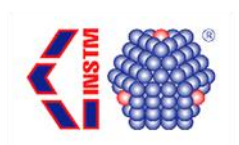




First Italian Workshop on Energy Storage - IWES 2021

BOOK OF ABSTRACTS

24-26 February 2021



BOOK OF ABSTRACTS

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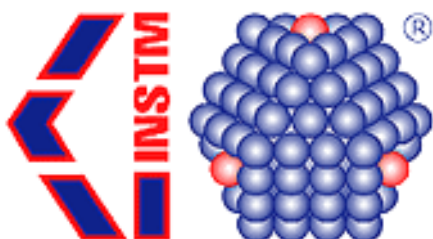
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Workshop proceedings

The Organizing Committee is happy to announce that the publication of the conference proceedings on a special dedicated issue of **Electrochimica Acta** (Elsevier publishing). This special issue (acronym EESC 2021) will be edited by **Prof. Sotiris Sotiropoulos** and **Prof. Vito Di Noto**, and co-edited by **Prof. Sergio Brutti, Dr. Chiara Ferrara, Prof. Enrico Negro, Dr. Gioele Pagot, Dr. Carlo Santoro and Dr. Cristina Tealdi**: the full title of the issue will be "**And Yet Electrochemical Energy Storage and Conversion Moves in 2021**". Contribution given at the IWES 2021 meeting will be welcome for peer-review following the standard careful procedures of the journal. The participation as speakers to the IWES2021 meeting does not guarantee the acceptance of manuscripts on the special issue. Submissions will be open from March the 20th 2021 to September the 20th 2021.

SCIENTIFIC PROGRAMME

DAY 1 - Wednesday 24th February

13:40-14:00	OPENING Prof. Piercarlo Mustarelli Prof. Catia Arbizzani Prof. Kristina Edström Prof. Vito Di Noto	
CHAIR: Kristina Edström and Vito Di Noto		
14.00-14.30	Janek	Solid-State Batteries – A Better Life without Liquids?
14.35-14.55	Appetecchi	Ionic liquid electrolytes for high-density lithium-ion battery systems operating at high voltages
15.00-15.15	Fracchia	Lithiation mechanism in high entropy oxides (HEOs) as anode materials for Li-ion batteries: an operando XAS study
15.15-15.30	Vezzù	Lithiated Fluorinated “Core-Shell” Nanoparticles as Single Ion-Conducting Electrolytes for Lithium Batteries
CHAIR: Claudio Gerbaldi		
15.40-16.00	Matic	Stabilization of Li-metal anodes with highly concentrated electrolytes and ionic liquids
16.05-16.20	Sharpe	Redox Chemistry and the Role of Trapped Molecular O ₂ in Li-Rich Disordered Rocksalt Oxyfluoride Cathodes
16.20-16.35	Amici	Composite solid electrolytes to enhance Lithium-metal cells safety
16.35-16.50	Darjazi	Improving high-voltage Ni-rich (LiNi _{0.8} Mn _{0.1} Co _{0.1} O ₂) cathode materials by modification for next-generation Li-ion batteries

DAY 2 - Thursday 25th February

CHAIR: Vincenzo Baglio		
09.45-10.00	Lingua	Unique carbonate-based single ion conducting block copolymers enabling high-voltage, all-solid-state lithium metal batteries
10.00-10.15	Mezzomo	Long life-cycle lithium metal batteries employing self-healing silica-based nanocomposite solid electrolytes
10.15-10.30	Falco	Enabling safe and stable Li metal batteries with protic ionic liquid electrolytes and high voltage cathodes
10.30-10.45	Lufrano	Nanocomposite Gel Polymer Electrolytes based on organo-clays: lithium ions transport study and mechanical properties
CHAIR: Gioele Pagot		
11.00-11.15	Triolo	Evaluation of electrospun Ge-doped Fe ₂ O ₃ nanofibers as anode in Na-ion batteries
11.15-11.30	Colombi	Autonomous self-healing strategy for stable Sodium-ion battery: a case study of Black Phosphorus anode
11.30-11.45	Staffolani	Fast Charging Anode for LIBs and NIBs Based on Fe ₃ O ₄ /rGO: Synthesis and Characterization
11.45-12.00	Touja	Sn-based protective layer for alkali metal electrodes
12.00-12.15	Soleimanzade	In-situ synthesis of nanowire Na ₄ Mn ₉ O ₁₈ and carbon nano fiber with exceptional rate capability used in aqueous sodium ion batteries
LUNCH		
CHAIR: Cristina Tealdi		
14.00-14.30	Stievano	Alkali-earth metal-sulfur batteries: tackling the drawbacks of inefficient Ca and Mg systems
14.35-14.55	Zeier	On influence of bonding interactions and structural disorders in solid ionic conductors
15.00-15.15	Baricco	Complex hydrides as electrolytes for solid-state batteries
15.15-15.30	Simari	NMR and electrochemical investigation of sodiated Nafion ionomer: toward a solid electrolyte for sodium-ion battery.
CHAIR: Lorenzo Stievano		
15.40-16.00	Arroyo De Dompablo	Recent progress on Calcium batteries: computational assessment of cathode materials
16.05-16.20	Fasulo	Singlet Oxygen release at Li-air battery cathode: new insights from first-principles calculations
16.20-16.35	Baglio	Bifunctional oxygen electrocatalysts prepared by electrospinning for alkaline metal-air batteries
16.35-16.50	Giorgetti	Electrochemical testing and characterization of Prussian blue analogues
16:50 – 17:00	Di Noto	EIT RawMaterials - The impact of Critical Raw Materials in Electrochemical Energy Storage and Conversion - An Introduction

DAY 3 - Friday 26th February

CHAIR: Maria Assunta Navarra		
09.45-10.00	Di Florio	Comparative Life Cycle Assessment (LCA) of a Redox Flow Battery with Semi-organic Electrolytes and a Vanadium Redox Flow Battery
10.00-10.15	Facchinetti	Thermally Regenerable Redox-Flow Batteries
10.15-10.30	Epoupa Mengou	An innovative membrane enhancing redox performance and reducing vanadium Crossover in Redox Flow Batteries
10.30-10.45	Crivellaro	Hybrid inorganic-organic proton-conducting membranes based on SPEEK doped with WO ₃ nanoparticles for application in vanadium redox flow batteries
CHAIR: Riccardo Ruffo		
11.00-11.15	Mele	Characterization of a laboratory flow zinc–air fuel cell and modelling of the polarization curves.
11.15-11.30	Morengi	Asymmetric supercapacitor with graphene-based electrodes
11.30-11.45	Dotoli	Online Electrochemical Mass Spectrometry for High Voltage Li-ion Battery cycle aging investigation
11.45-12.00	Lacarbonara	Gas Evolution in Li-ion batteries revealed by Electrochemical In-Situ Dilatometry
12.00-12.15	Bruni	Electrospun Carbon/CuxO Nanocomposite material as Sustainable and High Performance Anode for Lithium-Ion Batteries
LUNCH		
CHAIR: Francesca Pagnanelli and Sergio Brutti		
14.00-14.30	Kendrick	Sustainability of sodium and lithium ion batteries
14.35-14.55	Lanciotti	New challenges in battery production: an equipment manufacturer point of view
15.00-15.15	Curcio	Application of laser ablation in electrode materials processing
15.15-15.30	Tsurumaki	Development of all-solid-state batteries with Sn/C composite anodes
CHAIR: Sergio Brutti		
15.40-16.00	Pagnanelli	Innovative hydrometallurgical processes for the up-cycling of end of life Li-ion batteries
16.05-16.20	Morina	Extremely efficient deep eutectic solvents for a green approach to metal recovery from spent lithium batteries
16.20-16.35	Airoldi	Additive Manufacturing of Aqueous-Processed LiMn ₂ O ₄ Thick Electrodes for High-Energy-Density Lithium-Ion Batteries
16.35-16.50	Scaramuzzo	Advanced electrodes for Li-ion, Na-ion and Li-S batteries: from recycled materials to nanostructures

ABSTRACTS

Keynote Lectures (KN01-KN03)

Invited Talks (IT01-IT06)

Oral Presentations (OP01-OP34)

Solid-State Batteries - A Better Life without Liquids?

