IBA2016 | International Battery Association

Nantes, FRANCE

March 20-25

Nantes Events Center, France

IMN
INSTITUT DES MATÉRIAUX
JEAN ROUXEL

Abstracts
of poster presentations

Monday 21
Poster Session 1

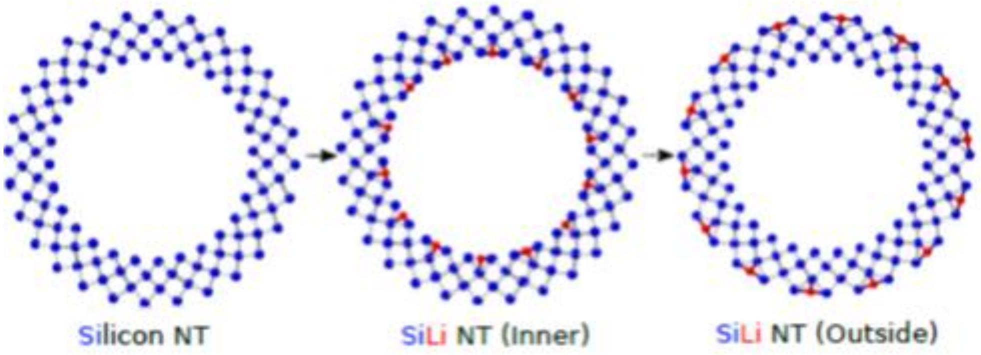
LI-ION REACTION MECHANISMS IN SILICON NANOTUBES

Maria Alfredsson[a], Jimmel Stewart[a] and Nanami Yokota[a]
[a] *School of Physical Sciences, University of Kent, Canterbury, CT2 7NH, UK*

m.l.alfredsson@kent.ac.uk

Rechargeable lithium-ion batteries are considered to be the most promising energy storage due to their long cycle life and high specific capacity [1]. However, existing lithium-ion batteries use graphite as anode material and this is not efficient enough to reach market level to be employed in vehicles. There are still some challenges to develop more in anode material to enhance their performance to meet the requirements for efficient energy storage [2]. Silicon has been regarded as one of the most promising candidate to replace graphite anode material due to its excellent merits in high theoretical electrochemical capacity. It is safe to use in high-power applications due to its low discharge potential [3]. However, the commercial application of silicon in the battery is still not progressed due to severe mechanical damage because of volume expansion and contraction of Si electrodes during cycling operation. This could cause pulverisation and loss of capacity [4]. An effective way to solve this problem is the employment of nanostructures, which are capable of minimising the volume change due to small size and available surrounding free space [5].

The aim of this study is to understand how the use of silicon nanotubes can improve the performance of Li-ion batteries. For this purpose we are using a combination of experimental techniques and atomistic simulations to determine the atomic processes involved in the insertion and extraction mechanisms of lithium ions in the silicon nanotubes. It is found that the strain energy in the tubes favour Li-ion insertion in the outer part of the tubes, as opposed from the inside of the tubes, which is in agreement with experimental observations. Experimentally, these findings are combined with electrochemical studies of silicon nanotubes, using a number of various electronic conducting binders and Li-ion salts.



[1] M..R. Palacin, Chem. Soc. Rev. 38 (2009) 2565-2575
[2] S. Flandrois, B.Simon, Carbon 37 (1999) 165-180
[3] J. Cho, J. Mat. Chem. 20 (2010) 4009-4014
[4] D. Billaud, E. Mcrae and A. Herold, Mater. Res. Bull. 14 (1979) 857–864
[5] J. Bae, J. Solid State Chem. 184 (2011) 1749–1755

V_2O_5 NANORIBBONS FROM REVERSE MICELLES AND ORGANIC OXIDANTS FOR BATTERY INSERTION ELECTRODEs

José Manuel Amarilla[a], Pedro Tartaj[a], and Beatriz Vazquez [a]
[a] *Instituto de Ciencia de Materiales de Madrid, (CSIC),* c/Sor Juana Inés de la Cruz, 28049 Madrid (Spain). email address of the presenting author: amarilla@icmm.csic.es

Single and mixed vanadium oxides have been extensively studied for insertion electrodes of rechargeable batteries due to its high capacity, low cost and wide availability [1]. In the last years, advances in Li-metallic anode stabilization, the continuous advances in solid-state electrolytes including those in combination with ionic liquids, and the advances in synthesis/processing routes have renewed the interest in vanadium oxides. Broad consensus exists that in order to maximize efficiencies in electrochemical properties, inorganic nanoscale materials must be used. Particularly, 1D-configurations (nanoribbons, nanoroads …) are very appealing as electronic and diffusive transports are enhanced, and they can withstand mechanical stresses during electrode cycling.

For this work, we have developed an original synthetic method based on reverse micelles for the growth at room temperature and atmospheric pressure of V_2O_5 nanoribbons [2]. Essential for the success of the method was the use of a soluble organic oxidant that acts as oxidant and co-surfactant during the synthesis, and facilitates surfactant removal with a simple washing protocol. An important feature of the synthesized V_2O_5 nanoribbons is that the red powder obtained after drying retains excellent solution-processable capabilities. Using this powder, we are able to process electrodes with three different configurations: Binder, Binder-free and Additives free (Figure 1). The electrochemical studies in Li-half cells shown that, a low rate (0.2C, 59 mA/g) the capacity of the V_2O_5 nanoribbons (ca. 200 mAh/g) was similar for the three electrode configurations. This result indicated that the nanoribbons were not altered during the different processing protocols. All the electrodes exhibited excellent rate capabilities and remarkable cycling performances [2]. Thus, the Additive free electrode retained 95% of the nominal capacity after 200 cycles at 5C charge/discharge rate.

Acknowledgment: Financial support from projects MAT2014-54994-R, PIE-201460E123 and MATERYENER3CM are gratefully acknowledged.

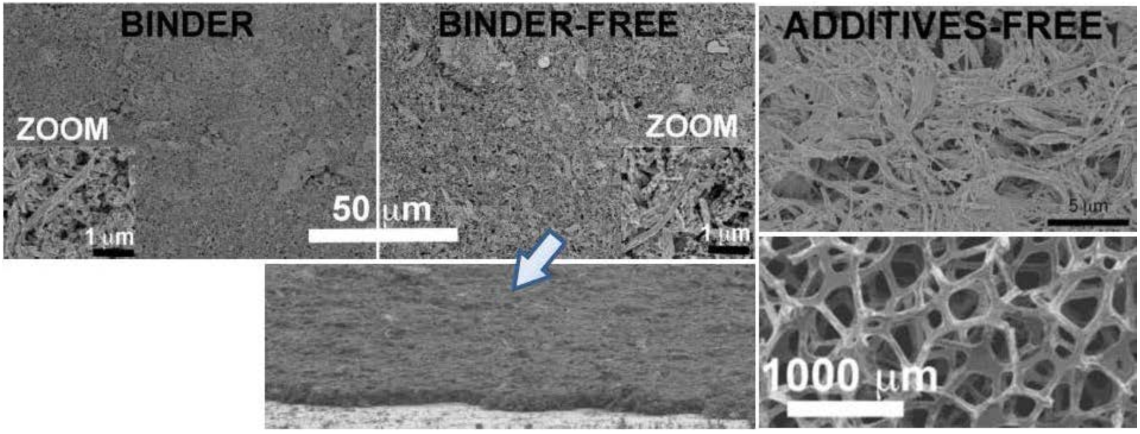


Figure 1: SEM micrographs of V_2O_5 nanoribbons electrodes manufactured following three different processing procedures

References :

[1] a) D. McNulty, D.N. Buckley, C. O'Dwyer, J. Power Sources 267 (2014) 831-873, b) J.M Amarilla, M.L. Pérez-Revenga, B. Casal, E. Ruiz-Hitky Catalysis Today 78 (2003) 571-579.
[2] P. Tartaj, J.M. Amarilla, B. Vazquez-Santos Langmuir (2015, submitted)

INFLUENCE OF DOPANTS ON THE STABILISATION OF HIGH ENERGY NCM $Li_x(Ni_aCo_bMn_c)O_2$

Juliette Billaud, Sébastien Sallard, Petr Novák, Claire Villevieille
Paul Scherrer Institut, Electrochemistry Laboratory, CH-5232, Villigen PSI, Switzerland

juliette.billaud@psi.ch

Lithium-ion batteries are nowadays the most advanced devices for portable energy storage and they started to enter the electric vehicle market. Current materials used on the positive electrode side have energy densities below 600 Wh kg^{-1} ($LiCoO_2$ and $LiFePO_4$), which represents one of main limitations in the improvement of their performance.

Amongst the compounds operating at high potential, a family of layered materials with the chemical formula $Li_xNi_aCo_bMn_cO_2$ (denoted HE-NCM) is the center of intensive investigations since the last decade.[1] They exhibit a specific charge of up to 250 mAh g^{-1}, corresponding to an energy density of *ca.* 900 Wh kg^{-1}.

