enhance the oxygen reduction reaction catalytic activity

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Platinum scarcity and its high cost have led to the requirement of alternative materials catalysing the Oxygen Reduction Reaction (ORR), which is the main rate-determining step occurring in electrochemical devices, including metal-air batteries and fuel cells [1,2].

Herein, we report a study on a sub-stoichiometric Calcium Titanate CaTiO3−δ (CTO) compound, having an orthorhombic phase, originally used as promoter for the ORR, in order to reduce the Pt loading and improve its electrocatalytic activity toward a 4-electron pathway. CTO was synthesized by a novel sol-gel method and characterized through X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and surface area analysis.

Composite electrodes based on Pt/C with different amounts of CTO were prepared and their catalytic activity was investigated by Rotating Disk Electrode (RDE). A commercial Pt/C catalyst was used as reference. The obtained results proved a higher catalytic activity for the composite electrode, with respect to pure Pt/C, in terms of electrochemically active surface area, oxygen reduction current density, onset potential and stability, associated to high corrosion resistance.

[1] M. Chen, L. Wang, H.Yang, S. Zhao, H. Xu, G. Wu, *J. Power Sources*, 2018, **375**, 277
[2] C. Lo Vecchio, A.S. Aricò, G. Monforte, V. Baglio, *Renew. Energy*, 2018, **120**, 342

# Nickel-based structured catalyst for indirect internal reforming of methane in solid oxide fuel cells

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Solid oxide fuel cells (SOFCs) have received considerable attention mainly for the high conversion efficiency and the capability of being powered by methane or biogas. Among the different routes for methane-syngas conversion, the dry reforming of methane (DRM) shows the combined advantages of syngas production and $CO_2$ utilization. Besides it is extremely endothermic and it requires temperatures as high as those of operating SOFCs. Thus, SOFCs can operate in indirect internal reforming mode: simultaneously performing DRM reaction in their anode sides and, partly, compensating the energy necessary for the reforming with the heat released during the electro-oxidation. Nickel supported on samarium doped ceria (SDC) is a highly performing anodic material showing a remarkable electro-catalytic activity due to the presence of oxygen vacancies that promote the $CH_4$ and $CO_2$ activation for carbon suppression [1].

Moreover, open-cell metallic foams are promising for application as catalyst carriers for endothermic reactions. Their high porosity and irregular structure ensure an intensive gas reaction with the catalytic surface and a high mass/heat transfer.

In the present work, 5wt% Ni-$Ce_{0.85}Sm_{0.15}O_{2-\delta}$ catalyst has been synthesized and supported on NiCrAl alloy foam by wash-coating method. Microstructural analysis of Ni-SDC/NiCrAl structured catalyst displayed a homogeneous catalytic layer (Fig. 1a). Catalytic tests were performed with a $CH_4$:$CO_2$ 1:1 mixture. $CH_4$ conversion was 87% at 800°C, close to thermodynamic equilibrium, and the yield of $H_2$ was 76%, indicating that the structured catalyst is suitable for indirect internal reforming in SOFCs (Fig. 1b).

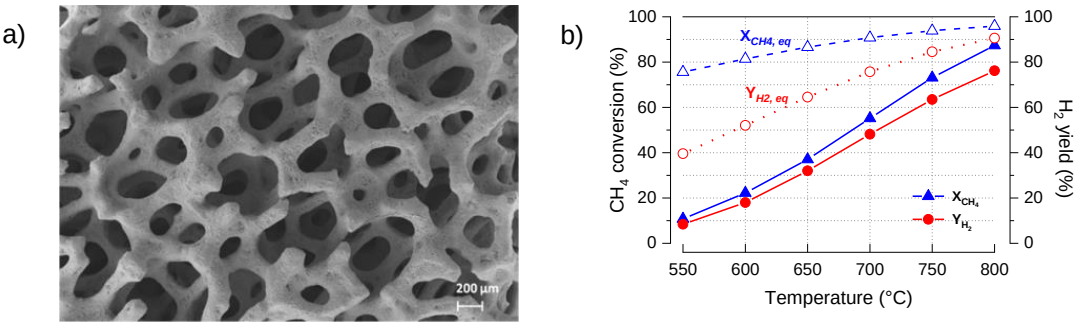


**Figure 1**: a) SEM image of NiCrAl foam coated with Ni-SDC; b) Catalytic measurements.

[1] I. Luisetto, S. Tuti, C. Romano, M. Boaro, E. Di Bartolomeo, *Journal of $CO_2$ Utilization*, 2019, **30**, 63-78.

# Cobalt electrodeposition on chars obtained from pyrolysis of waste tires: a study on the catalytic efficiency in ORR via hydrodynamic voltammetry

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In recent years the fossil sources dependence of our society for both fuels and essential raw materials and the global warming have led to an increasing use of renewable sources and waste valorization processes. Nowadays the outstanding increase in the number of vehicles worldwide is among the most environmental problem because of the emission of harmful pollutants and the solid wastes disposal, in particular the removal of the used tires. There are several technologies for tires recycling. Thermal treatments may be used such as pyrolysis: a thermal decomposition process performed at higher temperature in an inert atmosphere which allows the transformation of complex substances in simple molecules. These products can be easily stored, transported and used as a source of chemicals and energy. Among several heating technologies and apparatus used in pyrolysis process, microwave assisted pyrolysis (MAP) attracted attention, in recent years, due to the considerable advantages of this technology over conventional pyrolysis process [1]. The presence of specific metals together with a high carbon content are essential requirements for catalysts for ORR [2]. Selective electrodeposition of metal such as Cobalt on chars from MAP allows a better catalytic efficiency. A study on catalytic efficiency in alkaline environment has been led using Rotating Ring-Disk Electrode (RRDE) hydrodynamic electrochemical technique., In particular, electrochemical analysis of Co-chars catalyst showed good results as onset potential (Eon) and electrons number exchange for O2 molecule.

[1] A. Undri, B. Sacchi, E. Cantisani, N. Toccafondi, L. Rosi, M. Frediani, P. Frediani, *J. Anal. Appl. Pyrolysis*. 104 (2013) 396–404.
[2] M. Passaponti, L. Rosi, M. Savastano, W. Giurlani, H.A. Miller, A. Lavacchi, J. Filippi, G. Zangari, F. Vizza, M. Innocenti, *J. Power Sources*. 427 (2019) 85–90.

# Influence of A' cation substitution on promotion of supercapacitance of rare earth/$CoO_3$-based spray pyrolytic perovskite microspheres

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Considerable promotion of A' substituted $AA'BO_3$ perovskite-like structure of rare earth–$CoO_3$ composite supercapacitive performances is reported. The influence of cation substitution in perovskite structure on supercapacitance was also investigated. Spherical, sub-µm-sized, regular spheres of $La_{0.6}Sr_{0.4}CoO_3$ (LSCO) and $LaCoO_3$ (LCO) were synthesized by ultrasonic spray pyrolysis under different temperatures. The synthesis of Co-based oxide, namely $La_{0.6}Sr_{0.4}CoO_3$ (LSCO), was performed within single-step USP procedure. As starting precursors aqueous solutions with 0.10 M concentration of $La(NO_3)_3 \cdot 6H_2O$ (99.9% rare earth oxide), $Sr(NO_3)_2$ (99 %) and $Co(NO_3)_2$ (98%) were used for the synthesis of LSCO, and aqueous solutions with 0.10 M concentration of $La(NO_3)_3 \cdot 6H_2O$ (99.9% rare earth oxide) and $Co(NO_3)_2$ (98%) were used for synthesis of LCO. The solution for the LSCO and LCO synthesis were prepared by mixing starting precursor solutions in stoichiometric mole ratios. Synthesis temperatures were adjusted and kept to 600°C and 800°C.

LSCO and LCO composites were investigated for their supercapacitive performances in alkaline solution. Microstructure and surface morphology were studied by Scanning Electron Microscopy and X-ray Diffraction measurements. Electrochemical characterization of all LCO and LSCO samples included cyclic voltammetry (CV), galvanostatic charge-discharge (G-C/DC) and electrochemical impedance spectroscopy (EIS). The registered capacitance for LSCO reveals the promoting influence of Sr on A' position in perovskite on capacitance. The EIS analysis showed that Sr catalyzes the redox transition of Co species, with simultaneous proportional increase in capacitive abilities. This intrinsic interactive promotion introduces LSCO composite as unique supercapacitive material. Synthesis temperature plays important role on supercapacitive performances.

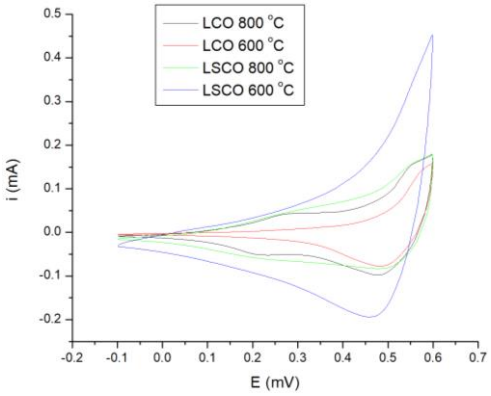


**Figure 1.** Cyclic voltammograms of LSCO and LCO synthetized at different temperatures at a scan rate of 50 $mVs^{-1}$ in 0.10 M KOH; room temperature.