Juergen Janek*

Institute of Physical Chemistry & Center for Materials Research Justus Liebig University Giessen, Germany & BELLA, Institute of Nanotechnology, Karlsruhe Institute of Technology, Germany

Lithium ion batteries (LIB) with liquid electrolytes are the state-of-the-art technology in electrochemical energy storage. 30 years of development have achieved LIB cells with excellent performance, lifetime and safety. However, the demand for improved energy density, fast charge ability and stability is ever growing, and therefore, alternatives or improved LIB concepts are intensively studied. Recently, solid-state batteries (SSB) with solid electrolytes replacing the organic liquid electrolyte experience strong interest, as they may enable the use of the lithium metal anode with very high specific capacity and may also allow fast charge and discharge kinetics in a wide temperature range. While solid electrolytes with very high lithium ion conductivity, even higher than in the case of liquid electrolytes, are well available, electrode interfaces of solid-state cells and their stability and kinetics still represent key challenges on the way to high-performance SSBs. In this presentation, the current status of SSB research will be briefly summarized, and the remaining challenges and hurdles on the route to competitive SSB will be discussed. Own results on the kinetics of the lithium metal anode, on the cathode/solid electrolyte interface and on the role of electrode interlayers will be presented.

Alkali-earth metal-sulfur batteries: tackling the drawbacks of inefficient Ca and Mg systems

Lorenzo Stievano (a,b)

(a) ICGM, Univ. Montpellier, CNRS, ENSCM, Montpellier; (b) RS2E, CNRS, Amiens, France

The increasing need in Li-ion batteries for nomad and stationary energy storage applications might face limited Li resources in the future, involving possible cost volatility and geopolitical tensions. In the search for sustainable and performing alternatives, the combination of cheap Mg or Ca anodes with inexpensive sulfur could produce a game-changing technology. In theory, Ca/S or Mg/S cells exhibit high energy densities competing with the Li-ion ones. Research on such systems, however, is facing major hurdles due to the passivation of the alkali-earth metals with common electrolytes which form a blocking layer hindering the diffusion of the corresponding cations. Two approaches are proposed to tackle these issue: 1) Developing new non-corrosive and non-nucleophilic electrolytes, able to plate the alkali-earth metals efficiently at room temperature without reacting with polysulfides. 2) Using alkali-earth metal alloys, less sensitive than pure metals to passivation, enabling the use of standard electrolyte formulations. A proof of concept will be given for both approaches, showing their advantages and drawbacks in terms of energy density, cycling performance and viability.

Sustainability of sodium and lithium ion batteries

Emma Kendrick

School of Metallurgy and Materials, University of Birmingham, B15, 2TT, UK

Sustainable improvements in battery or cell design can be made through materials, electrode or cell developments. Here we discuss the role of cell architectures and the manufacturing steps required to optimise the cell performance of lithium-ion and sodium-ion batteries. In all cases the sustainability of the cell chemistry is dependent upon not only the components and the elemental composition of those components, but the life-time performance required for the application and the ability to reclaim, reprocess and reuse those materials. This talk will address aspects of cell composition, electrode manufacturing, formation and recycling with a focus upon sustainability and the circular economy. Lithium, Cobalt, Phosphate and Natural Graphite are all materials on the critical materials list from 2020. Graphite composite electrode architectures made from traditional slurry cast methods are compared to a digital deposition methods, where microstructural control of the electrode coatings can be achieved through rheology and formulation in addition to deposition. Long cycle life can be achieved in high coat weight electrodes through optimisation of electrolyte transport pathways. Moving from lithium based anodes to sodium; hard carbon electrode composite electrode formulations are also discussed where additional additives are incorporated into the electrode coating to achieve greater life-time, rate with less sodium dendrite formation over time. In this case the zeolite addition, rather than being a channel for electrolyte transport, these additives control the formation of the interface layer on the hard carbon. This then leads us to the formation and conditioning process, which is the final and most expensive stage of the manufacturing process. The effect of electrolyte additives and formation conditions upon the life-time and operation of the cell are discussed. Using the same cell chemistry and cells designs, in this case a sodium-ion cell chemistry, small changes in the formation protocols can have a large effect upon the performance and the life-time. Finally we discuss some of the aspects of recycling, and reclamation and re-use of some of the critical materials contained within different battery chemistries.

Ionic liquid electrolytes for high-density lithium-ion battery systems operating at high voltages

G.B. Appetecchi* (a), E. Simonetti (a), M. De Francesco (a); S. Brutti (b,c), A. Sarra (b), A. Paolone (b), O. Palumbo (b); S. Fantini (d), R. Lin (d), A. Falgayrat (d); H. Choi (e,f), M. Kuenzel (e,f), S. Passerini (e,f); H. Geaney (g), K.M. Ryan (g)

(a) ENEA, Materials and Physicochemical Processes Technical Unit (SSPT-PROMAS- MATPRO), Via Anguillarese 301, 00123, Rome, Italy; (b) Consiglio Nazionale delle Ricerche, Istituto dei Sistemi Complessi Piazzale Aldo Moro 5, 00185, Rome, Italy; (c) La Sapienza University of Rome, Department of Chemistry, Piazzale Aldo Moro 5, 00185, Rome, Italy (d) Solvionic SA, Site Bioparc Sanofi, 195 Route d'Espagne, BP1169, 31036, Toulouse Cedex 1, France (e) Helmholtz Institute Ulm (HIU), Helmholtzstrasse 11, 89081, Ulm, Germany (f) Karlsruhe Institute of Technology (KIT), P.O. Box 3640, 76021, Karlsruhe, Germany (g) Materials and Surface Science Institute and the Department of Chemical and Environmental Sciences, University of Limerick, V94 T9PX Limerick, Ireland

Ionic liquid electrolytes based on imidazolium and tetra-alkyl-ammonium cations, coupled with bis(perfluoroalkylsulfonyl)imide anions, were specifically designed for application in safer, more reliable, high-density and high-voltage (up to almost 5 V) lithium-ion batteries. The quality control reveals moisture and halide contents below 5 ppm. The ion transport and electrochemical properties were herein reported and compared. Appealing conductivity values for practical battery systems were found for the EMI ($>10^{-3}$ S cm $^{-1}$) and N1114FSI ($>10^{-4}$ S cm $^{-1}$) electrolytes already at -10 °C. Anodic cyclic voltammetry experiments have revealed very low residual current values (< 10 μ A cm $^{-2}$) up to potentials above 4.8 V (vs. Li $^{+}$ /Li). Also, potential anodic dissolution phenomena of the aluminium current collector, due to the presence of the ionic liquid electrolytes, were preliminarily investigated. Battery cycling tests of the selected ionic liquid electrolytes employing large-capacity, silicon nanowire anodes and high-voltage, lithium-rich layered oxide (Li $_{1.2}$ Ni $_{0.2}$ Mn $_{0.6}$ O $_2$) cathodes are reported. Acknowledgements The authors would like to acknowledge the financial support from the European Union within the Si-DRIVE project. This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 814464.

Stabilization of Li-metal anodes with highly concentrated electrolytes and ionic liquids

Aleksandar Matic*, Shizhao Xiong, Matthew Sadd

Department of Physics, Chalmers University of Technology, 41296 Sweden

Metallic lithium is in many respects the ultimate anode material for high-energy-density batteries. The specific energy of Li-metal is required to match next generation high energy cathode concepts both when using liquid electrolytes and when trying to realise all solid-state batteries. However, the high reactivity of metallic Li, with both liquid and solid electrolytes, leads to low Coulombic used and safety concerns, which are connected to the unavoidable growth of Li dendrites during electrochemical plating process. Several strategies have been proposed to stabilize Li-metal anodes, based on new electrolyte formulations or the development of functional interlayers. In this contribution we present recent works aiming to understand the deposition process both at liquid-solid and solid-solid interfaces, targeting both conventional and solid-state batteries. We show how ionic liquid-based interlayers can be used to address interfacial issues in solid-state batteries and enable stable operation even at high current densities [1]. With a combination of phase-field modelling and electrochemical experiments we also show that a rapid depletion of Li-ions on the electrode surface, induced by e.g. low operating temperature, diluted electrolyte or high applied current density, is the underlying driving force for non-uniform electrodeposition of Li [2,3].

[1] Design of a multifunctional interlayer for NASICON-based solid-state Li metal batteries S. Xiong, Y. Liu, P. Jankowski, Q. Liu, F. Nitz, K. Xie, J. Song, and A. Matic, *Advanced Functional Materials*, 2001444 (2020); [2] Role of Li-ion depletion on electrode surface: underlying mechanism for electrodeposition behavior of lithium metal anode, X. Xu, Y. Liu, J-Y. Hwang, O. O. Kapitanova, Z. Song, Y-K. Sun, A. Matic and S. Xiong *Advanced Energy Materials*, 2002390 (2020) [3] Insight into the critical role of exchange current density on electrodeposition behavior of lithium metal, Y. Liu, X. Xu, M. Sadd, O. O. Kapitanova, V. A. Krivchenko, J. Ban, J. Wang, X. Jiao, Z. Song, J. Song, S. Xiong, and A. Matic, *Advanced Science*, 2003301 (2021)

On influence of bonding interactions and structural disorders in solid ionic conductors

W.G. Zeier

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The advent of solid-state batteries has spawned a recent increase in interest in lithium conducting solid electrolytes, especially in the lithium thiophosphates. However, many open questions remain when trying to optimize electrolytes and understand solid state battery chemistries. In this presentation, we explore the influence of inductive effects in superionic conductors showing that in $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, these can strongly affect the ionic transport. In addition, we show how a better understanding of how an underlying structural disorder can be used to tailor the ionic conductivities in superionic materials.

