

# IBA2016 | International Battery Association

Nantes, FRANCE

March 20-25

NANTES



Nantes Events Center, France



**IMN**  
INSTITUT DES MATÉRIAUX  
JEAN ROUXEL





# **Abstracts of oral presentations**



## Materials advanced for better Li(Na) ion batteries

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Batteries, Energy, Li-insertion, Electrodes, Oxides, Polyanions

Rechargeable lithium ion batteries, because of their high energy density, have conquered most of today's portable electronics and they stand as serious contenders for EV's and grid applications. Therefore, for this to happen, materials with higher energy densities while being sustainable, scalable, reliable and low cost must be developed. The challenges for chemists are enormous and this calls for new materials, new processes and new concepts. These different aspects will be addressed through this presentation.

Firstly, the strategy towards the design of novel high voltage polyanionic compounds will be described [1]. Turning to new concepts, we will show how discovery, of a reversible Li-driven anionic redox process among Li-rich layered oxides [3-4] represents a transformational approach for creating advanced electrode materials [5]. Lastly, concerning sustainability our new findings regarding Na-ion chemistry which enlists novel materials design (4) will be shared as well.

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## **Progress in moving scientific discovery into battery technologies: The risk and the opportunity.**

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In the energy storage research field, we have seen a blossoming of research both in materials discovery and materials and device engineering. In recent years this growth in research is complemented by rapid hunger for and progress in manufacturing quality and quantity of new battery technologies for the growing needs of commercial applications. This massive growth in commerce represents both great risk and enormous opportunity for research teams across the globe. The speaker will address the historical perspective of the kind of world-changing research and technology development that the battery field represents, and apply lessons learned for how research in lithium ion and beyond-lithium-ion batteries can best be balanced to ensure success for individual researchers and corporations alike.

## AN OVERVIEW OF THE BEHAVIOR OVERLITHIATED Li(Li,Mn,Co,Ni)O<sub>2</sub> LAYERED OXIDES IN LITHIUM-ION BATTERIES

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The materials belonging to the (1-x)LiMO<sub>2</sub>.xLi<sub>2</sub>MnO<sub>3</sub> system (M = Ni, Mn, Co) exhibit the largest capacity among all other layered oxides. These materials are overlithiated layered oxides (Li<sub>1</sub>(Li<sub>y</sub>Mn<sub>1-y-u-t</sub>Co<sub>u</sub>Ni<sub>t</sub>O<sub>2</sub>)) with a significant amount of lithium in the transition metal site. Depending on the starting composition, Mn ions can be tri- or tetravalent while Ni ions can be di- or trivalent. In the literature there is a strong debate about the existence of a solid solution or the presence of a composite structure.

A very general study of the synthesis and of the electrochemical characterization of the Li<sub>1.20</sub>Mn<sub>0.54</sub>Co<sub>0.13</sub>Ni<sub>0.13</sub>O<sub>2</sub> phase has been undertaken for several years in our lab. During the first charge, when all cations are oxidized to the tetravalent state, an overcharge of the cell leads to a structural modification that can be schematically described as a Li<sub>2</sub>O extraction occurs that cannot explain alone the oxidation process. Either oxidation of cations to a higher oxidation state or of oxygen is required. All experiments to detect cation oxidation state higher than four failed, so the oxidation of oxygen has been considered.

The contribution of oxygen to the redox activity in this material family is considered from several years. It was suggested in 2009 by Koyama *et al.* from first principle calculation in Li<sub>2</sub>MnO<sub>3</sub> [1], and more recently by Ito *et al.* from an XAS study on the Li<sub>1.20</sub>Mn<sub>0.56</sub>Co<sub>0.07</sub>Ni<sub>0.17</sub>O<sub>2</sub> phase [2]. In our lab we have clearly shown its occurrence in the case of the electrochemical (or chemical) cycling of the Li<sub>1.20</sub>Mn<sub>0.54</sub>Co<sub>0.13</sub>Ni<sub>0.13</sub>O<sub>2</sub> phase [3-4]. Sathiya *et al.* [5] also confirmed it in the case of the Li<sub>2</sub>Ru<sub>1-y</sub>Sn<sub>y</sub>O<sub>3</sub> system.

From all characterization we performed on can conclude that during the high voltage plateau in the first cycle, there is a partial densification on the external part of the particles followed by an oxygen oxidation in the bulk of the lattice without oxygen migration. This redox process is completely reversible in discharge. The contribution of nickel and cobalt and oxygen reduction leads to the huge specific capacity of this material family.

A general overview of all reactions mechanisms will be presented.

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## TEMPERATURE-DRIVEN ORDER-DISORDER TRANSITIONS IN $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ AND $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ POSITIVE ELECTRODES

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Both  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  and  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$  compositions represent very attractive positive electrode materials for Na-based high power-density applications. Although being close in chemical formulas, their crystal structures have nothing in common, besides being phosphate-based frameworks within which  $\text{Na}^+$  ions are distributed in a more or less ordered fashion. Given the critical impact of  $\text{Na}^+$  distribution schemes on ion transport properties and on response to high charge-discharge currents, we undertook precise temperature-controlled structural studies

Until very recently the crystal structure of  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$  was described in the tetragonal space group  $P4_2/mnm$ . We revealed, thanks to very high angular resolution synchrotron radiation diffraction, that a small orthorhombic distortion exists [1], described in the  $Amam$  space group: the structural framework is preserved but a different arrangement of the sodium ions was evidenced. Upon increasing slightly the temperature to  $\sim 130^\circ\text{C}$ ,  $\text{Na}^+$  are fully disordered and give rise to a more symmetrical structural form (space group  $I4/mmm$ ).

The crystal structure of the NASICON  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  phase (NVP) has been investigated as a function of T, combining laboratory and synchrotron X-ray powder diffraction as well as single crystal X-ray diffraction. The existence of four polymorphs from  $-30^\circ\text{C}$  to  $225^\circ\text{C}$  was demonstrated. While the high temperature  $\gamma$ -NVP crystallizes in the classical rhombohedral cell ( $R-3c$ ,  $200^\circ\text{C}$ ), the low temperature  $\alpha$ -NVP undergoes a monoclinic distortion (S.G.  $C2/c$ ,  $-10^\circ\text{C}$ ) together with a complete ordering of the  $\text{Na}^+$  ions [2]. Additionally, partial substitution of Al for V results in a significant increase of the energy density of this electrode by activating the  $\text{V}^{4+}/\text{V}^{5+}$  couple at 3.95 V vs.  $\text{Na}^+/\text{Na}$  [3].  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  was used to build all solid state symmetrical cells operating at  $200^\circ\text{C}$  together with NASICON  $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$  as the  $\text{Na}^+$  solid electrolyte. The battery operates at 1.8 V with 85 % of the theoretical capacity attained at C/10 with satisfactory capacity retention [4].

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## MECHANISTIC INSIGHTS INTO FAST ION CONDUCTION IN SOLID ELECTROLYTE AND CATHODE MATERIALS

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Major advances in rechargeable lithium (or sodium) batteries require the discovery and characterisation of new materials. It is clear that a complete understanding of the properties of electrode and electrolyte materials for both Li- and Na-ion batteries requires fundamental knowledge of their underlying structural, ion diffusion and surface properties on the atomic- and nano-scales. In this context, advanced materials modelling [1] combined with structural and electrochemical techniques are now powerful tools for investigating these properties. This talk will highlight recent studies [2-4] in the following areas: (i) structural and mechanistic insights into fast lithium-ion conduction in  $\text{Li}_4\text{SiO}_4$ - $\text{Li}_3\text{PO}_4$  solid electrolytes; (ii) ion diffusion pathways in polyanionic cathode materials such as Li-sulfates (e.g.  $\text{LiFeSO}_4\text{OH}$ ) and Na-phosphates (e.g.  $\text{Na}_2\text{FePO}_4\text{F}$ ,  $\text{Na}_4\text{M}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$ ). The presentation will aim to demonstrate how the strong synergy of computer modelling and experiment has helped us to shed new light on the structure-property relationships of battery materials.

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## Interfacial Engineering for Advanced Lithium-Ion Batteries

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High energy-density lithium-ion batteries have been long pursued worldwide to significantly improve the mobility of modern portable electronics. This global R&D effort was also driven by the emerging application of high energy-density lithium-ion batteries to electrify the transportation system so that a significant reduction on both the consumption of non-renewable fossil fuels and the emission of greenhouse gas can be achieved. From the perspective of engineering optimization, the energy-density of lithium-ion batteries can be improved from proper engineering designs to reasonably reduce the volumetric and gravimetric contribution the supporting components like current collectors and cell packaging materials. Optimization of the morphology of active materials is also reported as an effective approach to improve the packing efficiency of the active material for an improved volumetric energy-density. On the chemistry side, advanced non-aqueous electrolytes with better electrochemical/chemical compatibility with the electrode materials have been developed to extend the capacity/energy retention of lithium-ion cells so that small cells/packs can be designed to meet the end-of-life electrochemical requirements for targeted applications.

It is believed here that the continuous parasitic reactions between the active materials and non-aqueous electrolytes at the interface hold the major contribution to the performance degradation of lithium-ion batteries. It has been our major R&D focus to stabilize the solid-electrolyte interface for high-performance lithium-ion batteries. The first approach to achieve our goal is to develop functionalized electrolyte additives that can provide a more stable artificial SEI layer to protect active materials from reacting with the electrolyte [1,2]. An alternative approach is to develop functional coating layer on active materials [3,4]. In this talk, the latest advance on both areas will be discussed.

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## **GETTING BEYOND LIB FOR AUTOMOTIVE – COMMERCIALIZATION REALITIES**

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R&D scientists and engineers continue to develop new chemistries and materials claimed as potential replacements for today's LIB technology. However, many of these discoveries may have an uncertain future in automotive beyond the technical journal circuit due to practical barriers to commercialization that are not well understood early in the design process. Early identification of challenges and issues that must be overcome for manufacturing and commercialization success can prevent avoidable expenditure of research dollars, or redirect focus to more fertile avenues.

It is accepted that battery cost reduction is the key to enabling meaningful market penetration of electrified vehicles, and competitive battery costs cannot be achieved without state of the art mass production. The unique manufacturing and processing challenges associated with several commonly proposed replacements for today's LIB technology will be considered and contrasted with traditional LIB manufacturing processes. To support this comparison, an overview of incumbent high-volume battery manufacturing processes will be provided, and the 'new' steps required as next-gen technology enablers will be evaluated for promise and implementation potential. Some of the critical keys to successful battery technology transition from lab to pilot scale to market will be highlighted, with a focus on automotive applications for vehicle electrification.

## SUSTAINABILITY OF BATTERY SEGMENT AND RECYCLING OF STRATEGIC METALS

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Energy issues and climate changes are now asking urgent solution and one of the solutions is large growing of renewable energy part in the consumption models. However, major part of renewable energy equipment's contains strategic metals while they could be potential sources of negative environment impact when recycled with non-appropriate processes. Within this problematic we will present 2 segments related to Lithium ion and Ni-MH batteries.

Since its introduction 15 years before, lithium ion battery (LIB) become today the most largely adopted for portable electronic devices. Recently the new chemistry of both cathodes and anodes allow the LIB system to be among the best system candidate for in EV and HEV segment. However the composition of those batteries imposes a particular consideration of their end of life management due to the environment impact and valuable resource conservation for materials. Several processes were proposed for recycling LIB while in the meantime composition of li-ion batteries is strongly moving from lithium cobalt oxides / carbon portable segment to several kinds of cathodes materials, electrolytes and anodes materials. This means that we are in the need of new flexible processes. The sustainable way to recycle LIB must take account on next challenges:

- Lowest energy consumption
- CO2 emission (from organic solvents and carbon)
- Fluorine control (from anion of lithium salts and PVDF).
- Loss of valuable resources such as graphite lost as CO2, Mn and Li trapped into slag.

Nickel metal hydride batteries are also now more and more substituting the Ni-Cad system. Until now at industrial level the main efforts were devoted to recycling Nickel and the rare earths (RE) were generally lost in slag if metallurgical way is used.

The position of RE in critical metals classification imposes to consider the Ni-MH as high source of RE.

Geopolitical aspect will be presented for the main strategic metals of LIB and Ni-MH batteries

To achieve high recycling rate and low environment impact new processes obtained during involvement in several clusters and Networks<sup>1</sup> will be presented. Remaining challenges for recovery other valuable materials from advanced batteries will be discussed.

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<sup>1</sup> 1-National French Network Project (IRISBUS, FIAT, CEA, IFP, MICHELIN, RATP, EDF)

2- 7<sup>th</sup> FP European Cluster (Renault, Volvo, Solvay, Continental, University of Munster, University of Grenoble, University of Kiev, Cegasa Batteries, lithium balance)

## **BATTERY MATERIALS: INDUSTRIAL EVOLUTION FOR Li-ION AND POST Li-ION TECHNOLOGIES**

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Our objective is to show the evolution of materials used in lithium-ion batteries in parallel with the development of new applications and market demands. From a unique initial system (graphitized carbon/LiCoO<sub>2</sub>) introduced in 1991, more than ten are now available. They have been developed to fulfil the market requirements of portable applications exclusively in a first period and also for industrial applications from the 2000'.

Evolution is driven by demands of specific and volumetric energy increase (longer autonomy of portable devices or vehicles), safety, and cost decrease. Industrial applications have more stringent additional requirements: long or very long life cycling and/or calendar, high power, operation in extreme temperatures.

Manufacturers have a set of basic materials and play on blends, core/shell, surface layers, voltage range or additives to optimize for their application. Basic positive active materials are lithiated lamellar oxides, manganese spinel or olivine structures. The principal negative active material remains graphite but lithium titanate occupies a few niche markets.

Processing science is essential to draw the best of materials. A few examples will be shown concerning porosity of electrodes or surface treatment of separator or the need of large voltage stability windows electrolytes.

After many years of continuous improvements, the need of a breakthrough in specific energy leads researchers to investigate systems such as lithium-sulfur or lithium-air, promising for low power applications.

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## ENERGY STORAGE AND THE METAL ELECTRODE

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Lithium had been identified already in the 50's as an electrode leading to high capacities and voltages, but this was in primary primary cells and the positive electrodes (e.g. AgCl) were working on a phase change reaction, far from reversible.

The change came in the early 70's with the ushering of the concept of intercalation, giving in principle an immortal electrode without new phase nucleation <sup>[1]</sup>. In the same decade, the Li<sup>o</sup>/TiS<sub>2</sub> battery consecrated the principle <sup>[2]</sup>. However, this metallic lithium electrode system with liquid electrolytes was a dangerous failure, so was the subsequent Li<sup>o</sup>/MoS<sub>2</sub> batteries rapidly withdrawn from market. Thus, the "rocking chair" concept whose name evolved into "lithium-ion", known since 1978, was very well received by the community, then swept the market rapidly after 1992. Yet, the Li<sup>o</sup> electrode is still unsurpassed in energy density, not only for its intrinsic capacity, but as it can act as its own current collector, without the need for heavy and depletable copper.

From the early beginning <sup>[3]</sup>, polymer electrolytes would show good chemical compatibility with lithium and provided that remnant crystallinity sources of current inhomogeneities are absent and the lithium interface is made with a friendly SEI. A > 1000 cycle life was recently confirmed by spectacular *in operando* observation of a functioning cell <sup>[4]</sup>. Indeed, there are > 5000 EVs equipped with Li<sup>o</sup>/LFP batteries and the batteries are expected to last 10 years.

This utilization of lithium metal has been obtained with electrolytes that reach useful conductivities in the 60°- 80°C range, which limits the market to large systems. Though it is at a very early stage, a first family of polymers different from PEO have been recently shown to operate, though at low C/ rate, at room temperature <sup>[5]</sup>.

Lithium is not the only element considered for future storage systems. Na as a electrochemical vector must certainly play a role due to the gigantic demand for load-levelling of renewable energies, and Na<sup>o</sup>, though little information is presently known on its interface with electrolytes, is a candidate. The two other elements under consideration, Mg and Al, in contrast to the alkali metal have known electrolytes that can plate the metals in fine-grained, dendrite-free deposits, but both lack high capacity reversible positive electrodes. All these options will be discussed.

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## The Lithium Metal Polymer battery and its applications

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Building on its industrial expertise, over twenty years of research and development, and two billion euros of investment, the Bolloré Group developed LMP batteries. These batteries stand out in terms of power, high energy density and safety of use.

Metallic lithium is used as negative electrode. Lithium iron phosphate is the active material of the positive electrode. Between these two electrodes a polymeric film based on polyether served as separator and electrolyte. All these very thin films are dry which lead to a “solid-state” batteries, conferring numerous advantages, notably in safety terms. Another common point of all these films is that they are created using extrusion techniques. Compared to coating, extrusion is a process that uses no organic solvent which confers advantages in term of price and/or at ecological level.

### History

Started in the early nineties, R & D program at outlet on a first plant in 2001. The Bolloré Group launched manufacturing with the construction of this plant at its Pen-Carn site, located in Ergué-Gabéric, near Quimper. In 2009, with the viability of the technology proven, two production lines were deployed this site.

### Applications

#### Mobility

The Bolloré Group develops, manufactures and markets a series of electric vehicles using LMP batteries: a range of electric cars – Bluecars – a bus and even a boat currently at the prototype stage.

The bluecars are used in Autolib’ which is the first public service plan with electric vehicles to be developed in a large European metropolis. Since 2011 and the launch of the service, autolib’ it’s more than 12 millions of rentals and more than 120 million of kilometers.

#### Stationary

The LMP batteries are used in different stationary application: Blue Zone, Bluehouse and Bluestorage.

Bluestorage is developing a series of energy storage solutions, ranging from several kWh to multiple MWh of stored energy and aimed at different end customers: electricity consumers (individuals, companies, etc.) and stakeholders in electricity networks. Bluestorage allows consumption cut-off but also to make long-lasting the energy produced by the renewable energy.

## **Tribute to Michel Armand : From Solid Polymer Electrolyte to Carbon Nanopainting LiFePO<sub>4</sub>.**

K. Zaghib

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Michel Armand is a pioneer in the development of polymer electrolytes for battery applications. When John Goodenough discovered that olivine LiFePO<sub>4</sub> is a viable cathode for Li-ion batteries, Michel immediately recognized it had a redox energy well-matched to a polymer electrolyte. He used his experience in carbon coating (nanopainting) to increase the capacity and rate capability of LiFePO<sub>4</sub>. Research on lithium metal combined with polymer electrolytes in lithium rechargeable batteries started in 1979. Since that time, battery research has expanded worldwide. Several new polymers, solid electrolytes and ionic liquids with improved conductivity were identified. These advances resulted from a better understanding of the major parameters controlling ion migration, such as favorable polymer structure, phase diagram between solvating polymer and lithium salt, and the development of new lithium counter-anions. In spite of the progress so far, a highly conductive dry polymer is still not available for use at room temperature. However, effort is continuing, and developers of all-lithium polymer batteries (LPB) presently face a decision if the polymer electrolyte should be heated to enable high-power performance, as required for electric vehicle and energy storage. LPB developers have explored both the high-temperature and low-temperature options.