However, ageing of HE-NCM materials induces a fading of the specific charge and more challenging a depletion of the average discharge potential. This is due to the evolution of their structure upon cycling attributed to i) leaching of the transition metals at high voltage and ii) mobility of cations between slabs and interslabs.

In order to improve the performance of HE-NCM materials, we have developed various doping strategies in order to stabilise the potential upon cycling without compromising the specific charge. Various dopants (shown as Z in Figure 1) have been studied. The overall crystallographic structure is kept, although some minor changes are observed, as will be discussed in the presentation. Moreover, a mitigation of the potential dropping has been observed (see Figure 1.b): the average potential is not only higher but also fades less upon cycling. Besides the specific charge remains above 200 mAh g^{-1} (see Figure 1.a).

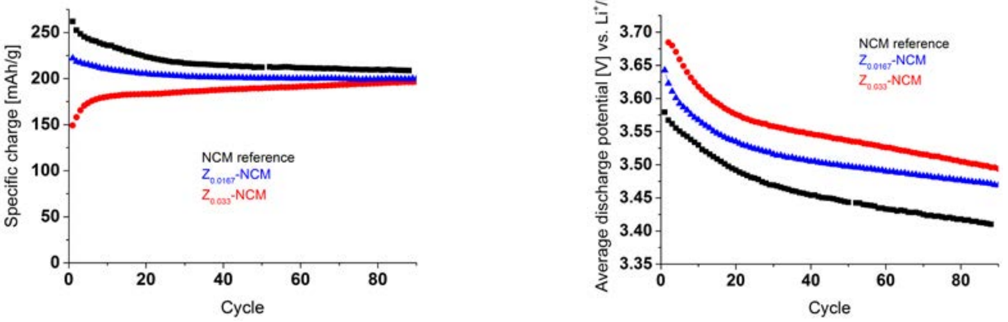

a) b)

Figure 1.a) Evolution of the specific charge as a function of cycle of standard HE-NCM and Z-doped NCM; b) Evolution of the average discharge potential as a function of the cycle number of standard HE-NCM and doped NCM

References:

[1] S.-H. Kang, P. Kempgens, S. Greenbaum, A. J. Kropf, K. Amine, and M. M. Thackeray, *J. Mater. Chem.*, **17**, 20 (2007) 2069.

Probing the degradation mechanisms of silicon anodes in Li-ion batteries by STEM-EELS mapping

Maxime Boniface[1], Julien Danet[1], Lucille Quazuguel[2], Philippe Moreau[2], Florent Boucher[2], Pascale Bayle-Guillemaud[1], Dominique Guyomard[2]

[1] CEA-INAC, 17 rue des Martyrs, F-38054 Grenoble 9, France
[2] Institut des matériaux Jean Rouxel (IMN), Université de Nantes-CNRS, 2 rue de la Houssinière, 44322 Nantes, France
Corresponding e-mail: maxime.boniface@cea.fr

Silicon represents one of the most promising anode materials for next generation lithium-ion batteries. However its colossal volume expansion (up to 300%) upon electrochemical reaction with lithium repeatedly exposes fresh surfaces and leads to continuous solid electrolyte interface (SEI) formation in which lithium is irreversibly consummated. This leads to very high irreversible capacities, compounded by the fact that parts of the silicon-based electrodes are progressively disconnected from both electrical and ionic transport networks.

In this characterization work, part of the European BACCARA project, we demonstrate the possibility to map major SEI components such as lithium carbonate (Li_2CO_3) and lithium fluoride (LiF) as well as quantifying lithium-silicon alloy compositions and Si crystallinity by combining scanning transmission electron microscopy and low-dose electron energy loss spectroscopy (STEM-EELS). Novel methods for careful dose control and rigorous sample preparation proved mandatory to preserve the integrity of the species of interest during measurements. Results on electrodes disassembled from full cells at their 1st, 10th and 100th charge at 1200 mAh/g indicate an early formation of patch-like LiF followed by continuous carbonate layer (fig 1.a). We observed a thicker SEI with increasing cycle number (fig 1.b-c). which is linked to poor cyclability of full cells. Observations of pristine c-Si as well as delithiated shells of a-Si at the end of the 10th and 100th charge (fig 1.d) also indicate disconnection of active material with cycling, which leads to over-lithiation of the remaining active material. Inhomogeneities in lithium content are present even at the single particle scale (fig 1.e), which highlights how critical both ionic and electronic transport are in Si anodes.

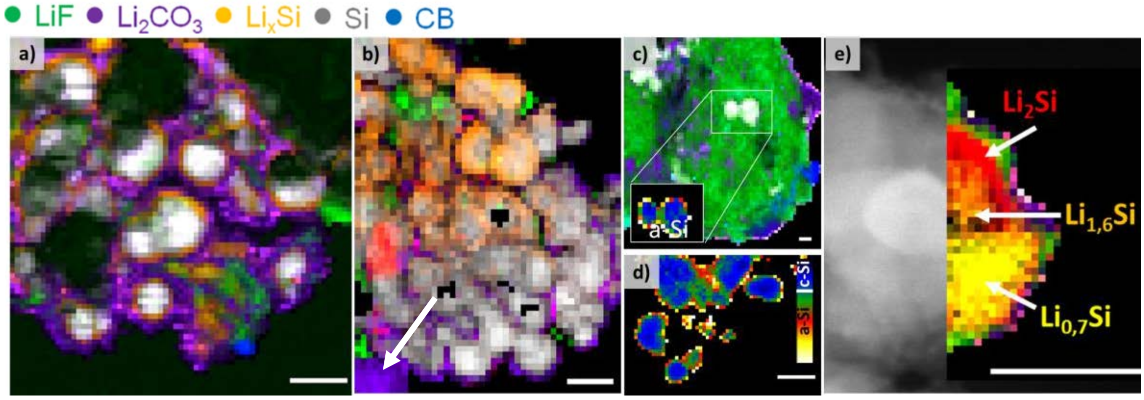


Figure 1: STEM-EELS maps representing: a) Li_xSi shells, Si cores and LiF/carbonate SEI after the 1st charge. b) Inhomogeneous lithiation and carbonate buildup after the 10th charge. c) Thick LiF buildup isolating formerly active Si after the 100th charge. d) c-Si/a-Si delithiated core-shell nanoparticles after the 100th charge. f) Inhomogeneous lithiation of a single SiNP after the 10th charge. All scale bars are 100 nm.

Reference: J. Danet et al., PCCP, 2010, 12-1, 220-6

COUPLING SURFACE IMAGING, FIB, AND SPECTROSCOPIES TO UNDERSTAND SILICON ANODES LITHIATION AND AGEING MECHANISMS

Arnaud Bordes[a,b], Eric De Vito[a], Cédric Haon[a], Alexandre Montani[a], Philippe Marcus[b]
[a] Univ. Grenoble Alpes, F-38000 Grenoble, France
CEA, LITEN, Minatec Campus, F-38054 Grenoble, France.
[b] Groupe de Physico-Chimie des Surfaces, Institut de Recherche de Chimie Paris,
CNRS-Chimie ParisTech, 75005 Paris.

Arnaud.bordes@cea.fr

To follow growing energy demand of new devices, batteries energy density needs to be improved. Silicon-based anode is a serious option since it offers a specific capacity almost ten times higher than carbonaceous materials. Even so silicon anodes suffer from a drastic capacity fading making it unusable after few cycles. A fine understanding of the lithiation mechanism of silicon could participate to the elaboration of more robust architectures.

In this work, composite silicon electrodes have been electrochemically cycled vs Li. After a transfer from a glove box to a ToF-SIMS by using an air-tight vessel, chemical mapping of the inside of silicon grains can be done by achieving an *in-situ* FIB cut.

The first lithiation has been extensively studied. By stopping lithiation at different stages it is possible to follow the evolution of the core-shell structure (*ie* LiSi alloy shell and pure Si core) as shown in fig.1. This method also permits to observe the Si particles, considering their position within the depth of the electrode. To complete this study, cross analysis with Auger spectrometer and SEM have been performed, allowing to quantify Li presence in the Li_xSi alloy and better understand the pure Si core morphology. At the end, a complete mechanism for silicon micron-sized particles is proposed.

In a second time, Si electrodes have been observed after 3, 5 and 10 cycles (limited capacity of 1000 $mAh.g^{-1}$) in both lithiated and delithiated states. After three cycles the core-shell structure is still visible in lithiated state. After 10 cycles the presence of Si particles containing lithium at the end of the charge are observed and associated to particle getting out of the conductive grid and trapping lithium. This phenomena is detrimental to battery lifespan.