Recent progress on Calcium batteries: computational assessment of cathode materials

M. Elena Arroyo-de Dompablo

Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040 Madrid (Spain)

To meet the increasing energy and power demand at lower cost advances in electrochemical energy storage systems are urgently needed. A desirable alternative to Li-ion batteries is to develop metal-anode rechargeable batteries based on abundant elements such as Na, K, Ca or Mg. Calcium is an attractive candidate due to its low cost, natural abundance and low reduction potential. The development of rechargeable batteries based on a Ca metal anode demands the identification of suitable cathode materials [1]. In the last years we have investigated the potential application of a variety of compounds, which are selected from the Inorganic Crystal Structural Database (ICSD) considering 3d-transition metal oxides, oxysulphides, pyrophosphates, silicates, nitrides, and phosphates with a maximum of four different chemical elements in their composition. Cathode performance is evaluated throughout the DFT-calculation of operation voltages, volume changes associated to the redox reaction and mobility of Ca²⁺ ions. The major downside of the materials is the hampered diffusion of Ca²⁺ ions. Some Fe-based materials exhibit attractive specific capacities and intercalation voltages combined with energy barriers for Ca migration around 1 eV (Ca₄Fe₉O₁₇, CaFeSO, Ca₂FeSi₂O₇, Ca₂Fe₂O₅). In this presentation we will discuss DFT results that signify αI-VOPO₄ as a promising Ca-cathode.

[1] M.E. Arroyo-de Dompablo, A. Ponrouch, P. Johansson and M.R. Palacin, Achievements, Challenges, and Prospects of Calcium Batteries. Chem. Rev. 120 (2020) 6331-6357.

New challenges in battery production: an equipment manufacturer point of view

Stefano Saguatti, Claudio Lanciotti

Manz, Italy

How to bring a new technology or innovative cell design or improvement to mass production? Battery manufacturing and their implication are identified, process flows are selected, manufacturing proof of concept tools are developed to test and validate individually critical processes and their relevant limiting factors. Initially, few samples are made per day to verify the quality and scalability of the new technology. When the key principles have been proven then they will be transferred into Pilot R&D equipment. The POC concept tools are integrated to demonstrate the capability of the new manufacturing sequence, already fully machine-controlled, to produce prototype components in an R&D environment. The next step is a single Pilot Production Line with a capability of 15 to 30 cells per minute that will allow in-depth evaluation of product quality. Mass production at the Giga factory level needs to integrate multiple Pilot production lines with automatic material handling and logistics. The driving factors for process development mainly focused on cost reduction now need to be paired with sustainability and recyclability issues. Several tools like full digitalization of the production, power requirement optimization, and digital twins will shape and make better the new battery production plants.

Innovative hydrometallurgical processes for the up-cycling of end of life Li-ion batteries

Francesca Pagnanelli

Department of Chemistry, La Sapienza University of Rome

Lithium ion batteries are the dominant technology for portable electronics, stationary storage and electric and hybrid vehicles. However, the production of these batteries requires critical raw materials such as cobalt, lithium and graphite, which imposes their recycling. In this line, the proposed adaptation of the Battery Directive introduces specific recycling targets for critical metals. Today in EU, LIB recycling processes are based on pyrometallurgical approaches that burn graphite and slug lithium (down-cycling) with significant environmental impacts for energy consumption and release of greenhouse gases. Low temperature hydrometallurgical processes can be a sustainable alternative allowing the integral recovery of all components of LIB. Nevertheless, these processes suffer from the complexity and heterogeneity of LIBs, which involve expensive plants for the separation of the different metal components in the starting salts necessary for the production of new batteries. A change of vision is needed towards simple processes for the production of high-value products, moving from pyrometallurgical down-cycling to hydrometallurgical up-cycling. An example of this change in vision is an integrated process of cryomechanical treatment, leaching and recovery of cathodic and anodic materials with application for the production of new LIBs.

Lithiation mechanism in high entropy oxides (HEOs) as anode materials for Li-ion batteries: an operando XAS study

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High entropy oxides (HEOs) are a new class of materials firstly discovered in 2015 [1]; the first explored material is $\text{Co}_0.2\text{Cu}_0.2\text{Mg}_0.2\text{Ni}_0.2\text{Zn}_0.2\text{O}$, that can be obtained by mixing in equimolar ratio the correspondent parent compounds. The contribution of the configuration entropy, particularly large for a mix of 5 components, leads to the formation of a single-phase with rock salt structure. Due to its high specific capacity and cycling reversibility, this material has drawn great attention as potential anode in Li-ion batteries [2,3]. However, its lithiation/ delithiation mechanism is still controversial. Here I will present our recent work [4], where we carried out an operando XAS (X-ray absorption spectroscopy) investigation into HEO anodes for Li-ion cells with the aim of elucidating the working mechanism during the first lithiation/delithiation cycle. The spectroscopic measurements, coupled to electrochemical and microstructural characterization, revealed the occurrence of a complex redox mechanism, developing through the reduction of the transition-metals, which triggers the conversion reaction below 1 V. The conversion is irreversible and incomplete, leading to the final collapse of the rock-salt structure. However, it was observed that, before collapsing, the structure is retained up to the 60% of charge, thus proving the beneficial role of the configuration entropy.

[1] C. M. Rost, E. Sachet, T. Borman, A. Moballegh, E. C. Dickey, D. Hu, J. L. Jones, S. Curtarolo and J. P. Maria, *Nat. Commun.*, 6 (2015), 8485. [2] A. Sarkar, L. Velasco, D. Wang, Q. Wang, G. Talasila, L. de Biasi, C. Kubel, T. Brezesinski, S. S. Bhattacharya, H. Hahn and B. Breitung, *Nat. Commun.*, 9 (2018), 3400. [3] A. Sarkar, Q. Wang, A. Schiele, M. R. Chellali, S. S. Bhattacharya, D. Wang, H. Hahn, L. Velasco and B. Breitung, *Adv. Mater.*, 31 (2019), 1806236. [4] P. Ghigna, L. Airoidi, M. Fracchia, D. Callegari, U. Anselmi-Tamburini, P. D'Angelo, N. Pianta, R. Ruffo, G. Cibin, D. Oliveira de Souza and E. Quartarone, *ACS Appl. Mater. Interfaces*, 12 (2020), 50344-50354

Lithiated Fluorinated “Core-Shell” Nanoparticles as Single Ion-Conducting Electrolytes for Lithium Batteries

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The development of high-performing functional materials for application in solid lithium-ion secondary batteries is nowadays one of the most active fields in the scientific research panorama [1]. Recently, a ceramic material based on lithiated fluorinated-TiO₂ (LiFT) was proposed acting both as a solid-state electrolyte and as a nanofiller (NF) to obtain nanocomposite electrolytes [2-4]. LiFT consists of fluorinated anatase nanoparticles (NPs), whose surface is functionalized with Li⁺ ions through an innovative one-step process involving metallic Li [5]. When used as a NF, LiFT act both as the source of Li⁺ and as a plasticizing agent of the solvent. Accordingly, LiFT allowed us to devise innovative composite with a high thermal stability and conductivity (>40 mS/cm). In this work, we present our recent studies on two different applications of LiFT NPs in Li-secondary batteries: a) pristine ceramic solid-state electrolyte and b) NF as source of Li⁺ in a family of ionic liquid-based electrolytes (EMImBF₄ and EMImTFSI). The correlation between structure, thermal properties and conductivity mechanism of the resulting electrolytes is elucidated by a variety of techniques. Finally, the most promising electrolytes go through electrochemical studies and are adopted in the fabrication of battery prototypes, that undergo charge/discharge cycles in operative conditions at different C rates.

[1] V. Di Noto, S. Lavina, G.A. Giffin, E. Negro, B. Scrosati, *Electrochimica Acta* 57 (2010) 4. [2] F. Bertasi, G. Pagot, K. Vezzù, E. Negro, P.J. Siders, S.G. Greenbaum, H. Ohno, S. Scrosati, V. Di Noto, *J. Power Sources*, 400 (2018) 16. [3] F. Bertasi, K. Vezzù, G.A. Giffin, T. Nosach, P.J. Siders, S.G. Greenbaum, M. Vittadello, V. Di Noto, *Int. J. Hydrogen Energy*, 39 (2014) 2884. [4] F. Bertasi, K. Vezzù, E. Negro, S. Greenbaum, V. Di Noto, *Int. J. Hydrogen Energy*, 39 (2014) 2872. [5] V. Di Noto, F. Bertasi, E. Negro, M. Piga, M. Bettioli, F. Bassetto, *Solid- State Electrolytes based on Fluorinated doped Oxides* (2012), PCT/IB2012/053542.