# High-surface area carbon materials as alternative counter electrode for electrochemical characterization of electrode materials for sodium-ion cells

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Among the most promising post-lithium-ion batteries, sodium-ion batteries (SIBs) are attracting great interest for grid-scale energy storage systems thanks to the high abundance and the low-cost of sodium, and its environmentally friendly nature.

Although Na metal is widely used as anode and, sometimes, it is preferred instead of hard carbon since it can enable energy densities 30% higher, issues concerning efficiency, service life, and safety still affect its further development. Indeed, it suffers from dendritic formation and great volume change along with high reactivity that is detrimental to the surrounding cell environment. These concerns may lead to the electrolyte decomposition and constant breaking and reforming of the solid electrolyte interface, resulting in low coulombic efficiency and huge capacity fading over cycling.

Also for the characterization of electrode materials for Na-ion cells the substitution of Na metal with a sodium-free counter electrode would be preferable. Here we investigate the feasibility of using an alternative electrode to perform the lab-scale electrochemical characterization of cathode and anode materials for SIBs. This approach allows to decrease the electrolyte reactivity both during the assembly and over cycling. Specifically, the use of high-surface area carbonaceous materials, which show a capacitive behavior that may be also interesting for the exploitation in Na-ion supercapacitors, is investigated in half-cell with sodium intercalation electrodes and with an electrolytic medium based on organic carbonates and $NaPF_6$.

[1] J. W. Choi and D. Aurbach, *Nature Reviews Materials*, 2016, **1**, 16013.
[2] X. Dou, I. Hasa, D. Saurel, C. Vaalma, L. Wu, D. Buchholz, D. Bresser, S. Komaba and S. Passerini, *Materials Today*, 2019, **23**, 87-104.
[3] X. Zheng, C. Bommier, W. Luo, L. Jiang, Y. Hao, and Y. Huang, *Energy Storage Materials*, 2019, **16**, 6–23.

# New evidences on the growth of oxide layers via oxide-oxide galvanic exchange reactions

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Metal-metal galvanic exchange reactions are well-known processes quite common in fields as diverse as corrosion, metal recovery and preparation of metal nanoparticles, with a variety of structures, including hollow and bimetallic ones. Analogous reactions may occur between solid sacrificial oxides and dissolved cations, and may be represented by the general equation:

$$nMe_1O_{x(solid)} + mMe_{2\,(aq)}^{n+} \rightarrow mMe_2O_{y(solid)} + nMe_{1\,(aq)}^{m+}$$

In this process, partial or total replacement of the sacrificial oxide takes place, either by oxidation or by reduction, with the formation of a secondary oxide.

Papers about oxide-oxide galvanic exchange reactions are not numerous and mainly concern nanometric objects. In recent years, our group has reported on the conversion porous $PbO_2$ layers, tens of micrometres thick, to some secondary oxides i.e. $MnO_2$, $SnO_2$ and $Co_3O_4$ [1,2].

To collect new evidences on the mechanism of oxide-oxide galvanic exchange reactions and on the growth of secondary oxides, we have studied the reaction of $PbO_2$ layers with (i) a single low-valent cation, (ii) two cations used in successive reactions or (iii) two cations dissolved in the same solution, using electrochemical methods, SEM-EDS and XPS. This study has provided new data on: (i) the effect of the thermodynamic driving force on the growth rate of the secondary oxide, (ii) the location of the exchange reaction, (iii) the species that are transported through the growing oxide layer (iii) the rate-determining step of the overall process.

[1] N. Comisso, S. Cattarin, P. Guerriero, L. Mattarozzi, M. Musiani, E. Verlato, *Electrochem. Commun*. 2016, **73**, 59-62.
[2] N. Comisso, L. Armelao, S. Cattarin, P. Guerriero, L. Mattarozzi, M. Musiani, M. Rancan, L. Vazquez-Gomez, E. Verlato, *Electrochim. Acta* 2017, **253**, 11-20.

# Experimental study for environmentals friendly silver electroplating for the production of jewels

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This electrochemical research is part of the Regional POR CREO GADGET - ERDF 2014-2020 Call No.2 project. One of the objectives of this project is to set up a new formulation for cyanide-free silver electroplating bath. Usually for the electrodeposition of silver are employed cyanide baths because they produce mirror bright, compact, smooth, and adhesive deposits, a the lowest cost. Unfortunately cyanide compounds have strong toxicity and a large amount of the cost is required for securing safe working conditions and for waste treatment. Due to the strong toxicity of cyanide compounds, various formulations of electroplating silver baths without cyanide have been studied in recent years. Most of this formulation suffer from instability, and poor quality of the deposits. It is presented voltammetry study of silver electrodeposition from cyanide-free bath with 5,5-dimethylhydantoin (DMH) as the complexing agent Fig.1. For obtaining good quality deposits is very important a clear understanding of nucleation and growth during silver electrochemical deposition. The nucleation and growth mechanism plays an important role on the structure and properties of deposited metal thin films. Current transient measurements were used to obtain the kinetic parameters of the electrodeposition process Fig. 2. These parameters were calculated using existing models for three-dimensional multiple nucleation with diffusion-controlled growth. Furthermore, the influence of the polyethyleneimine additive (PEI) on the silver growth nucleation mechanism is also examined. The electrochemical behavior of PEI and its interaction with DMH were characterized using galvanostatic measurements. The optimal concentration of PEI is studied to obtain a luminous mirror deposit.

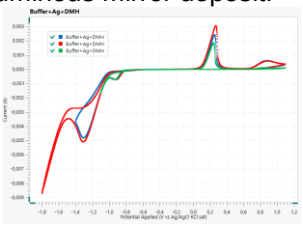

**Figure 1**: CVs for the electrodeposition of silver on GCE. Scan rate 50mV $s^{-1}$

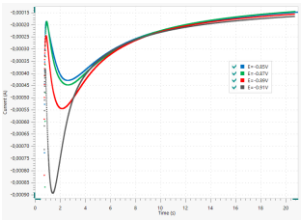

**Figure 2**: Potentiostatic current transients for silver deposition on GCE

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# Bromate-ion ($BrO_3^-$) reduction in acidic solution at RDE. Theoretical predictions vs. experimental data for maximal current density

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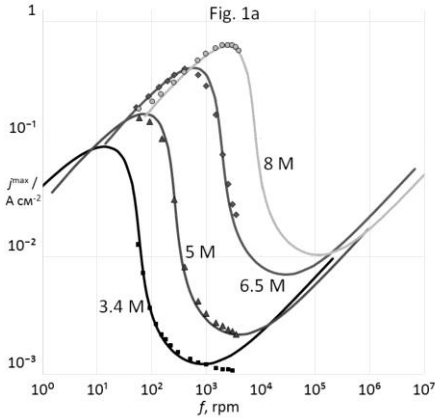
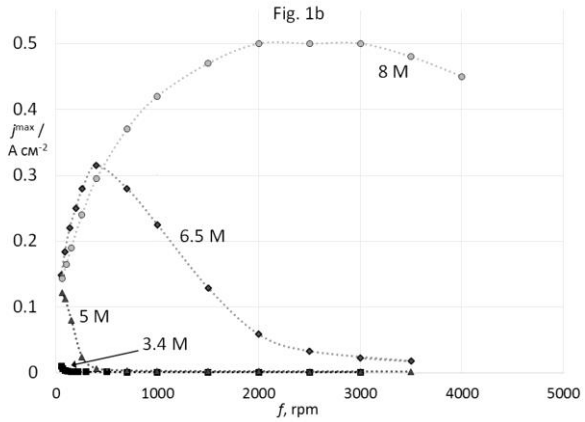
Recent theoretical analysis [1] has demonstrated that the electroreduction process of the inactive bromate ($BrO_3^-$) anion at an uniformly accessible electrode (such as rotating disk electrode, RDE) can be realized via an autocatalytic cycle (EC" mechanism) composed of the reversible electrode reaction of couple, $Br_2/Br^-$, and the comproportionation reaction between $BrO_3^-$ and Br- inside solution generating $Br_2$ so that $BrO_3^-$ transformation may be accompanied by progressive accumulation of high amounts of $Br_2$ and $Br^-$ near the electrode surface, resulting in high areal current (~ several A / $cm^2$) and power density (> 1Wt/$cm^2$) for such a system [1].

The theory [1] predicts strikingly unusual features for the dependence of the steady-state maximal current density jmax (limit for high cathodic overpotential) of the RDE rotation frequency f (curves in Fig. 1a calculated for various $H_3PO_4$ concentrations). In particular, there is a relatively narrow range of f where its diminution leads to a drastic increase of $j^{max}$ so that for less intensive agitation of solution the current may become comparable to the $BrO_3^-$ diffusion-limited one. Experimental study of $NaBrO_3$ reduction from $H_3PO_4$ solutions (from 3 M to 8 M, Fig. 1b) has both confirmed these unusual features and been in full agreement with theoretically predicted curves (Fig. 1a).