This presentation discusses the challenges and opportunities in developing lithium ion and thin lithium metal with stable SEI as negative electrodes for three battery technologies:

1. Li-ion batteries containing dry polymer and ionic liquid-polymer electrolytes
2. All solid-state Li-sulfur batteries
3. Li-air batteries.

In addition, we will discuss the safety implications of lithium ion, lithium metal, dendrite mechanism, interface phenomena, side reactions, protection of lithium metal, and lithium alloys.



## RECENT PROGRESSES ON LITHIUM SALTS OF PERFLUORINATED SULFONIMIDE ANIONS FOR RECHARGEABLE LI AND LI-ION BATTERY

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In the present work, we report recent progresses on lithium salts based on various kinds of perfluorinated sulfonimide anions (see Figure 1) as conducting salt for Li and/or Li-ion batteries. We will cover a wide range of electrolytes of these new anions from non-aqueous liquid (including conventional carbonate solutions, ionic liquids, and molten salts) to solid polymer electrolytes (including classic lithium salt/PEO, and single Li-ion conducting polymer based on polyanions).

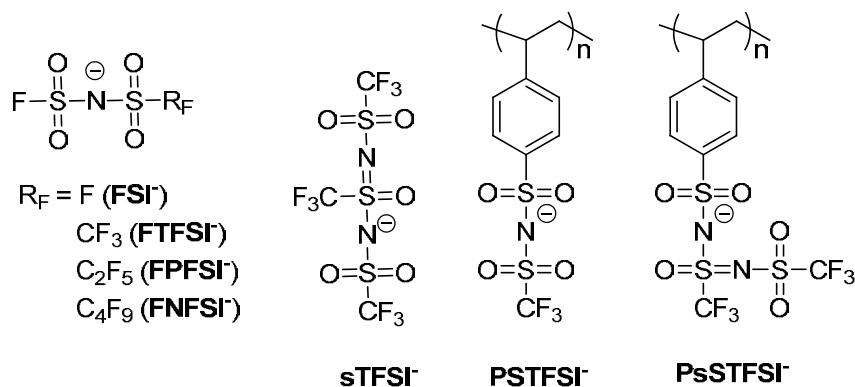


Figure 1. Structures of various kinds of perfluorinated sulfonimide anions.

In liquid carbonate electrolytes, both LiFSI and LiFNFSI as conducting salt or additive for improving the high-temperature performances of Li-ion cells will be discussed. In both ionic liquid and molten salt electrolytes, the electrochemical performances of natural graphite/LiFePO<sub>4</sub> Li-ion cells will be detailed. In solid polymer electrolytes, the electrochemical performances of Li/LiFePO<sub>4</sub> cells will be described. The mechanisms behind the improvements of electrochemical performances of Li and Li-ion cells by using these lithium salts will be discussed, in terms of various chemical, electrochemical and surface analyses.

## **Electrolytes enabling Li and Na metal devices – from polymer electrolytes to ionic liquids.**

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The holy grail of energy storage is battery technology based on Lithium metal anodes, with Sodium metal being a close second contender electropositive metals, both Li and Na provide possibilities for reversible, high energy density devices for use from electric vehicles to grid storage. These may include in conventional devices where an intercalating cathode is used, or in Li/Na-sulphur or Li/Na-air configurations.

A significant problem with both metals is the ability to cycle the electrode without creating dendritic morphology, which can cause poor cycling efficiency, dangerous short circuits and failures in a battery. Polymer electrolytes, and more recently ionic liquid based systems, have shown great promise for stable cycling of Li and Na. This talk will span the trajectory of polymer and ionic liquid electrolytes, from the early, traditional polyethylene oxide based electrolytes through to novel single ion conducting ionomers and finally the highly concentrated mixed ionic liquid electrolytes that appear to produce a stable interphase layer, so that, despite somewhat lower ionic conductivities than the traditional organic solvent electrolytes, excellent device performance is achievable.

## Single-ion block copolymer electrolytes

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Today the environment is a major society concern and the polluting fossil energy consumption, more and more expensive, is a drag on our economy, thereby the development of alternative transportation such as electric or hybrid vehicles, has become a key need for a sustainable long term development<sup>1</sup>. The increase of energy density necessary to promote this future revolution imposes to develop “new” chemistries for both the active electrode materials and electrolyte<sup>2,3</sup>. However, for high scale applications a safety issue comes from the liquid electrolytes as they embedded organic solvents that can likely leak or generate flammable reactions. The use of a solid polymer electrolyte (SPE) could solve most of the safety issues encounter with liquid electrolyte. However, the development of SPE has been hampered by two hurdles i/ the inability to design a SPE that has both a high ionic conductivity and good mechanical properties<sup>3</sup> and ii/ the motions of lithium ions carry only a small fraction of the overall ionic current which leads during battery operation to the formation of strong concentration gradient with highly noxious effects like favored dendritic growth<sup>4</sup> and limited energy density, especially when power increases. In this context, we are developing nanostructured multifunctional block copolymer electrolytes (BCE), B-A-B comprising a central A block based on poly(ethylene oxide) (PEO) that brings ionic conductivity and a B block that brings other functionalities like mechanical properties, electrochemical stability, increase of transport number etc. We will present our approach in improving the performances of BCEs starting from neutral BCEs like PS-POE-PS<sup>5,6</sup> laden with a lithium salt to the single-ion BCEs (SIEL) comprising grafted lithium trifluoromethanesulfonylimide (TFSILi)<sup>7</sup>. Especially, we analyse the impact of the BCEs composition (ie proportion of PEO) and the effect of molecular weigh on the physical properties such as the morphology, the thermodynamic transitions, the mechanic stability and the ion transport. At last, for a complete analysis, the results obtained with several prototypes of batteries will be presented.

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# NOVEL EQCM-D-BASED METHODOLOGY FOR IN-SITU GRAVIMETRIC, VISCOELASTIC AND HYDRODYNAMIC PROBING OF BATTERY AND SUPERCAPACITOR ELECTRODES

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During about 3 years out of 6 we were focused on the use of electrochemical quartz-crystal microbalance (EQCM) for in-situ dynamic tracking of ions adsorption into nanoporous carbons during their charging. [1-5] Here EQCM served as a gravimetric probe of the compositional changes in the nanoporous carbon (resonance width was almost constant). A number of gravimetric problems related to charging mechanisms in nanoporous carbons (hardly assessed by other techniques) were solved: partial ions desolvation during adsorption, perm-selective behavior of carbons at high charge density, and its failure near the potential of zero charge, full gravimetric modeling of ions adsorption with incorporation of Gouy-Chapman-Stern model, the origin of selective ions adsorption, and many others.

However, we realized very soon that in case of a typical Li-ion battery electrode such as  $\text{LiFePO}_4$  olivine, the change in the resonance peak width was comparable with the change of the resonance frequency, implying strong periodic, intercalation-induced deformation of the composite electrode [6,7]. The arising electrode deformation modifies solid-liquid interactions in the boundary hydrodynamic layer between the porous/rough electrode and the solution. When solid porous electrode is completely rigid, these interactions are fully tracked by the potential-dependent shifts of the resonance frequency and resonance peak width described in terms of the hydrodynamic admittance model which quantifies the electrode deformations. [7,8] Using this method a strong dependence of the deformation of  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene electrode on the ion's charge-to-size ratio has been found, contributing to the understanding of the "capacitive paradox" of this unique one-dimensional electroactive material. [8] We also extended this methodology to identification of the effect of mechanical properties of the polymeric binders on the intercalation-induced expansion/contraction of the intercalation particles, and thereby, the entire deformation of the composite electrode (non-invasive in-situ dynamic monitoring of elastic properties of composite battery electrodes by EQCM-D). [9] This unique non-destructive technique has a potential to serve for early diagnostics of cycling life durability of batteries and supercapacitors.

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## FROM BULK TO NEAR-SURFACE INVESTIGATIONS OF $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ USING *OPERANDO* TECHNIQUES (NEUTRON/X-RAY/RAMAN/OEMS)

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The Li-ion technology still needs improvements to fulfil the requirements for electric mobility, especially in terms of energy density.  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  (LNMO) is a promising cathode material thanks to its high potential during cycling and thus its high energy density [1]. However, it suffers from stability problems in long-term applications, especially in full-cell configuration against a graphite electrode. The understanding of the main and side reaction mechanisms is crucial to develop this cathode further and to this, *operando* techniques are the most suitable ones to follow the structural and/or surface changes occurring during the lithiation/delithiation processes.

For the structural changes and especially to follow the lithium, a cylindrical cell for neutron powder diffraction measurements was developed. A representative result from such *operando* diffraction experiments is shown in Figure 1, left. During cycling, LNMO undergoes a solid-solution reaction from pristine to half-delithiated states followed by a two-phase reaction occurring from half to fully delithiated states with a total shrinkage of the lattice parameter of ca. 6 %. Similar results were obtained from our in house *operando* XRD measurements.

The near-surface region of the LNMO was investigated using *operando* Raman spectroscopy (Figure 1, right). The assignment of the peaks and their intensities were confirmed by first principle calculations. Finally, *online* electrochemical mass spectrometry (OEMS) was used to follow the gas evolution from LNMO during cycling. All these results, combining information from bulk and surface, will be discussed, to demonstrate that LNMO could be a cathode of choice for future of Li-ion batteries.

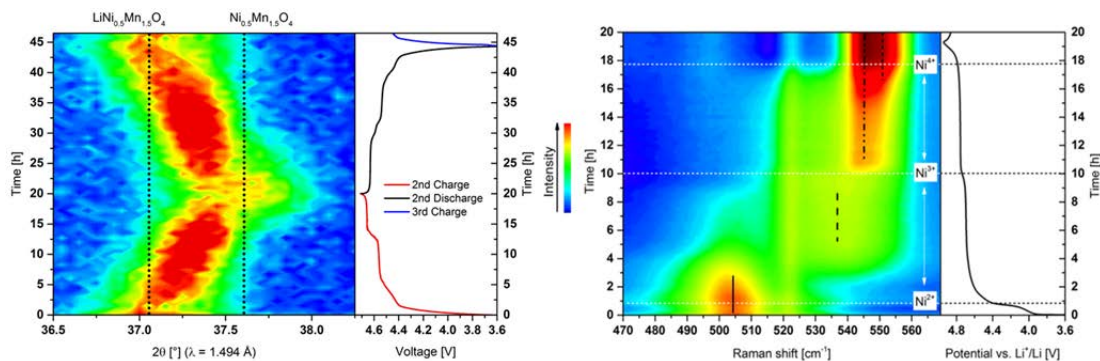


Figure 1: Contour plot obtained from *operando* (left) neutron diffraction measurement of (222) LNMO peak; (right) Raman spectroscopy measurement of LNMO.



### **3D MICROSTRUCTURE OF BATTERY ELECTRODES ANALYZED BY FIB-SEM AND *IN OPERANDO* X-RAY TOMOGRAPHY**

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Batterie electrodes, and in particular Lithium based batteries, have a complex microstructure. They are composed of different solid functional constituents (C, Si, LFC, conductive binders, ...etc) irrigated by a network of interconnected pores. During operation, the pores are filled with liquid electrolyte allowing ionic reactions and transport.

The microstructure of these complex structures should be analyzed at different important length scales. The morphology of the initial pristine electrodes is first a key information allowing to understand and then optimize the electrode behavior. The changes in this microstructure is then another important indicator of the degradation of the performance of the battery in service.

This microstructure and its evolution being complex in nature and the connectivity of the phases being of utmost importance for electrical transport, 3D imaging techniques could be interesting tools to use.

For all these reasons, analyzing the microstructure of the electrodes has been carried out in the present study using non destructive X Ray Tomography (XRT) at different scales and *in operando*. Because the resolution in XRT is sometimes not good enough for the smallest scales in these electrodes, FIB-SEM destructive tomography has also been used to analyze the microstructure and its evolution.

## In Operando Monitoring of the Pore Dynamics in Ordered Mesoporous Electrode Materials by Small Angle X-Ray Scattering

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To monitor dynamic volume changes of electrode materials during electrochemical lithium storage and removal process is of utmost importance for developing high performance lithium storage materials. Small angle X-ray scattering (SAXS) is one of the most useful analytical techniques to investigate properties of nano materials since the SAXS technique works very well in characterizing unique nanostructures of materials with the probing range of 1 – 100 nm. In order to further gain insights on the nanostructural changes of materials during cycling, it is highly required to develop a new analytical technique with *in operando* capability to monitor physical changes of mesopores in the electrode material. We herein report an *in operando* probing of mesoscopic structural changes in ordered mesoporous electrode materials during cycling with synchrotron-based small angle X-ray scattering technique. *In operando* SAXS studies combined with electrochemical and other physical characterizations straightforwardly show how porous electrode materials underwent volume changes during the whole process of charge and discharge, with respect to their own reaction mechanism with lithium. Moreover, the changes of mesoscopic cell volumes upon lithiation and delithiation also can be exactly measured, from which we can get direct evidence that proves the role of mesopores in the active materials to effectively accommodate the volume expansion of crystalline frameworks by the reaction with lithium. Such a precise *in operando* probing technique for pore dynamics of ordered porous materials can be also utilized to study nanostructural changes of the electrode materials in other electrochemical systems adopting porous materials, such as electrode of the fuel cells, supercapacitor and metal-air battery systems. We also believe that *in operando* investigation of dynamic changes in the mesoscale order will help us to deeply understand physical behaviors of lithium storage materials, thereby providing valuable guidance for designing innovative nanostructured materials for next generation energy storage system.

## Nanostructured Si-Based Negative Electrodes for Li-ion Batteries

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The use of Si alloy negative electrodes in practical high energy density Li-ion cells has now been well-established [1]. Their successful implementation requires combining materials, binder, coating, electrolyte and cell design. This presentation will focus on recent advances in Si alloy materials.

Optimization of Si alloys requires a detailed understanding of the interaction of Si with other active and inactive phases. We have found that internal stresses can develop between active Si and an inert inactive phase can be as high as 2 GPa during lithiation, and can shift the voltage curve of Si by hundreds of mV [2], as shown in Figure 1 below. This voltage shift can result in the  $\text{Li}_{15}\text{Si}_4$  formation peak, which usually resides at about 50 mV [3], to be shifted below 0 V, thus inhibiting  $\text{Li}_{15}\text{Si}_4$  formation. Moreover, the stress induced voltage shift can cause a significant portion of the Si lithiation voltage curve to be shifted below zero volts, resulting in capacity reduction [2]. Different inactive phases were found to shift the Si voltage curve by different amounts, implying that the interaction between Si and inactive phases can vary substantially, depending on composition [4]. Such results have important implications regarding the design of new alloy materials.

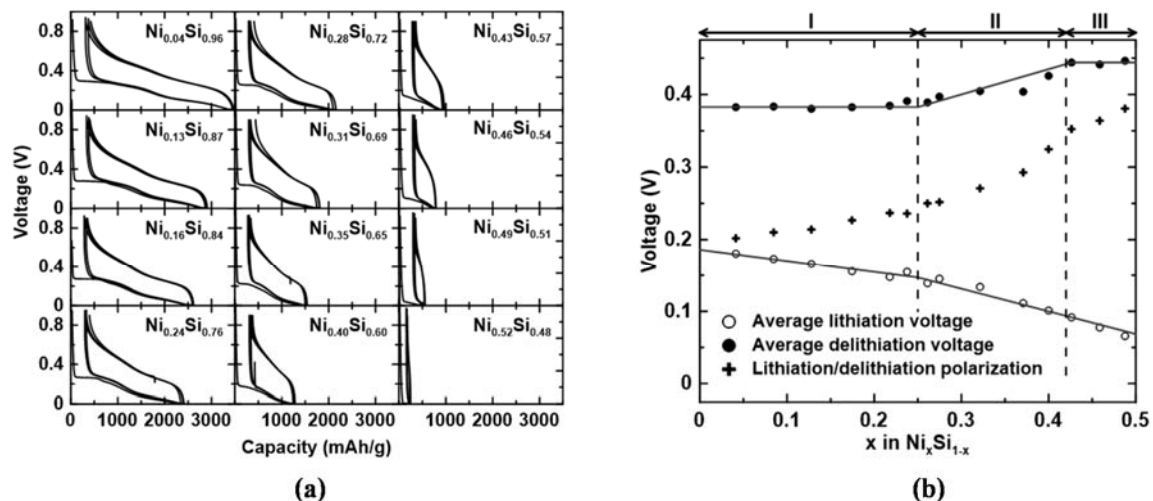


Figure 1 (a) The voltage curves and (b) the average lithiation and delithiation voltages of  $\text{Ni}_x\text{Si}_{1-x}$  alloys as a function of composition. Reproduced with permission from Reference 2.

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## Interface Optimization Principles of Si Anode for Li-ion Batteries

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The high gravimetric capacity of lithiated silicon (Si) has motivated research as a potential anode for lithium ion batteries; however, major challenges remain for the implementation of Si in commercial devices. The large irreversibility associated with the formative cycles of Si anodes is primarily due to mechanical pulverization and chemical instability. The mechanical pulverization of the Si active material has largely been improved by adopting nanostructures and thin films which can accommodate the strain of full lithiation.<sup>1-2</sup> Conversely, the chemical instability due to the consumption of Li ions as the electrolyte is reduced to inactive side products,<sup>4</sup> forms the solid electrolyte interphase (SEI) leading to poor capacity retention and Coulombic efficiency. Therefore, a direct investigation of the SEI morphology and composition to improve Si electrodes has been carried out.