Redox Chemistry and the Role of Trapped Molecular O₂ in Li-Rich Disordered Rocksalt Oxyfluoride Cathodes

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In the search for high energy density cathodes for next-generation lithium-ion batteries, the disordered rocksalt oxyfluorides are receiving significant attention due to their high capacity and lower voltage hysteresis compared with ordered Li-rich layered compounds. However, a deep understanding of these phenomena and their redox chemistry remains incomplete. Using the archetypal oxyfluoride, Li₂MnO₂F, we show that the oxygen redox process in such materials involves the formation of molecular O₂ trapped in the bulk structure of the charged cathode, which is reduced on discharge. The molecular O₂ is trapped rigidly within vacancy clusters and exhibits minimal mobility unlike free gaseous O₂, making it more characteristic of a solid-like environment. The Mn redox process occurs between octahedral Mn³⁺ and Mn⁴⁺ with no evidence of tetrahedral Mn⁵⁺ or Mn⁷⁺. We furthermore derive the relationship between local coordination environment and redox potential; this gives rise to the observed overlap in Mn and O redox couples and reveals that the onset potential of oxide ion oxidation is determined by the degree of ionicity around oxygen, which extends models based on linear Li–O–Li configurations. This study advances our fundamental understanding of redox mechanisms in disordered rocksalt oxyfluorides, highlighting their promise as high-capacity cathodes [1]. [1] R. Sharpe, R. A. House, M. J. Clarke, D. Förstermann, J. J. Marie, G. Cibir, K. J. Zhou, H. Y. Playford, P. G. Bruce and M. S. Islam, *J. Am. Chem. Soc.*, 142 (2021) 21799-21809

Composite solid electrolytes to enhance Lithium-metal cells safety

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Electrical energy storage is a critical issue to answer global warming by effectively replacing fossil energies by renewable ones. The Li-ion technology, widely studied and available on the market is now reaching its limits and does not represent alone a viable option toward energetic transition. In this perspective, Li metal anode represents the “holy grail” of battery research for its extremely high theoretical specific capacity, and its low gravimetric density. However, it also presents many challenges derived primarily from dendrite formation upon cycling causing both safety issues and poor cycling performance. The use of a solid electrolyte has been recognized as an effective approach to address the above problems even though, solid polymer electrolytes suffer from poor ionic conductivity at room temperature and inorganic ceramic electrolytes from poor interfacial contact with electrodes. Solid composite electrolytes on the contrary benefit from good ionic conductivity, flexibility, and intimate contact with the electrodes. For example, the preparation of methacrylate-based polymer matrix, in a solvent free, thermally induced, radical polymerization, allows the addition of a wide range of additives up to high ratio. The simplicity of the formulation and the preparation method open the road to highly versatile electrolytes, adaptable in function of the final application.

Improving high-voltage Ni-rich ($\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$) cathode materials by modification for next-generation Li-ion batteries

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Due to the cost and safety concerns together with the increasing demands on the Li-ion batteries (LIBs) high energy density, Ni-rich $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (NMC811) have been considered promising cathode materials for next-generation commercial LIBs, thus as to elevate the market influence of zero-emission electric vehicles [1–3]. However, their low cycling stability stands in their large-scale applications way [4]. Herein, we enhanced the structural stability of NMC811 by applying lattice doping and surface coating, which can suppress multi-phase transformation. Comprehensive structural and electrochemical characterizations are performed. The modified NMC delivers a specific capacity of 232 mAh/g, at 0.1C and high charge cut-off voltage of 4.8 V vs Li/Li⁺, and significant-good cycling stability after 100 cycles; better than standard NMC811. In order to identify the origin of the improvement, we have evaluated the ionic and electronic transport properties, as well as the solid electrolyte interphase layer behavior correlated with structural changes [5], electrochemical impedance spectroscopy measurements have been carried out by recording spectra every 25 mV during Li-ion extraction. The main finding of this study is an improved charge/discharge performance due to doping and coating, which hinders phase transition.

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Unique carbonate-based single ion conducting block copolymers enabling high-voltage, all-solid-state lithium metal batteries

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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 requires batteries with improved energy density at reduced cost, 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. These issues are prompting research on the development of new electrolyte materials. Within the context of solid state battery technology development, a variety of solid-state electrolytes have been investigated to date; in principle, they enable extension of the operating temperature range of a device, also ensuring higher safety even in the case of fire, together with enhanced energy and power densities. Among solid polymer electrolytes (SPEs), the new class of “single ion conducting polyelectrolytes” (SICPs) has deserved considerable attention [2-5]. SICs are composed of a polymer backbone bearing a covalently bonded anionic functional groups along with a lithium counterion free to move and responsible for ion mobility. Because of their single-ion nature, the lithium transport number values approach unity; this accounts for remarkable benefits to the electrochemical performance, because Li⁺ ions are predominantly engaged in the redox reaction while anions remain relatively inactive. Other fundamental features of SICPs include a wide electrochemical stability and compatibility with the active materials, particularly lithium metal. In this work we focus on the development of novel poly[(carbonate)-b-(ionic liquid)] block copolymers with single Li-ion conducting features, showing greatly enhanced performance towards the state of the art solid state systems in terms of compatibility with high voltage cathodes (e.g., LiNiMnCoO₂, NMC) as well as lithium metal anode and operating at almost theoretical capacity in lab-scale cells. Ring opening polymerization (ROP) has been exploited on trimethylene carbonate (TMC) monomer directly using a RAFT-agent having hydroxyl terminal group to obtain poly(carbonate)-based macro RAFT precursor. Then the features of the polycarbonate based block were matched with the ones of the specifically designed ILM, namely lithium 1-[3-(methacryloyloxy)propylsulfonyl]-1-(trifluoromethylsulfonyl)-imide (LiMTFSI). The poly(carbonate)-based macro RAFT precursor was further utilized to synthesize a series of block copolymers comprising LiMTFSI and poly(ethylene glycol) methyl ether methacrylate (PEGM) via controlled RAFT polymerization. The obtained ionic block copolymers, named poly[TMC_n-b-(LiM_m-r-PEGM_k)] were thoroughly characterized from the chemical-physical viewpoint by NMR, DSC, TGA, AFM, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). The electrochemical behaviour of the SICPEs was then evaluated by means of constant-current (galvanostatic) charge/discharge cycling in lithium metal lab-scale cells using lithium iron phosphate (LFP) and NMC catholytes with excellent reversible cycling.

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Long life-cycle lithium metal batteries employing self-healing silica-based nanocomposite solid electrolytes

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The inherent limitations linked to the chemistry of Li-ion batteries and the growing demand for devices with high energy density have recently brought renewed interest in the exploitation of lithium metal anode for next-generation secondary batteries. Unfortunately, uncontrolled growth of Li dendrites on the anodic surface is preventing its practical implementation [1]. This can be overcome using mechanically strong solid electrolytes, such as nanocomposite polymeric ones that hinder dendrite growth thanks to the homogenous dispersion of strengthening ceramic fillers into a soft polymeric matrix, otherwise prone to dendrite piercing [2]. Following an approach similar to the one previously exploited for the incorporation of TiO₂ nanoparticles into polymeric matrices [3], relatively high content (20-30 wt%) of PEO-grafted silica nanoparticles have been successfully encompassed into high-Mw PEO to produce ceramic-in-polymer solid electrolytes that display an ionic conductivity comparable to polymeric analogues and a highly improved stability upon cycling. Moreover, these electrolytes present a notable self-healing behaviour, often regarded as an important feature for next-generation batteries [4]: thanks to the well-known SiO₂ reaction with Li [5], the dendrites grown into the separator are disrupted and several cells autonomously restarted their operation after failure.