Acknowledgement: The work was supported by Mendeleev University of Chemical Technology of Russia. Project Number X020-2018.

References:

[1] M.A. Vorotyntsev; D.V. Konev; Y.V. Tolmachev, Electrochim. Acta, 2015, **173**, 779-795.

# Long-lasting oxygen evolving titanium anodes activated by Mn and Sn oxides by hydrothermal air-pyrolytic brushing

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Dimensionally stable anodes (DSA®s), are type of anodes based on Ti substrate coated by transitional/noble metal oxides acting as the catalyst for anodic gas evolution [1].Due to their excellent performances, DSA®s have been extensively used as oxygen-evolving electrodes in metal recovery processes, water electrolysis, copper powder electroproduction and sewage treatment [2].The coatings may be composed of one or more active metal oxides, but is important to develop cheap anodes of an excellent electrochemical activity and stability for oxygen evolution reaction [3]. Usually, these electrodes are commercially available as Ti/$IrO_2$–$Ta_2O_5$.The aim of this work is to find acceptable replacement of $IrO_2$ and $Ta_2O_5$ by $MnO_2$ and/or $SnO_2$, or by far to reduce the amount of $IrO_2$. New hydrothermal air-pyrolytic brushed (HtAPB) Ti/$IrO_2$–$TiO_2$(TIR), Ti/$MnO_2$–$IrO_2$–$TiO_2$(TMIR) and Ti/$MnO_2$–$IrO_2$–$SnO_2$–$TiO_2$(TMIRS) were characterized by linear sweep voltammetry (LSV) and cyclic voltammetry (CV). Preliminary electrochemical experiments were carried out to evaluate electrocatalytic activity, and stability for oxygen reaction.

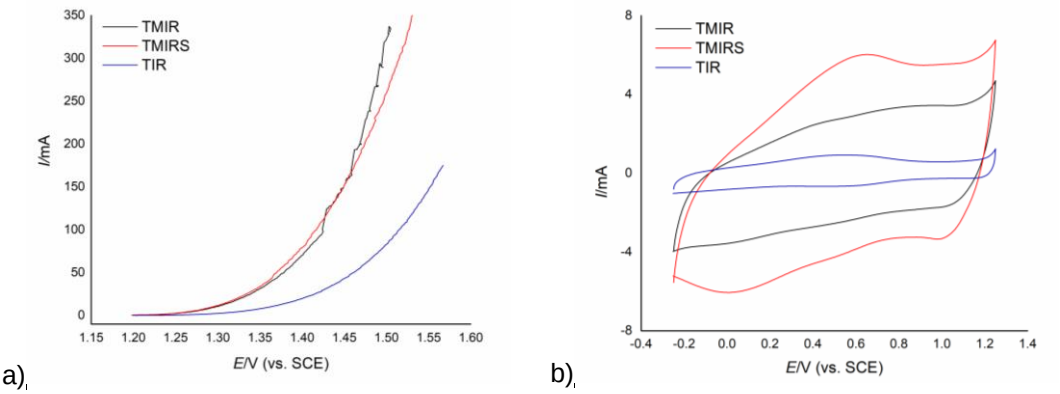


**Figure 1**: LSV and CV of different electrodes TIR, TMIR and TMIRS in 0.2 M $H_2SO_4$.

The CV and LSV results indicate that $MnO_2$ and $SnO_2$ can replace successfully $Ta_2O_5$, with a potential to reduce the $IrO_2$ loading in oxygen-evolving DSA®s.

[1] Y. Zhao, Q. Fan, X. Wang, W. Zhang, X. Hu, C. Liu, W. Liang,*Chem. Eng. J.,* 2019, **368**, 968-979.
[2] R.Zhao, X. Zhang, F. Chen, X. Man, W. Jian, *Int. J. Environ. Res. Public Health,* 2019, **16(3)**, 343.
[3] A. A. El-Moneim and H. M. Soliman, *Int. J. Sustain. Water Environ.Sys.* 2011,**2**, 43-48.

# Can biofilm be modelled as a porous conductive layer?

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Electrochemically active biofilms (EAB) exchange electrons with conductive surfaces such as electrodes and are commonly used in bioelectrochemical systems such as Microbial fuel cells (MFCs). The transfer of electrons between EA bacteria and the electrode can be direct or indirect. Direct electron transfer takes place via extracellular conductive connections called conductive pili or bacterial nanowires.

In the biofilm matrix, the biomass components (made up of communities of bacteria, the extracellular polymeric substances (EPS) and nanowires) form the solid conducting phase. The wastewater (substrate solution) that enters the porous biofilm matrix is oxidized by the active bacteria and releases electrons and hydrogen ions. The biofilm matrix thus works as a porous catalyst layer on the anode surface and can be characterized by two separate current balances, one for the solid phase and one for the liquid electrolyte phase. In standard fuel cells, the porosity of the electrodes or the catalyst layers has a strong influence on the mass transfer characteristics and thereby on the performance of the cell.

In this study we considered the biofilm on the surface of the anode as a porous conductive matrix with a fixed porosity ($\phi$) and conductivity, and derived the expressions for MFC cell voltage and power density. Effect of substrate concertation was also studied. The model results showed that increasing porosity has a negative influence on the voltage generated from the MFC. Also initial COD concentration has a strong influence on the MFC performance. Increasing initial COD concentration improves the power density and the COD removal rate, however it decreases the Coulombic efficiency of the system. These results are in agreement with literature. The proposed model considering biofilm as a porous conductive matrix was able to predict system performance in accordance with experimental studies.

# Synthesis of micro- and mesoporous carbons from PEO-b-PS soft template and resorcinol-formaldehyde resins for the *in situ* generation of hydrogen peroxide

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The aim of this work is the realization of porous carbons through a soft template approach. A polyethyleneoxide-polystyrene block copolymer (PEO-b-PS) was selected as a soft template because of the influence of PS chain length over the pore dimensions of the carbon product. Resorcinol-Formaldehyde (RF) thermosetting resin was selected as a non-doped carbon source. Several $PEO_{125}$-b-$PS_x$ templates were synthesized through bulk Supplemental Activator and Reducing Agent Atom Transfer Radical Polymerization (SARA-ATRP) of styrene on $PEO_{125}$-Br macroinitiator. Different PS chain lengths were obtained by increasing the polymerization time to promote different porosity systems in the final carbons [1]. The carbon products were obtained through homemade-autoclave treatment, followed by pyrolysis of PEO-b-PS/RF composite materials. Further pyrolysis treatments were performed in the presence of melamine or thiophene in order to insert N or S dopants, respectively.

Transmission Electron Microscopy (TEM), Brunauer-Emmett-Teller (BET) model and elemental analysis were performed to assess surface morphology, micro/mesopore area and volume and elemental composition of the carbon products. Oxygen reduction activity and $H_2O_2$ production were electrochemically tested through Rotating Ring Disk Electrode (RRDE) in acid environment. Preliminary BET analysis showed an improved surface area from 611 $m^2/g$ to 966 $m^2/g$ as the carbon product obtained from $PEO_{125}$-b-$PS_{160}$ was treated with melamine. RRDE analysis on the doped carbon toward oxygen reduction reaction showed an improved catalytic activity and a slightly higher selectivity for $H_2O_2$ with respect to the undoped catalyst [2].

The final goal of this project is the realization of Gas Diffusion Electrodes (GDEs) to test their activity toward $H_2O_2$ production and pollutant degradation [3].

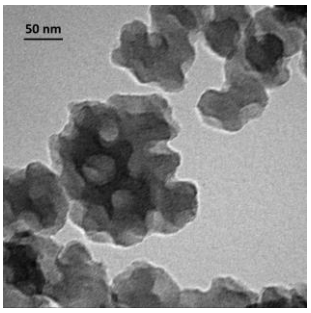


**Figure 1** TEM image of non-doped porous sample from $PEO_{125}$-b-$PS_{160}$/RF composite.

**Acknowledgement:** Fondazione Oronzio e Niccolò De Nora and Industrie De Nora S.p.A. are cordially acknowledged for granting a fellowship supporting this research activity

[1] C. Liu; M. Yu; Y. Li; J. Li; J. Wang; C. Yu; L. Wang, *Nanoscale*, **2015**, 7, 11580 – 11590.
[2] V. Perazzolo; C. Durante; R. Pilot; A. Paduano; J. Zheng; G. A. Rizzi; A. Martucci; G. Granozzi; A. Gennaro, *Carbon*, **2015**, 95, 949 – 963.
[3] V. Perazzolo; C. Durante; A. Gennaro, *J. Electroanal. Chem*., **2016**, 782, 264 – 269.