We have improved the performance of Si anode by optimizing electrode fabrication, incorporating electrolyte additives, and coating for Si nanoparticles. The optimized parameters improved the initial Coulombic efficiency to 88.8 % without the use of additives or coatings. A series of advanced characterization techniques was used to investigate the material and interface properties. Using atomic resolution scanning transmission electron microscopy and electron energy loss spectroscopy (EELS) demonstrates that a uniform dense SEI consisting of primarily inorganic compounds improves longterm cycling performance (Figure 1(a)). Anoxic X-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectrometry depth profiling techniques were used to accurately characterize effect fluoroethylene carbonate (FEC) on amorphous Si thin films (Figure b,c)), giving evidence to fast reduction kinetics of FEC, leading to the improving silicon's conductivity via silicon native oxide etching and improved Li-ion transport through the SEI via a shuttling mechanism. The use of conformal coating to form an artificial SEI through molecular layer deposition can further improve both the mechanical and chemical instability of Si electrodes. The understanding of the SEI morphology and chemical composition will shed light on the design of future Si electrodes.

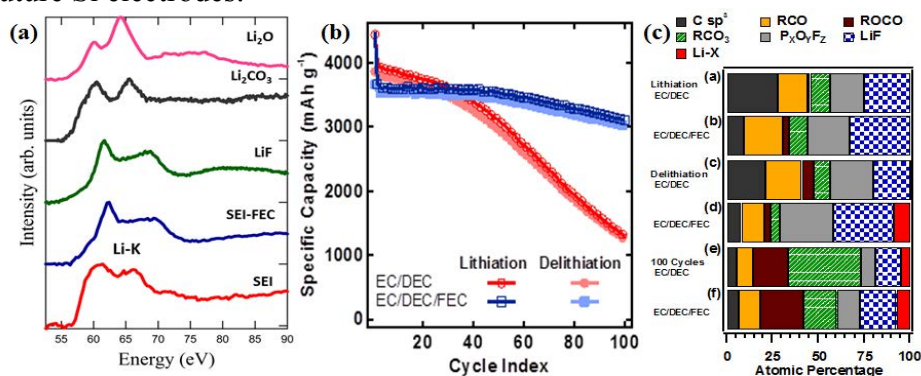


Figure 1(a) EELS spectra Li-K edge of cycled Si composite electrode (b) Specific capacity versus cycling of a-Si thin films at C/2 rate and (c) relative SEI composition after cycling.

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## **Analytical multi-probe study of the SEI on silicon based electrode in full cell configuration**

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Over the past years, lithium-ion battery became one of the most promising energy storage technology addressing a large range of applications, from hybrid electric vehicles, electric vehicles to Plug-in Hybrid Electric Vehicles, which are essential to reduce the fossil oil dependency. In order to meet requirements of these automotive applications, it is necessary to find both higher capacity and higher capacity retention electrode materials for Li-ion batteries. Providing new materials for the negative electrode of Li-ion cells has therefore been the subject of many investigations for more than a decade. Among the candidates for negative electrode, silicon appears as an attractive alternative to graphite due to its natural abundance, high specific gravimetric capacity (3579 mAh.g<sup>-1</sup> vs. 372mAh.g<sup>-1</sup> for graphite) and a large volumetric capacity (2081 mAh.cm<sup>-3</sup> vs. 779 mAh.cm<sup>-3</sup>). Silicon based electrodes however suffer from poor cyclability due to the large volumetric expansion of Si particles upon cycling as well as an unstable solid electrolyte interphase (SEI) caused by a continuous liquid electrolyte degradation at the surface of the Si phase leading to the increase of the amount of electrolyte-degradation products. Although the interface between Si particles and the electrolyte is playing a major role in the electrochemical performance, it has rarely been characterized in depth and the failure mechanism of silicon-based electrodes has been studied only in a half-cell configuration. In the present work, a combination of analytical techniques, <sup>7</sup>Li, <sup>19</sup>F MAS NMR, XPS, TOF-SIMS and STEM-EELS, provides an in-depth characterization of the SEI forming on the surface of silicon particles as well as its evolution upon cycling in a full Li-ion cell configuration with LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> as the positive electrode.

## Silicon-based lithium ion battery anode active materials – an industry perspective

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The introduction of silicon as an anode active material with high volumetric capacity and low charge/discharge potential will enable cell manufacturers to increase the energy density of lithium-ion batteries up to 40% depending on cathode chemistry and cell design [1].

Besides technical challenges resulting from the volume change during (de-)lithiation, several prerequisites like scalability, reproducibility and economic attractiveness of the active material have to be met to allow introduction into a broad range of applications.

Up to now, three major challenges resulting from the extreme volume change of silicon (~300%) during de-/lithiation hamper the use of silicon-based anode active materials. These are: (i) loss of electrical contact by electrochemical milling, (ii) loss of electrical contact by insufficient electrode stability and (iii) loss of capacity by initial and continuous irreversible lithium-ion loss due to SEI effects.

Different approaches to solve these problems are currently under investigation [2,3]. First of all, the use of nano-sized or nano-structured silicon should reduce the mechanical stress leading to the fracture of silicon. Furthermore, an optimized binder and/or a matrix incorporating the active material should allow for compensating the silicon volume change. Finally and most challenging, industrial feasible concepts have to be developed in order to reduce the initial as well as continuous capacity loss by SEI (re-)formation. Material concepts avoiding or minimizing the contact between the nano-silicon as well as electrolytes for a stable SEI on the silicon surface are viable attempts to solve this problem.

In agreement with literature [4] our findings show that nanosized Si particles with a diameter < 200 nm and carbon composites incorporating these particles proved to be stable during cyclization. In contrast to carboxymethyl cellulose, an in-house developed binder [5] enables high cycle stabilities at application-relevant area loadings (~2 mAh/cm<sup>2</sup>). By optimized electrolytes the capacity loss can be considerably reduced. Evidently, even after 300 full cycles silicon significantly contributes to the anode capacity. Combinations of advanced Si-based electrodes with an optimized electrolyte enable to reduce the initial capacity loss to a level comparable to graphite. Several hundred cycles with 80% capacity retention depending on the cathode material (e.g. NMC-111, NCA) have been achieved in full cells with industry-relevant area loading and balancing.

Despite significant progress, the investigated material concepts are still under development and need to be fully implemented in order to achieve the performance required for market introduction (at least 500 cycles at 80 % capacity retention).

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## Metastable Intermediate in $\text{Li}_x\text{FePO}_4$ Structure, Electrochromism, and Transport Properties

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In  $\text{Li}_x\text{FePO}_4$ , the ground state phase separation and metastable solid solution are energetically competitive, and the solid solution phase is induced in a non-equilibrium electrochemical reaction. However, until now, there has been no discussion or experimental report of the crystal structure, optical and transport properties of the metastable solid solution phase due to the following extreme technical difficulties. First, the solid solution phase  $\text{Li}_x\text{FePO}_4$  is metastable during electrochemical process and disappears within a few seconds after relaxation. We overcame this limitation by quenching  $\text{Li}_x\text{FePO}_4$  ( $x = 2/3$ ) at 350 °C to room temperature. This quenched phase remained stable for a couple of weeks, which enabled sufficient time to measure the several intrinsic properties. Second, conductive carbon may form during sintering at high temperature from possible carbon sources such as polyolefin worn from jars, organic solvent used in milling and carbon-containing precursors (e.g., oxalate  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ). Finally, impurities such as  $\text{Li}_3\text{PO}_4$ ,  $\text{Li}_4\text{P}_2\text{O}_7$  and  $\text{Fe}_x\text{P}$  resulting from off-stoichiometric mixing or the carbon reduction effect above 800 °C will largely increase the apparent optical absorption and conductivity of  $\text{Li}_x\text{FePO}_4$  by several orders of magnitude. The scattering of the conductivity data resulting from the above extrinsic effects has troubled and confused scientists for a long time. In our present study, pure carbon-free  $\text{LiFePO}_4$  and  $\text{FePO}_4$  were prepared using carbon-free precursors and controlling sintering parameters, and the intrinsic superstructure [1], optical properties [2], and conductivity [3] of quenched single phase  $\text{Li}_x\text{FePO}_4$  ( $x = 2/3$ ) was evaluated.

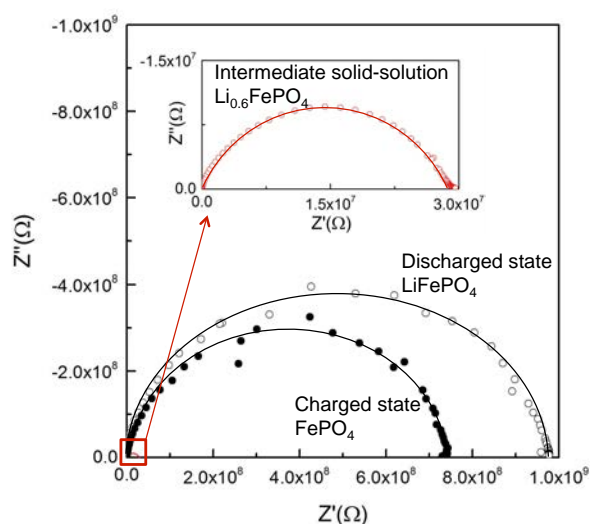


Figure 1 Nyquist plots for thermodynamically stable  $\text{FePO}_4$ ,  $\text{LiFePO}_4$ , and the isolated intermediate solid solution  $\text{Li}_{0.6}\text{FePO}_4$ . The non-equilibrium solid solution  $\text{Li}_{0.6}\text{FePO}_4$  shows approximately two orders of magnitude lower resistance than the equilibrium end members  $\text{FePO}_4$  and  $\text{LiFePO}_4$ .

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## ELECTROLYTE ADDITIVES FOR LITHIUM- AND MANGANESE-RICH LAYERED CATHODE MATERIALS: AN XPS STUDY

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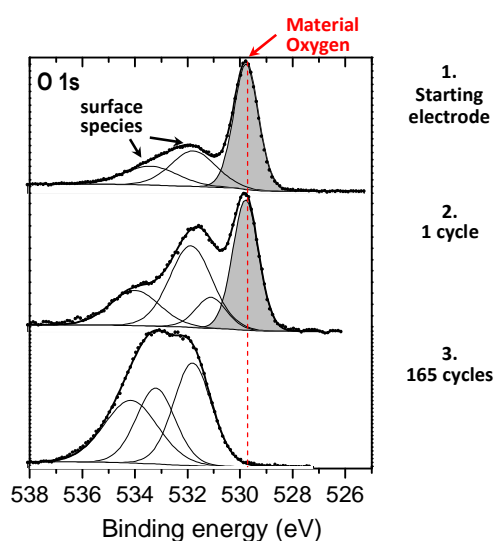
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Lithium- and manganese-rich layered oxides  $\text{Li}_{1+x}(\text{Mn}_{1-y-z}\text{Ni}_y\text{Co}_z)_{1-x}\text{O}_2$  (LMR-NMC) are able to reach reversible capacities higher than  $250 \text{ mAh.g}^{-1}$ , much more than conventional positive electrode materials. To achieve such capacities, they need an electrochemical activation by increasing the upper voltage limit of the first cycle (up to 4.8 V vs.  $\text{Li}^+/\text{Li}$ ). Further cycling also requires rather high potentials to take full advantage of the great capacities of these materials. However, usual liquid electrolytes (organic carbonate solvents mixtures) undergo oxidative reactions at the electrode surface at high potentials ( $\sim 4.5\text{V}$  vs.  $\text{Li}^+/\text{Li}$ ). To prevent such reactions, one solution is to use electrolyte additives that are able to form a passivating film at the positive electrode/electrolyte interface.

In this presentation, I will discuss the effect of three additives. Two organic: Vinylene Carbonate (VC), Succinic Anhydride (SA), and one inorganic: Tris(2,2,2-trifluoroethyl) phosphite (TTFP). Electrochemical characterisation revealed the beneficial effect of such additives. X-ray Photoelectron Spectroscopy (XPS) investigation of surface/interface mechanisms has shown that these additives not only improve the anodic stability of the electrolytes in contact with the positive electrode surface, but also act on the LMR-NMC material itself. Especially, it was shown that the presence of the additive improves the efficiency of the electrochemical activation step on the material.



XPS O 1s spectra of LMR-NMC electrodes before cycling, and after 1 cycle and 165 cycles, in half cells with EC/PC/EMC/DMC + 1M  $\text{LiPF}_6$  + 5 wt. % TTFP electrolyte



## HIGHLY CONCENTRATED ELECTROLYTES FOR 5-V CATHODES

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Highly concentrated electrolytes have many unique properties,<sup>1-4</sup> such as Li<sup>+</sup>-intercalation into graphite anode without EC,<sup>1,3</sup> suppression of S<sub>8</sub><sup>2-</sup> ion dissolution in Li-S batteries, etc., and is attracting much attention of many researchers. In highly concentrated electrolytes, all solvent molecules are strongly coordinated with Li<sup>+</sup> ions, and hence the stability of the electrolytes against oxidation is improved significantly. Yoshida et al. reported that LiCoO<sub>2</sub>, which is a 4-V cathode, can be charged and discharged in a LiTFSI/triglyme (1:1) electrolyte with good cycleability,<sup>3</sup> though triglyme is an ether compound and usually cannot be used as solvent. 5-V cathodes, e.g. LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> and LiCoPO<sub>4</sub>, are promising for the next-generation LIBs with high energy densities. Unfortunately no electrolyte systems that tolerate the highly oxidative 5 V cathode have been reported so far. In the present study, we investigated the effect of concentration on the stability of highly concentrated electrolytes, LiPF<sub>6</sub>/PC and LiBF<sub>4</sub>/PC, against a 5-V cathode, LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> to realize 5-V LIBs with high energy densities.

Figure 1 compares charge/discharge curves of a 5-V spinel LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> in standard (0.83 mol kg<sup>-1</sup>, 1 M, Li/PC = 11.8) and highly concentrated (4.9 mol kg<sup>-1</sup>, Li/PC = 2) LiBF<sub>4</sub>/PC at 30°C. The charge/discharge rate of C/10 was employed to emphasize electrolyte decomposition. Though the LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> can be charged and discharged in both electrolytes, the irreversible capacity (Q<sub>irr</sub>) in 1 M LiBF<sub>4</sub>/PC was high (76 mAh g<sup>-1</sup>) because of vigorous electrolyte decomposition. In contrast, Q<sub>irr</sub> was significantly reduced in the concentrated electrolyte, which indicated that stability against oxidation was improved in the highly concentrated electrolyte. Similar tendency was also observed in highly concentrated LiPF<sub>6</sub>/PC electrolytes, though polarization on charging and discharging were much higher.

A fresh half-cell was fully charged to 5.0 V, and kept at 60°C for 3 days in LiPF<sub>6</sub>/PC electrolytes. The amount of Mn deposited on lithium counter electrode was evaluated by ICP as a measure of dissolved Mn ions. The amount of dissolved Mn ions decreased with increasing Li/PC ratio, which indicated that the use of highly concentrated electrolytes is also effective for suppressing Mn ion dissolution.

This work was supported by a Kyoto Area Super Cluster Program, Japan Science and Technology Agent (JST), Japan.

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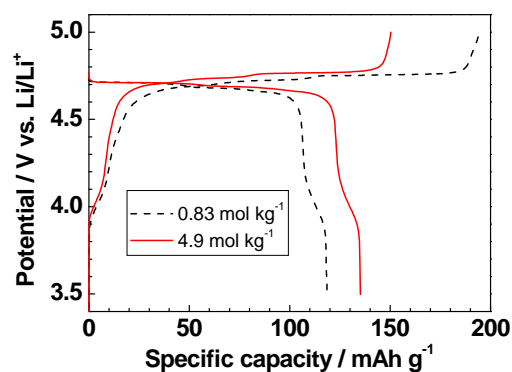


Fig. 1 Charge and discharge curves of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> in 0.83 mol kg<sup>-1</sup> (1 M) and 4.9 mol kg<sup>-1</sup> LiBF<sub>4</sub>/PC at 30°C. Charge and discharge rate: C/10.

## THE ELECTROCHEMICAL LITHIUM INSERTION PROPERTIES OF A NEW VANADIUM OXYFLUORIDE WITH $\text{ReO}_3$ -TYPE STRUCTURE

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Transition metal (TM) fluorides have been investigated in the search of new chemistries for lithium ion rechargeable batteries. In spite of the characteristic insulating behavior of these typical ionic compounds they are highly interesting. Fluorine ligands tend to raise intercalation potential opening new possibilities to find high energy electrode materials. However, the increment of intercalation potential with respect to similar oxides may drive the operating window out of the electrochemical stability window of the commonly used liquid electrolytes. A controlled effect on potential increase may be reached through the partial substitution of oxygen by fluorine. Thus proper oxygen by fluorine substitution may produce an increase of the intercalation potential but keeping it below the high voltage stability limit of the electrolyte. An important drawback is that stoichiometric control is not easily achieved and the chemistry of oxyfluorides is not as well-known as the chemistry of oxides. Academy has to make an effort to develop basic knowledge on these interesting materials and in particular reliable, reproducible and safer (HF free) synthesis methods. Note that due to crystal chemistry differences between oxygen and fluorine, crystalline structures with different features for insertion reaction may exist.

In this connection we have been working in the past few years on cryolites  $\text{Li}_3\text{MF}_6$  (M=Fe and V) and in the partial substitution of F by O which it proved to be difficult. However, we contribute now to the research on oxyfluorides by presenting a new oxyfluoride  $\text{VO}_2\text{F}$  for which non previous evidences of its existence had been reported. It fills the gap in the  $\text{MO}_2\text{F}$  compounds of Group 5 elements: V, Nb and Ta. Intercalation of lithium into  $\text{NbO}_2\text{F}$  has been reported, but vanadium is much more interesting owing to its lightness.

The synthesis procedure consists in simultaneous high temperature and high pressure treatment of  $\text{V}_2\text{O}_5$  and  $\text{VF}_3$  mixture at 4 GPa and 1073K. Vanadium dioxyfluoride is isostructural with  $\text{TiO}_2\text{F}$  exhibiting a hexagonal structure related to the  $\text{ReO}_3$  structure.

A complete chemical and microstructural study has been undertaken to fully characterize the new oxyfluoride. Regarding its electrochemical behavior, it is characterized by a long discharge from 4 to 1.5 V that develops ca. 450 mAh/g. However, the voltage-composition curve during the whole first discharge – charge cycle and further cycling (reversible capacity of 350mAh/g) indicate that  $\text{VO}_2\text{F}$  transforms irreversibly, similarly to the case of  $\text{NbO}_2\text{F}$ . In the high voltage region a kinetically limited intercalation reaction takes place. Mechanical milling enables intercalation and thus a reversible capacity of 250 mAh/g has been observed in the 4-2.25 V range. Nevertheless cycleability has been found to be limited in the high voltage region. Changes of vanadium oxidation state upon intercalation are presently being investigated by XAS to shed light in the intercalation reaction mechanism.