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Enabling safe and stable Li metal batteries with protic ionic liquid electrolytes and high voltage cathodes

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In the present global scenario, batteries are identified as high-performance systems that can efficiently store and deliver energy on demand along with reducing the carbon footprint of the transportation sector, stabilize the power grid and support a wide range of strategic industries. Lithium-ion batteries (LIBs) are dominating the portable consumer electronic market, being most promising for the realization of hybrid-electric, plug-in and full electric vehicles, as well as for advanced delocalized energy storage units. Commercially available LIBs employ electrolytes based on organic carbonate mixtures that guarantee high ionic conductivity and low charge-transfer resistance at the interface with the active materials. However, the presence of flammable and volatile organic solvents accounts for serious safety hazards, which are prompting research on the development of new electrolyte materials. Ionic liquids (ILs) are amongst the most promising candidates to replace conventional organic liquid electrolytes [1]. ILs are an interesting class of salts having melting points lower than 100 °C, with negligible vapour pressure at low/moderate temperature, high chemical and thermal stability, and, in some cases, hydrophobicity; as a result, they are considered safe due to non-flammability [2]. In this work we investigate the subset family of protic ionic liquids (PILs), which is receiving increasing attention, as they possess all the attractive features of aprotic ionic liquid (AILs), while being cheaper and easier to prepare, thus more sustainable. The main advantage of PILs over AILs is the presence of less shielded cations, intrinsically responsible for the “cation competition effect”, which, in a mixture of PIL-Li salts, results in loosely coordinated Li⁺ ions along with improved mobility [3]. The use of PILs as electrolytes in high-energy Li metal battery was never considered due to the presence of acidic protons, which are strongly reactive towards the Li metal electrode. Considering the highest theoretical capacity (3860 mAh g⁻¹) and the lowest electrochemical potential (-3.04 V vs. SHE) of the Li metal anode, the promising combination with PILs as electrolyte is a great challenge, possibly leading to high-energy density devices, with improved performances compared to the systems with AILs [4]. Here we present for the first time the use of pyrrolidinium-based PILs with Li metal as anode in two different Li-metal cell configurations, using either LiFePO₄ (LFP) or LiNiMnCoO₂ (NMC) as cathodes. The electrolytes consist of solutions of N-butylpyrrolidinium-bis(trifluoromethanesulfonyl)imide (PYRH4TFSI) or N-butylpyrrolidinium-bis (fluorosulfonyl)imide (PYRH4FSI) in combination with LiTFSI or LiFSI, respectively. The electrolyte solutions are combined with vinylene carbonate (VC) that has the fundamental purpose of promoting the formation of a stable protective layer on the Li metal anode, preventing detrimental reactions due to the protic ILs, by means of electrochemically induced reductive decomposition upon initial cycling [5]. Remarkably stable ambient temperature cycling at different current regimes is firstly demonstrated even with >4 V class NMC composite cathodes, as well as in comparison with the corresponding AIL-based cells. The same PILs were used in combination with crosslinked polymers demonstrating their use also in Li-metal solid-polymer cells [6].

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Nanocomposite Gel Polymer Electrolytes based on organo-clays: lithium ions transport study and mechanical properties

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One of the biggest challenges lithium batteries face is related to their safety. The flammability and low vapor pressure of the liquid electrolytes are responsible for the explosion and re-ignition risks of a battery. Many attempts have been made in recent decades to replace the liquid electrolyte based on organic solvents with a solid one. GPEs are a promising and concrete concept of electrolytes for lithium-battery technology. In this work, we applied the strategy of the nanocomposite membranes, to prepare advanced GPEs. The starting gel electrolyte is based on polyethylene-oxide (PEO)/polyacrylonitrile (PAN) blend polymers as matrix to incorporating an organic electrolyte solution, LiTFSI in EC-PC. Nanocomposite gels were obtained by dispersion of a nanoscale organic/inorganic filler based on montmorillonite (MMT) clay. Specifically, the organo-modified MMT clay was synthesized by intercalation of CTAB molecules in the interlamellar space of sodium montmorillonite (Na-MMT) through a cation-exchange reaction. The self-standing composite GPEs were investigated by a combination of thermal (DSC), morphological (SEM) and mechanical analysis (DMA), while the ion transport properties were investigated by AC impedance spectroscopy and multinuclear (^7Li and ^{19}F) PFG-NMR spectroscopy. A complete description of the ions dynamics in so complex systems was achieved according to the Nernst-Einstein equation.

Evaluation of electrospun Ge-doped Fe₂O₃ nanofibers as anode in Na-ion batteries

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Although Na-ion batteries (NIBs) represent the electrochemical energy storage systems with the highest level of maturity and sustainability among post-lithium rechargeable batteries, the development of highly performing anode materials is one of the barriers to still be overcome for their commercialization at the large scale. In this scenery, transition metal oxides are gathering increasing attention thanks to their high theoretical reversible capacities and low cost. In this work, electrospun Ge-doped Fe₂O₃ nanofibers (Fe₂O₃:Ge NFs) are comprehensively characterized and evaluated as active anode material in NIBs. Germanium, incorporated in the iron oxide lattice mainly as a dopant impurity, favors the formation of α - and γ -phases of the iron oxide; an amorphous component is also present. Ge⁴⁺ ions occupy tetrahedral sites of the maghemite lattice and the defective hematite surface sites. The NFs, consisting of fine and elongated nanostructures developing along their axis, exhibit good specific capacity (320 mAh g⁻¹ at 50 mA g⁻¹ rate) and excellent rate capability (still delivering 140 mAh g⁻¹ at 2 A g⁻¹) thanks to the synergy between their nanostructured morphology, electronic transport properties and the pseudo-capacitive nature of the charge storage mechanism.

Autonomous self-healing strategy for stable Sodium-ion battery: a case study of Black Phosphorus anode

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Self-healing polymers have attracted increasing attention for their potential use as polymer electrolytes within Li- (LIB) or Na-ion (SIB) batteries. The development of functional polymers with suitable characteristics has proven to be a promising strategy for making safe and high-performance batteries. The polymer electrolytes, consisting of fragile polymers, can break during charging cycles, making direct contact between the electrodes causing serious safety problems. The difficulty in designing self-repairing polymer electrolytes, with high healing efficiency and excellent electrochemical performance without the aid of external stimuli, has led the attention to supramolecular polymer chemistry. This type of self-healing polymers could be used in high-performing anode active materials like Phosphorus. This material undergoes by volume expansion and phase changes upon ion insertion. To avoid the capacity decay and short lifetime, generated by the volumetric expansion/contraction upon sodiation/desodiation, a solution could be a self-healing strategy, based on the dynamic quadruple hydrogen bonding. Instead of a common binder, an innovative ureidopyrimidinone (UPy)-telechelic system, with a robust polyethylene glycol content, and related blends with poly(ethylene oxide) lead to obtain an BP anodes with impressively improved capacity retention.

Fast Charging Anode for LIBs and NIBs Based on Fe₃O₄/rGO: Synthesis and Characterization

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In this study we present the synthesis and characterization of a Fe₃O₄-based nanocomposite anode for LIBs and NIBs. Several transition metal oxides have been studied for both mentioned alkali-ion batteries because of their high specific capacity such as Co₃O₄ (890 mAh g⁻¹), SnO₂ (1494 mAh g⁻¹) and Fe₃O₄ (924 mAh g⁻¹)[1,2]. The latter is certainly a good candidate thanks to its low toxicity, low cost and earth abundancy. Anyway, several issues must be faced to make it suitable for real application e.g., the remarkable structural change and volume expansion which can lead to the electrode pulverization and eventually capacity decay[3]. Herein we report a facile one-pot synthesis of Fe₃O₄ nanoparticles (Fe₃O₄ nps) by a base-promoted coprecipitation, and a facile and quick embedding of Fe₃O₄ nanoparticles into reduced graphene oxide (Fe₃O₄/rGO), given by a sonochemical approach and chemical reduction. The obtained materials are structurally characterized by XRD, SEM and Raman spectroscopy. The electrochemical behaviour is studied by CV, galvanostatic cycling, rate capability and PEIS. Thanks to this rapid and simple approach, the Fe₃O₄ nps and rGO are linked together without the need of any other molecular linkers, leading to remarkable properties such as a specific capacity of \approx 980 mAh g⁻¹ at 4C (3.7 A g⁻¹) in LIBs and \approx 300 mAh g⁻¹ at 1 A g⁻¹ in NIBs.

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Sn-based protective layer for alkali metal electrodes

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The increasing demand for better batteries has generated a renewed interest in Li metal batteries. Thanks to its high specific capacity (3860 mAh g⁻¹), in fact, Li metal can increase their energy density. The growth of dendrites on Li anodes during charge and discharge cycles, however, does not only lower the coulombic efficiency but also raises safety issues (short circuits, thermal runaway and fire hazards). Therefore, many efforts have been led to find strategies for protecting Li and controlling dendrites' growth [1]. In this study, a Sn-based protective layer covering the electrode surface, obtained by dropping a SnCl₄ solution on top of the electrode, was applied to Li anodes and extended to sodium and potassium systems. The nature of the layer, characterized using X-Ray Diffraction and Mössbauer spectroscopy, proves the formation of the Sn-alkali alloy as well as the alkali-chloride salts on the surface of the electrodes. These protective layers have a positive effect on the performance of protected electrodes compared to that of bare alkali metal anodes.