# Structure properties correlation in MXenes: 2D anodic materials for sodium ion batteries

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Recently, MXenes [1], a class of 2D materials obtained by the chemical exfoliation of carbide MAX phases, have been proposed as suitable anodic materials for SIBs devices [2]. The $M_{n+1}AX_n$, or MAX phases are transition-metal carbides and nitrides with a layered, hexagonal structure where ''M'' is a transition metal, ''A'' is a 13 or 14 group's element, and ''X'' is C and/or N. M-X based MXenes can be obtained by the corresponding MAX phase by chemical or electrochemical etching of the A element, forming a layered structure with large space between two M-X sandwiches (around 1 nm) suitable for ion pseudo-intercalation. The lamellar structure of MXenes facilitates the intercalation of many alkaline and earth-alkali metal ions, on an extended range of charge-recharge rates for thousands number of cycles [3]. Although there are several papers on the use of MXenes as active materials in both SIBs and supercapacitors devices, the correlations among their structure, chemical composition, and the electrochemical properties are seldom investigated.

In the present contribute we discuss how different etching processes of starting $Ti_3AlC_2$ phase to produce $Ti_3C_2T_x$ (T=F, Cl, OH) have a deep influence on the chemical composition ($T_x$), the crystalline structure, and the morphologies, which in turns rule the electrochemical behavior towards the reaction with the sodium ion. The $Ti_3C_2T_x$ phase obtained by chemical etching shows a reversible capacity of about 150 mAh $g^{-1}$ with very low potential hysteresis and an average anodic potential of 1.4 V vs. $Na^+/Na$ (figure 1).

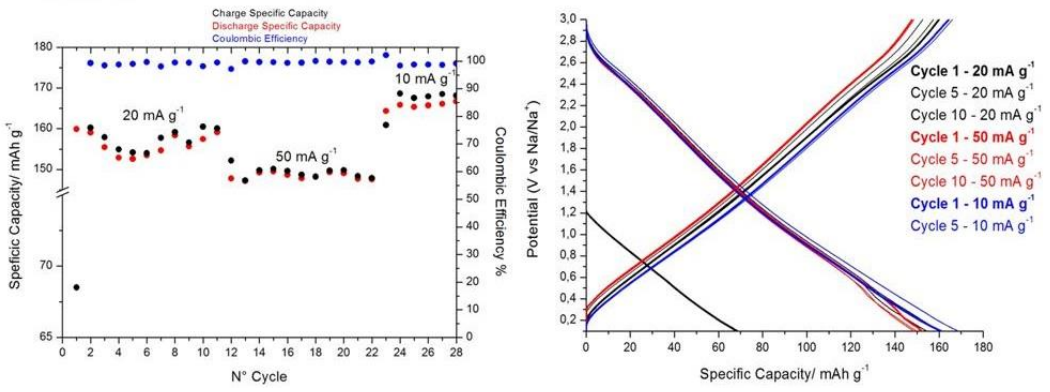


**Figure 1**: Rate profile of the MXene electrode for Na-ion cell (on the left), voltage profiles of MXene at different cycling rates (on the right)

[1] M. M. Doeff, Y. Ma, S. J. Visco and L. C. De Jonghe, *J. Electrochem. Soc.,* 1993, **140**, L169–L170.
[2] M Naguib, M Kurtoglu, V Presser, J Lu, J Niu, M Heon, L Hultman, Y Gogotsi, M. W. Barsoum, *Adv. Mater.* 2011, **23**, 4248–4253
[3] M. R. Lukatskaya, O. Mashtalir, C. E. Ren, Y. Dall'Agnese, P. Rozier, P. L. Taberna, M. Naguib, P. Simon, M. W. Barsoum, Y. Gogotsi, *Science*, 2013, **341**, 1502–1505.

# n-p $BiVO_4$-$CuBi_2O_4$ nano-heterojunction as an efficient photoanode in photoelectrochemical water oxidation

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We report on the nanostructured $BiVO_4$-$CuBi_2O_4$ heterojunction (*nano*$BiVO_4$-$CuBi_2O_4$) photoelectrode with significantly enhanced photoelectrocatalytic properties towards water oxidation. *nano*$BiVO_4$-$CuBi_2O_4$ was synthesized by the electrodepostion of BiOI nanosheets (*nano*BiOI) template and subsequent conversion of *nano*BiOI template into *nano*$BiVO_4$-$CuBi_2O_4$ by drop-casting $Cu^{2+}$ and $V^{4+}$ solution and follow-up thermal treatment. The n-p conductivity and composition of the resultant *nano*$BiVO_4$-$CuBi_2O_4$ can be tuned simply by adjusting the nominal $Cu^{2+}$/ $V^{4+}$ molar ratios (r) in the precursor solution. The preliminary results (Figure 1) indicate that *nano*$BiVO_4$-$CuBi_2O_4$ with Cu content exhibited significantly ehanced photocurrent response, which can be attributed to the improved charge separation efficiency and interfacial charge transfer efficiency. Further mechanistic study and optimization are under investigation.

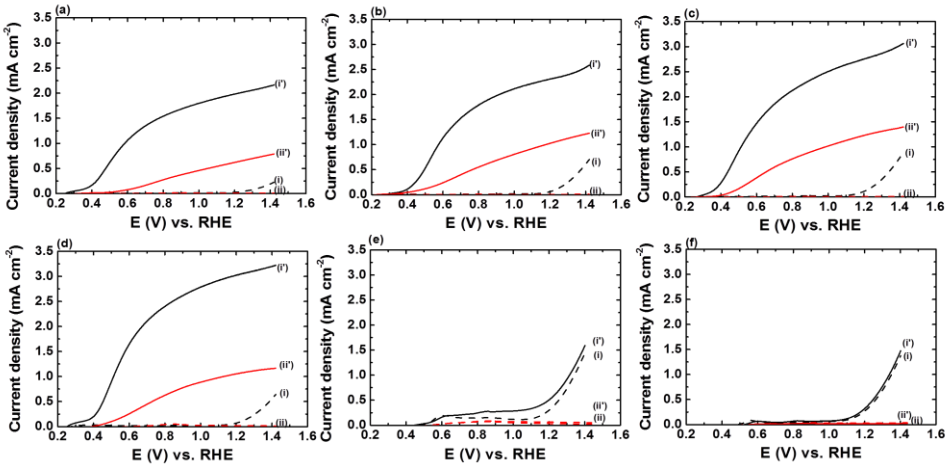


**Figure 1**: Linear sweep voltammetry, recorded at a scan rate of 10 mV $s^{-1}$, of *nano*$BiVO_4$-$CuBi_2O_4$ (a: r= 0, b: r= 0.0714, c: 0.167, d: 0.5 , e: 1.5, f: 3.5 ) in the dark (curves i' and ii') and under light illumination (curves i and ii). Curves i & i' were recorded in 0.1 M $Na_2SO_3$ solution whereas curves ii & ii' were recorded in borate buffer (0.1 M, pH 9.2).

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# Interaction between $La_{0.6}Sr_{0.4}FeO_3$ and $La_{0.6}Ba_{0.4}CoO_3$ and investigation of $Ba_{0.99}Sr_{0.297}La_{0.594}Co_{0.8}Fe_{0.2}O_{3-\delta}$ as cathode for intermediate temperature solid oxide fuel cells

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$La_{0.6}Sr_{0.4}Fe_{0.8}O_3$ (LSF64) [1] and $La_{0.6}Ba_{0.4}CoO_3$ (LBC64) [2] were tested in several thin film electrode configurations as Solid Oxide Fuel Cells cathode. Particular attention has been dedicated to evaluate interaction between these two materials in different conditions. Microstructural results showed a strong interdiffusion between materials in two particular conditions. Indeed, interdiffusion occurred (i) when two powders were sintered after mixing process at 1200 °C, and (ii) in Pulse Laser Deposition (PLD) chamber depositing LSF64 and LBC64 simultaneously starting from two difference pellets.

Microstructural analysis identified a new perovskite phase (NPP) with a stoichiometry of $Ba_{0.099}Sr_{0.297}La_{0.594}Fe_{0.8}Co_{0.2}O_3$. NPP electrode was electrochemically tested in a porous thin film configuration (100 nm) and compared with reference materials. Impedance results highlighted an improvement of performance for the new electrode material; a possible explanation of this enhancement is the increase of chemical capacitance directly associable with oxygen vacancy concentration involved in the electrode process at low frequency, controlling the global kinetic.

Interactions between LSF64 and LBC64 were avoided in a bilayer system, preserving both phases. Two different bilayer systems were prepared and compared with pure dense thin LSF film of 200 nm. They consisted in a LSF64 layer (150 nm) covered by a LBC64 top layer (50 nm): in the first case top layer had a dense structure, in the second case the layer was porous. The presence of LBC64 at gas/electrode interface drastically decrease electrode polarization resistance. Distribution of Relaxation Times (DRT) [3] analysis and then equivalent circuit modeling (ECM) of impedance data at different temperature and oxygen partial pressure attributed this performance improvement to the enhancement of low frequency process, related with oxygen surface phenomena. This explanation is in accordance with material properties; indeed, LBC64 surface is more active towards oxygen surface exchange than LSF64. Then, these kind of systems can provide an interesting way to exploit complementary strengths of the two materials.