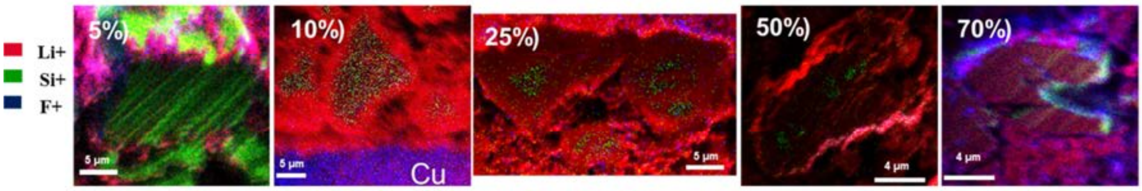


Figure 1: Evolution of the core-shell structure upon first lithiation

COATED CURRENT COLLECTOR FOR LITHIUM-ION BATTERIES

Christophe Busson[a,b], Bernard Lestriez[a], Olivier Crosnier[a], Dominique Guyomard[a], Patrick Soudan[a], Marie-Anne Blin[b], Pierre Guichard[b]

[a]*Institut des matériaux Jean Rouxel (IMN), 2 rue de la Houssinière, 44322 Nantes Cedex 3, France*
[b]*Armor SA, 7 rue de la Pélissière, 44118 La Chevrolière, France*

christophe.busson@armor-group.com

Through the challenges of electric mobility and renewable energy storage like solar or wind energy, lithium-ion batteries are growing up in interest and are one of the most acclaimed devices. Requirements of this technology are to achieve high specific energy density and specific power in order to fit the various applications. Since the 90's a lot of studies on lithium-ion energy storage devices are focused on the optimization of electrolytes, active materials and also on the electrode formulation. Although they are effective ways to improve the performance of these systems, they usually put aside the current collector influence. Several shortened lifetime, failures, or reduced performance can be ascribed to the metallic current collector. We can take as an example the electrode delamination [1], the metallic corrosion [2] or the electrical contact resistivity between the current collector and the electrode [3]. To avoid these problems, a conductive and protective coating of the metallic current collector (fig.1) can be added to obtain a better interface between the electrode and its substrate. Armor company is specialized in complex liquid formulations and thin coating industrial processes, and has a growing interest in producing such coated current collectors for energy storage devices (batteries/ultracapacitors). In this work, various types of carbon coated aluminum current collectors for positive electrodes will be presented and compared to battery grade aluminum. Their characteristics such as physical properties, chemical resistivity, electrode affinity or electric resistivity will be presented. The influence of these current collectors on the electrochemical performance will be assessed in half cells with a standard $LiFePO_4$ – polyvinylidene fluoride electrode and carbonate-based electrolyte. Results of electrochemical impedance spectroscopy, cycling and ageing experiments will be discussed. Both the coating formulation and properties have a great influence on the electrode performance, and an adapted coating allows achieving better performance of a given system.

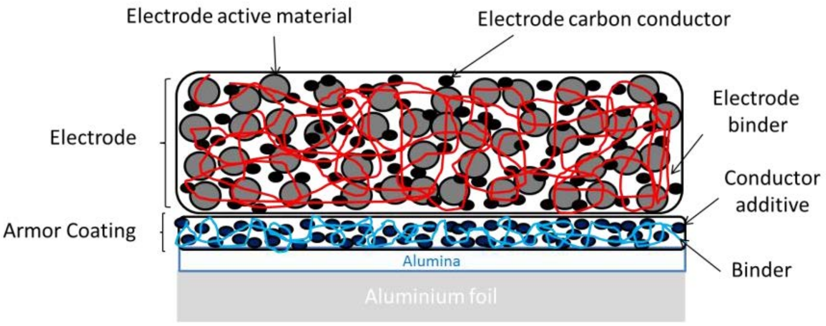


Figure 1 : Schematic coating on aluminum current collector

[1] S. Lee, E-S. Oh, J. Power Sources 244 (2013) 721-725.
[2] I. Doberdò, N. Löffler, N. Laszczynski, *et al.,* J. Power Sources 248 (2014), 1000-1006.
[3] S. Wennig, U. Langklotz, G-M. Prinz, *et al.,* J. Appl. Electrochem 45 (2015), 1043-1055

GRAFTED CARBON-SILICON NANOCOMPOSITES FOR Li-ION BATTERIES

Olivier Crosnier[a,d], Cédric Martin[a], Mélanie Alias[a], Martin Weissmann[a,d], Richard Retoux[b],
Daniel Bélanger[c], and Thierry Brousse[a,d]
[a] *Institut des Matériaux Jean Rouxel (IMN), CNRS, Nantes, France*
[b] *Département Chimie, Université du Québec à Montréal, Montréal, Québec, Canada*
[c] *Laboratoire CRISMAT-CNRS/UMR 6508 ENSICAEN, Caen, France*
[d] *Réseau sur le Stockage Electrochimique de l'Energie (RS2E), CNRS, Amiens, France*

olivier.crosnier@univ-nantes.fr

The recent development of silicon-based negative electrodes has already shown the possibility to enhance the specific capacity of standard graphite electrodes by nearly one order of magnitude [1]. In order to enhance both the cycling stability and the power capability of such composite electrodes, the concept of coupling silicon with a carbon material (graphite, carbon nanotubes, graphene) with a chemical bond developed by using a phenyl group [2-4]. Such a bridge can be formed by a two-step procedure (Figure 1) which makes use of the diazonium chemistry [5].

The chemical and electrochemical modification of silicon and carbon-based materials by the reduction of a diazonium salt involves the formation of an aryl radical which subsequently reacts with the surface to form a covalent carbon-carbon bond. For example, the first step consists in the grafting of aminophenyl groups onto carbon multiwalled nanotubes in p-phenylenediamine followed by sodium nitrite addition. The second step consists in the grafting of silicon on aminophenyl modified carbon (MWCNTs-φ-NH_2) which yields MWCNTs-φ-Si [3].

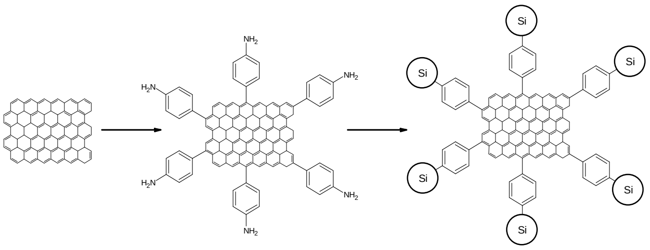


Figure 1: Step 1: functionalization of carbon; Step 2: construction of a molecular bridge between carbon particles and silicon

The MWCNTs-φ-Si nanocomposite electrode shows improved electrochemical performance compared to a simple mixture of the two compounds: higher specific capacity, better cycling ability and rate capability.

The obtained silicon-based nanocomposite materials (using graphite, carbon nanotubes or graphene) have been characterized by different physical and electrochemical techniques (TGA-MS, BET, SEM, IR / Raman spectroscopy, electrochemical experiments...) at different stages of the synthesis in order to confirm the presence of the grafted molecules and to determine their influence on the cycling performance when used in lithium-ion batteries.

[1] J. Li, J. R. Dahn, J. Electrochem. Soc. 154 (2007) A156-A161.
[2] C. Martin, M. Alias, F. Christien, O. Crosnier, D. Bélanger, T. Brousse, Adv. Mater. 21 (2009) 4735-4741.
[3] C. Martin, O. Crosnier, R. Retoux, D. Bélanger, D. M. Schleich, T. Brousse, Adv. Func. Mater. 21 (2011) 3524-3530.
[4] M. Weissmann, O. Crosnier, B. Lestriez, B. Humbert, C. Agnès, F. Duclairoir, L. Dubois, G. Bidan, T. Brousse, in preparation.
[5] D. Bélanger, J. Pinson. Chem. Soc. Rev. 40 (2011) 3995-4048.

PROTECTION OF 5V CATHODE MATERIALS WITH ATOMIC LAYER DEPOSITION OF DIFFERENT OXIDES

Philippe Dumaz[a, b], Cécile Rossignol[a], Arnaud Mantoux[b], Anass Benayad[c], Renaud Bouchet[a]
[a] LEPMI, 1130 rue de la piscine, BP 75, F-38402 Saint-Martin d'Hères
[b] SIMaP, 1130 rue de la Piscine, BP 75, F-38402 Saint-Martin d'Hères
[c] CEA, Centre de Grenoble, 17 rue des Martyrs, 38054 Grenoble Cedex 9
philippe.dumaz@lepmi.grenoble-inp.fr

In order to increase the energy density of lithium-ion batteries, a promising solution is to use positive materials with high potential (4.5 to 5.2 V vs Li + / Li) [1]. However, this operating potential is largely above the stability range of conventional electrolytes. Degradation to the surface of the positive material causes a decrease in coulombic efficiency and a rapid drop in the amount of stored energy. One of the strategies proposed by the scientific community is to deposit a protective nano-layer of oxide to limit interfacial reactivity [2].

High voltage spinel $LiNi_{1/2}Mn_{3/2}O_4$ shows good electrochemical properties but suffers from capacity loss induced by transition metal dissolution, and efficiency loss induced by electrolyte oxidation. In order to exacerbate these phenomena, different ways to charge the material were used. Figure 1 shows a faster degradation with a 1 hour 5V holding at the end of charge. The loss of capacity is speeded up after few cycles, compared to usual cycling.