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In-situ synthesis of nanowire $\text{Na}_4\text{Mn}_9\text{O}_8$ and carbon nano fiber with exceptional rate capability used in aqueous sodium ion batteries

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Although research on aqueous sodium ion batteries is not completely new, fundamental challenges such as the choice and combination of electrode materials remain to be addressed. While some materials have been introduced for using as cathode, the channeled structure $\text{Na}_4\text{Mn}_9\text{O}_{18}$ (NMO) is still one of the promising candidates, meeting the screening criteria for using in aqueous sodium batteries. [1] However, NMO suffers from low rate capability especially for high speed applications. In this study, by choosing the right precursors and optimum treatment parameters, ultra-long (~50nm thickness and ~20 μm length) single crystals of nanowire NMO had been synthesized by hydrothermal treatment. In contrary to satisfactory cyclic stability of obtained nanowires in aqueous electrolyte, the bare NMO presents relatively low rate capability, due to low electrical conductivity. To solve this, we, for the first time, report an in-situ synthesis of NMO nanowires with carbon nano fiber (CNF). By changing the raw materials and hydrothermal parameters, nanowire NMO had been synthesized in presence of CNF. In addition, by optimizing the CNF load, the electrical conductivity of synthesized NMO + CNF is increased to more than 10,000 S/cm. As a result, the rate capability is significantly improved and at 20C (charge or discharge in 3 min), more than 50% of theoretical capacity (25mAh/g) had been preserved.

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Complex hydrides as electrolytes for solid-state batteries

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Solid-state electrolytes (SSEs) are candidates to substitute organic liquids currently employed in batteries. Complex hydrides (CH) are suggested as SSEs for all-solid state batteries (SSB), due to their high ionic conductivity close to room temperature (RT). A combination of DFT and topological calculations allowed to identify correlations between crystal structures and Li-ion conductivity in CH [1]. The hexagonal phase of LiBH₄, which is stable at temperatures above 110 °C, has a high ionic conductivity (~10⁻³ S cm⁻¹ at 120 °C). The halogenation of LiBH₄ with Br⁻ and Cl⁻ of LiBH₄ allows the synthesis SSEs operating at RT, suggesting possible applications in Li-ion SSB [2]. To access a RT SSB, the Li-ion conductivity of LiBH₄ can be enhanced with the development of highly conductive interfaces by mixing it with oxide nanoparticles (e.g. SiO₂, Al₂O₃ and MgO) [3]. The optimal composition of the mixture results 53 v/v % of MgO, showing a Li-ion conductivity of 2.86 10⁻⁴ S cm⁻¹ at 20 °C. The mixture has been incorporated as SSE in a TiS₂/Li all-solid-state Lithium metal-ion battery. A stable solid electrolyte interphase has been obtained by a pre-conditioning cycling at 60 °C and a capacity retention of about 80 % at the 30th cycle was obtained at RT [4]. DFT and topological calculations are in progress for Mg(BH₃-NH₃)₂(BH₄)₂, suggested as SSE on Mg-ion SSBs [5].

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NMR and electrochemical investigation of sodiated Nafion ionomer: toward a solid electrolyte for sodium-ion battery

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The safety and stability issues of conventional liquid electrolytes for sodium batteries, have prompted researchers for the development of durable, safe and good performing sodium-conducting polymer electrolytes (SPEs) [1]. In the early stages of SPE-based sodium batteries, high Na⁺ availability and ionic conductivity were generally achieved by dissolving the appropriate sodium salts in a suitable polymer matrix [2]. More recently, a new concept for polymer electrolytes has been proposed based on a single ion conducting-SPEs, which have anions covalently bonded to the polymer backbone [3]. In this regard, great attention should be devoted to Nafion® ionomer, a perfluorinated ion exchange membrane with ionizable groups (–SO₃[–]), which combines fast cation transport and unity transference number with good thermal and electrochemical stability. De facto, some preliminary studies have recently demonstrated Nafion membrane might be effectively used as both electrolyte and separator for the sodium-ion batteries [4]. Here, a sodiated Nafion membrane was synthesized and its ionic conductivity and sodium transference number investigated in common non-aqueous solvents. Stripping/plating tests, galvanostatic cycling vs. NaTFSi, and stability tests were carried out to characterize the electrochemical performance of Na⁺-Nafion, whereas the Pulsed Field Gradient (PFG) NMR technique allowed a thorough and systematic study of the sodium-ions transport mechanisms in such systems. Finally, dynamic mechanical analysis (DMA) were carried out to investigate the mechanical properties of the film.

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Singlet Oxygen release at Li-air battery cathode: new insights from first-principles calculations

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Several recent experiments have shown that singlet oxygen (1O_2) is formed at Li-air battery cathode upon charging. Such highly reactive specie undermines the performance and the long-term stability of the battery [1,2]. Nevertheless, studying the elusive mechanism of singlet oxygen release represents a challenging task for both experiments and theory. In this contribution we focus on such process from a computational perspective. In particular, we address the formation of 1O_2 from the lithium peroxide (Li_2O_2) surface, considering the facets that are among the most exposed ones in Li_2O_2 nanoparticles [3,4]. We report the release of triplet- and singlet-oxygen species and compare the results of two different ab initio approaches, the periodic DFT and the embedded cluster approach at the CASPT2 level of theory. A first important result of our study is that the starting oxygen bond length is a key descriptor to predict the formation of the singlet specie over the triplet. Further analysis of our results highlights that the charging mechanism with release of oxygen occurs via the formation of superoxide species, as also suggested by recent experiments [5]. In particular, this mechanism is well characterized by the CASPT2 method that is able to predict an energy barrier and a singlet/triplet states degeneration, which are not properly described by the standard periodic DFT approach. Beside the interesting computational comparison, our results offer interesting insights for the optimization and further development of nanostructured cathodes for the promising Li-air battery technology.

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Bifunctional oxygen electrocatalysts prepared by electrospinning for alkaline metal-air batteries

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Rechargeable alkaline metal–air batteries can be considered one of the most promising next energy storage systems owing to their extremely high energy densities compared with lithium-ion batteries. Despite their advantages, they do not still offer adequate practical energy density and life cycle; in fact, critical problems arise from the positive electrode, such as slow kinetics of the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). In the last few years, Co-based catalysts were thoroughly investigated for the ORR/OER, and Co₃O₄ was the most employed formulation. Because of the European Commission included cobalt in the list of critical raw materials (CRMs) in terms of high supply risk and economic importance, the substitution of cobalt with cheaper and more available alternative elements is highly desirable. In particular, as widely reported in the literature, the partial replacement of Co, in spinel Co₃O₄, with Ni, Fe, or Mn can enhance the electron conductivity and electrocatalytic activity thanks to the formation of a ternary spinel oxide structure in which two distinct cations coexist [1, 2]. Another approach is to combine these oxides with carbon nanostructures, in particular graphitic ones, in order to maintain suitable stability under cycling operation. These approaches are evaluated and presented here.

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Electrochemical testing and characterization of Prussian blue analogues

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Prussian blue analogues (PBAs) or metal hexacyanoferrates are bimetallic cyanides with a three-dimensional cubic lattice of repeating -Fe-CN-M-NC- units (where M=transition metals). Because of their peculiar structure exhibiting large ionic channels, interstices in the lattice and redox-active sites they have been proposed as active materials for electrodes in batteries. In our group, a series of PBAs have been synthesized, such as copper hexacyanoferrate (CuHCF), manganese hexacyanoferrate (MnHCF), titanium hexacyanoferrate (TiHCF), multi-metal doped hexacyanoferrate, as well as copper nitroprusside etc. Their electrochemical properties have been studied in both organic and aqueous electrolytes [1-5]. Operando X-ray absorption spectroscopy (XAS) and synchrotron X-ray powder diffraction (XRPD) indicates that the copper is also active in CuHCF playing a remarkable role in the redox process. MnHCF has shown excellent cathode properties with large specific capacity (>130 mAh g⁻¹) and high discharge potential (3.68 V vs. Li⁺/Li). The Jahn-teller distortion of Mn site only causes local distortion and does not produce a macroscopic distortion in the long range. The activation of titanium-site inside TiHCF and electrochemical active ligand of -NO inside of copper nitroprusside have also been demonstrated.

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The impact of Critical Raw Materials in Electrochemical Energy Storage and Conversion - An Introduction

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The various families of Electrochemical Energy Storage and Conversion (EESC) devices, including secondary batteries and fuel cells, are playing a major role in the implementation of the Sustainable Development Goals (SDGs) of the UN’s Agenda 2030 [1]. SDGs lay the foundations of today’s energy transition away from non-renewable sources, to decarbonize the energy sector and mitigate global warming. EESC devices, like all the SDGs, are enabled by Raw Materials [2]. Some Raw Materials, known as “Critical Raw Materials” (CRMs), are particularly susceptible to trigger supply bottlenecks, which run the risk to jeopardize the large-scale rollout of EESC devices [3]. This presentation highlights the rationale behind the identification of CRMs in the EU perspective and briefly overviews their implementation in EESC devices and in the associated technologies. The main strategies to mitigate the occurrence of supply bottlenecks affecting EESC devices due to CRMs are reviewed. Finally, a few case studies describing the practical implementation of such mitigation strategies for prominent EESC devices such as proton exchange membrane fuel cells (PEMFCs) and secondary lithium batteries are outlined.