# LAYERED OXIDES FOR Na-ION BATTERIES

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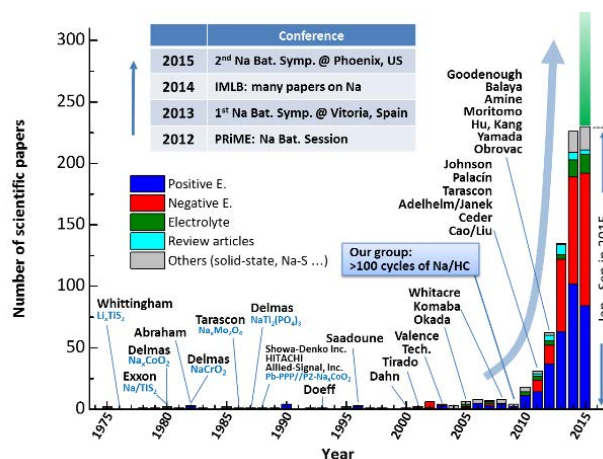
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Na-ion batteries are attracting much more interests as lithium-free high-voltage batteries because lithium resource is not abundant in the Earth's crust. Indeed, we found many papers on Na batteries reported even in the last IMLB. When we look back on the history of Na-ion batteries in Figure 1, there have appeared to be a few pioneering reports to demonstrate Na-ion full cells by Shacklette, Doeff, Alcántala, and Barker's groups in 1988, 1993, 2001, and 2003, respectively [1]. We note that the sodium-ion battery of Pb-polyphenylene//P2-Na<sub>x</sub>CoO<sub>2</sub> developed by Japanese and U.S. companies demonstrates good cycle-life according to their patents submitted in 1987-1988. In 2009, we succeeded in high performance Na-ion batteries by the development of sodium insertion shuttle-cock battery with adequate electrolyte [2]. Our present motivation is to achieve highly energetic Na-ion made from abundant materials free from toxicity.

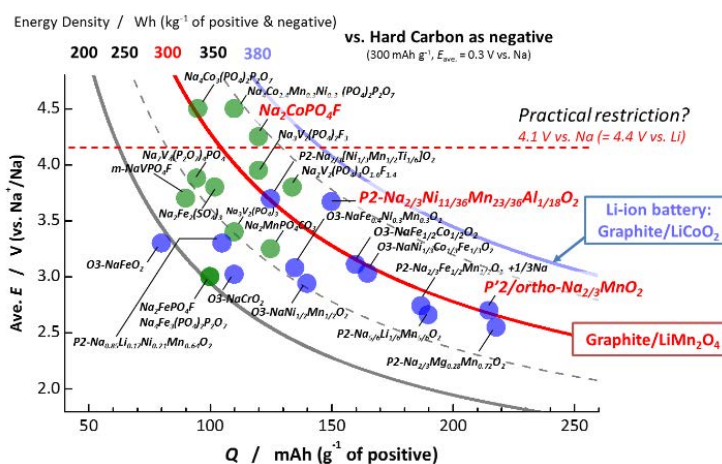
Layered transition metal oxides are promising candidates as positive electrode materials for Na-ion batteries because of the relatively high capacity, good cycle stability, and acceptable voltage range. Considering a difference in the standard potential between Li and Na, high operating voltage is required for positive electrodes to realize high energy Na-ion batteries. By studying on composition and structure of layered oxides, P2-Na<sub>2/3</sub>Ni<sub>11/36</sub>Mn<sub>23/36</sub>Al<sub>1/18</sub>O<sub>2</sub> shows ca. 150 mAh/g of reversible capacity with relatively high operating voltage of more than 3.5 V vs. Na as shown in Figure 2. Furthermore, calculated energy density (Wh/kg) of the Na-ion batteries of hard-carbon//P2-Na<sub>2/3</sub>Ni<sub>11/36</sub>Mn<sub>23/36</sub>Al<sub>1/18</sub>O<sub>2</sub> is approaching about 90% of the conventional Li-ion graphite//LiCoO<sub>2</sub>. We will present and discuss our recent progress and perspective in the layered oxides for positive electrodes of Na-ion batteries.

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**Figure 1** Yearly number of papers on sodium batteries. Data are based on Web of Knowledge in Oct. 2015 and summarized by our MS students, Mr. Hashimoto, Asari, Hashimoto and Hironaka. Conferences on Na are also inserted.



Updated plots from Chem. Rev., 114, 11636 (2014).

**Figure 2** Average voltage ( $V_{ave}$ ) and energy density (Wh/kg) versus gravimetric capacity (mAh/g) for selected positive electrode materials for Na-ion batteries. Energy density was calculated with the hard carbon (reversible capacity of 300 mAh/g with  $V_{ave} = 0.3$  V vs Na metal) as negative electrode materials.

## NEW INSIGHTS INTO VANADIUM FLUOROPHOSPHATES OF FIRST INTEREST DEVELOPED FOR Li AND Na-ION BATTERIES

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LiVPO<sub>4</sub>F and Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F<sub>3</sub> are respectively positive electrode materials for Li-ion and Na-ion batteries, which are attracting strong interest due to their high capacity, rate capability and long-term cycling stability.<sup>1,2</sup>

We will show how challenging is the control of oxygen over fluorine stoichiometry in these fluorophosphates. Existence of characteristic lithium defect environments has been for instance recently revealed using solid-state <sup>7</sup>Li nuclear magnetic resonance in well-crystallized Tavorite LiVPO<sub>4</sub>F,<sup>3</sup> despite they were not seen by high resolution X-ray and neutron diffraction as well as scanning transmission electron microscopy. The nature of these defects will be discussed, considering different possible sources of aging of LiVPO<sub>4</sub>F.

We already showed a complex phase diagram as a function of the charge state for Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F<sub>3</sub>, on the contrary to the straightforward solid solution described in the literature.<sup>4</sup> From structural determination based on high resolution X-ray powder synchrotron data and bond valence sum analysis we proposed for instance in NaV<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F<sub>3</sub> two vanadium environments, V<sup>3+</sup> and V<sup>5+</sup>, instead of a single one (i.e. V<sup>4+</sup>). We will report on the *operando* investigation of the redox processes involved during sodium deintercalation and on the charge compensation mechanism on the V site, considering X-ray absorption near edge structure measurements collected at the V k-edge.

### Acknowledgements:

This research is performed in the frame of the French network RS2E (<http://www.energie-rs2e.com>) and of the European network ALISTORE-ERI (<http://www.alistore.eu>). This project is partly funded by the French National Research Agency ANR (Descartes project SODIUM and Progelec project HIPOLITE) and by the H2020 European Program (Project NAIADES).

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## NON-AQUEOUS K-ION BATTERIES

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Mobile electronics and increasing interest in electromobility have substantially pushed battery research in recent years. Since the 1970s, lithium- and sodium-based materials for rechargeable batteries have been studied in parallel. The commercialization of the first lithium-ion battery (LIB) in 1991 shifted the focus of the research community solely towards this battery technology. However, the use of LIBs for large-scale applications leads to concerns about the availability and price stability of lithium and other materials (e.g. cobalt), which are commonly used in LIBs. As a result of these concerns, room temperature sodium-ion batteries are facing great interest as the specific materials needed for the sodium based batteries are generally cheaper and less toxic in contrast to lithium based systems [1]. Unfortunately, to date, Na-ion cathodes still show a tendency to deliver lower potentials than comparable Li-ion compounds.

This recently shifted researchers' attention to the investigation of potassium-ion battery (KIB) materials, which could possibly combine the higher potential of Li-ion cathodes and the feasibility of graphite as anode typical of lithium-ion batteries (LIBs) and the lower cost of sodium-ion battery (SIB) materials. In fact, the higher ionic radius and mass of  $K^+$  might result in negligible decrease of the gravimetric capacity but could also give access to new advantageous material properties. By that, KIBs could show similar cell performance to LIBs at the lower costs of SIBs.

So far, reported K-ion cells were still using K metal as counter electrode. Since the use of K metal as electrode material is related to severe safety concerns, which are even higher than for the use of Na metal, we will present an organic electrolyte based full cell without the use of K metal and give an outlook on possible perspectives in this new field of battery related chemistry.

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## IN SITU Fe K-EDGE XAS STUDY DURING CYCLING OF $\text{Li}_2\text{FeSiO}_4$

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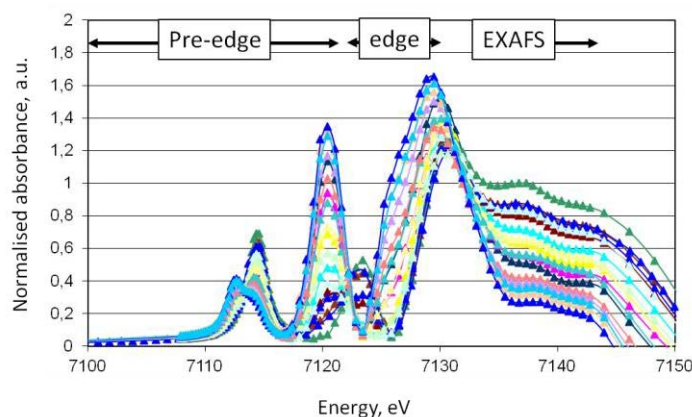
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Lithium iron silicates ( $\text{Li}_2\text{FeSiO}_4$ ) offer many benefits as novel cathode materials in Li-ion batteries. By using abundant elements, like iron and silicon, they offer an economic alternative to the Co based system currently employed in most commercial batteries. Another driving factor in battery development is associated with their safety and the Si–O bond provides stability similar to the P–O bond in  $\text{LiFePO}_4$  compounds [1].

Another advantage of the iron silicates, is the theoretical possibility to remove two Li ions from  $\text{Li}_2\text{FeSiO}_4$ , by utilizing the  $\text{Fe}^{+2}/\text{Fe}^{+3}$  and the  $\text{Fe}^{+3}/\text{Fe}^{+4}$  redox couples, thus, producing a higher capacity than 166 mAh/g for one Li ion. Although capacities greater than 200 mAh/g have been reported by several groups [2-4] it has yet to be clarified whether it was due to  $\text{Fe}^{+4}$  formation or electrolyte degradation [1]. Pouch cells were made to study the XANES and EXAFS of the Fe K-edge of  $\text{Li}_2\text{FeSiO}_4$ -based batteries cycled between 3.5 and 4.8 V, so as to show the eventual suggested  $\text{Fe}^{+3}/\text{Fe}^{+4}$  redox couples or whether the additional capacity originates from electrolyte degradation [5]. In addition, the pre-edge features of the XANES signal will be used in that regard.



XANES spectra of the Fe K-edge for  $\text{Li}_2\text{FeSiO}_4$ , cycled between 3.5 and 4.8V and measured at various state of charge.

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## The Rechargeable Aprotic Li-O<sub>2</sub> Battery

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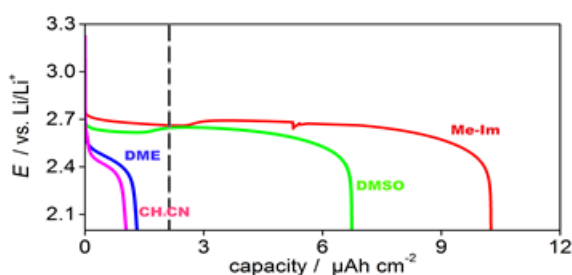
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### ABSTRACT

Li-ion and related battery technologies will be important for years to come. However, society needs energy storage that exceeds the capacity of Li-ion batteries. We must explore alternatives to Li-ion if we are to have any hope of meeting the long-term needs for energy storage. One such alternative is the Li-air (O<sub>2</sub>) battery; its theoretical specific energy exceeds that of Li-ion, but many hurdles face its realization.<sup>[1-5]</sup> One spin-off of the recent interest in rechargeable Li-O<sub>2</sub> batteries, based on aprotic electrolytes is that it has highlighted the importance of understanding the fundamental electrochemistry at the positive electrode within the battery.<sup>[6-15]</sup>

The challenges of obtaining efficient, reversible charge and discharge are well-documented in the field. Here, we describe how our recent studies into the electrochemical mechanism of O<sub>2</sub> reduction to form Li<sub>2</sub>O<sub>2</sub> at the positive electrode might allow us to design new strategies to overcome these limitations.<sup>[16]</sup>

For example, exploiting the effect of solvent donor number, Fig. 1. We will describe our recent results using redox mediators<sup>[17]</sup> to facilitate the electrochemistry along with the implications of the results for the future of rechargeable Li-O<sub>2</sub> batteries.



**Figure 1.** Potential vs. time at a planar Au electrode in various O<sub>2</sub> saturated aprotic solvents, 100 mM LiClO<sub>4</sub> showing early cell death for low donor number solvents but sustained capacity beyond the 7  $\mu\text{Ah cm}^{-2}$  limit (dashed line) for a Li<sub>2</sub>O<sub>2</sub> film in high donor number solvents.

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## RECHARGEABLE MAGNESIUM BATTERIES: ACHIEVEMENTS AND CHALLENGES

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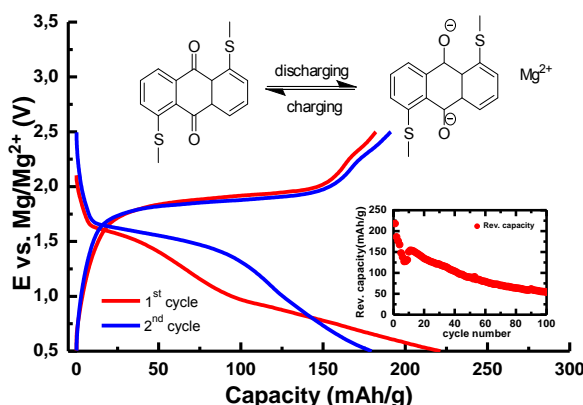
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Mg batteries are currently considered as one of the possible next generation electrical energy storage devices since they have high theoretical energy density and Mg is also highly abundant and relatively cheap when compared to Li. Highly passivating nature of magnesium metal surface requires special attention to the electrolyte development which should go along with a development of active cathode materials. Recently a major progress has been made in the field of non-nucleophilic electrolytes with high oxidative stability.<sup>1,2</sup> This opened the possibility to employ these types of electrolytes with organic materials where weak intermolecular forces enable the reversible electrochemical interaction of Mg cations coupled with fast diffusion.<sup>3,4</sup>



In this contribution we demonstrate use of several different anthraquinone based polymers as an active cathode material which presents a robust approach towards sustainable Mg batteries with high power and good cycling properties. Redox active quinone groups in the polymer matrix together with Mg powder anode separated by non-nucleophilic electrolytes show excellent electrochemical activity and stability during cycling. All electrochemical tests were performed in the two electrode modified Swagelok laboratory cells. Capacities between 150 and 200 mAh/g at a voltage from 1.5 – 2.0 V with stability over 100 cycles are realistically obtainable in the system used in our work. The present results pave the way for the use of other organic active materials and the further development of electrolyte systems. In particular, by broadening the range of organic solvents used, we expect that even better stability and higher capacity of organic materials can be achieved.

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## REVISIT MULTIVALENT BATTERY SYSTEM

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In the quest for new rechargeable battery technology to overcome Li-ion batteries, multivalent batteries are one of the possible options. Indeed in multivalent systems, the ions transport more than one charge such as 2 in the case of divalent  $Mg^{2+}$  or  $Ca^{2+}$  ions and even 3 in the case of trivalent  $Al^{3+}$ . [1, 2] For magnesium, proof-of-concept has been achieved with complex electrolyte compositions enabling electrodeposition (plating) coupled to covalent host cathodes to diminish columbic interactions. [3, 4] Recently Mg-type battery has known a regain of interest with especially the development of several new classes of electrolytes. [5] The latest one is based on a halogen free electrolyte which presents the advantage to diminish strongly the corrosion of current collector and/or battery casing. [6] On the other hand, the possibility of developing a secondary battery based on calcium has been much less investigated since a previous study concludes about the impossibility to electrodeposit calcium. [7] Being the 5<sup>th</sup> most abundant element on earth and having the second most electronegative theoretical potential after  $Li^+/Li$ , we decide to revisit the possibility to use Ca metal as an anode in rechargeable system. In this report, we will demonstrate the possibility to plate and strip calcium in conventional alkyl carbonate electrolytes at moderate temperature. Finally, the prospects of developing a new calcium based rechargeable battery technology will be discussed. [8]

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## Extending stability of cathode electrode materials in high-voltage region for Li/Na-ion batteries

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To further develop high-energy density Li/Na ion batteries, a feasible strategy is to develop cathode materials is able to work at high-voltage. For example, the upper limit voltage of commercial LiCoO<sub>2</sub> has been extended to 4.4 or 4.45(vs. Li). In order to achieve this target, highly stable electrode/electrolyte materials are necessary. In this talk, we will present some results about understanding how to keep high stability of electrode/electrolyte at high voltage with alivalent doping and electrolyte additives.

In the first example<sup>[1]</sup>, suberonitrile (SUN) and LiBOB were investigated as binary additives for Li-ion batteries that used LiCoO<sub>2</sub> as a cathode, cycled at high cutoff potentials and utilized LiPF<sub>6</sub>-based electrolyte. In the electrolyte with binary additives, the electrochemical performance of LiCoO<sub>2</sub> was enhanced significantly, and the initial coulombic efficiency increased to 94% compared with 90% in reference electrolyte. The cell also exhibited capacity retention of 62% after 500 cycles, a strong contrast with the 25% measured in reference electrolyte. EIS, SEM, TEM and XPS analyses indicated that the combination of the two additives had a unique influence on the structure and composition of the cathode-electrolyte interface on LiCoO<sub>2</sub>. Ex situ XRD confirmed that structural change of the LiCoO<sub>2</sub> material was not the main reason causing poor cycling performance when charging to the 4.5 V cutoff potential. In addition, some new progress<sup>[2]</sup> in the controlling cycling stability of P2-type Na<sub>0.66</sub>Ni<sub>0.33</sub>Mn<sub>0.67</sub>O<sub>2</sub> with Zn<sup>2+</sup>-doping and its working mechanism will be also presented.

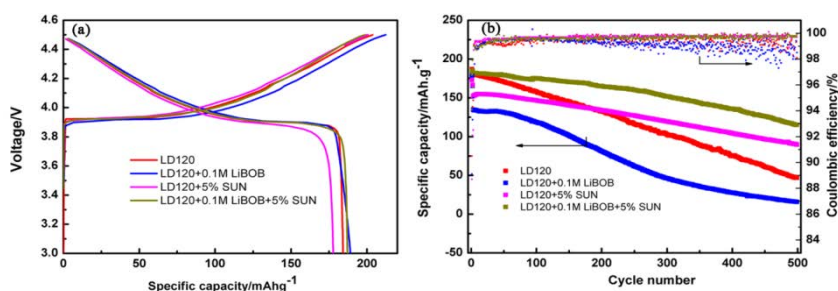


Figure 1. Comparison of (a) the initial voltage profiles at 14 mA g<sup>-1</sup>, (b) the cycling performance and coulombic efficiencies of LiCoO<sub>2</sub>/Li half cells at 140 mA g<sup>-1</sup>.