In order to mitigate this loss of capacity, the electrode surface was covered with ultrathin layer of different oxides, such as Al2O3, deposited by atomic layer deposition (ALD). Thickness of such oxides is a key factor. 5, 10, 20 & 50 ALD cycles were used for reaching different thickness. Coverage, physical properties and chemical composition of each of these layers were investigated by means of XPS, EIS, and TEM. The role of different oxides on LNMO's electrodes is discussed according to their chemical, physical and electrochemical properties.

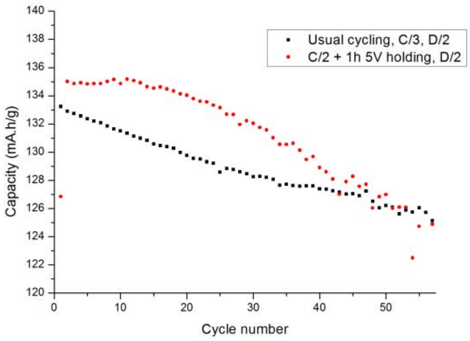


Figure 1 Capacity of LNMO spinel with different cycling parameters

[1] Nanotechnology for Sustainable Energy, Hu, Y., et al., ACS Symposium Series, American Chemical Society, Washington, DC, 2013

[2] Ultrathin Coatings on Nano-LiCoO2 for Li-Ion Vehicular Applications, Isaac D. Scott, Yoon Seok Jung, Nano Lett. 2011, 11 (2), pp 414–418

RELAXATION EFFECTS OF THE NEGATIVE ELECTRODE TiSnSb USING ^{119}Sn MÖSSBAUER AND ^{7}Li MAS NMR SPECTROSCOPIES

Nicolas Dupré,[1,4] Karen E. Johnston,[1,3,4] Ali Darwiche,[2] Lorenzo Stievano,[2] Clare P. Grey[3,4] and Laure Monconduit[2,4]

[1]Institut des Matériaux Jean Rouxel (IMN), CNRS UMR 6502, Université de Nantes, France,
[2]Institut Charles Gerhardt Montpellier-UMR 5253 CNRS, Université Montpellier 2, 34095, Montpellier, France
[3]University of Cambridge, Department of Chemistry, Lensfield Road, CB2 1EW, UK
[4] *ALISTORE-ERI European Research Institute*

Conversion type materials have recently been considered as a plausible alternative to conventional electrode materials, owing to their strong gravimetric and volumetric energy densities. The ternary alloy TiSnSb was recently proposed as being a suitable negative electrode material in Li-ion batteries owing to its excellent electrochemical performance. Using complementary *in situ operando* X-ray diffraction (XRD) and *in situ operando* ^{119}Sn Mössbauer spectroscopy, it was determined that during the first discharge, TiSnSb undergoes a conversion process leading to the simultaneous formation of Li-Sb and Li-Sn intermetallic compounds.

However, some ambiguities remain: A shifted, group of resonances appear in the ^{7}Li NMR spectra at approx. 20 ppm, in addition to a contribution from Li_3Sb at 3.5 ppm and a resonance at 8.5 ppm (assigned to Li_7Sn_2), and could correspond to intermediate phases. In addition, changes in the local environments of Sn and Li nuclei have been detected upon OCV relaxation after the lithiation process, using ^{119}Sn Mössbauer and ^{7}Li NMR spectroscopies, respectively. These results suggest an intrinsic instability of the phases formed at the end of the lithiation process. *Ex situ* ^{7}Li NMR indicates that this evolution is stopped or at least slowed down when the active material is in contact with the electrolyte. Both "*in situ*" and "*ex situ*" type experiments have been completed using the two techniques in order to understand the influence of small changes in composition on Mössbauer signal and ^{7}Li NMR shifts. Following this approach, the ternary alloy NbSnSb was investigated and directly compared to TiSnSb to determine the influence of the inactive metal on the ^{7}Li NMR shift. The obtained results highlight the sensitivity of ^{7}Li NMR to the chemical or electronic environment around the Li_3Sb phase or clusters and not only to the direct local environment (Li_3Sb). This result shows the crucial importance of interfaces between the phases formed along the redox processes in the case of conversion materials. A systematic study using both Mössbauer spectroscopy and NMR the phases formed during discharge and subsequent relaxation will be presented and discussed.

References

[1]: M. Sougrati, et al. *J. Mater. Chem.* **2011**, *21*, 10069.
[2]: C. Marino et al. *Chem. Mater.* **2012**, *24*, 4735.
[3]: C. Marino et al. *J. Phys. Chem. C* **2013**, *117*, 19302.
[4] : H. Wilhelm, et al. *Electrochem. Commun.* **2012**, *24*, 89.

NEW POLYMORPHS OF A_xMPO_4F FLUORIDE PHOSPHATES AS CATHODE MATERIALS FOR RECHARGEABLE BATTERIES

Stanislav S. Fedotov[a,b], Nellie R. Khasanova[a], Alexandr Sh. Samarin[a], Sergey M. Kuzovchikov[a], Alexey I. Manoilov[a], Oleg A. Drozhzhin[a], Artem M. Abakumov[a,b], Evgeny V. Antipov[a]
[a] *Crystal Chemistry Laboratory, Chemistry Department, Lomonosov Moscow State University, Moscow, Russia*
[b] *Center for Electrochemical Energy Storage, Skolkovo Institute of Science and Technology, Moscow, Russia*

email: fedotov.msu@gmail.com

In the pursuit of low-cost, eco-friendly and chemically stable cathode materials, a huge variety of candidates was thoroughly inspected starting from layered oxides to complex polyanion and mixed anion compounds. At the same time the crystal structure of the cathodes have evolved from close packages into much more sophisticated arrangements, which opened up opportunities to tune the electrochemical properties of the resulting electrode materials. Fluoride phosphates based cathode materials with A_xMPO_4F general formula (x = 1, 2; A – alkali metal; M – 3d transition metal)[1,2,3] are in focus due to the several advantages arising from the combination of phosphate and fluoride anion moieties as well as the richer structural diversity. The phosphate group is responsible for a structural, chemical and thermal stability; the fluoride anion anticipates a better kinetics of the mobile ion and brings about an increase of the working potential.

Within the scope of this work we investigated mixed $(Li,Na)_2Co_{1-x}M_xPO_4F$ (M = Mn, Fe) and $AVPO_4F$ fluoride-phosphates as cathode materials for Li-ion batteries and found two new polymorphs crystallizing in the orthorhombic system with quasi-2D and 3D frameworks respectively. A freeze-drying assisted ceramic route was applied to the synthesis of the materials, which allowed lowering sintering temperatures and stabilizing new structural modifications. The crystal structure was studied by X-ray, electron and neutron diffraction, chemical composition was verified by TEM-EDX and ICP-AES methods. The materials were tested in Li-anode cells by galvanostatic cycling and voltammetry techniques. The new polymorphs demonstrated a reversible electrochemical activity in 2.0÷4.8 V potential range with good capacity retention and high rate capability up to 40C preserving more than 50% of the theoretical specific capacity. Composition-structure-property relationships in these fluoride-phosphate systems will be discussed with a special focus to the interrelation between structure peculiarities and electrochemical properties.

[1] B. L. Ellis, W. R. Michael Makahnouk, W. N. Rowan-Weetaluktuk, D. H. Ryan, L. F. Nazar, Chem. Mater., 22 (2010) 1059.
[2] S. Okada, M. Ueno, Y. Uebou, J. Yamaki, J. Power Sources, 146 (2005) 565.
[3] J. Barker, M. Y. Saidi, J. L. Swoyer J. Electrochem. Soc. 150 (2003), A1394

SURFACE INVESTIGATION OF AMORPHOUS SI THIN FILMS CYCLED AS ANODES FOR LI-ION BATTERIES

Giulio Ferraresi[a], Lukas Czornomaz[b], Petr Novák[a], Claire Villevieille[a], Mario El Kazzi[a]

[a] *Paul Scherrer Institut – Electrochemical Energy Storage Section – CH-5232 Villigen PSI, Switzerland*

[b] *IBM Research-Zürich – Säumerstrasse 4 – CH-8803 Rüschlikon, Switzerland*

giulio.ferraresi@psi.ch

The search for alternative negative electrodes to replace graphite in Li-ion batteries is ongoing. So far, silicon is one of the most promising candidates due to its availability and its high theoretical specific charge of ca. 4200 mAh g^{-1} (up to 4.4 Li per Si), the highest value among the already known candidates. However, its commercial application is still very limited because of its large volume change upon lithiation (up to 300%) and its low electronic conductivity [1]. To overcome those issues, one can both decrease the thickness of the electrodes, thus increasing the cycling stability, and also insert a dopant to enhance the conductivity. Moreover the investigation of Si thin film can be of great interest for the application in all-solid-state Li-ion batteries.