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Comparative Life Cycle Assessment (LCA) of a Redox Flow Battery with Semi-organic Electrolytes and a Vanadium Redox Flow Battery

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Deployment of renewable power sources will experience a rapid growth in the next years. This epochal change in energy generation will not become effective without the support of energy storage technologies, which are able to redeem renewables from their discontinuity. Vanadium RFBs have established as the technological standard for flow batteries. However, systems based on metals pose environmental and socio-political problems, especially in view of an economy of scale. Therefore, recently research has put in focus the search for new safer redox materials, shifting the attention from metal-based electrolytes to organic materials. However, up to now a complete environmental assessment of an organic or semi-organic electrolyte RFB has not been carried out. In the present study, an organic/halogen RFB, based on anthraquinone disulfate (AQDS) and HBr, is analyzed via Life Cycle Assessment (LCA) and compared to an equivalent vanadium RFB, as a benchmark. The analysis shows that the production of a semi-organic RFB might be a valid environmental alternative to full vanadium RFB, and the results demonstrate lower impacts in several categories (ReCiPe 2016). Nevertheless, the results are strongly affected by AQDS synthetic route. As a result of this study, we are confident that greener chemical pathways are decisive to assert the benefits of switching from metal to organic RFBs.

Thermally Regenerable Redox-Flow Batteries

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Low-Temperature Heat (LTH), heat below of 100°C, has recently elicited great interest among the scientific community, as a source of energy since it actually does not see any form of utilization as it is currently simply released into the environment. The conversion of such form of energy from various sources thus becomes of utmost importance as its efficient recycling would allow to decrease the environmental footprint caused by humankind during energy production, and it would open the doors to the exploitation of a huge amount of heat as well, such as geothermal, solar, and industrial waste heat. Thermal regenerable Redox-Flow Batteries (TRBs) are flow batteries that store energy in concentration cells that can be recharged by distillation at temperature <100°C, exploiting LTH. TRBs are composed by a selective ion-exchange solid-state electrolyte which divides two half cells where two water solutions at different concentration of a suitable redox couple (such as LiBr/Br₂ or NaI/I₂) are injected. The initial experiments prove an unprecedented heat-to-electricity efficiency for both the systems: 3% for TRB-NaI and 4-5% for TRB based on LiBr water solutions, depending on the thickness of the membrane with a power density output of almost 10 W m⁻² for both technologies, which opens various possibilities to implement further improvements into this new class of energy storage/converter devices.

An innovative membrane enhancing redox performance and reducing vanadium Crossover in Redox Flow Batteries

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In a redox flow battery, the ion exchange membrane prevents electrolyte mixing while supporting proton transport to maintain electro neutrality. The most common used commercial membranes suffer for low selectivity leading to vanadium ions permeation from one half cell to the other [1,2] then causing decreased in coulombic efficiency and capacity decay during cycling [3,4]. In order to overcome these problems, the innovative membrane LP has been designed based on a new concept, to adjust charges in the bulk of the membrane like a zip, through the reaction of two main block with specific properties. VO_2^+ permeabilities at different electrolyte concentration, measured by UV-Vis, are dramatically lower in the LP series than for Nafion®212. The same trend is confirmed by the self-discharge test. The membranes are also tested in a vanadium redox flow cell according to a standard test protocol. Compared to Nafion®212 used as reference, at the same current density of $80 \text{ mA}\cdot\text{cm}^{-2}$, the LP membrane showed better coulombic efficiency (98,3% vs 96,8%), and energy efficiency (77% vs. 69%). At different SOC, the cell open circuit voltage is higher for LPs than for Nafion®212, both at the beginning of test and after more than 72 hours. These results once again underline a lower cross over for the LP membranes.

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Hybrid inorganic-organic proton-conducting membranes based on SPEEK doped with WO₃ nanoparticles for application in vanadium redox flow batteries

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One of the most challenging issues of vanadium redox flow batteries (VRFBs) is the poor ion selectivity of the commercially available membranes [1]. The development of innovative and cost-effective proton-conducting membranes exhibiting an improved [H⁺/VO₂⁺] ion selectivity is critical to prompt the large-scale implementation of VRFBs. In this work, a new family of hybrid inorganic-organic membranes consist of a sulfonated poly (ether ether ketone) (SPEEK) matrix hosting between 0 and 23.6 wt% of WO₃ nanoparticles (NPs) is prepared and characterized. It is found that the [SPEEK/(WO₃)_{0.20}] membrane presents the highest ion selectivity (2.1×10^4 S min cm⁻³), that is more than three times higher than that of recast Nafion (6.5×10^3 S min cm⁻³). [SPEEK/(WO₃)_{0.20}] is then mounted in a single cell VRFB, that is tested extensively under realistic operating conditions. These tests demonstrate a consistent improvement in coulombic efficiency upon all current densities which renders (i) much larger cyclability and (ii) much more stable open circuit potential if compared to a VRFB incorporating a Nafion 212 membrane. The [SPEEK/(WO₃)_x] membranes described in this work are promising low-cost and high performance proton-conducting separators for application in VRFBs owing to their good conductivity, outstanding [H⁺/VO₂⁺] ion selectivity and cyclability.

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Characterization of a laboratory flow zinc–air fuel cell and modelling of the polarization curves

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The pollution issues due to fossil fuels and the intermittent nature of renewable energy sources are driving the scientific community to look for new environmentally friendly and low-cost devices able to store and convert energy. In this context, zinc-air devices are promising energy storage systems, due to their high theoretical energy density, low cost and safety. In this research, a laboratory flow zinc–air fuel cell (ZAFC), mechanically refuelable with Zn microspheres, has been set-up. The electrochemical characterization of the ZAFC has been performed by long-term discharge tests. A morphological and spectroelectrochemical characterization of the Zn anode spheres has been carried out. The effect of electrolyte aging and electrolyte flow rate on the behaviour of the Zn anode and on the polarization curves has been analysed. A model based on mixed-control kinetics for describing the polarization curves has been proposed. The model has been tested on the polarization curves obtained by running our laboratory ZAFC at several operating conditions and it has also been validated on the polarization curves reported in several significant papers from the literature.

Asymmetric supercapacitor with graphene-based electrodes

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Supercapacitors (SCs) are able to store electrochemical energy with higher power density and longer cycle life than batteries. The major SCs issue is the poor energy density, due to the physical origin of their capacitance. Graphene-based porous materials are remarkable candidates as SCs electrodes, thanks to high graphene specific surface area and superior electronic conductivity [1]. Graphene decoration with transition oxide nanoparticles is expected to further enhance capacitance by introducing red-ox reactions [2]. Then, the voltage working window can be further enlarged coupling two electrodes with different potential ranges [3]. In this study, thermal exfoliated graphite oxide (TEGO), having a specific surface area of 500 m²/g, has been employed as active material in SCs electrodes, displaying a capacitance of 105 F/g at 10 mV/s. Moreover, owning a great amount of defects, TEGO is able of anchoring Ni nanoparticles (NPs) [4]. During the early voltammetric cycles in KOH 3.5 M electrolyte, metal Ni-NPs converted in Ni(OH)₂, reaching a high reversible specific capacitance of 1340 F/g at 10 mV/s. Coupling an electrode of pure TEGO with another of TEGO decorated with Ni-NPs we made an asymmetric supercapacitor which reached an extended voltage window of 1.6V in KOH 3.5 M aqueous electrolyte [5].

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Online Electrochemical Mass Spectrometry for High Voltage Li-ion Battery cycle aging investigation

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Ni-rich Lithium Nickel Cobalt Manganese Oxide (NMC) and Lithium Nickel Manganese Spinel (LNMO) are among the most investigated materials for High Voltage Li-ion batteries with high specific energy density. Cycle aging can cause the evolution of gaseous species, coming from the oxidative degradation of the electrolyte at high potentials (up to 5 V). This phenomenon degrades the performances of the cell and creates safety concerns. Online Electrochemical Mass Spectrometry (OEMS) represents a powerful tool for the in-situ evaluation of gases developed at the electrode-electrolyte interface upon cycling of electrochemical cells. Following the literature 1–5, a custom-made bench-test has been built up and coupled to a Mass Spectrometer (MS), capable to sample evolved gases at ambient pressure. Volatile species are sent from the cell to MS using He as carrier gas. A commercial lab-scale cell, equipped with gas inlet and outlet, has been tested and full-cell configuration batteries will be investigated (Graphite or Silicon-Graphite at anode), to approach real Li-ion battery conditions. First results obtained on commercial electrolyte formulations (1M LiPF₆ in EC/DMC; 1M LiPF₆ in EC/DMC +3%wt FEC; 1M LiPF₆ in EC/DMC +3%wt VC) will be extended to new ionic liquid formulation (LiTFSI-EMIFSI/EMITFSI based), developed as part of Si-DRIVE H2020 EU-Project.