[1] S. Kogler, A Nenning, G.M. Rupp, A.K. Opitz, J. Fleig, *J. Electrochem. Soc.,* **162** (2015) F317-F326
[2] G.M. Rupp, A. Schmid, A. Nenning, J. Fleig, *J. Electrochem. Soc.,* **163** (2016) F564-F573
[3] F. Ciucci, C. Chen, *Electroch. Acta* **167** (2015) 439-454

# Plastic derived carbon materials for oxygen reduction reaction: effect of pre- and post- treatments

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Closing the resource loop by transforming plastic waste into higher added value products is an important step for changing from linear to circular economy. One way to achieve such a goal is to convert waste plastic into carbon nanomaterials via pyrolysis [1]. Among different employments, the carbon-nanomaterials can be used in electrocatalysis, such as in fuel cell electrodes. In particular, the use of plastic as precursors for platinum free FC catalysts (non-PGMCs) meets also the economic requirements of FC technologies, being inexpensive materials [2]. Among non-PGMCs, Fe-N-C materials have attracted interest, as alternative to Pt-based materials, due to their high activity, selectivity and good tolerance to poisoning. The synthesis of Fe-N-C materials from plastic can be accomplished according to several routes. In this work we follow a two-step pyrolysis synthesis using polyethylene (PE) and polyurethane (PU) as nitrogen-carbon precursors in the presence of an iron salt. The obtained material was then activated with an acid wash and $H_2$ thermal reduction. The mixing of precursors was done by using both a wet mechanical mixing and a Brabender. The formation of iron phases was investigated by XRD analysis and Mössbauer spectroscopy. XRD spectra showed the formation of $Fe_3C$ and $Fe_3O_4$ along with α-Fe, which was for the most part removed after the acid wash (Fig. 1a). The catalysts were tested by RRDE showing to be active towards ORR (Fig. 1b).

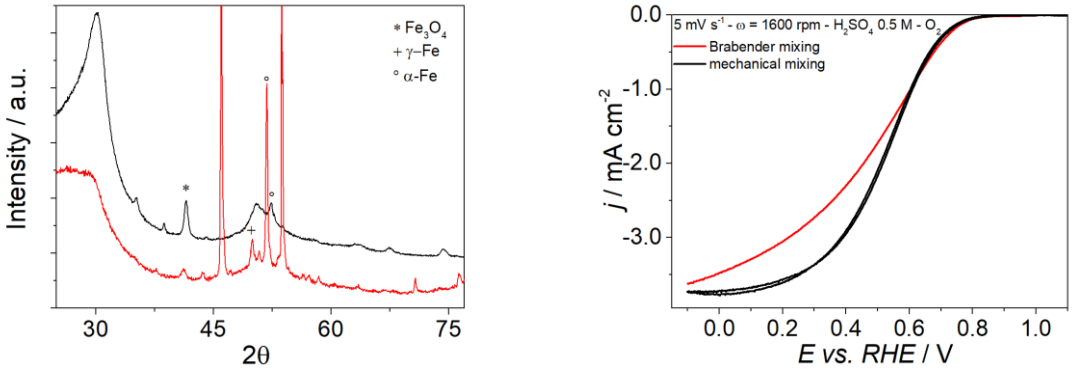


Figure 1: (a) XRD spectra before (red line) and after activation treatments (black line). (b) LSV at RDE in $O_2$ saturated 0.5 M $H_2SO_4$ of catalysts prepared by using two different pre-treatments.

**Acknowledgments**
The research leading to these results has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking under Grant Agreement No 779366, CRESCENDO

[1] J.G.S. Moo, A. Veksha, W. Da Oh, A. Giannis, W.D.C. Udayanga, S.X. Lin, L. Ge, G. Lisak, Electrochem. Commun., 2019, **101**, 11–18..
[2] F. Jaouen, E. Proietti, M. Lefevre, R. Chenitz, J.-P. Dodelet, G. Wu, H.T. Chung, C.M. Johnston, P. Zelenay, Energy Environ. Sci., 2011, **4**, 114–130.

Promoted to oral presentation

# Preparation of electrodes for the reduction of $CO_2$ to formic acid at low overpotential by electroprecipitation of nanostructured $CeO_2$ onto BDD electrodes

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Many groups are actively investigating catalytic materials for the electrochemical reduction of $CO_2$ ($CO_2$RR). Although the $CO_2$RR is unlikely to provide a major contribution to the limitation of $CO_2$ concentration in the atmosphere, the conversion of a waste like $CO_2$ to useful compounds to be used in industrial processes is interesting in a circular economy perspective, especially if powered by renewable energy sources.

We have investigated the deposition of ceria onto boron doped polycrystalline diamond (BDD) and glassy carbon cathodes. Ceria deposits were formed through electrochemically induced precipitation processes from nitrate solutions of $Ce^{3+}$ ions, and then characterized using SEM-EDS, HRTEM, XRD and XPS. Using appropriate combinations of deposition potential and deposition charge, we obtained deposits with accurately controlled composition and properties. XRD analyses revealed the presence of some $Ce(OH)_3$, besides $CeO_2$, when the deposits were prepared at very negative potential (Fig.1). Thin, compact, well-adhering films with negligible $Ce(OH)_3$ content were obtained at moderately negative reduction potential and with low deposition charges.

Thin $Ce(OH)_3$-free ceria films allowed $CO_2$ electrochemical reduction at overpotential below 50 mV, yielding formic acid with faradaic yield higher than 40% (Fig. 2) and stable performance during many hours. Formaldehyde and molecular hydrogen were detected as side products. Ceria-coated glassy carbon electrodes did not lead to comparable results, failing to produce formic acid. This suggests that ceria acted as co-catalyst that adsorbed $CO_2$ and activated it towards reduction by hydrogen-terminated BDD.

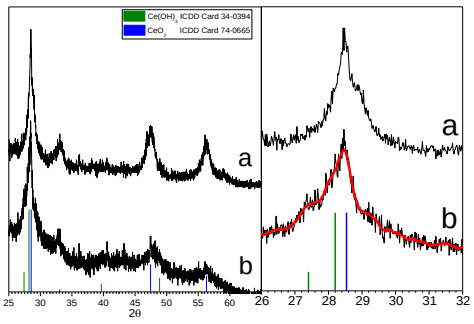


**Figure 1**: X-ray diffractograms of ceria deposits obtained at less (a) and more (b) negative potential

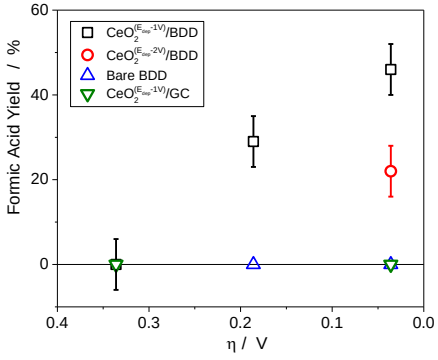


**Figure 2**: Faradaic yield for CO2 reduction to HCOOH with various electrodes

# Exploiting N-doped carbon spheres for supercapacitors

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The development of high energy supercapacitors requires the use of high specific capacitance electrode materials and electrochemically stable electrolyte for high cell voltages. Many electrode nanostrucutres, like activated carbons, carbon aerolges, graphene, have been investigated with the aim of improving the surface area as needed for high electrical double-layer capacitance. In turn carbon doping by heteroatoms is expected to have an effect on carbon conductivity and to contribute to the capacitive response by providing reversible faradic reactions. These reactions can have an effect on the energy storage performance and cycling stability of the supercapacitor. This is mainly observed in the case of the use of aqueous electrolytes.
Here we present a chemical-physical and electrochemical study on nitrogen doped mesoporous carbons, prepared from templating propylamine functionalized silica. We report about the capacitive features of these N-doped carbons in ionic liquids to demonstrate a new class of electrode materials for high-voltage supercapacitors.

**Acknowledgments**
The research has been carried out under the Italy-South Africa joint Research Programme 2018-2020 and the Executive Bilateral Program Italy-Quebec 2017-2019, Italian Ministers of Foreign Affairs and of the Environment.

# $Pd_3Y$ alloyed NPs synthetized by laser ablation: toward zero platinum in PEMFC cathode catalysts

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

In this paper $Pd_3Y$ nanoparticles were for the first time successfully prepared by laser ablation synthesis in organic solvent starting from a $Pd_3Y$ target and tested as active electrocatalyst for ORR in both acid and alkaline electrolytes [2,3].The formation of alloyed NPs was confirmed by TEM, XRD and XPS analyses Fig. 1b. XPS analysis revealed that when ethanol was used, the superficial $Pd_3Y$ alloy reaches its maximum (46 %). TEM measurements confirmed the formation of NPs in the range 10-20 nm, while XRD diffraction patterns estimated from the Rietveld analysis agree with the cell parameters of $Pd_3Y$ alloy.

The ORR investigation, in KOH 0.5 M and $H_2SO_4$ 0.1 M, showed that the catalyst containing the highest amount of $Pd_3Y$ alloy exhibits higher catalytic activity expressed in term of half wave potential, mass and specific activity, when compared to a standard Pd/C (146 A $g^{-1}$ vs. 15 A $g^{-1}$ in acid electrolyte). The effect of $ClO_4^-$ and $Cl^-$ anions was also investigated revealing the surprising poisoning effect of $ClO_4^-$ for the $Pd_3Y$ alloys. LaSiS was confirmed as a fruitful synthetic route for the preparation of electrocatalysts for both proton and anion exchange fuel cell.