In this context, we investigated amorphous Si thin films deposited by sputtering or chemical vapour deposition techniques on two different substrates: copper and titanium. Those thin films, which can also be doped to increase their conductivity, were electrochemically characterized in test cells vs. Li metal (Figure 1a-b). Remarkable results were obtained for the thin films prepared by chemical vapour deposition on copper substrate which show high stability and reversible specific charge of ~ 4000 mAh g^{-1} after 30 cycles. After 500 cycles more than 50% of the initial specific charge was maintained. The surface evolution during the early stages of lithiation and delithiation was probed by scanning electron microscopy (SEM) and in-house x-ray photoelectron spectroscopy (XPS). Combining ex situ XPS characterization analysis (Figure 1c) with post mortem SEM surface morphology we were able to develop a model describing the mechanism behind the SEI evolution as well as the Li-Si alloy reaction.

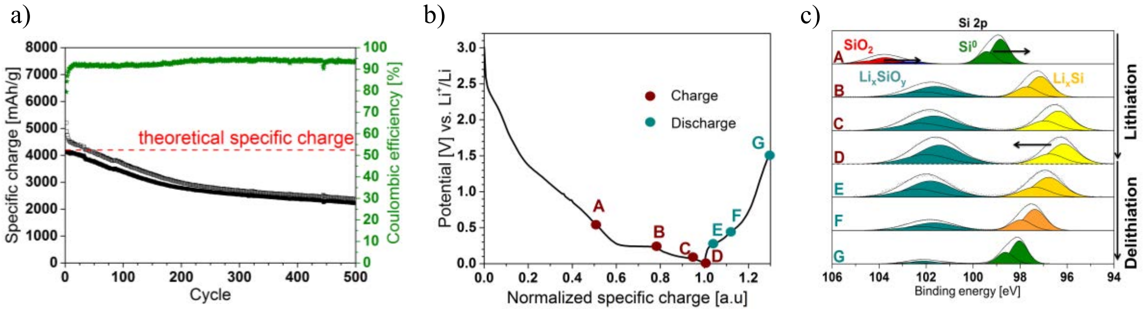


Fig. 1 - a) Cycling stability of Si thin films cycled vs. Li at 1C rate; b) Galvanostatic profile of the first cycle of Si thin films in LP30 electrolyte; c) Evolution of the XPS Si2p core level during first lithiation and delithiation.

References:

1. J.O. Besenhard, J. Yang, M. Winter, J. Power Sources 68 (1997) 87

CORE SHELL AMORPHOUS SILICON-CARBON NANOPARTICLES SYNTHESIS BY DOUBLE STAGE LASER PYROLYSIS, APPLICATION TO ANODE MATERIAL

Julien Sourice[1,2], Willy Porcher[2], Cedric Haon[2], Arnaud Bordes[3], Eric De Vito[3], Adrien Boulineau[2], Nathalie Herlin-Boime[1], Cécile Reynaud[1]

[1]CEA, IRAMIS, NIMBE, CNRS UMR 3685, F- 91191, Gif sur Yvette, France
[2]CEA, LITEN, 17 rue des Martyrs, F-38054 Grenoble, France
[3]CEA, MINATEC, 17 rue des Martyrs, F-38054 Grenoble, France

Cedric.haon@cea.fr

Li-ion battery is reaching a limit in its energy density. In particular the capacity of graphite is too low (372 mAh.g-1) to meet the increasing energy demand. Silicon (Si) anode appears as a possible solution as carbon replacement in LIB thanks to its high theoretical specific capacity (3579 mAh.g-1). However, rapid pulverization of the particles and SEI instability cause capacity fading in few cycles. Silicon nanostructuration together with association of carbon to Si greatly enhance the performances in terms of both cyclability and capacity. Using a-Si as core material, instead of c-Si, is a less considered option but appears promising to enhance cyclability. Indeed, a-Si is not subject to the drastic crystalline state alteration upon its first lithiation. In order to cumulate all the benefits cited above, active material should be a composite of an a-Si core covered with a carbon shell. A major drawback of such structures is related to their synthesis processes not meeting the quantity requirement for industrial development. Having this point in mind, the Laser Pyrolysis (LP) process was adapted for the one step synthesis of C-coated nanoparticles. This versatile process was used with success to synthetize many types of nanoparticles. Interestingly, the amount of final product is directly correlated to the flow of gas precursor, thus leading to easily scalable process. However the synthesis of a complex material such as nanoparticles composed of a-Si core covered with a carbon shell implies the development of specific reactor. We demonstrate here the successful use of a two stage reactor. This reactor, composed of two reaction zones, allow the synthesis of Si@C nanoparticle in a one-step process, without manipulation of nanopowders. We develop the synthesis of a-Si and a-Si@C core shell nanoparticles, with the exact same silicon core, and we bring in evidence the protective effect of the carbon shell. The two active materials were characterized and studied as anode materials versus metallic lithium in cyclic voltammetry and galvanostatic experiment. We highlighted the beneficial effects related to the use of a-Si over c-Si and the beneficial of a carbon covered active material over a bare one. Results show that a-Si without any carbon coverage presents very poor cycling capacity, due to the presence of a thick and electronically insulant silicon oxide shell. At the opposite, a-Si protected with a carbon shell presents outstanding electrochemical properties: In coin cell configuration, it can be cycled for more than 500 cycles, with a specific capacity superior to 1000 mAh.g-1 and with an exceptional coulombic efficiency of 99,91% at the end of the 500th cycle. This very high stability can be explained by the low oxidation of silicon through the carbon shell that act as an efficient barrier to oxygen diffusion. In good agreement with the stability of the device, post mortem SEM analysis shows an important residual porosity in the electrode.

Rapid and facile microwave synthesis of high performing nanostructured SnO_2/C composite anode materials for Li-ion battery

Mesfin A. Kebede[a], Mkhulu K. Mathe[a], Kenneth I. Ozoemena[a]
[a] *Energy Materials, Materials Science and Manufacturing, Council for Scientific and Industrial Research, P.O.Box 395, Pretoria, South Africa*

E-mail: mkebede@csir.co.za

SnO_2 operates by adopting the alloy/de-alloy reaction mechanism and it has attracted intensive research interest as a promising next-generation anode material for LIBs due to its high theoretical specific capacity of 782 mAh g^{-1}[1], which is more than twice the theoretical capacity of currently used graphite (372 mAh g^{-1}). Interestingly, tin-based lithium storage compounds need reasonably low potentials for Li^+ insertion and they have high storage capacities. However, the practical use of SnO_2 based anodes is challenged by their capacity fading due to the large volume change during repeated charge-discharge cycling process. Such volume variation causes cracking and result in electrical disconnection from the current collector, and eventually limit the cycling capability of electrodes.

In this work an attempt have been made to synthesize a high capacity, good cycle performance, and good rate capacity tin-based anode materials for LIB applications. Accordingly, nanostructured SnO_2 anode materials were synthesized using fast microwave synthesis technique and then SnO_2/C nanocomposites have been prepared to improve the cyclability of the anode materials. The morphology, structural and electrochemical properties of the as-synthesized anode materials were characterized by means of SEM, X-ray diffraction (XRD), and galvanostatic charge/discharge battery tester.

[1] I. A. Courtney, J. R. Dahn, J. Electrochem. Soc. 1997, 144, 2045

ALTERNATIVE BINDERS FOR LITHIUM IRON SILICATE (Li_2FeSiO_4) CATHODES

Tayfun Kocak,[b], Fabian Jeschull[a], Mario Valvo[a], , Anti Liivat[a], Servet Turan[b]
[a] Department of Chemistry - Ångström, Uppsala University, Sweden
[b] Department of Material Science and Engineering, , Anadolu University, Turkey
tayfunk@anadolu.edu.tr

The vast increase in the use of portable electronic devices over the last decade has multiplied the demand for rechargeable lithium-ion batteries. While increasing the energy density of such batteries has been the main target, there is an increasing concern about the environmental impact regarding the production and recycling of Li-ion batteries. The interest in adopting battery materials environmentally more sustainable, such as iron-based, has therefore been expected. Beside the active material, however, the rest of the cell components need to be revised as well with sustainability in mind.

Here, we investigate greener cell chemistries, such as fluorine-free binders and non-aromatic solvents for a cathode material with low environmental footprint: Li_2FeSiO_4. [1]. The alternative fluorine-free binders studied here are poly(ethylene oxide) (PEO), a cellulose-based ETHOCELL™ and poly(vinylpyrrolidone) (PVP) polymers instead of the conventional PVdF-HFP [2,3].

The electrodes have been cycled in half cells using 1M LiTFSI electrolyte salt in EC:DEC at 60 °C under different C-rates. The performance of the electrodes with fluorine-free binders is similar to that of the one based on PVdF showing good capacity retention under such demanding cycling conditions (Fig. 1).