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Gas Evolution in Li-ion batteries revealed by Electrochemical In-Situ Dilatometry

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Gas evolution in Li-ion cells, arising from many sources in lithium-ion batteries, is one of the most important safety issues, given that several originated gases (e.g. H₂, ethene) are highly flammable [1]. The monitoring of is phenomenon is usually carried out by in situ differential electrochemical mass spectroscopy (DEMS) [2]. Also, the volumetric changes of electrodes during insertion/deinsertion of lithium ion are important for the battery safety and in this field several equipments have been developed to detect the volumetric changes of the cell or of the electrodes [3, 4]. A novel electrochemical dilatometer with controlled and variable pressure applied to the electrochemical cell has been designed and validated with graphite model electrodes [5]. We carried out a study on the thickness variation of all the cell components under different applied pressure. We demonstrated that various phenomena such as solvent evaporation, SEI formation, and gas evolution can be emphasized. Specifically, we performed experiments under controlled hydrogen evolution to demonstrate that the presence of gassing can be detected by applying different forces that affect the gas uptake and release from the porous separator [5]. Acknowledgements: The authors would like to thank Marposs Spa for kindly providing the equipment for electrochemical dilatometry.

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Electrospun Carbon/Cu_xO Nanocomposite material as Sustainable and High Performance Anode for Lithium-Ion Batteries

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The increase in energy density of the next generation of battery materials to meet the new challenges of the electrical vehicles era requires innovative and easily scalable materials with sustainable processes [1]. In this way, transition metal oxides (TMOs) has been subject of intensive research in these last few years, due to their advantage to be fairly easy to be found, to be cheap and to possess high theoretical specific capacities [2]. To easily obtain innovative morphologies while implementing effective 3-D support and conducting frameworks, electrospinning has gained much attention due to its relatively easy experimental setup, operational straightforwardness and scale up capabilities [3,4]. In this work we present the electrospinning synthesis procedure of a Cu₂O/PAN derived carbon nanocomposite, coupled with an improved and sustainable electrode processing procedure based on the PolyAcrylic Acid (PAA)-Ethanol binder/solvent couple which ensured high performance on a long cycling life perspective. The nanocomposite has been fully characterized and the electrochemical performance shows high specific capacity values over 450 galvanostatic cycles at 500 mA g⁻¹ specific current with capacity retention values over 80%. In addition, the composite shows remarkable high rate performance and highly stable interface, which has been studied by impedance spectroscopy.

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Application of laser ablation in electrode materials processing

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Starting from its discovery in 1960, when it was defined "a solution seeking a problem", laser has found widespread applications in several fields including energy storage. Among laser processing technique, laser ablation allows the production of electrodes in form of thin film and the morphological, structural and chemical modification of electrode materials. Pulsed Laser Deposition (PLD) is a well-known technique used to obtain compact and dense films, particularly suited for depositing solid materials with a complex stoichiometry. Here titania anodic films as well as cathodic lithium metal phosphate were successfully deposited by PLD. Different post-deposition treatments were evaluated and films structure and composition were investigated with a multi-technique approach, cyclic voltammetry and galvanostatic technique were used to demonstrate the electrochemical activity. Moreover pulsed laser can be used to irradiate particles suspended in a liquid medium to modify their size, shape and composition. For this purpose carbonaceous particles were processed with laser irradiation in acetonitrile to obtain an anode material with improved electrochemical properties. Irradiated carbonaceous particles present higher active surface and nitrogen functionalization as a result of the irradiation process. The electrochemical performances were tested by galvanostatic technique

Development of all-solid-state batteries with Sn/C composite anodes

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Improvement of safety and reliability of lithium ion batteries (LIBs) has become a major concern because of the exponential growth in their energy density. One of the most promising strategies to improve the thermal stability of LIBs is the replacement of carbonate-based electrolytes with non-flammable solid-state electrolytes. Lithium thiophosphate-based electrolytes, such as LiI-Li₃PS₄ (LPSI), are recently gathering attentions because of their remarkably high ionic conductivity at room temperature (>1 mS/cm) without high temperature sintering, which arises from their amorphous solid properties [1]. In this study, the composite anode, namely Sn/C, was prepared via a straightforward, one-step, hand grinding. Bulk-type all-solid-state LIBs, employing the Sn/C anode and LPSI electrolyte, exhibited a capacity of 400 mAh/g in the 1st cycle at 0.033C. Throughout the course of 30 cycles, the cell retained a capacity above 320 mAh/g and a coulombic efficiency above 98%. The suppressed fade in capacity suggests that the pulverization of Sn, which is generally caused by the large volume expansion of Sn, was physically suppressed by using solely solid state materials. It was demonstrated that the combination of LPSI electrolyte and Sn/C enables a facile preparation of all-solid-state LIBs with a stable and safe performance.

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Extremely efficient deep eutectic solvents for a green approach to metal recovery from spent lithium batteries

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LIBs present various critical raw materials (CRMs) (eg Li, Mn, Co, Ni, graphite), not present as massive and primary resources in Europe. The common recovery methods for the extraction of Co, Li, Ni metals are thermal/chemical methods like pyro and hydrometallurgical approaches. They are based on the metal leaching by solvent, supercritical fluid-extraction or chemical precipitation, with the use of strong acids and reducing agents to improve the metal dissolution. However, these processes are highly energy-consuming, require harsh conditions and produce toxic materials. In addition, they do not lead to easily recoverable elements [1]. In our work we are study a green, cheap and safe approach of extraction by using a new type of organic solvents as lixiviant, the Deep Eutectic Solvents (DES). DESs are obtained by simply mixing two safe components (cheap, renewable, and biodegradable), which are capable of forming a eutectic mixture, in our case we combine the acid lactic:choline chloride. We decide to focus the recovery of Li, Ni and Co in a LNC cathode (LiNi_{0.8}Co_{0.2}O₂) and the use of the obtained precursor for the realization of a second life cathodes.

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Additive Manufacturing of Aqueous-Processed LiMn₂O₄ Thick Electrodes for High-Energy-Density Lithium-Ion Batteries

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Enhancing electrode areal capacity of lithium-ion batteries will result in cost saving and better electrochemical performances. Additive manufacturing (AM) is a very promising solution, which enables to build structurally complex electrodes with well-controlled geometry, shape and thickness. Here we report on 3D-printed cathodes based on LiMn₂O₄ (LMO) as the active material, which are fabricated by robocasting AM via aqueous processing. Such a technology is: i) environmentally friendly, since it works well with water and green binders; ii) fast, due to very short deposition times and rapid drying process because of low amount of solvent in the printable pastes; iii) easily scalable. The cathodes are produced by extruding pastes with higher solid loadings (>70 vol.%) than those typically reported in literature. The printing efficiency is strongly affected by both the binder and the carbonaceous additive. The best cathode is composed by LMO, Pluronic as the binder, and a mixture of graphite/carbon black as the electronic conductor, which is critical for achieving optimal electrochemical performance. The cathode with thickness of 200 μm and mass loading of 13 mg cm⁻² exhibits good electrochemical areal capacity (2.3 mAh cm⁻²) and energy density (>32 J cm⁻²). Our results may boost the development of greener, lower cost and more efficient new generation of LIBs for applications as household energy storage or even micro-battery technology.

Advanced electrodes for Li-ion, Na-ion and Li-S batteries: from recycled materials to nanostructures

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Efficiency and cycle life of batteries strongly depend on the composition and quality of electrodes: as such, electrode materials should be characterized not only by high capacity, but also by low cost and high safety level. Since many years our group has been involved in the design and fabrication of advanced electrode materials for sustainable and efficient alkali-ion and Li-S batteries. Recently, we developed an innovative, green procedure for recycling of exhausted tires to produce a carbonaceous material which proved to be extremely promising as anode for both Li and Na batteries [1]. Moreover, we are investigating the great potentialities of nanostructured materials in this field. As an example, we fabricated cathodes based on nanometric S or core-shell S@TiO₂ particles for Li-S batteries, showing that dimensions and monodispersity of sulfur affect the overall performances, while the shell guarantees a good retention of capacity during cycling [2]. Finally, we are focusing on nanostructured C-Si composite anodes, such as Cu or Sn catalyzed binder free Si nanowires on carbon paper. The anodes obtained by mean of either chemical vapor deposition [3] or solvent vapor growth [4] showed high irreversible capacity mainly in the first cycle due to the formation of the SEI layer on the silicon surface, while in the other cycles they showed good capacity retention and high charge efficiency.

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