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## Advanced Materials for Electrodes in Na-ion batteries.

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Energy storage possesses an important role in order to rationalize the use of both fossil and renewable energy sources. Scientists are looking for inexpensive and green energy storage systems. At CIC-Energigune we are working on electrochemical energy storage: batteries and supercapacitors. A brief description of the activity developed at CIC-Energigune and fundamentally on sodium-ion batteries will be presented.

The development of sodium ion batteries is moving at a much faster rate and its use in the market is expected to be in near future. Very promising results have been reported in the recent past showing the performances of the sodium ion batteries very competitive for stationary energy storage [1, 2].

Energy density values of 210 Wh/kg can be obtained by using some specific electrode materials with an average cell potential of 3.3 V. A great range of compounds is being studied as possible cathode materials for Na-ion batteries, from oxides  $\text{Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$  to phosphates  $\text{NaFePO}_4$ , fluorophosphates  $\text{Na}_3\text{V}_2\text{O}_{2x}(\text{PO}_4)_2\text{F}_{3-2x}$  (where  $0 \leq x \leq 1$ ). Regarding the negative electrode, unlike the lithium ion batteries, the inability of sodium to insert into graphite is promoting the use of hard carbons, titanates and sodium alloys composites as anode materials.

In this talk we will present a general overview of the most interesting materials for electrodes in Na-ion batteries and the relationship between the structure and the electrochemical properties of these compounds.

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## TITANATE SYSTEMS FOR SODIUM STORAGE

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Room temperature sodium-ion batteries (NIBs) are expected to play a significant role in the future as an alternate battery technology to lithium-ion batteries, especially in applications where the weight and size of a battery are not crucial parameters. In this context, implementation of NIBs as large scale electrical energy storage (EES) devices for handling the intermittent nature of power generation from power plants running on renewable sources such as solar and wind will be especially attractive. Factors such as globally abundant sodium reserves and the identification of some newly discovered high energy density NIB cathodes<sup>[1]</sup> could make NIBs feasible for future EES. However, such high performance NIB cathodes would need an equally capable anode. In this talk, we will present our results on the sodium storage characteristics and performance of some phases within the sodium titanate family operating as low voltage NIB anodes. In particular, we will discuss three separate NIB anodes from this family which have individually attractive features for different EES applications.

The first such anode,  $\text{Na}_2\text{Ti}_6\text{O}_{13}$ , demonstrates an ultra-long cycle life of 5,000 cycles with a fast response time of 30 C (2 min).<sup>[2]</sup> We will discuss the cause of this excellent performance through structural studies. Its capacity close to 50 mAh/g at an average voltage of 0.85 V vs  $\text{Na}/\text{Na}^+$  may be attractive for regulating the minute-by-minute fluctuations of power generated from solar/wind farms, where a fast response time is most important rather than storage capacity. The second such NIB anode involves the two mole sodium storage per mole of the  $\text{Na}_2\text{Ti}_3\text{O}_7$  phase. This  $\text{Na}_2\text{Ti}_3\text{O}_7 \rightleftharpoons \text{Na}_4\text{Ti}_3\text{O}_7$  sodium storage pathway has an attractively high capacity of 178 mAh/g with a very low charge plateau at 0.4 V vs  $\text{Na}/\text{Na}^+$ .<sup>[3]</sup> We will discuss our attempts at stabilizing its cycling performance through electrochemical and synthesis-related approaches. The third NIB anode discussed will be the recently discovered  $\text{Na}_2\text{Ti}_3\text{O}_7 \rightleftharpoons \text{Na}_{3-x}\text{Ti}_3\text{O}_7$  pathway ( $x \leq 1$ ) which exhibits a moderate-high capacity of 89 mAh/g with the lowest voltage redox activity for any non-carbon based NIB anode at 0.2 V vs  $\text{Na}/\text{Na}^+$ .<sup>[4]</sup> We will discuss its sodium storage mechanism and show its excellent performance punctuated with a response up to 80 C (45 s) with a decent cycle life till 1,500 cycles. Furthermore, we will discuss our analyses on the unreliability of sodium metal acting as a counter electrode with special considerations to the possibility of erroneous data interpretations in sodium half cells<sup>[5]</sup> with some specific examples.

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## RECENT FINDINGS IN SODIUM BATTERY ELECTRODE MATERIAL TESTING

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Sodium metal anodes are widely used as counter (or also reference) electrodes in the so termed *half cell* tests, performed mostly at laboratory scale to assess the electrochemical performance of a given compound avoiding the assembly of *full cells* in which electrode balancing can severely affect performance. The reliability of extrapolating such half cell testing results to potential performance in full cells relies on the stability of the Solid Electrolyte Interphase (SEI) formed on the surface of sodium metal anodes as a result of electrolyte degradation reactions.

A comparative study of the composition, morphology and stability of the SEI formed on lithium and sodium metal anodes with state-of-the-art electrolytes using a range of techniques will be presented. The impact of the use of metal anodes (Li or Na) in half cell configuration on the impedance of a standard carbonaceous negative electrode (hard carbon, HC hereafter) was also discussed. Our results clearly point at the existence of significant differences which cast some doubts on the representativity of half-cell tests and call to exercise care in the interpretation or extrapolation of their results.<sup>1</sup>

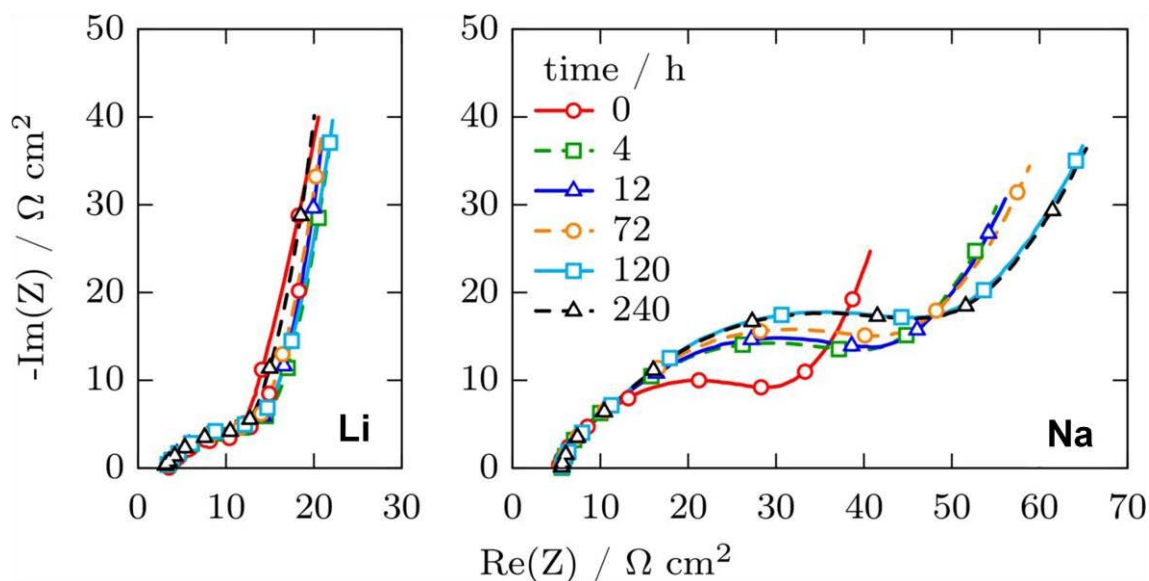


Figure 1. Impedance of hard carbon measured on the 500 kHz to 10 Hz frequency range in 3 electrodes configuration with reference and counter electrodes of metal M, at different times of storage in open circuit. In (a): M = Li, electrolyte is LP30; in (b): M = Na, electrolyte is 1M NaPF<sub>6</sub> in EC<sub>0.45</sub>PC<sub>0.45</sub>DMC<sub>0.1</sub>.

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## Crystal Water for Advanced Sodium and Magnesium Rechargeable Batteries

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Although Li-ion batteries have been successful in various applications, their shortcomings with regard to high cost and global maldistribution of raw materials, as well as safety concerns have stimulated alternative rechargeable batteries based on other carrier ions represented by sodium and magnesium ions, targeting grid-scale energy storage systems (ESSs). However, many electrode materials in these emerging systems often suffer from sluggish kinetics due to the larger size or bivalency of carrier ions, limiting electrochemical performance particular in specific capacity and operation voltage. In this talk, I will introduce a new approach of engaging crystal water in layered cathode materials. The crystal water improves the performance of the given materials substantially by shielding electrostatic interactions or maintaining the crystal frameworks over repeated cycles. Detailed effects of crystal water will also be described [1,2], along with promising potentials towards aqueous operations. Electron microscopy characterization for in-depth understanding of these materials will also be introduced [3].

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## Electrolytes: A key component for improved safety and longer life of lithium ion batteries

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LiPF<sub>6</sub> based non-aqueous organic carbonate solvent based electrolytes solutions are the state-of-the-art in lithium ion batteries. With the help of various, to most part novel analytical techniques, qualitative and quantitative information of the electrolyte degradation products could be gathered and eventually resulted in the proposal of mechanisms for related electrolyte aging reactions outside and inside the cell [1-3]. Furthermore, reducing the flammability and reactivity of the organic solvents, improving overcharge protection and developing more protective electrode/electrolytes interfaces plays a key role for the intrinsic (= passive) safety of the battery [4]. New electrolyte additives were investigated in terms of their flame retardant abilities and their influence on electrochemical performance. The electrolyte was analyzed as a whole system, as well as in view of its single constituting components. Novel safety/abuse tests and analytical methods were developed to better understand the effect of individual electrolyte components [5]. In this presentation, we will discuss the role of liquid organic solvent based electrolytes for safety and for cycle and calendar life of lithium ion batteries and how to conduct experiments elucidating this role. For instance, experiments to determine the self-extinguishing time of the electrolyte as well as nail penetration tests and heat-wait-search tests in an adiabatic reaction calorimeter (ARC-HWS) were carried out at different states of health to prove the functionality of specific electrolyte additives after long term cycling experiments.

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## Thermal energy balance, internal short and thermal runaway

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Battery reliability and safety are crucial for market acceptance for battery applications. Yet, these two important issues are difficult to manage, due to the lack of quantification methods to address them. Here we attempted to define the problem and search for better solutions to quantify reliability for battery functionality and performance. By establishing this practice, we are confident that battery reliability issues could be addressed more definitively and clearly for the goal of battery management. Once the reliability quantification was established, the safety issues and criteria for maintaining safety operation of the battery systems could be addressed with proper context.

The problems of internal short and thermal runaway in a battery are two severe safety issues that need better solutions to handle these potential hazards. Current solutions are more or less based on empirical solutions with a two-prong approach: from bottom up, by choosing better materials for cell design; and, from the top down, by using tests to regulate the requirements for prevention and protection. However, as often a battery may age differently in degree due to different duty schedules, user habits, and operating environments, the condition of a battery and its state might not be well defined. Thus, the effectiveness in prevention of internal short and thermal runaway cannot be assessed confidently. To address the severity of internal short and potential for thermal runaway, we began with detailed considerations of thermal balance in a cell. We believe that understanding and controlling the heat generation in a cell is the first step to deal with these safety hazards. The sources of heat, from Joule heating and chemical reactions, should be identifiable and quantifiable before we can design a safer cell for thermal management.

In this presentation, we shall begin with the discussion on how to define the state of a battery system and to quantify battery state in the system [1-3], followed by the subject on how to determine the amount of heat generation from each attributes and model the thermal balance in the battery system according to the cell chemistry [4] and design. At the end, a mechanical hypothesis on how thermal runaway proceeds in a battery cell would be provided for further discussion on how to quantify thermal behavior of a battery in the practice of commercial product development.

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## Hybrid Organic-Inorganic Gel Polymer Electrolytes for Lithium Batteries

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Hybridization of organic and inorganic materials is a way to produce polymeric compounds having enhanced mechanical and thermal properties. Solvay proprietary functionalized PVDF is able to be linked to silica through i.e. sol-gel reaction. This approach has been selected, in combination with the use of several liquid electrolyte, notably ionic liquids and organic carbonates, to produce a safe gel polymer separator for lithium ion and lithium metal batteries.

The Ionobrid membrane, obtained combining N-Propyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr13TFSI), LiTFSI, tetraethyl orthosilicate and Solef® functionalized PVDF, exhibits homogeneous surface with no defects (Fig.1), while high ionic conductivity (Fig.2), high flexibility and good mechanical strength can be obtained and tuned by adjusting the formulation. The Ionobrid has been successfully tested in lithium batteries and results will be presented.

A comparative study with carbonate based films will be done, focusing on the similarities and differences in term of cyclability and physico-chemical properties of the hybrid networks.

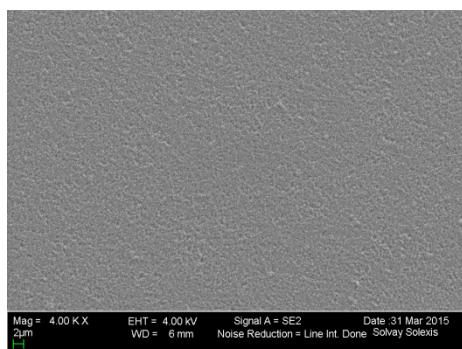


Fig. 1: SEM image of Ionobrid membrane (magnification 4.0k)

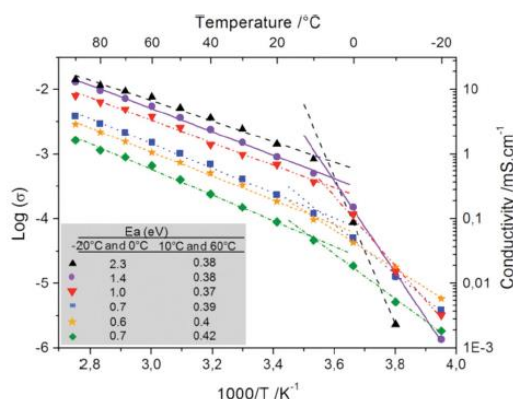


Figure 2. Ionic conductivities of different Ionobrid membrane compositions.

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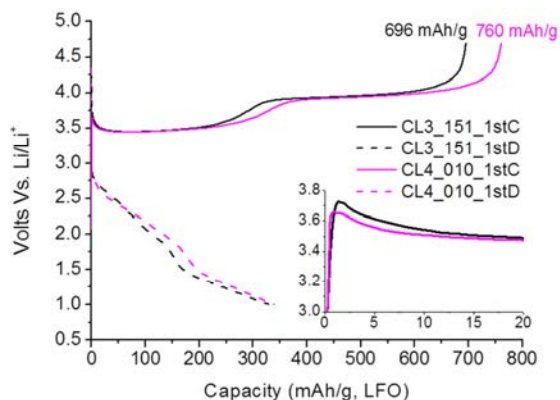
## Li-rich $\text{Li}_5\text{FeO}_4$ (LFO) cathode material as pre-lithiation additive for enabling high-energy Si-C/NMC batteries

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Silicon containing anodes employed in Li-ion cells are known to drastically boost the energy density of a full LIB battery by providing a high intrinsic capacity via  $\text{Li}_x\text{Si}$  intermetallic alloy formation/utilization compared to capacity-limited graphite anodes. However because a >300% volume change occurs between (de)lithiated  $\text{Li}_x\text{Si}$  states, a irreversible trapping of cyclable Li in the full cell negatively impacts performance, potentially by lowering cycle life. In this new approach, we enable new high-energy Si-containing Li-ion full cell systems with NMC cathodes by supplementing the lithium content in the cell from the cathode side via *co-blending* NMC powder with the anti-fluorite compound,  $\text{Li}_5\text{FeO}_4$  (LFO) that contains a tremendously high gravimetric capacity. For example, in a Li/LFO half cell, we observe a huge gravimetric capacity on the first charge (Figure 1 and Ref. 1). The LFO can release upwards of 750 mAh/g usable capacity on this sacrificial first charge. Note the LFO on discharge is electrochemically inactive above 3.0 V (vs  $\text{Li}^\ominus$ ), and thus will not contribute *reversible* capacity in a typical Si-C/NMC(LFO) cell cycled in a voltage range above about 2.5 V. The Li in LFO also provides small aliquots of Li during long-term cycling in Si cells that spares NMC from overcharge. This presentation will highlight the features of LFO, an effective lithium-source additive material.



**Figure 1.** First charge and discharge voltage profile of Li/ $\text{Li}_5\text{FeO}_4$  cell between 4.7 and 1.0 V; C rate is C/40; black curve: standard LFO material, and cyan curve: optimized LFO material.

[1] C. S. Johnson et al. *Chem. Mater.*, **22**, 1263-1270 (2010)

Support from the Vehicle Technologies Program, Hybrid and Electric Systems, in particular, David Howell, Tien Duong, and Peter Faguy, at the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy is gratefully acknowledged.

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## Overcharge Study in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Based Lithium-Ion Pouch Cell

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The Hawai'i Natural Energy Institute (HNEI) is leading a team engaged in the research, development, deployment, and analysis of grid-scale battery energy storage systems (BESS) that are designed for system control and power quality support at the generation, transmission, and distribution levels. The program aims to identify high value BESS applications at various system levels, develop control algorithms that maximize the benefit to the grid/customer and the lifetime of the BESS, and evaluate and optimize those algorithms under real world operating conditions.

Overcharge tolerance has often been studied from a safety standpoint (e.g. thermal runaway), but rarely from a durability standpoint. A quantitative battery diagnosis was developed to analyse an overcharge event in a commercial  $\text{Li}_4\text{Ti}_5\text{O}_{12} \parallel \text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  lithium-ion pouch cell and the subsequent cycle aging behaviour [1].

Using an electrochemical inference technique and the degradation emulation 'alawa toolbox [2-4], quantitative diagnoses of two cells enduring the same cycle aging conditions, with or without the overcharge event, were performed. From this analysis, a hypothesis of localized blockage of the ionic conduction pathway due to gas accumulation was proposed as the mechanism driving the degradation [1], Figure 1. This hypothesis was then validated using X-ray computerized tomography (CT scan) and half-cell experiments.