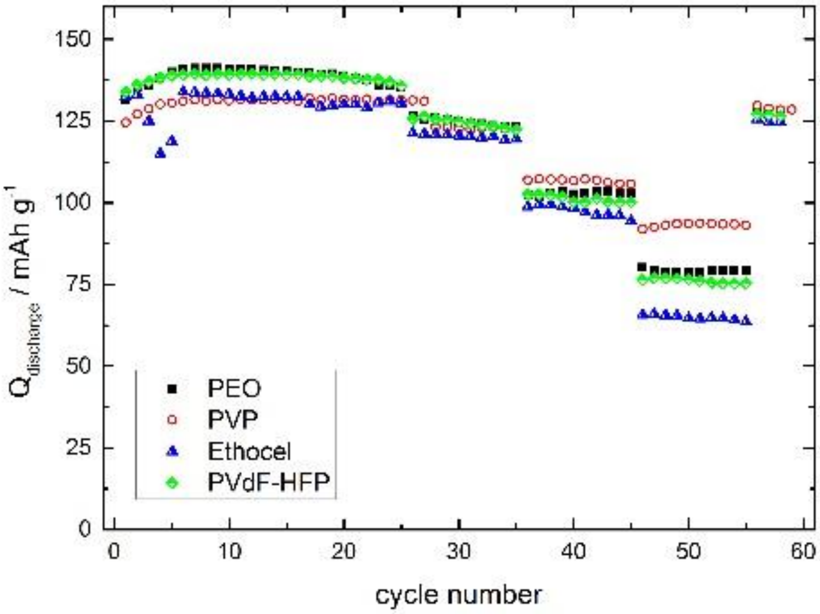


Figure 1, Capacity retention for Li_2FeSiO_4 electrodes made of different binders.

[1] A. Nytén, A. Abouimrane, M. Armand, T. Gustafsson, J.O. Thomas, Electrochem. Commun., 7 (2005) 156-160.
[2] S.-L. Chou, Y. Pan, J.-Z. Wang, H.-K. Liu, S.-X. Duo, Phys Chem Chem Phys 16 (2014) 20347-20359.
[3] F. Jeschull, M.J. Lacey, D. Brandell, Electrochim. Acta 175 (2015) 141-150.

Towards Improved Cycling Performances of Silicon Electrodes after Electrochemical Pre-formatting

Florent Lepoivre[a,b], Dominique Larcher[c,d], Jean-Marie Tarascon[a,b,d]
[a] *Chimie du Solide et Energie, Collège de France, 11 Place Marcelin Berthelot, 75005 Paris, France*
[b] *Sorbonne Universités – UPMC, Université Paris VI, 4 Place Jussieu, 75005 Paris, France*
[c] *Laboratoire de Réactivité et Chimie des Solides (LRCS), UMR CNRS 7314,33 rue Saint Leu, 80039 Amiens, France*
[d] *Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, France*

email address of the presenting author: lepoivre@zoho.com

Li-ion batteries are the cornerstone of the mobility market due to their high performances out-ranging any other battery technology. Yet, they hardly meet the gluttonous demand of portable devices in term of autonomy, requiring development of higher capacity materials. Negative electrode materials such as alloys would allow for large gain in capacity if they were not hampered by intrinsic limitations[1]. For instance, silicon suffers from large volumetric expansion[2] altering the electrode microstructure hence limiting its cycling performances.

In our work, that swelling was minimized using Si nanoparticles and an environmentally friendly electrode preparation[3] enabling superior cycling retention of Si half-cells, yet at the price of capacity lower than the theoretical one. Two methodologies were developed to counter this capacity loss consisting in i) lithium plating/stripping during the 1st cycle or ii) constant load 1st discharge. The morphological and chemical changes induced by the aforementioned formatting steps were investigated by TGA analysis and TEM observations. It revealed the formation of a protective SEI layer along with the activation of extra silicon otherwise inactive, triggered by the sustained low potential applied to the Si electrode. Moreover, tremendous improvements of the cycling performances were observed with formatted electrodes, which exhibit capacities greater than 2100 $\mathrm{mAh/g_{of\ Si}}$ for several hundreds of cycles without any capacity constraints.

We therefore demonstrate that such electrochemical formatting steps are a viable and well-controlled alternative to chemical and texturing routes previously developed for silicon anodes. Such results echo with the need for high energy density anode materials, emerging from the improvements on the positive side and the development of new technologies such as Li-Air, for which lithium metal is still mostly used.

References :
[1] J. O. Besenhard, J. Yang and M. Winter, J. Power Sources 68 (1997) 87–90.
[2] L. Y. Beaulieu, K. W. Eberman, R. L. Turner, L. J. Krause and J. R. Dahn, Electrochem. Solid-State Lett. 4 (2001) A137.
[3] A. Touidjine, M. Morcrette, M. Courty, C. Davoisne, M. Lejeune, N. Mariage, W. Porcher and D. Larcher, J. Electrochem. Soc. 162 (2015) A1466–A1475.

MULTI-SCALE CHARACTERIZATION OF ELECTRONIC AND IONIC LIMITATIONS TO POWER PERFORMANCE OF COMPOSITE ELECTRODES

A. Etiemble,[a] N. Besnard,[b,c] A. Bonnin,[d] J. Adrien,[a] T. Douillard,[a] P. Tran-Van,[c] L. Gautier,[e] O. Dubrunfaut,[f] J.-C. Badot,[g] E. Maire,[a] B. Lestriez[b]

[a] *Laboratoire MATEIS, CNRS UMR5510, Institut national des sciences appliquées de Lyon, F-69621 Villeurbanne, France.*
[b] *Institut des Matériaux Jean Rouxel (IMN), CNRS UMR 6502, Université de Nantes, 44322, Nantes Cedex 3, France.*
[c] *Renault technocentre, 78084 Guyancourt, France.*
[d] *Swiss Light Source, Paul Scherrer Institut, 5232 Villigen, Switzerland*
[e] *Umicore Rechargeable Battery Materials, 1000 Brussels, Belgium*
[f] *Laboratoire de Génie Electrique de Paris, CNRS, SUPELEC, Sorbonne Universités-UPMC Univiversité Paris 06, Université Paris-Sud, 11 rue Joliot-Curie, Plateau de Moulon, 91192 , Gif-sur-Yvette , France*
[g] *Institut de Recherche de Chimie Paris, CNRS, Chimie ParisTech, 11 rue Pierre et Marie Curie, 75005, Paris, France*

Bernard.lestriez@cnrs-imn.fr

Blending different active materials is an approach followed by several automotive battery suppliers intended to optimize the performance of the battery with respect to the automotive operating requirements.

In this communication, the 3D morphology of pure NMC, pure LFP and blended NMC/LFP electrode is characterized by both synchrotron X-ray tomography and FIB/SEM tomography for rational interpretation of their electrical properties and electrochemical performance.

Their electrical properties are measured by broad band dielectric spectroscopy, which allows to discriminate the contact resistance at the electrode/current collector interface and the electrode through-thickness electronic conductivity, both in the dry and the wet state (infiltrated by the liquid electrolyte) [1-3].

The rate performance is shown to be critically influenced by the inter-connectivity between the active mass and the CB+PVdF conductive network, and by the porosity tortuosity.

[1] K.A. Seid, J-C. Badot, O. Dubrunfaut, S. Levasseur, D. Guyomard, B. Lestriez, « Multiscale electronic transport mechanism and true conductivities in amorphous carbon-$LiFePO_4$ nanocomposites », *J. Mater. Chem.*, 2012, 22, 2641

[2] K. A. Seid, J. C. Badot, O. Dubrunfaut, M. T. Caldes, N. Stephant, L. Gautier, D. Guyomard and B. Lestriez, "Multiscale electronic transport in $Li_{1+x}\,Ni_{1/3-u}\,Co_{1/3-v}\,Mn_{1/3-w}O_2$: a broadband dielectric study from 40 Hz to 10 GHz", *Phys. Chem. Chem. Phys.*, 2013, 15, 19790.

[3] K-A. Seid, J-C. Badot, C. Perca, O. Dubrunfaut, P. Soudan, D. Guyomard, B. Lestriez. "In-situ multiscale study of ion and electron motions in a lithium-ion battery composite electrode", *Adv. Energy Mater*, 2015, 5, 1400903

OPTIMIZATION OF SILICON-BASED COMPOSITE ELECTRODES

D. Mazouzi,[a] Z. Karkar,[a,b] C. Real Hernandez,[b] L. Roué,[b] D. Guyomard,[a] B. Lestriez[a]

[a] *Institut des Matériaux Jean Rouxel (IMN), CNRS UMR 6502, Université de Nantes, 44322, Nantes Cedex 3, France.*
[b] *INRS-Énergie, Matériaux et Télécommunications, 1650 boulevard Lionel-Boulet, Varennes, Québec, J3X 1S2, Canada.*

Driss.Mazouzi@cnrs-imn.fr

Over the last few years, silicon (Si) has attracted considerable attention since it has potentially about 10 times the gravimetric capacity of conventional graphite anodes (3578 mAh g^{-1} *vs.* 372 mAh g^{-1} for graphite) [1].

Several strategies have been undertaken to solve the large capacity fading observed during cycling of silicon electrodes. More than for any other active material for lithium battery, silicon has stressed the importance of carefully addressing the formulation and the engineering of the composite electrode [2].

In this communication we will report the study of the influence of a pre-treatment of the silicon powder and of the conductive additive choice on the cyclability of silicon based electrodes of various active mass loadings (between 1 and 3 mg cm^{-2}).