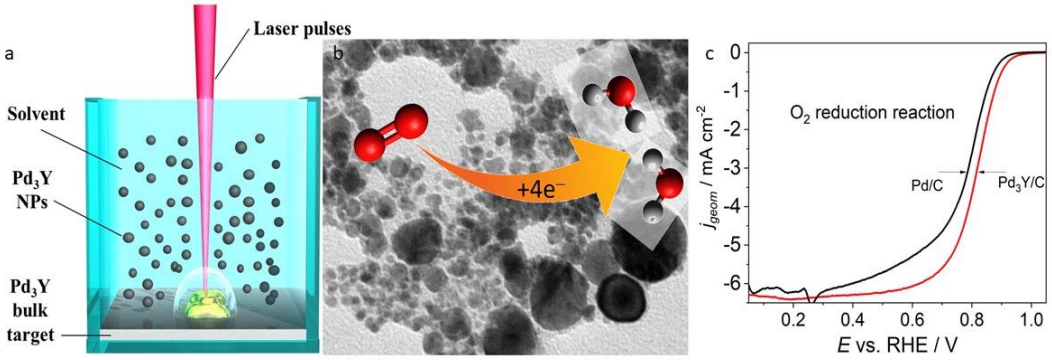


Figure 1: a) Sketch of PdY NPs preparation by LASiS; b) TEM image $Pd_3Y$; c) LSV at RDE of $Pd_3Y$ NPs and Pd NPs in $O_2$-saturated 0.1 M $H_2SO_4$ solution at 20 mV $s^{-1}$ and 1600 rpm.

**REFERENCES**

[1] R. Brandiele, C. Durante, E. Grądzka, G.A. Rizzi, J. Zheng, D. Badocco, P. Centomo, P. Pastore, G. Granozzi, A. Gennaro, *J. Mater. Chem. A.*, **2016**, 4 12232–12240.
[2] J. Zhang, M. Chaker, D. Ma, *J. Colloid Interface Sci.*, **2017**, 489, 138–149.
[3] M. Shao, *J. Power Sources.*, **2011**, 196, 2433–2444.

# A new monolayer-protected clusters: the 145th gold atom matters

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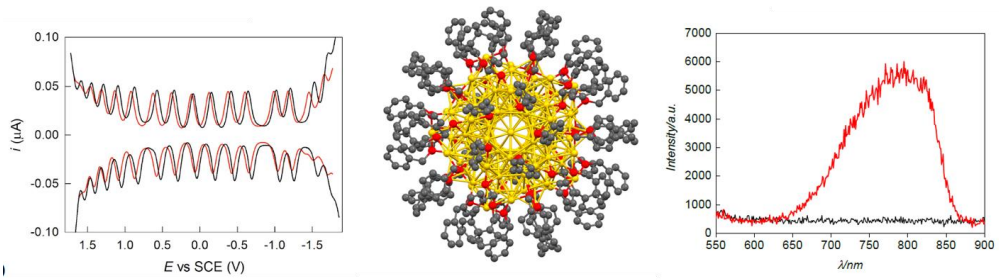
Monolayer protected clusters (MPCs), consisting of a core with a few gold atom capped by a pattern of protecting motifs, are one of the most actively researched areas in chemistry. When the number of gold atoms is small, quantum confinement makes these clusters display properties that cannot be seen in larger gold nanoparticle systems such as peculiar UV-Vis absorption spectra and very regular electrochemistry patterns. Interestingly, these properties can be tuned precisely by exchanging one single gold atom with a other metal atom, without affecting the original structure. Therefore, they have the potential to be the next generation of building blocks for future highly miniaturised electronic devices and for being used in biosciences, as effective drug carriers and sensors [1]. Among thiolate-protected metal clusters prepared with atomic precision, one of the most studied is $Au_{144}(SR)_{60}$. It was prepared long time ago, but its X-Ray structure was reported only a few months ago [2] showing a peculiar structure with an empty 12-atom icosahedron core. The absence of the central atom in $Au_{144}$ is a mystery because all other cases of known icosahedral Au clusters have an inner core of 12+1 atoms.

For the very first time, our group could prepare the missing $Au_{145}$ cluster. We prepared it protected by n-butanethiolates (SBu) as a cation of formula $[Au_{145}(SBu)_{60}]^+Br^-$. For comparison, we also prepared the corresponding $Au_{144}(SBu)_{60}$ cluster, which is neutral. The stoichiometry of both clusters has been unequivocally determined by high-resolution ESI mass spectrometry. We found that the NMR spectrometry pattern of $Au_{145}$ is similar, yet clearly




distinguishable from $Au_{144}$ [3]. Electrochemistry (differential pulse voltammetry, DPV, Figure on the left) shows the same sequence of nicely spaced charging peaks, though shifted and with some perceivable interpeak potential differences. The addition of one single Au atom, however, is not just changing the NMR and electrochemical behaviors. The most striking difference is a huge difference in the luminescence spectrum. Whereas $Au_{144}$ virtually does not emit, $Au_{145}$ emits (Figure, on the right) as no other known Au cluster of the same type. This is an extremely important aspect that by itself fully justifies the interesting on this new $Au_{145}$ with respect to the apparently very similar $Au_{144}$ and, more in general, points out the fascinating relationship between the optical, electrical and structural properties in such MPCs.

[1] Special issue “Toward Atomic Precision in Nanoscience” *Acc.Chem.Res.* ***2019***
[2] Z. Lei, J.-J. Li, X.-K. Wan, W.-H. Zhang and Q.-M. Wang *Angew. Chem., Int. Ed.* **2018**, *57*, 8639.
[3] T. Dainese, M. Agrachev, S. Antonello, D. Badocco, D. M. Black, A. Fortunelli, J. A. Gascón, M. Stener, A. Venzo, R. L. Whetten and F. Maran *Chem. Sci*. **2018**, *9*, 8796.

# Catalytic vs. electrocatalytic reduction of $CO_2$ to added-value products

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The increase of $CO_2$ concentration in the atmosphere after industrial revolution plays a critical role in global climate crisis, which can be mitigated by exploiting $CO_2$ as a raw material to synthesize high added-value products [1]. The electrochemical (EC) reduction of $CO_2$ is a sustainable and technologically interesting process for the production of chemicals or fuels using renewable electricity sources [2]. The main challenge is to find a suitable electrocatalyst (with a high selectivity, stability and activity) to establish this technology at an industrial level. We are investigating for this EC process nanostructured Cu-based catalysts that are active for the thermocatalytic (TC) $CO_2$ reduction reaction ($CO_2$RR) to $CH_3OH$. A commercial Cu-Zn-Al-based material was tested for these two processes for comparison purposes. The TC $CO_2$RR in $H_2$ atmosphere (25 bars and 250 $^oC$) leads to a methanol selectivity of 50% and CO as side-product, while the EC $CO_2$RR (at ambient conditions) yields different alcohols and other C-based products ($C_1$ to $C_3$) with an overall faradaic efficiency of ~ 70%. The chemical-physical properties of the catalyst were studied before and after both experiments by several characterization techniques (e.g. X-rays diffraction, X-ray Photoelectron Spectroscopy, Field-Emission Electron Microscopy, among others) to understand the role of the modification of the catalyst components during operation in the final selectivity and activity. These results demonstrated that there are synergies between the TC and the EC processes that can be exploited to develop new electrocatalysts compositions for producing useful liquid products (e.g. alcohols) from $CO_2$. In addition, from our primary data we perform a Life Cycle Assessment (LCA) for comparing the TC and EC processes from the environmental and energy consumption viewpoints, demonstrating that the EC $CO_2$RR technology is a more promising approach than the TC one to reduce the impact of global warming, with additional energetic advantages.

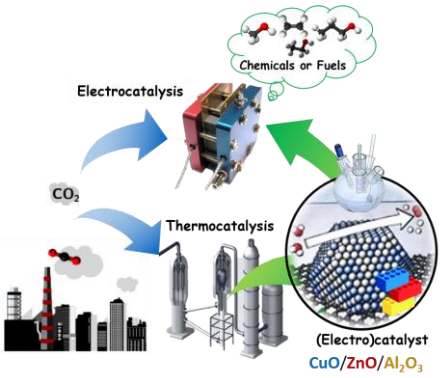


**Figure 1**: Synergies between thermo- and electro- catalysis for $CO_2$ conversion to added-value products.

[1] S. Hernandez, M.A. Farkhondehfal, F. Sastre, M. Makkee, G. Saracco, N. Russo, Green Chemistry. 2017, 19, 2326 - 2346.
[2] I. Ganesh, Renewable and Sustainable Energy Reviews. 2016, 59, 1269-1297.

# PEO-grafted $TiO_2$ filler as solid polymer electrolyte for lithium rechargeable batteries

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The formation of lithium dendrites represents one of the drawbacks for the use of lithium anode in rechargeable batteries. To block their grown a possible solution is the increase of the Young's module of the electrolytes by creating hybrid ceramic-polymer systems, such as inert ($SiO_2$, $Al_2O_3$ [1]) or active nano-fillers (LATP [2]) in the polymer matrix. Another alternative is the "polymer into ceramic" which exploits a ceramic main phase with polymer as binder [3].