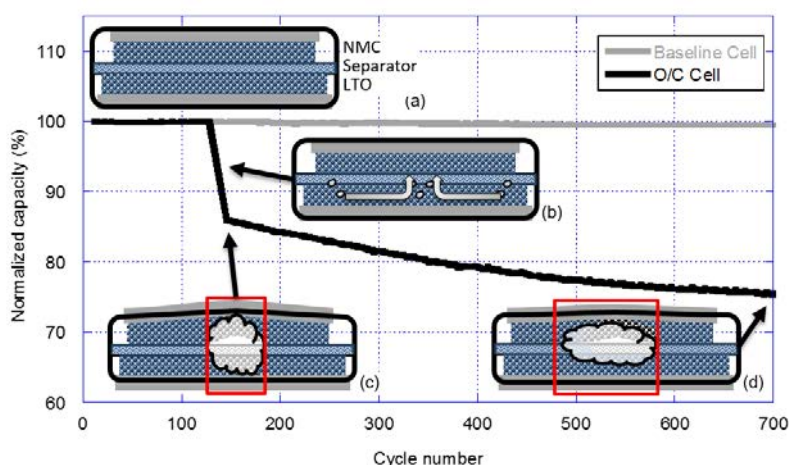


Figure 1: Proposed overcharge degradation mechanism.

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## **HIGH-RATE CAPABILITY ENABLED BY POLYSULFIDE CHEMISTRY FOR LI-S BATTERIES**

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S lithiation during the operation of Li-S battery is a multi-step electrochemical process that involves different lithium polysulfide (PS) intermediates. Some of the PSs are highly soluble in the aprotic organic electrolyte, leading to PS dissolution from the electrode. PS dissolution has been a major issue in the research of Li-S battery. It has been considered as an unfavorable process that is directly linked to the deterioration of several key performance indexes, such as cycle life, self-discharge and coulombic efficiency, of the battery. However, as revealed in this presentation, the PS dissolution process could have a profound effect on the rate capability of the Li-S battery. With properly designed electrode architecture, the rate capability of a Li-S battery can in fact be substantially enhanced by taking advantage of PS dissolution.

## Bypassing methods of polysulfides dissolution in improved lithium sulfur batteries

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In this paper, we will present the electrochemical performance of an electrode consisting of sulfur confined within hollow-mesoporous TiO<sub>2</sub> (HMT) spheres that are interconnected via multi-wall carbon nanotubes (MWCNTs), designated hereafter as HMT@CNT. We successfully synthesized and characterized (i) a S-HMT@CNT sulfur cathode comprised of hollow, spherical, nanostructured TiO<sub>2</sub> and carbon nanotubes and (ii) DF-PCW interlayer comprised of highly porous carbon spheres and carbon nanotubes. We use a highly porous carbonaceous interlayer to improve the wettability with the electrolyte and hence to further improve the rate capability. We selected the chitosan binder in our electrode formulations in order to reduce the electrode volume expansion and loss of active material caused by dissolved lithium polysulfides. Moreover, the pores of TiO<sub>2</sub> allowed for high sulfur loadings and accommodation of the volume expansion at the electrode level. The CNT component provided an overlapping network that improved both the electronic conductivity and mechanical strength of the S-HMT@CNT and DF-PCW. The pores in the carbon interlayer played the role of a medium that scavenged the dissolved lithium polysulfides, while improving Li-ion and electron transports. Owing to our cathode characteristics and cell design, the lithium-sulfur cell fabricated demonstrated good cycle life, high efficiency, and high rate capability. Of significance, the excellent cycling realized at the 2C and 5C rates is appealing for utilizing the lithium-sulfur batteries in high power applications (Fig. 1).

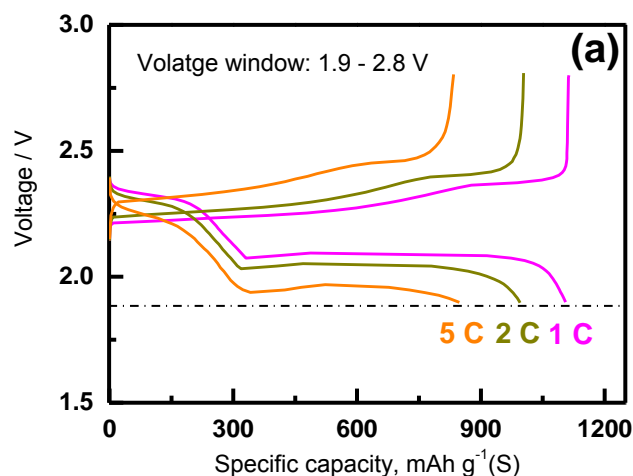


Figure 6. Voltage profiles of the S-HMT@CNT electrode in a cell constructed with DF-PCW interlayer and cycled between 1.9 and 2.8 V under increasing rates

## ADVANCES IN NA, LI-S AND ZN BATTERY SYSTEMS

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There is a great interest in developing alternative low cost, high energy solutions for EV and grid storage. This presentation will review progresses on the fundamental understanding of full battery reactions mechanisms and materials issues in non-lithium battery systems. Examples may include Na-ion, Li-S and Zn batteries. In Na-ion batteries we will discuss high capacity electrode materials, but will highlight the properties and influence of SEI layers in full battery cells. In Li-S batteries we will focusses on the electrochemical properties with high S loading and low electrolyte amount for high energy density considerations. Several key factors will be discussed: (1) electrode architecture, (2) surface modification of the electrode materials, (3) solubility of the polysulfides and their control, and (4) role of dual function binders. In Zinc batteries we will discuss a highly reversible aqueous system and the reaction mechanisms in the cathodes, anodes and electrolytes.



## HOW DO YOU SOLVE A PROBLEM LIKE LITHIUM POLYSULFIDES?

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The drive to identify high energy batteries remains an on-going challenge. Whilst companies and researchers continue to pursue intercalation materials that can operate high voltages (5 V vs Li|Li<sup>+</sup>), these materials and devices don't offer the step change in energy density that a battery hungry world requires.

Although a 10 fold increase in specific energy is possible with recent advances in Li-Sulfur (2567 Wh per kg) technologies, there are several challenges in the development of these devices. The most vexing of these challenges is the generation of lithium polysulfides which are highly prone to irreversibly move into the electrolyte media. These can have deleterious effects on the performance of the device such as reduced capacity and cycle-life. To overcome this problem, numerous different approaches have been trialled to "lock" S within a conductive structure / matrix whilst still making it available to lithium ions from the electrolyte to form the required lithium polysulfides that deliver the high capacity of the device.

At CSIRO, we have been looking at a range of different methodologies to understand the formation of polysulfides both in the electrolyte and the cathode and then examine various methods to keep them electrically connected within the cathode. In this presentation, we will highlight our work in various cathode structures, both organic and inorganic based, methods to prevent polysulfide dissolution, changes to the electrolyte and the effect on cycling and *in-situ* studies at the Australian Synchrotron.

Reference to a journal publication:

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## ORIGINS OF HCMR™ CATHODES DEGRADATION

V. Battaglia, G. Chen, W. Chen, G. Liu, D. Membreno, K. Persson, A. Shukla, L. Terborg,  
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High capacity manganese rich (HCMR™) materials are promising candidates for commercial Li-ion battery positive electrodes for applications in electric and plug-in hybrid electric vehicles.<sup>1</sup> These oxides, also denoted as  $x\text{LiMO}_2 - (1-x)\text{LiMnO}_3$  ( $M = \text{Co}, \text{Mn}, \text{Ni}$ ), deliver a high discharge capacity ( $>240$  mAh/g) at operating voltages exceeding 3.5 V vs.  $\text{Li}/\text{Li}^+$ .<sup>2</sup> However, these materials have significant limitations and suffer from high first cycle irreversible capacity loss, impedance rise and voltage fade during cycling.<sup>2-4</sup>

This study provides an overview about possible scenarios which could lead to the DC resistance rise observed within a cycle and with cycle life in high capacity manganese rich positive electrode materials (HCMR™). The structure and possible structural changes of the pristine and aged HCMR™ material are discussed. Preliminary evaluations of the material suggest a single phase, aperiodic crystal consisting of monoclinic domains. *In situ* Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR) and potentiostatic intermittent titration technique (PITT) are discussed providing information about structural changes of the surface, surface layer formation and  $\text{Li}^+$  diffusivity. Raman spectroscopy suggests transformation to a spinel like structure after aging and FTIR spectroscopy indicates dynamic formation of a surface film, growing with cycle number. The  $\text{Li}^+$  diffusivity in HCMR™ varies as a function of potential and correlates strongly with DC-R behavior. Changes in impedance as well as in cell parameters during and with cycling show morphology and topology changes of the HCMR™ material. The electrode composite and the material itself contribute to the long term impedance rise with prolonged cycling.

### Acknowledgements

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231, under the Applied Battery Research for Transportation (ABR) Program and Award Number DE-EE0006443.

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## MICROSTRUCTURAL CHANGE OF $\text{Li}(\text{NiCo})\text{O}_2$ BASED MATERIALS OF LI ION BATTERIES.

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The performance of  $\text{Li}(\text{Ni},\text{Co})\text{O}_2$  materials as positive material has been studied by many authors. For example, we have reported the fading mechanism of lithium ion batteries with  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ [1-3], and pointed out that the reaction and diffusion resistances of positive electrode drastically increased during durability test at high temperatures. It was revealed that the microstructural change of positive material played a important role for resistance increase. In this presentation, the microstructural change of  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  material investigated by various methods, such as electrochemical techniques, STEM, EELS, and XAFS. The cylindrical cells (18650-type) of  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  and artificial graphite with carbonate electrolyte were used for durability tests at high temperatures. The electrodes taken out of the cells before and after durability tests were evaluated by using various methods. The  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  materials before and after 1 cycle were also evaluated by STEM-EELS to compare with the materials after long durability test. The importance of non-uniform reaction, especially at low temperature will be discussed.

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## Lithium- and Manganese-Rich Cathodes: A Deep Dive and a Look Forward

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Lithium- and manganese-rich cathode materials have been extensively studied for the past decade or more. Due to the promise of substantial capacity and energy gains this class of cathodes still commands interest despite the possibly, insurmountable challenges that remain. One reason for continued interest is the fact that there are very few alternatives within the space of conventional lithium-ion that have the potential to meet the demands of next-generation technologies; namely, transportation applications. In 2012 the U.S. Department of Energy commissioned a “Deep Dive” study into the now well-known phenomenon of voltage fade associated with this class of cathodes<sup>1</sup>. This presentation will give an overview of the insights gained from that recently-concluded, ~3-year study and discuss a few, as-of-yet, unanswered questions. A current strategy moving forward will be presented and state-of-the-art comparisons will be made.

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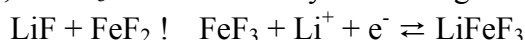
## COMPOSITE CATHODES AS A SUBSTITUTE CATHODE

Shigeto Okada<sup>a</sup>, Ayuko Kitajou<sup>a</sup>, Hironobu Hori<sup>a</sup>, Nikolay Dimov<sup>a</sup>,  
Takahiro Yamashita<sup>a</sup>, Daisuke Tsunoe<sup>a</sup>, and Prabeer Barpanda<sup>b</sup>

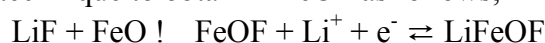
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As far as we know, composite cathode with LiF was first reported by Kim [1]. According to his report, LiFeF<sub>3</sub> was obtained by the mixing of LiF and FeF<sub>3</sub> as follows;



Here, we tried similar technique to obtain LiFeOF as follows;



Because it is also difficult to synthesize the LiFeOF single phase as well as LiFeF<sub>3</sub> [2].

As the substitute cathode for rocksalt-type LiFeOF, LiF and FeO composite was prepared by the dry ball-milling method under ambient pressure. The reversible capacity was 274 mAh/g with an average voltage of 2.6 V. As shown in Table 1, the energy density was over 712 mWh/g and it means that the composite cathode has the highest energy density among iron-based insertion-type cathode active materials. The electrochemical activity was also confirmed by the charge and discharge reactions in the full cell with LiFeOF cathode and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> anode. In this presentation, the other examples of iron-based composite cathode will be introduced such as and LiSO<sub>4</sub>-FeSO<sub>4</sub> and LiF-Fe [3].

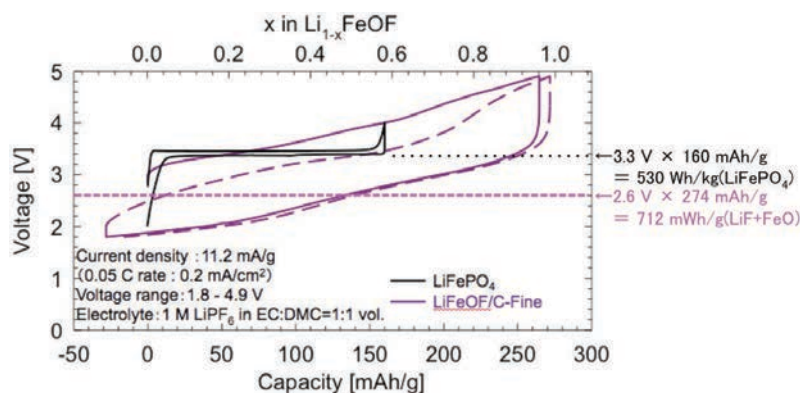


Fig. 1 Charge/discharge profiles of LiFePO<sub>4</sub> and LiF-FeO composite cathode vs. Li.

Table 1 Comparison of the cathode properties between LiFePO<sub>4</sub> and LiF-FeO composite cathode.

Cathode	Discharge capacity	Discharge voltage	Energy density
LiFePO <sub>4</sub>	150 mAh/g	3.3 V	495 mAh/g
LiFeOF(LiF + FeO)	290 mAh/g	2.5 V	725 mAh/g

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## UNDERSTANDING OF THE MECHANISM OF SODIATION OF p-BLOCK ELEMENT BASED ELECTRODES

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Na-based storage systems working at ambient temperature have lately regained interest. Recent research on Na-ion systems was focused on the development of negative electrode materials, firstly based on the insertion of Na into hard carbon structures able to develop a capacity as high as ~300 mAh/g, but limited volumetric energy density.[1]The large ionic radius of Na with respect to Li leads to a higher volume expansion upon cycling, which is expected to strongly affect insertion as well as alloying or conversion reactions. Surprisingly, p-element-based electrodes have shown to be viable alternatives to hard carbon, providing very interesting performances with reversible capacities largely exceeding 400 mAh/g.[2-3]We have investigated several phases containing P, Sb, Pb and/or Sn as electrode materials for Na batteries. The thorough investigation of both mechanism (through in situ XRD and Mössbauer spectrometry) and performances of Sband Pb will be presented (Figure 1). The good electrochemical performances of such electrode materials arevery surprising if one take into account the huge volume expansion expected from the reaction with Na (200-400 %). An XPS analysis will be presented to compare the solid electrolyte interphase (SEI) formed in the Sb based battery versus Li and Na.[4]

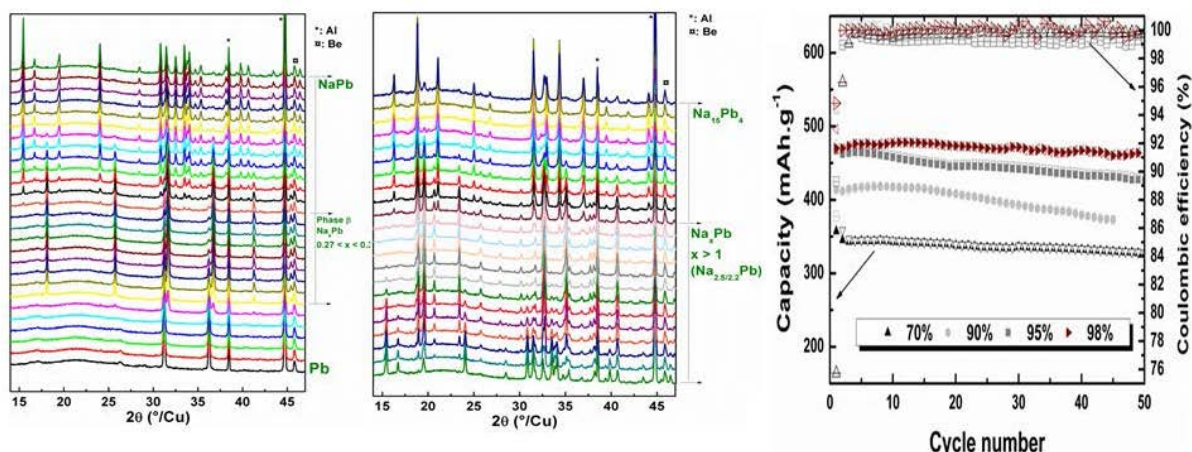


Fig. 1: a) XRD *in situ* of Pb/Na and b) capacity as function of number of cycles for various electrode formulations and coulombic efficiency.

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## ALLUAUDITE FRAMEWORKS FOR SODIUM BATTERIES

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Sodium-ion batteries are widely seen as an alternative to Li-ion batteries. In this scenario, the development of sodium batteries relies on discovery and optimization of oxide/ polyaionic insertion materials. Guided by the inductive effect principle, the redox potential of polyanionic cathodes can be altered with the electronegativity of constituent anions. Here, electronegative  $\text{SO}_4$ -based materials can deliver the highest redox potential vis-à-vis other polyanionic materials. In this spirit, alluaudite framework  $\text{Na}_2\text{Fe}_2(\text{SO}_4)_3$  cathode has been recently reported offering  $\sim 100$  mAh/g capacity with high rate kinetics and cycling reversibility [Nature Communications, 5, 4358, 2014]. It marks the highest  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox potential (ca. 3.8 V vs. Na/Na+). We have pursued this high-voltage Na-M-S-O quaternary alluaudite insertion family using low temperature solvothermal synthesis ( $T_r < 300^\circ\text{C}$ ) like (i) ionothermal method, (ii) spray drying route and (iii) Pechini synthesis. Using these green synthesis routes, we have explored other 3d metal homologues in Na-M-S-O quaternary system. Using experimental and DFT calculations, we will summarise the crystal structure, magnetic properties and electrochemical performance of high-voltage alluaudite framework cathode materials for sodium batteries.