Furthermore, it has been discovered that storage for a few days in humid air before cell assembling of Si-carboxymethyl cellulose (CMC) composite electrode prepared with a slurry buffered at pH 3 has a major positive impact on its cycle life and coulombic efficiency [3].

[1] U. Kasavajjula, C. Wang and A. J. Appleby, J. Power Sources, 163 (2007) 1003.
[2] D. Mazouzi, Z. Karkar, C. Reale Hernandez, P. Jimenez Manero, D. Guyomard, L. Roué, B. Lestriez, “Critical roles of binders and formulation at multiscales of silicon-based composite electrodes”, *J. Power Sources*, 2015, 280, 533-549.
[3] C. Real Hernandez, Z. Karkar, D. Guyomard, B. Lestriez, L. Roué, “A film maturation process for improving the cycle life of Si-based anodes for Li-ion batteries”, *Electrochem. Commun.*, 61 (2015) 102-105.

HONEYCOMB ORDERING TO TRIGGER OXYGEN REDOX CHEMISTRY IN LAYERED CATHODE MATERIALS

Benoit Mortemard de Boisse[a,b], Guandong Liu[a], Jiangtao Ma[a], Shin-ichi Nishimura[a,b],
Sai-Cheong Chung[a,b], Hisao Kiuchi[a], Yoshihisa Harada[c], Jun Kikkawa[d], Yoshio Kobayashi[e], Masashi Okubo[a,b] and Atsuo Yamada[a,b]
[a] *The University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo 113-8656, Japan*
[b] *ESICB, Kyoto University, Nishikyo-ku, Kyoto 615-8245, Japan*
[c] *The University of Tokyo, Kashiwa, Chiba 277-8581, Japan*
[d] *National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan*
[e] *The University of Electro-Communications, Chofu, Tokyo 182-8585, Japan*

email address of the presenting author: benoit.mortemard@battery.t.u-tokyo.ac.jp

Even though Na_xMO_2 ($x \leq 1$, M = transition metal) materials have been studied for a long time as positive electrode candidates for Na-ion batteries, the available capacity is still limited. Partial substitution of M by Na^+ is an appealing strategy to overcome this issue: the excess Na^+ ions in the MO_2 layer could participate in the (de)intercalation process while lowering the weight of the battery, thus greatly enhancing the gravimetric capacity. This strategy, applied to Li-ion batteries for many years, is still poorly transferred to Na-ion battery materials.

In order to establish a model for the study of Na_2MO_3 materials, we prepared two polymorphs of O3-Na_2RuO_3[1,2], distinguished by the honeycomb-like ordering of the $[Ru_{2/3}Na_{1/3}]O_2$ layers. We identified that the ordered phase induces the spontaneous formation of an ilmenite-type intermediate which facilitates highly reversible oxygen redox chemistry associated to large extra capacity (Figure 1).

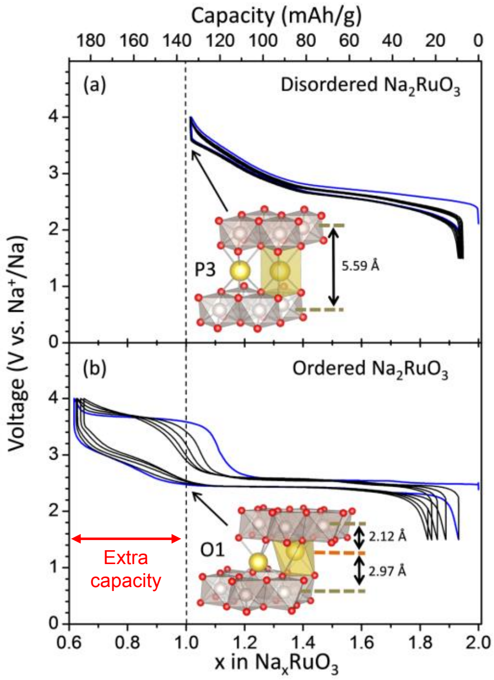


Figure 1. Galvanostatic cycling curves for (a) disordered and (b) ordered O3-Na_2RuO_3 (first cycle highlighted in blue). The insets represent the coordination environment of Na at x = 1.

[1] M. Tamaru, X. Wang, M. Okubo, A. Yamada, Electrochem. Comm. 33 (2013) 23 – 26.
[2] B. Mortemard de Boisse, G. Liu, J. Ma, S.-i. N, S.-C. Chung, H. Kiuchi, Y. Harada, J. Kikkawa, Y. Kobayashi, M. Okuboand A. Yamada, Submitted.

Irreversible structural transformation of Li-rich NMC electrodes during cycling: the role of manganese

Guy Ouvrard[a], Alexandre Pradon[a], Maria Teresa Caldes[a], Florent Boucher[a], Philippe Moreau[a], Camille La Fontaine[b], Stephanie Belin[b], Eric El Kaim[b], Erwan Dumont[c], Cecile Tessier[c].

[a] *Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, 2, rue de la Houssinière BP 32229, 44322 Nantes Cedex 3, France.*
[b] *Synchrotron SOLEIL, St. Aubin-BP 48, 91192 Gif-sur-Yvette Cedex, France*
[c] *Saft, 33074 Bordeaux Cedex, France*

guy.ouvrard@cnrs-imn.fr

Li-rich layered oxides $Li_{1+x}M_{1-x}O_2$ (M = Mn, Co, Ni) can be considered as good candidates for use as positive electrode in LIBs regarding on their high specific capacity (250mAh/g), only achieved by loading at high potential (> 4.3 V). Under these charging conditions, a voltage plateau appears at the end of the charge and an extra capacity is obtained. However, the first cycle is performed with a significant irreversible capacity and coulombic efficiency ranges between 85-90 %. Moreover, Li-rich compounds undergo notable capacity loss and voltage decay during cycling. These drawbacks prevent these materials to be commercialized so far and need further understanding. Redox phenomena at the origin of voltage plateau, have been extensively studied in literature [1]. However, even if irreversible capacity is often related to irreversible structural transformations undertaken by these compounds during the plateau, some questions still remain. What is the exact nature of this structural transformation? Are all chemical elements involved in the same way into the irreversible structural changes? How does this transformation impact redox mechanisms?

In this work, *operando* X-ray diffraction (XRD) and high resolution electron microscopy (HREM) were combined to *operando* X-ray absorption spectroscopy (XAS) to study the structural modifications undertaken during the first charge-discharge cycle. DFT calculations have used to validate proposed structural models.

Our results confirm that these compounds must be considered as nano-composites Li_2MnO_3-$LiMO_2$ from both structural and electrochemical viewpoints. As shown by operando XRD, irreversible structural modifications occur mainly during the plateau. They concern particularly Li_2MnO_3 since its characteristics diffraction peaks are no longer observed in XRD patterns at the end of the charge**.** Furthermore, only manganese spectra are notably modified during the plateau as observed in *operando* XAS. HREM shows that structural transformations undertaken at the end of the charge corresponds to a 3D migration of cations into lithium layers, which are partially delithiated. DFT calculations performed on Li_2MnO_3 delithiation process have shown that 3D migration of manganese atoms is coupled with a 2D one inside transition metal layers.

A structural model containing 2D and 3D defects, validated by DFT and HREM image calculations, was used to simulate XAS spectra. From comparison between experimental and calculated XAS spectra, we can conclude that cationic migration mainly involves manganese atoms. These results suggest that new electrochemical phenomena observed during discharge (irreversible cycle) could be related to an irreversible change of the local structure of the manganese (defects 2D, 3D) during the plateau. Moreover, that may also explain why manganese atoms are more redox-active during discharge as probed by operando XAS.

[1] H.Yu, H.Zhou, J. Phys. Chem. Lett.. 4, (2013) 1268−1280

TRANSITION METAL DISSOLUTION IN THE $Li_{1+x}(Ni_aCo_bMn_{1-a-b})_{1-x}O_2$ / GRAPHITE FULL-CELL

H.-J. Peng[a,b], S. Trabesinger[a], C. Villevieille[a], H. Wolf[b], K. Leitner[b], P. Novák[a]
[a]*Paul Scherrer Institut, Electrochemistry Laboratory, CH-5232 Villigen PSI, Switzerland,*
[b]*BASF SE, D-67056 Ludwigshafen, Germany*

hai-jung.peng@psi.ch

Despite the high specific charge and good thermal stability, the application of lithium-rich transition metal oxides ($Li_{1+x}(Ni_aCo_bMn_{1-a-b})_{1-x}O_2$, called hereafter HE-NCM) as cathode materials for future lithium-ion battery is impeded by the substantial specific charge and voltage decay. In the full-cell containing HE-NCM as cathode and graphite as anode, transition metal (TM) dissolution have been proposed to be the primary cause for the significant specific charge loss. [1] While most of the studies on TM dissolution in lithium transition-metal oxides focus on the electrode/electrolyte interaction at various states of charge (SOC) [2], information about influence of cycling itself is limited. In this study, the effect of cycle number and cycling rate on the TM dissolution in HE-NCM vs. graphite was investigated using ICP-OES. The overall dissolution rate is higher during the initial cycles, and Ni-dissolution can already be detected after the formation cycle performed at C/15 rate. During the extended cycling at both C/2 and C/10 rates, Mn-dissolution exceeds Ni and Co (Figure 1b). However, considering the relative TM dissolution, Ni-dissolution is more than twice as high comparing to Mn and Co (Figure 1c), suggesting an easier Ni removal. Comparison of TM dissolution while cycling at two different rates, C/2 and C/10, leads to additional conclusions: first, worse specific charge retention is observed at C/10 rate despite the decreased TM dissolution, indicating that TM dissolution is not the only cause of fading; second, comparing TM dissolution within the same total cycling time of 400 h, TM loss of 4.5 atomic % was detected at C/2 rate (100 cycles) as compared to 0.9 atomic % at C/10 (20 cycles). Therefore, the total time that HE-NCM stays at high SOC does not have significant influence on the overall TM dissolution. Instead, repeated lithium insertion and extraction governs the extent of TM dissolution.