In this work, we investigate PEO-grafted $TiO_2$ as filler for PEO/LiTFSI-based systems as Solid Polymer Electrolyte. This approach allows the realization of small PEO-chain-grafted filler having a branched structure, which gives a better chemistry affinity with the polymer matrix and increases the mechanical resistance with respect to the nano-dispersed filler. The first characterizations are carried out by impedance spectroscopy ranging from 1 MHz to 100 Hz, with 25 mV of amplitude and between 20 °C and 70 °C. Our preliminary results suggest that the 6 % w/w PEO-grafted $TiO_2$ sample reaches the best conductivity values (Fig. 1).

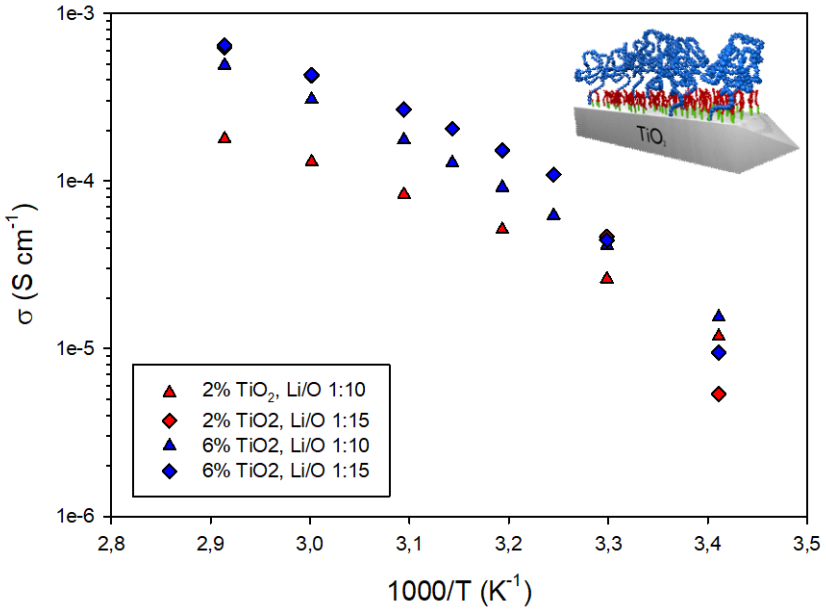


**Figure 1**: Arrhenius plot of conductivity for different TiO2 concentration and Li/O ratio. The inset shows a sketch of the PEO-grafted $TiO_2$ filler.

[1] P. A. R. D. Jayathilaka, M. A. K. L. Dissanayake, I. Albinsson and B.-E. Mellander, *Electrochimica Acta*, 2002, **47**, 3257–3268.
[2] W. Wang, E. Yi, A. J. Fici, R. M. Laine, e J. Kieffer, *J. Phys. Chem. C*, 2017, **121**, 2563–2573.
[3] S. Bonizzoni, C. Ferrara, V. Berbenni, U. Anselmi-Tamburini, P. Mustarelli, e C. Tealdi, *Phys. Chem. Chem. Phys.*, 2019, **21**, 6142–6149

# Behavior of Fe(III)-octaethyl porphyrin adsorbed on HOPG towards ORR probed by electrochemical scanning tunneling microscopy

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Metal-phthalocyanines and metal-porphyrins are the most common sources for $MN_4$ sites (transition metal atom coordinated by four nitrogen atoms), and they are regarded as versatile molecules. For this reason, they have been and are also currently employed as model catalysts for many reactions involving both inorganic and biological applications [1]. That of $MN_4$ is often regarded as a "redox catalysis", since the catalytic effect is exerted by the central metal atom, which is able to reach different oxidation states.

In this paper, Fe(III)-octaethyl porphyrin chloride (Fe-OEP) was characterized in its ability to adsorb on an HOPG substrate, with the primary aim to form an ordered monolayer. Self-assembled adlayers were visualized via electrochemical scanning tunneling microscopy (EC-STM) in 0.1 M $HClO_4$ electrolyte, allowing the Fe-OEP/HOPG system to behave as working electrode in the "four-electrode setup" [2]. On this regard, EC-STM provides a direct correlation between the macroscopic electrochemical response of the Fe-OEP/HOPG electrode and its changes at single molecular level. Preliminary cyclic voltammetry characterization showed the activity of the Fe-OEP adlayer with respect to bare HOPG towards ORR. In $O_2$ saturated electrolyte, a high-current density cathodic peak was found at $E_p = 0.28\ V$ vs RHE, indicating a net catalytic activity of the Fe-OEP adlayer. Potentiodynamic imaging at EC-STM was performed first in deaerated electrolyte, and then in $O_2$-saturated electrolyte. In Ar purged electrolyte, fig. 1.a and 1.b, molecules were visualized as crosses connected at each vertex with each other. Two main arrays were detected, producing differences in the image contrast. In both cases, the ethyl groups were protruding outwards of the molecular plane (brighter dots, indicated with solid circles) or inwards (dimmer spots, indicated with dashed circles). The Fe center did not show any particular feature. In $O_2$ saturated electrolyte, fig. 1.c, molecules maintained the same shape, but differences can be pointed out in the topographic profiles. A brighter spot is in fact visualized in a shifted position from the center of each cross, indicating the presence of an $O_2$ molecule adsorbed on the Fe catalytic site.

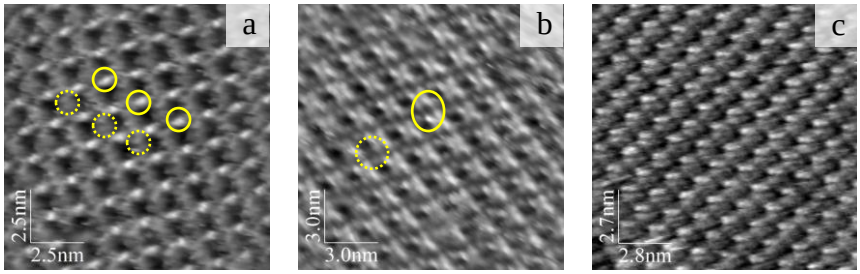


Fig. 1. EC-STM image of Fe-OEP adlayer on HOPG in a) deaerated and b) $O_2$ saturated 0.1 M $HClO_4$.

[1] J.H. Zagal, S. Griveau, J.F. Silva, T. Nyokong, F. Bedioui, *Coord. Chem. Rev. 254*, 2010, 2755–2791.
[2] M. Wilms, M. Kruft, G. Bermes, K. Wandelt, *Rev. Sci. Instrum. 70*, 1999, 3641–3650.

# Electrodeposited nickel molybdenum sulfide for electrochemical and photoelectrochemical hydrogen generation in near-neutral medium

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Solar water splitting is an attracting technology as it generates clean and sustainable energy vectors of hydrogen. Immense efforts, therefore, have been made in developing hydrogen evolution catalysts (HECs) that are efficient in acidic and/or alkaline solutions [1]. A molybdenum incorporated nickel sulfide (Ni-Mo-S) electrode which is prepared from scalable and low-cost electrodeposition shows highly efficient activity toward hydrogen evolution in acid medium [2. However, many photoelectrodes are only stable and functional under benign conditions. It is, therefore, essential to further explore the activities of this type HECs in neutral and/or near-neutral medium before it can be applied onto photoelectrode for solar water splitting [3].

In this study, we report on the effects of synthetic conditions and chemical composition on the electrocatalytic activity of resultant Ni-Mo-S towards hydrogen evolution reaction in borate buffer (pH 9.2). The optimised Ni-Mo-S has a hemisphere morphology with an elemental ration of 1: 0.08: 0.17 on a Fluorine-doped tin oxide (FTO) substrate, which is denoted as $NiMo_{0.08}S_{0.17}$. The $NiMo_{0.08}S_{0.17}$ electrode generates 10 mA $cm^{-2}$ at an overpotential of 250 mV with a Tafel slope of 86 mV/dec, outperforming Ni and NiS counterparts. The Ni-Mo-S were further integrated to a $CuBi_2O_4$ photoccathode through a photo-assisted electrodeposition to achieve photoelectrochemical hydrogen generation.