## SIMULATED SYNTHESIS AND CHARACTERISATION OF Li-Mn-O NANOSTRUCTURES

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Simulated amorphisation recrystallization methods, are now routinely used to generate models of various nano-architectures for metal oxides with complex microstructural details [1,2]. In the current studies the approach is used to generate nanostructures of manganese dioxides, and those associated with the  $\text{Li}_2\text{MnO}_3$  and spinel  $\text{LiMn}_2\text{O}_4$  for Li-ion battery application. Firstly, lithium transport and mechanical properties of pure and lithiated nanorods and nanoporous  $\text{MnO}_2$  are discussed and compared with the bulk structure. In particular, stresses related to lithium insertion and how these impact on electrochemical properties are outlined. Secondly, a nanosphere of the ternary  $\text{Li}_2\text{MnO}_3$  was synthesised and molecular dynamics (MD) simulations of its charging reveal that the reason nanocrystalline- $\text{Li}_2\text{MnO}_3$  is electrochemically active, in contrast to the parent bulk- $\text{Li}_2\text{MnO}_3$ , is because in the nanomaterial the tunnels, in which the Li ions reside, are held apart by Mn ions, which act as a pseudo 'point defect scaffold'. Lastly, nano-architectures, i.e. nano- sphere, sheet, porous and bulk, associated with the Li-Mn-O ternary were synthesised from amorphous spinel nanosphere. The resulting crystallised nanostructures are characterised from visual images, radial distribution functions, XRDs and simulated microstructures. A preliminary analysis reveals the presence of the layered  $\text{Li}_2\text{MnO}_3$  and spinel  $\text{LiMn}_2\text{O}_4$  together with a wide variety of defects, including grain boundaries and ion vacancies.

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## **MECHANICAL ACTIVATION AND MECHANOCHEMICAL REACTIONS: FUNDAMENTALS AND APPLICATION FOR LITHIUM-ION BATTERIES**

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Recently, many methods for preparing materials for lithium-ion batteries have been explored. High-energy solid-state mechanical activation (MA) is one of the modern and promising synthetic methods to prepare different nanostructured functional materials [1]. This is due to the potential application of mechanochemical reactions in technology, in particular, for the development of so-called dry processes, which are more environmentally friendly and cost-efficient than the currently adopted technologies. MA provides better contacts between the reagents as a result of mixing, decreasing particle size, generating fresh surface for the contacts, and also by inducing melting and sublimation of reagents. MA affects solid-state reactions by improving diffusion, generating strain, structural, electronic and ionic defects, as well as by creating pulses of pressure and temperature. A peculiar feature of mechanochemical reactions is that the products can be formed in a metastable state, similar to what happens during fast crystallization, when there is no time for an equilibrium structure to be formed. This can bring to novel materials with new structures and new electrochemical properties. When MA is combined with other techniques, its advantages can be more fully displayed.

To optimize the process, the choosing of the appropriate reagents for the fast-propagating mechanochemical reactions is important. In this study, different mechanochemical reactions were used to prepare nanostructured electrode materials for lithium-ion batteries, including acid-base reactions, redox reactions, association reactions, ‘core’-‘shell’ and composite materials formation [2-4].

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## Re-Thinking Lithium Ion Battery Design and Manufacturing

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A multiyear research and development effort at MIT and 24M Technologies has demonstrated a new lithium-ion cell architecture and manufacturing method based on semisolid electrodes. Originally studied for flow battery applications, semisolid electrodes have been developed with high electronic conductivity ( $t_e \sim 1$ ) and lower tortuosity than conventional calendered electrodes, thereby allowing thick electrodes with several times the thickness and area capacity of today's lithium ion electrodes to have transport kinetics useful for all but very high power applications. Figure 1 illustrates the area capacity ( $\text{mAh}/\text{cm}^2$ ) of semisolid Li-ion cells compared to several conventional cells as a function of current density, with the diagonal lines indicating constant C-rate contours. Cells built on this electrode platform have significantly fewer inactive component layers than conventional lithium-ion cells of similar performance, and can be produced by a radically simpler process that obviates most of the electrode fabrication unit operations in conventional Li-ion, thereby lowering both materials and manufacturing cost. Semisolid Li-ion cells also possess unique physical properties including deformability and high abuse tolerance. Cell test results for LFP/graphite grid cells and NCA and NMC based EV cells will be presented.

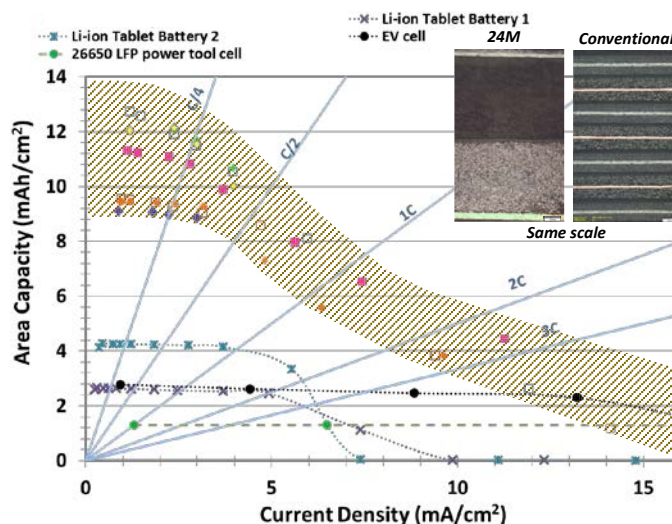


Figure 1. Area capacity vs. current density for semisolid electrodes (shaded band) and several conventional Li-ion cells. Inset shows cross-sections of semisolid cell stack compared with conventional cell at the same magnification.

### Acknowledgements:

Support by the U.S. Department of Energy through the ARPA-E program, the Vehicle Technologies Office of EERE, and the Advanced Battery Materials Research (BMR) program is gratefully acknowledged.

## REACTION DISTRIBUTION IN COMPOSITE ELECTRODES OF LIB

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Various kinds of application-oriented lithium ion batteries (LIBs) are produced in large scale. Uniform reaction inside the battery leads to the maximum performance of the battery. It is difficult so far, however, to observe phenomena and examine their distribution inside *operando* LIBs. High-energy X-ray from storage ring and neutron beam can penetrate the depth of LIB and clarify reactions and their distribution inside LIB even covered with metal case. The authors devised some new technology to examine reactions inside LIB using SPring-8 beam line[1-3].

Reaction distribution has a hierarchy; crystallite, primary particle of polycrystalline, secondary particle, one dimensional depth distribution of composite electrode, two dimensional facial distribution of composite electrode, battery-to-battery in battery pack, and module-to-module in battery system.

We focus on the distribution through the depth of LiCoO<sub>2</sub> (LCO), LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> (NMC), and LiFePO<sub>4</sub> (LFP). Space sensitive X-ray absorption spectroscopy and X-ray diffraction revealed that the distribution is more remarkable for the composite of low porosity than for the one of high porosity[4, 5]. Charge and discharge at high rate causes large reaction distribution through the depth of composite electrode. The distribution is relaxed under potential resting or open circuit for the composite electrode for LCO and NMC active materials but not for LFP. This different behavior is ascribed to the potential change depending on lithium content of the materials. A local cell formed inside the composite electrode relaxes the distribution. Very flat potential change with lithium content of LFP gives little motive force for relaxation of the distribution.

This work was carried out as a part of Research and Development Initiative for Scientific Innovation of New Generation Batteries (RISING project) financially supported by New Energy and Industrial Technology Development Organization (NEDO).

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## EFFECTS OF ADDITIVES ON ELECTROCHEMICAL PERFORMANCE OF ANODE MATERIALS IN PC-BASED ELECTROLYTES

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We have developed a high throughput virtual screening technique, based on quantum chemical calculations, to identify potential electrolyte additives for PC-based electrolytes. This screening method is cost effective, time saving and can be used for all additive applications. Based on high throughput screening, 11 compounds were selected as potential lead structures from the first Pareto front and crucial properties were examined and compared using DFT calculations. Among these compounds, two additives were selected, synthesized and experimentally tested to illustrate the potential of the selected additives and hence the screening technique. The additives were tested using 1M LiPF<sub>6</sub> /PC and 1M LiPF<sub>6</sub> /PC: dimethyl carbonate (DMC) (1:1 v/v). The CV of 1 M LiPF<sub>6</sub>/PC:DMC (1:1) and 1 M LiPF<sub>6</sub>/PC, with and without, different additive concentrations are carried out in this work. The cell without the additive cannot be cycled which is consistent with the charge/discharge test. No reduction peak is observed in the potential region above 1 V; however, a broad feature starts to appear below 0.8 V, in the region where reduction of PC occurs. However, lithium intercalation and deintercalation is not observed which can be related to the exfoliation of the MCMB electrode. The cells with different additive concentrations all show a peak, due to additive reduction, in the potential region between 1.8-1.4 V centered at 1.7 V for CMDO and at 1.6 V for BCMDO. This observation is consistent with the calculated reduction potential and the charge/discharge profile. The intensity of the peak increases as the additive concentration increases. In the lower potential region (below 0.8 V), the broad feature observed for the cells without the additives, correlated with the decomposition and cointercalation of PC, disappears with the addition of the additives. This result suggests that the additive can suppress the cointercalation and decomposition of PC, while lithium intercalation and deintercalation can be maintained. The mesocarbon microbead electrode showed an excellent electrochemical performance in a PC based electrolyte with 2% additives. The first cycle coulombic efficiency of the proposed additives was >84%, increasing to 99% after the second cycle. When compared with previously reported sulfur or halogen containing additives, the computationally designed additives resulted in better coulombic efficiency. The MCMB electrode's electrochemical performance improvement is therefore attributed to additive decomposition products.

## **ELECTRODEPOSITION AND DEVELOPMENT OF METAL ANODES**

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Various metals have been used as battery anodes in electrochemical cells ever since the birth of batteries with Volta's pile and also in the first commercialized primary (Zn/MnO<sub>2</sub>, Leclanché 1866) and secondary (Pb/acid, Planté 1859) batteries. The idea and prospects of building a technology based on lithium are much more recent, as it required moving away from aqueous electrolytes. However, the first Li-MoS<sub>2</sub> cells with specific energy two or three times higher than the current Ni/Cd or Pb/acid cells were withdrawn from the market after safety difficulties were experienced with overheating on recharge related to dendrites growth. As an alternative, secondary Li-ion batteries avoiding the use of lithium metal anodes were commercialized by Sony in 1991 [1]. In contrast with Li and Na metal anodes, electrodeposition of Mg and Ca does not seem to be plagued with dendrite formation [2,3,4]. These metals are thus interesting candidates as metal anodes in rechargeable batteries.

Despite issues to develop viable anodes, metal (Li, Na, Mg or Ca) electrodes are commonly used within the battery community as reference and counter-electrodes to investigate the performance of potential electrode materials using the so called half-cell configuration. While this protocol has proved to be reliable in Li based cells, the essential properties for the use of Na, Mg and Ca pseudo reference electrodes remain to be fully assessed. A systematic evaluation of the non-polarizability and stability in the electrolytic environment will be presented for these metal electrodes and the effect of several factors influencing the electrochemical deposition/stripping process will be discussed.

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## PUSHING THE LIMIT OF OPERANDO TECHNIQUES TO PROBE BATTERY MATERIALS

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The Li-ion chemistry is thus far the most advanced chemistry employed in battery technology. To date, Li-ion batteries dominate the market of the electronics and portables devices. However, in the field of electric and hybrid vehicles further improvements are required in terms of performance, safety, and cost. Advanced Li-ion batteries and the novel systems (Li-S and Na-ion) utilize less explored electroactive materials and thus show new reaction mechanisms during electrochemical cycling, the understanding of which requires new characterization tools and techniques.

Development of a reliable electrochemical cells is thus of a prime importance when studying battery materials in *operando* mode during cycling. This is never an easy task, since the design of such cells has to be adequate to the technique of a choice and meet all necessary requirements.

Herein we present different cell designs developed in our laboratory and used for *operando* studies. Having overcome many obstacles, our *operando* cells are able to sustain more than 100 cycles and simultaneously to perform structural studies such as X-ray and neutron diffraction. For the latter one, we also tested and adapted a new set-up called stroboscopic mode. It allows *operando* study of the batteries that are cycling at very high rates (e.g. 10C) with a neutron patterns collected each 1 s along 200 cycles and more.

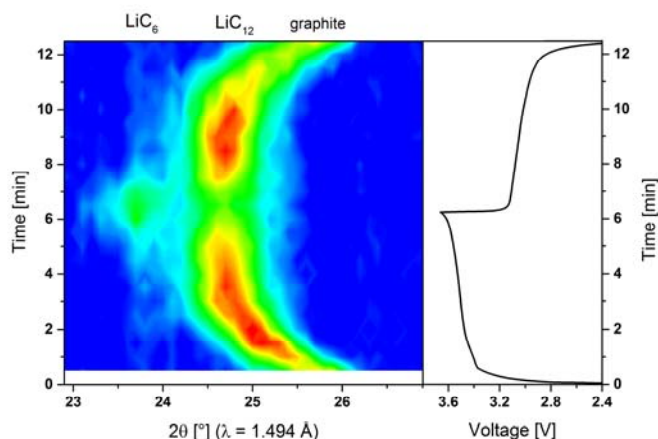


Figure 1. *Operando* neutron powder diffraction measurements using stroboscopic mode (cell cycled at roughly 10C rate) performed in a full cell  $\text{LiFePO}_4$  vs. graphite (the plot shows the evolution of the main peak of the graphite (002) along charge and discharge).

Moreover,  $\text{Li}_2\text{MnO}_3$  will be given as an example of the material that requires the activation at elevated temperature in order to be properly cycled. We modified our X-ray diffraction cell to be able to cycle it at temperatures higher than  $25^\circ\text{C}$  and thus to study the activation mechanisms of  $\text{Li}_2\text{MnO}_3$ . Other than that examples based on different *operando* techniques used to characterize Li-ion, Na-ion, and Li-S batteries will be also presented during the talk.

*Acknowledgment:* The authors would like to express their gratitude to Dr. Denis Sheptyakov from HRPT, SINQ, PSI beamline and fruitful help/discussions regarding neutron experiments. Mr. Hermann Kaiser and Christoph Junker are acknowledged for their help in all technical aspects of this study and the development of the cells. SAFT, SNF and SCCER Heat and Storage are thanked for financial support.

## LITHIUM RICH LAYERED CATHODE MATERIALS - HIGH PRESSURE AND EPITAXIAL FILM SYNTHESSES

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Structures, electrochemical properties and reaction mechanism of lithium rich layered cathode materials were studied for the samples synthesized by high pressure and epitaxial thin film synthesis methods.

Lithium-rich layered rock-salt type oxides,  $\text{Li}_{1.2+x}\text{M}_{0.8-y}\text{O}_2$  ( $M = \text{Mn/Co/Ni}$ ), were synthesized using a high-pressure method and the relationship of the phases appeared in the ternary system,  $\text{Li}_2\text{MO}_3\text{-LiMO}_2\text{-Li}_2\text{MO}_2$ , was clarified. The phases were synthesized by changing Li/M/O ratios, Mn/Co/Ni ratios, and reaction conditions, and their structures were characterized by synchrotron X-ray and neutron diffraction analyses. The amount of excess lithium in the transition metal layer increased with increasing lithium content. Furthermore, additional Li was detected at the tetrahedral site in the transition metal layer in the structure. X-ray absorption near-edge structure spectra confirmed that the oxidation state of the transition metals increased with the increase in the amount of excess lithium. The effects of the excess lithium and the Mn/Co/Ni ratio to the electrochemical properties were investigated.

The reaction mechanism of the lithium excess phases was studied using epitaxial-films fabricated by pulsed laser deposition method. The initial lithium intercalation-deintercalation reaction was investigated using surface X-ray diffraction and hard X-ray photoelectron spectroscopy. The charge and discharge capacities drastically increased with decreasing film thickness for the  $\text{Li}_2\text{MnO}_3$  system. The 12.6 nm thick film showed a high capacity of  $300 \text{ mAh g}^{-1}$  during over 50 cycles, indicating that the surface region is actively reconstructed to generate a high-capacity phase. Surface structural changes at the initial cycling have a pronounced effect on the power characteristics and the capacity of lithium-rich layered rocksalt type cathodes. Based on the materials synthesized by high pressure and thin film methods, the reaction mechanisms of the lithium excess cathode materials will be discussed.



## IMPROVED CATHODE MATERIALS FOR NEXT GENERATION LITHIUM-ION BATTERIES

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Due to their high energy and power density, excellent efficiencies and long life time lithium ion batteries have become the dominating energy storage technology for the new generation of Plug-in hybrid electric vehicles (PHEV) and full electric vehicles (EV). However, there is still considerable improvement needed to achieve extended driving range and to reduce significantly the cost of battery packs. For these reasons, the development of new high capacity, safe and lower cost cathode materials is necessary.

Among various cathode materials under development, high voltage  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$  (LMNO) with spinel structure is one of the most promising candidates, because of the high operating voltage, high rate capability and good thermal stability. Moreover, it is easy to obtain via low cost synthesis methods from abundant raw materials.

However, the high voltage can also lead to side reactions with the electrolyte, which cause impedance increase and capacity fading during cycling or storage especially in full cells using graphite as anode. The long term stability can be significantly improved by adjusting the composition, the particle morphology and by surface coating. In this presentation, we discuss intensively the effect of composition, particle morphology and surface modification on the electrochemical performance, structural and thermal stability of LNMO.

Another approach towards high energy and lower cost is the development of  $\text{Li}_{2-x}\text{Mn}_{1.5-y}\text{M}_y\text{Ni}_{0.5}\text{O}_4$  ( $0 \leq x \leq 0.5$ ) materials. These materials combine both the high voltage and the high specific capacity approach, reaching reversible capacities up to  $280 \text{ mAhg}^{-1}$ . Morphological features can be easily adjusted to meet industrial needs. These materials show high coulombic efficiency, high rate capability and excellent cycling stability. More than 150 cycles without any capacity loss could be demonstrated for complete cells consisting of graphite as anode material. We will report the influence of stoichiometry, structure and particle morphology on electrochemical performance, structural stability and ageing behavior.