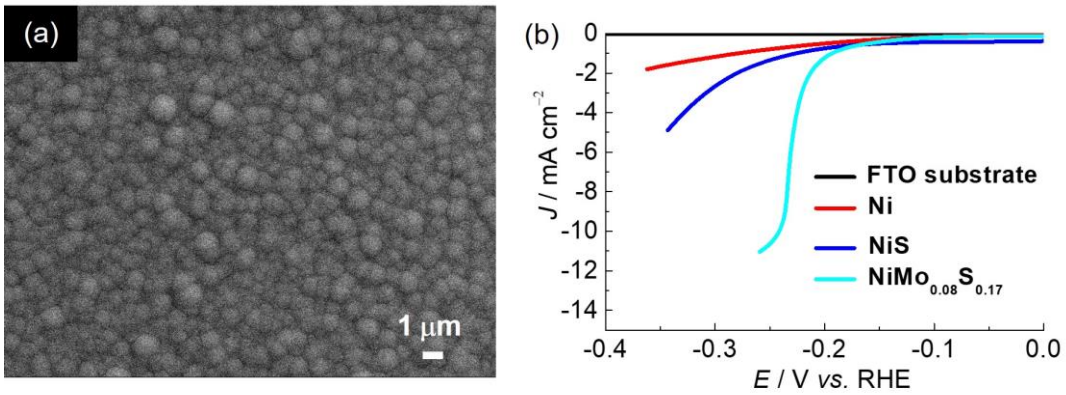


**Figure 1**: (a) The scanning electron microscopy image of $NiMo_{0.08}S_{0.17}$. (b) The linear sweep voltammetry of FTO substrate, Ni, NiS, and $NiMo_{0.08}S_{0.17}$ in a borate buffer solution (pH 9.2) with a scan rate of 10 $mVs^{-1}$

[1] N. Mahmood, Y. Yao, J.-W. Zhang, L. Pan, X. Zhang and J.-J. Zou, *Adv. Sci.* 2018, **5**, 1700464.
[2] A. P. Murthy, J. Theerthagiri, K. Premnath, J. Madhavan and K. Murugan, *J. Phys. Chem. C*, 2017, **121**, 11108-11116.
[3] W.-H. Huang and C.-Y. Lin, *Faraday Discuss.*, 2019, DOI: 10.1039/C8FD00172C.

# Lithium rich transition metal oxides as high capacity positive electrode materials in Li-ion cells

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Development of new materials for Li-ion batteries is mandatory to satisfy the increasing demand for devices with higher capacity, energy, prolonged calendar life and increased safety. One of the bottlenecks to improve lithium ion technology is the development of positive electrode materials with improved eco-compatibility, reduced costs and enhanced performance.

Promising candidates are Li/Mn-rich layered oxides with a general stoichiometry $Li_{1+x}M_{1-x}O_2$, in which M is a mix of transition metal as Ni, Mn, Co. From the structural point of view, these materials belong to the family of layered materials and attract growing attention for their large specific capacity (typically >200 mAh $g^{-1}$), and high working potentials (4-5V vs. Li) [1]. Nevertheless their practical use in a Li-ion device is still limited by several issues: (i) large irreversible capacity loss in the first cycle, (ii) poor rate capability, (iii) mean working potential decay upon cycling and (iv) large Co content [2]. Several strategies to mitigate these issues have been proposed, including tailored synthetic strategies, doping with other metals (like Fe, Cr, Zr and others) and coatings [3].

In this communication we present the synthesis and characterization of a lithium rich layered phase with stoichiometry $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$. The goal is to investigate the electrochemical performance in lithium cells in comparison to the available literature on similar materials.

Materials have been synthesized with a sol-gel synthesis. Composition, structural and morphological analyses have been carried out by the means of ICP-OES (inductive coupled plasma optical emission spectroscopy) XRD (X-ray diffraction) and SEM (Scanning electron microscopy). The electrochemical properties have been studied by cyclic voltammetry and galvanostatic tests.

[1] P. Rozier, J-M. Tarascon, Journal of The Electrochemical Society, 2015, 162 (14), A2490-A2499.
[2] P. Nayak, E. Erickson, F. Schipper,…. & D. Aurbach, Adv. Energy Mater., 2017, 8 (8), 1702397.
[3] P. K. Nayak, J. Grinblat, M. Levi, E. Levi, S. Kim, J. Choi, & D. Aurbach, Adv. Energy Mater., 2016, 6(8), 1502398.

# Hybrid inorganic-organic proton-conducting membranes based on SPEEK doped with $WO_3$ nanoparticles for application in vanadium redox flow batteries

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Nowadays, electrochemical energy storage (EES) systems are critical to improve the robustness and efficiency of the electrical distribution grid by peak shaving and load leveling. Owing to their fast response times, freedom from geographical constraints, facile scalability and high turnover efficiency, EES systems are very promising [1]. Vanadium redox flow batteries (VRFBs) exhibit a high safety, a long cyclability and include components that can be easily reprocessed [2]. The fundamental working principle of VRFBs is the exploitation of solutions based on vanadium species as the feeds for both the anode and the cathode, that undergo reversible redox reactions. One of the primary research hot spots in VRFBs is concerned with the proton-exchange membrane (PEM) [3]. Well-recognized issues that hinder the commercialization of VRFBs are the high cost and poor selectivity of the Nafion membrane used in the state of the art. Therefore, in order to make VRFB technology commercially viable, technical and economic barriers including high capital costs and rapid capacity decay need to be addressed.

This work reports the development of innovative and low-cost PEMs exhibiting an improved [$H^+/VO^{2+}$] ion selectivity in comparison with perfluorinated ionomers (*e.g.*, Nafion). SPEEK-based membranes containing a dispersion of tungsten oxide nanoparticles (NPs) in various molecular contents are prepared, that are labeled "[SPEEK/$(WO_3)_x$]" and consist of a SPEEK matrix hosting between 0 and 23.6 wt% of $WO_3$ nanoparticles (NPs). The effect of $WO_3$ nanofiller incorporation on the physicochemical properties, vanadium permeability, thermal stability and structure of the composite membranes is elucidated. It is found that the ion selectivity of hybrid membranes (up to $2.1 \cdot 10^4$ S·min·cm$^{-3}$ for [SPEEK/$(WO_3)_{0.20}$]) is much improved in comparison with recast Nafion ($6.5 \cdot 10^3$ S·min·cm$^{-3}$). The VRFB single cell assembled with [SPEEK/$(WO_3)_{0.20}$] exhibits a higher coulombic efficiency (CE, 98.2%) and energy efficiency (EE, 71.8%) than that assembled with Nafion212 as reference (CE 96.6% and EE 68.4%) at the current density of 80 mA cm$^{-2}$. Taken all together, the proposed [SPEEK/$(WO_3)_x$] hybrid membranes could be used as promising low-cost and high-performance membrane for VRFBs, owing to their good conductivity, remarkable ion selectivity and long-term stability.

**References**

[1] B. Dunn, H. Kamath and J.M. Tarascon, *Science.* 2011, **334**, 928-935.
[2] P. Leung, X. Li, C. Ponce De León, L. Berlouis, C.T.J. Low and F.C. Walsh, *RSC Adv.* 2012, **2**, 10125-10156.
[3] X.L. Zhou, T.S. Zhao, L. An, Y.K. Zeng and L. Wei, *J. Power Sources.* 2017, **339**, 1-12.

# Interplay between activation processes, physicochemical properties and electrochemical performance of *"core-shell"* carbon nitride Pt-Ni ORR electrocatalysts based on hierarchical graphene supports

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This work explores the effect of different EC activation approaches on ORR performance and on the reaction mechanism, aiming at a robust upscaling of the preparation process [1]. The ECs described here exhibit a *"core-shell"* morphology: a hierarchical graphene-based support (H-GR) *"core"* is covered by a carbon nitride *"shell"* stabilizing the active sites in *"coordination nests"* [2]. The *"core"* comprises highly defected graphene nanoplatelets [3] and carbon black nanoparticles; the latter improve the charge and mass transport phenomena that occur during the EC operation. A very low platinum charge characterizes these ECs, on the order of *ca.* 5% by weight, that is the *"active metal"*; Ni is introduced as the *"co-catalysts"* to improve the ORR performance [2]. An extensive post-synthesis activation process (**A**) is applied to the ECs, significantly affecting their chemical composition, structure and morphology.

The proposed ECs are extensively characterized both before and after **A** to study the complex interplay between the synthetic/activation parameters, the physicochemical properties, and the electrochemical ORR performance both *"ex-situ"* and in single PEMFC. The bulk chemical composition of the ECs is determined by means of Inductively-coupled plasma atomic emission spectroscopy (ICP-AES) and CHNOS microanalyses; the structure is investigated through wide-angle X-ray diffraction (WAXD) and vibrational spectroscopies (*e.g.*, confocal micro-Raman); the surface composition and oxidation states are probed with X-ray photoelectron spectroscopy (XPS); morphology is observed by high-resolution transmission electron microscopy (HR-TEM); the details of the ORR performance and reaction pathway as a function of the pH of the environment are elucidated by cyclic voltammetry with the rotating ring-disk electrode (CV-TF-RRDE). Finally, the ECs are used to fabricate membrane-electrode assemblies (MEAs) that are tested in single PEMFC in operating conditions.

**References**

[1] V. Di Noto, E. Negro, K. Vezzù, F. Bertasi, G. Nawn, L. Toncelli, S. Zeggio, F. Bassetto, Patent application PCT/IB2016/055728 (2016).
[2] V. Di Noto, E. Negro, K. Vezzù, F. Bertasi, G. Nawn, *The Electrochemical Society Interface*, 2015, **Summer 2015**, 59-64.
[3] V. Di Noto, E. Negro, A. Bach Delpeuch, F. Bertasi, G. Pagot, K. Vezzù, Patent application PCT/EP2017/084801 (2017.

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