### Acknowledgements

Financial support of the BMBF within the project “Li-EcoSafe” (FKZ: 03X4636A) and by the European Community within the Seventh Framework Program APPLES Project (contract number 265644) are gratefully acknowledged

## Advanced concentration gradient cathode material with two-slope for high-energy and safe lithium batteries

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Li[Ni<sub>x</sub>Co<sub>y</sub>Mn<sub>z</sub>]O<sub>2</sub> cathode with two-sloped full concentration gradient (TSFCG), maximizing the Ni content in the inner part of the particle and the Mn content near the particle surface was synthesized via a specially designed batch-type reactor. The cathode delivered a discharge capacity of 200 mAh g<sup>-1</sup> (4.3 V cutoff) with excellent capacity retention of 88% after 1500 cycles in a full-cell configuration. Overall electrochemical performance of the TSFCG cathode was benchmarked against conventional cathode (CC) with same composition and commercially available Li[Ni<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>]O<sub>2</sub> (NCA). The TSFCG cathode exhibited the best cycling stability, rate capability and thermal stability of the three electrodes. Transmission electron microscopy analysis of the cycled TSFCG, CC and NCA cathodes showed that the TSFCG electrode maintained both its mechanical and structural integrity whereas the NCA electrode nearly pulverized due to the strain during cycling. While the chemical partitioning of the composition generated the observed high capacity and thermal stability, the unique microstructure of the TSFCG secondary particle provided excellent cycle stability and rate capability. TEM analysis of the cycled TSFCG, CC and NCA cathodes revealed that the TSFCG electrode remained intact with minimal surface deterioration whereas the NCA electrode experienced severe damage during cycling, resulting in pulverization of the particles.

## Polymer electrode material for energy storage

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Polymer material, as a rather new member in energy storage family, has attracted much attention and efforts because of its special property in many aspects comparing with other inorganic electrode material.<sup>[1,2]</sup> In our recent study, different polymer material has been investigated and used for lithium/sodium secondary battery and even all-organic battery. Owned to the optimized molecular structure, the polymer with quinone moiety increased from about 190mAh/g for previous polyanthraquinone sulfide<sup>[3]</sup> to more than 250mAh/g for the latest poly(1,4-anthraquinone). In addition, the film-forming property of this polymer phase endows it with a possible application in membrane battery. Another recent study was focused on the application of polymer electrode material in some new energy storage system, such as aqueous Li<sup>+</sup> battery and magnesium battery. It was found that the aqueous Li<sup>+</sup> battery with polymer anode showed a greatly improved electrochemical performance than previously reported analogues due to its high reaction reversibility, very suitable working voltage, as well as its extremely stable polymer framework. Generally, polymer electrode material, with diversified structure, has promising prospective in energy storage.

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## Development of Non Polymeric Positive Electrode Materials for Rechargeable Organic Batteries

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Most of traditional batteries are based on the redox chemistry of inorganic species (mainly metals), of which some are scarce natural resources, often costly (even toxic) and energy greedy at the process level. Alternatively, organic chemistry provides great opportunities for finding innovative electrode materials and developing potentially greener electrochemical storage systems. Based on the tailoring of naturally abundant chemical elements (*e.g.*, C, H, N, O), organics give the true possibility of being prepared from renewable resources and eco-friendly processes. Additionally, a better recycling management is expected for such batteries because organic compounds can thermally be eliminated with possible heat recovery. Last but not least, two types of electrochemical mechanisms can be used in practice: n-type structures with cations release/uptake and p-type structures with anions uptake/release.

These last ten years, significant progress has been achieved on redox-active organics bringing them positively to the attention of the energy storage community as demonstrated by the rapid increase in the number of studies and recent reviews on the topic [1]. However, the search for efficient organic electrode materials is still a burgeoning field and one of the most challenging tasks remains the fabrication of long lasting and high energy organic batteries.

For the past few years, we have been revisiting selected n-type organic structures based on carbonyl/carboxyl functional groups and identified stable redox-active organic structures able to reversibly accommodate lithium. For instance, efficient lithiated positive electrode materials have been developed [2]. Beyond this class of organic materials, this contribution will be more importantly focused on the development of novel p-type non polymeric compounds able to intercalate anions at average operating potentials  $> 3.2$  V vs.  $\text{Li}^+/\text{Li}$  giving rise to organic electrode materials exhibiting higher energy densities.

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## NMR BEYOND LI: NA, MG AND LI-AIR BATTERIES

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This talk will describe the use of NMR spectroscopy to characterize a series of “beyond-Li” electrode materials. The NMR results are combined with complementary techniques such as pair distribution function analysis of (X-ray) scattering data. In the sodium-ion battery case,  $^{23}\text{Na}$  NMR spectroscopy can be used to follow changes in local structure in a manner very similar to that performed on lithium-ion battery materials. Our work using the method to study local structure and  $\text{Na}^+$  and electronic ordering in positive layered materials and intermetallic anodes will be described.  $^{25}\text{Mg}$  NMR is more challenging, but the use of DFT calculations to predict shift positions and help interpret the spectra speeds up the analysis considerably. This will be illustrated for paramagnetic positive electrode materials. The use of NMR and MRI (magnetic resonance imaging) to link structural changes with electrolyte concentrations will be demonstrated for lithium metal anodes. Finally, new developments in the field of lithium-oxygen batteries will be described. In particular NMR spectroscopy allows the different discharge products and many side-reactions to be followed. For example,  $^1\text{H}$  and  $^7\text{Li}$  NMR spectroscopy can be used to separate  $\text{Li}_2\text{O}_2$  from  $\text{LiOH}$ , allowing batteries that cycle via  $\text{LiOH}$  to be characterized. Our recent studies with  $\text{LiI}$  redox mediators and r-GO electrodes will be described.

## NOVEL BATTERY CONCEPTS – SAME OLD ELECTROLYTES?

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Li-ion batteries have enjoyed decades of electrolyte development and the basic standard electrolyte recipes have more or less converged. On the other hand, the prerequisites on the electrolytes for the next generation batteries differ substantially and hence also the motivations for the choices needed to be made. But still the salts and solvents to be used are much the same – or not?

This presentation will detail out the main new relevant physico-chemical demands on the electrolytes from the perspective of the novel battery concepts of Li-metal, Li-S, Li-O<sub>2</sub>, and Na-ion [1-3]. This includes the different electrochemical stability windows (all), the stability vs. the superoxide radical anion (Li-O<sub>2</sub>), the various solubility issues (Li-S), the different cation-solvent interaction strengths (Na-ion), *etc.*

To be concrete a “smorgasbord” consisting of results from i) experiments using very specific model systems [4], ii) experiments using special *operando* set-ups [5], and iii) computations based foremost on quantum chemistry (DFT) but also combined with thermodynamics will be presented [6]. The information will be used to outline if, why, and how we can/should change the basic electrolyte chemistry for each of the novel battery concept – or not.

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## Na-Air Batteries: Understanding of Mechanisms and Rechargeability

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Alkali metal-oxygen (Li-O<sub>2</sub>, Na-O<sub>2</sub>) batteries have attracted a great deal of attention recently due to their high theoretical energy densities, which is comparable to gasoline, making them attractive candidates for use in electrical vehicles. However, the limited cycling life and low energy efficiency (high charging overpotential) of these cells hinder their commercialization [1,2]. Li-O<sub>2</sub> battery system has been extensively studied in this regard during the past decade. Compared to the numerous reports of Li-O<sub>2</sub> batteries, the research on Na-O<sub>2</sub> batteries is still in its infancy. Although Na-O<sub>2</sub> batteries show a number of attractive properties such as low charging overpotential and high round-trip energy efficiency, their cycling life is currently limited to a few tens of cycles. Lithium and sodium elements share similar chemical properties, however, the chemistry and electrochemistry of Li- and Na-O<sub>2</sub> batteries are not the same. While the discharge product of Li-O<sub>2</sub> cells is well-recognized to be lithium peroxide (Li<sub>2</sub>O<sub>2</sub>), both sodium peroxide (Na<sub>2</sub>O<sub>2</sub>) and superoxide (NaO<sub>2</sub>) have been detected as the discharge product of Na-O<sub>2</sub> cells in a number of different studies. Therefore, understanding the chemistry behind Na-O<sub>2</sub> cells is critical towards enhancing their performance and advancing their development.

Our group applied nanostructured carbon materials as cathodes to investigate various effects including surface area of porous carbon black [3], current density on CNTs [4] and functional groups on graphene [5], 3D electrodes [6] and humidity on rechargeability [7]. Furthermore, the determining kinetics factors for controlling the chemical composition of the discharge products in Na-O<sub>2</sub> cells will be discussed and the potential research directions toward improving Na-O<sub>2</sub> cells are proposed. The perspectives will also be discussed.

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## **BEYOND LI-ION : RECENT DEVELOPMENTS AND DEEPER UNDERSTANDING OF THE LITHIUM/SULFUR RECHARGEABLE BATTERY TECHNOLOGY.**

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Firstly reported in the 80's, rechargeable lithium/sulfur (Li/S) batteries have received ever-increasing attention since 10 years. Indeed, elemental sulfur (S<sub>8</sub>) is a promising positive electrode material due to its high theoretical specific capacity of 1675 mAh.g<sup>-1</sup>. Assuming full conversion of S<sub>8</sub> to Li<sub>2</sub>S, complete Li/S cells are expected to reach practical gravimetric energy densities from 300 up to 600 Wh.kg<sup>-1</sup>. Those values, combined with low cost, non-toxicity and environmentally abundance of sulfur, make Li/S batteries one of the most promising candidates for next-generation energy storage systems. A review of the recent developments done at CEA-LITEN on the lithium/sulfur cell will be presented, at different levels starting from the optimization of coin cell components up to assembly of prototypes.

In parallel, review of last characterization methods that have been applied via *in situ* and *in operando* methods to the lithium/sulfur (Li/S) battery will be reported, allowing deeper understanding of Li/S cell cycling mechanism.

## High Energy Density Lithium-Sulfur Batteries for Aerospace Applications

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NASA's upcoming missions need energy storage systems with enhanced performance, especially higher specific energies and energy densities, beyond the capabilities of Li-ion cell. One such application involves astronaut Extra Vehicular Activity (EVA), wherein the astronaut's Portable Life Support System (PLSS) is expected to support 8 hours of EVA. The state of art (lithium-ion) batteries with ~200 Wh/kg at the cell level can support only four hours of EVA. To address these needs, we are developing high-energy and long-life lithium-sulfur cells, with the following performance targets: cell specific energy of 400 Wh/kg ii) cycle life exceeding 200 cycles and iii) ability to operate safely over a wide temperature range of -10 to +30 °C. We have been developing improved cell components for Li-S cells, e.g., a protected Li anode, a dense sulfur cathode and compatible electrolytes, mainly addressing the key technological hurdles of poor utilization at high cathode loadings (necessary for a practical high energy cell) and limited cycle life.<sup>1-4</sup> We have developed new sulfur cathodes with metal sulfide blends that show high specific capacities of  $\geq 800$  mAh/g at C/3 rates with practical material loadings, ii) a Li anode protected with a polymer electrolyte that displays efficient Li cycling and durability in laboratory Li-S cells, and iii) Electrolytes and new proprietary coatings serving as polysulfide blocking layers which inhibit the deleterious effects of sulfur redistribution and contribute to a good cycle life. In this paper, we will describe some of these material developments and their performance in laboratory cells and later in prototype cells.

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## DEVELOPMENT OF FREE STANDING ELECTRODES FOR LI-ION ANODE STORAGE

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In an attempt to reduce materials that are not directly involved in the electrochemical reactions in a lithium-ion battery, such as the current collectors, the Ångström Advanced Battery Centre (ÅABC) at Uppsala University is currently working on developing free standing flexible electrodes [1,2,3,4]. Our first attempts have been to address the negative electrode and the challenge of the large volume expansion experienced when alloying lithium with tin and silicon. We show some promising results.

Size tunable nanocrystals of SnO<sub>2</sub> or Si encapsulated in 3d macroporous carbon have been synthesized and tested as free-standing negative electrodes for lithium-ion batteries. The synthesis of SnO<sub>2</sub> is based on a rapid, scalable combustion method by using the biodegradable and recyclable polyvinyl alcohol (PVA) foam as the carbon source. The electrostatic forces between the copious hydroxyl groups of purified PVA sponge and tin precursor guaranteed the uniformly and intimate integration of tin oxide nanocrystals on the carbon matrix. The combustion process carbonized the processed PVA molecules into a 3d carbon matrix, which not only encapsulated tSnO<sub>2</sub> nanocrystals as a way to buffer the volume changes during the lithiation/delithiation process, but also served as a way to preserve the interconnected pore system for the facile electrolyte percolation. The best performing electrode based on the composite with optimized size range of SnO<sub>2</sub> NCs and graphitization degree of carbon delivered a rate performance up to 8 A g<sup>-1</sup> and long term cycleability up to 500 cycles for Li<sup>+</sup> storage. Silicon nanocrystals were attached to grapheme layers with a sol gel process and then freeze dried with PVA before the combustion step. In this case the silicon particles were protected from direct contact with the electrolyte. This gave the free-standing electrode a cycling stability vs. lithium for more than 1400 cycles but also a stable cycling performance in a full cell where the cathode was LiFePO<sub>4</sub> also made as a free-standing electrode. The results will be discussed based on detailed electrochemical analysis, in-situ technique and post-mortem morphological characterizations. We confirmed and quantitatively analyzed the contributions from traditional alloying/de-alloying mechanisms and non-diffusion controlled pseudocapacitive behavior for high rate Li<sup>+</sup> storage.

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## Development of novel electrolyte additives via ex-situ analysis of electrodes

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### **Abstract**

An investigation of the effect of electrolyte on performance of lithium ion batteries will be presented. The electrochemical performance of common electrolyte formulations will be discussed along with detailed ex-situ surface analysis of the cycled electrodes. The ex-situ analysis allows the development of an understanding of the role of the electrolyte and common additives in the structure of interfacial electrode films on both the anode (solid electrolyte interphase, SEI) and on the cathode. Correlation of the structure of the surface films with the performance limiting reactions in lithium ion batteries affords insight into the mechanism of interfacial film formation and function. The mechanistic insight is used to systematically develop novel additives designed for specific electrode surface modification to afford optimized electrochemical performance. The electrochemical performance and ex-situ surface analysis of electrodes cycled with novel Additives for Designed Surface Modification (ADSM) will be presented.

## NEW INSIGHTS INTO SEI FORMATION ON GRAPHITE IN ALKYL CARBONATES AND DINITRILES BASED SOLVENTS

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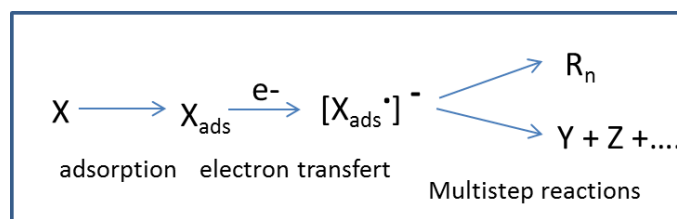
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In order to increase the energy density of Li-ion batteries for portable applications the use of higher cell voltages or larger specific capacities is required. Most anodes material, like graphite, silicon or tin are working out of the electrochemical stability range of the commonly used electrolytes. Then, stable cycling cannot be achieved without the formation of a stable and  $\text{Li}^+$  conducting solid electrolyte interphase (SEI). Using high voltage cathode ( $>5\text{V}$ ) cannot be achieved with alkyl carbonates (AC) as electrolyte solvent as they are not enough stable. Alternative solvents which are more resistant to oxidation, like dinitriles (DN), may be used instead of AC but the formation of a stable SEI on the negative electrode has to be re-considered.

The simpler manner to stabilize the anode/electrolyte interface is to use additives such as vinyl or fluorinated derivative of ethylene carbonate (EC) which have already identified to be efficient for increasing batteries performances and cycle life.

The mechanism of action of SEI former compounds is not completely understood today. Nevertheless some recent works [1-4] are able to provide new insights based on the scheme reported below:



$\text{R}_n$ : insoluble polymeric network

$\text{Y}, \text{Z}$ : small molecules and ions, oligomers

where X represents the SEI former additive. When the applied potential is driven to sufficiently low value, X is reduced in a multistep process which leads to a polymeric 3D network ( $\text{R}_n$ ) and by products (Y, Z). Some of the byproducts have been already identified in solution or at the electrode/separator surface by mean GC-MS analysis, IR spectrometry and XPS analysis but nothing is known at this time about the polymer molecular weight.

In this presentation, it will be shown that SEI former additives are often strongly adsorbed at the electrode interface before being reduced and this explain why they are efficient even at very low concentration and in the presence of various solvents including DN.

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## NEW INSIGHTS INTO THE ELECTRODE/ELECTROLYTE INTERFACE ON POSITIVE ELECTRODES IN LI-ION BATTERIES

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Understanding and controlling the reactivity at the electrode/electrolyte interface (EEI) is one of the key issues for the development of high capacity and efficient lithium-ion batteries. The heterogeneous and partially catalytic reaction of the electrode with the electrolyte triggers the formation of surface films on the electrode surface which can cause degradation of the cell performance. Whereas the EEI layer properties are quite well known for negative electrodes such as lithium metal and graphite [1,2], the EEI layer on positive electrode materials is still puzzling. Especially the interface layers on high voltage and high capacity positive electrodes, whose potentials approach the limit of electrolyte stability against oxidation [3], is quite unexplored. One of the challenges in understanding the reactions at the surface of the electrode is the complicated composition of the positive electrodes, containing not only the active material but also conductive agents and polymeric binders, that can modify the EEI layers on the electrode. To bypass these ambiguities, there is a need for study model electrodes such as thin films or pure active material electrodes, which allow for investigating solely the reactivity of the electrolyte at the active material surface. Here, combining X-ray Photoelectron Spectroscopy (XPS and X-ray Absorption and Emission Spectroscopy (XAS/XES), of model electrodes, we will show how the species formed at the electrode/electrolyte interface are affected by change in charging potential and the structure and nature of the transition metal in the material. XES and XAS will be used to shed light on the change of electronic structure upon delithiation.

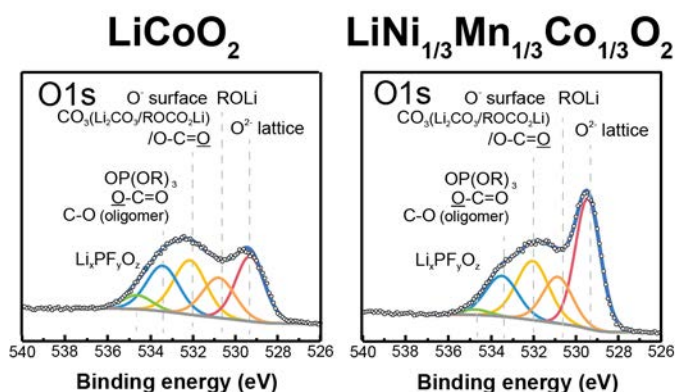


Figure 1: O1s XPS spectra photoemission lines for 100% LiCoO<sub>2</sub> or LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> electrodes charged at 4.6 V<sub>Li</sub> at a rate of C/100 in 1M LiPF<sub>6</sub> 3:7 EC:EMC.

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