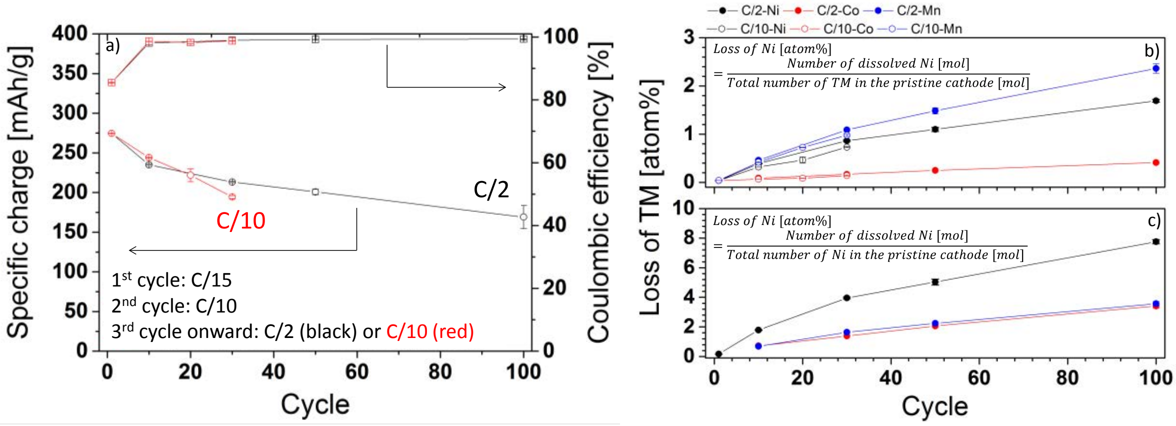


Figure 1. a) Specific charge retention and coulombic efficiency of HE-NCM full cells cycled between 1.0 and 4.8 V at C/2 and C/10 rates. The corresponding amounts of Ni, Co, and Mn detected on the graphite anode in discharged state are normalized to b) the total active mass and c) the total mass of the specific transition metal within the cathode.

[1] Y. Li, M. Bettge, B. Polzin, Y. Zhu, M. Balasubramanian, D.P. Abraham, J. Electrochem. Soc., 160 (2013) A3006-A3019.

[2] N.P.W. Pieczonka, Z. Liu, P. Lu, K.L. Olson, J. Moote, B.R. Powell, J.-H. Kim, J. Phys. Chem. C, 117 (2013) 15947-15957.

HOMO- AND HETEROVALENT DOPING OF NANOSTRUCTURED $LiCoPO_4$

Olga A. Podgornova, Nina V. Kosova
Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, 18 Kutateladze, Novosibirsk 630128, Russia

E-mail: podgornova.nsk@gmail.com

Among the olivine cathodes $LiMPO_4$ (M = Fe, Mn, Co, Ni), $LiCoPO_4$ is characterized by high working potential (~4.8 V vs. Li/Li^+) and relatively high theoretical specific capacity (167 mAh/g). Many efforts have been done to improve its low intrinsic electronic conductivity and Li-ion diffusion, including carbon coating, cation doping and particle size reduction. The atomistic simulations showed favorable energies only for divalent ion substitution for M^{2+} at M site in the olivines but are against the possible substitution of supervalent ions on either M or Li sites [1]. Homogeneous doping does not require any charge compensation and hence does not increase the number of charge carriers. On the contrary, supervalent doping is energetically unfavorable, suggesting that these ions are unstable within the $LiMPO_4$ crystal structure. This leads to formation of secondary phases.

In the present study, the effect of homo- (Fe^{2+}) and heterovalent ($V^{3+,4+}$) doping on the structure and electrochemistry of $LiCoPO_4$ has been studied. Fe and V doped $LiCoPO_4$ were prepared by mechanochemically assisted carbothermal reduction of Co_3O_4, Fe_2O_3 and V_2O_5 using a high-energy AGO-2 planetary mill. The activated reagent mixtures were subsequently annealed at 750 °C under Ar flow. The samples were characterized in detail by XRD using Rietveld refinement, FTIR and Mössbauer spectroscopy, SEM, TEM, EDX, NEXAFS (BESSY II), galvanostatic cycling and GITT. Phase transformations upon cycling were studied by *in situ* synchrotron diffraction (PETRA III, DESY).

All as-prepared $LiCo_{1-y}Fe_yPO_4$ ($0 \leq y \leq 1$) samples are single-phase solid solutions, crystallized in the orthorhombic structure (S.G. *Pnma*). All Fe ions are in 2+ oxidation state. Fe-doped $LiCoPO_4$ samples show improved electrochemical performance due to enlarged 1D Li diffusion channels and the reduced cell volume changes upon Li extraction/insertion. A systematic decrease in the Co^{2+}/Co^{3+} average potential vs. y is observed. *In situ* synchrotron diffraction shows that upon charging of $LiCo_{0.5}Fe_{0.5}PO_4$, a two-phase mechanism changes for a single-phase one.

When doped with vanadium, the $(1-y)LiCoPO_4/yLi_3V_2(PO_4)_3$ composites were formed. The EDX elemental maps showed that $LiCoPO_4$ and $Li_3V_2(PO_4)_3$ are finely mixed with the $Li_3V_2(PO_4)_3$ phase predominantly segregated at the surface. According to NEXAFS, V ions in the composites are in 3+,4+ oxidation state. On charge-discharge curves, all plateaus, characteristic of phase transformations for $LiCoPO_4$ and $Li_3V_2(PO_4)_3$, are maintained. In contrast to $LiCo_{1-y}Fe_yPO_4$ solid solutions, no noticeable shift of the Co^{2+}/Co^{3+} redox potential was observed for the composites.

[1] C.A.J. Fisher, V.M.H. Prieto, M.S. Islam, J. Chem. Mater. 20 (2008) 5907–5915.
[2] N.V. Kosova, O.A. Podgornova, E.T. Devyatkina, V.R. Podugolnikov, S.A. Petrov, J. Mater. Chem. A 2 (2014) 20697-20705.

An active Li-Mn-O compound for high energy density Li-ion batteries

M. Freire[a,c], N.V. Kosova[b], C. Jordy[c], D. Chateigner[a], O.I. Lebedev[a], A. Maignan[a] and V. Pralong[a]

[a] Laboratoire de Cristallographie et Sciences des Matériaux CRISMAT, ENSICAEN, Université de Caen, CNRS, 6 Bd Maréchal Juin, F-14050 Caen, France.
[b] Institute of Solid State Chemistry and Mechanochemistry SB RAS, 18 Kutateladze, Novosibirsk 630128, Russia.
[c] Saft, Direction de la Recherche, 111/113 Bd Alfred Daney, 33074 Bordeaux, France.

email address of the presenting author: melanie.freire@ensicaen.fr

Due to their low weight, high energy densities and long cycle life, the battery scientific community is still trying to develop new high capacity cathodes materials in order to increase the energy density of storage devices [1].

After a composition screening, a new material family has been discovered in the Li-Mn-O system and has been investigated as potential new material for Li-ion batteries to replace conventional NMC materials ($LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$) [2]. In this study, we report for the first time the synthesis, structural and electrochemical characterizations of a new non-lamellar oxide with the highest capacity observed ever before in the Li-Mn-O system. This new patented [3] material with the composition of $Li_4Mn_2O_5$ shows a discharge capacity of 300 mAh/g. It is a rock-salt type nanostructured material, prepared by a direct mechanochemical synthesis. The typical crystallite size is about 5-10nm (from Transmission electron microscopy TEM and electron diffraction ED). The ring ED pattern of this individual phase can be indexed on the cubic F*m-3m* structure, with a rock-salt cell parameter of *a*=4.16Å, according to Rietveld refinement.

The electrochemical performances were performed at a C/20 rate, and show a reversible discharge capacity about 300 mAh/g. A gradual increase in the cut-off voltage up to 4.8V activates the material and prevents the electrolyte degradations. During cycling, the derivative curves indicate at least 2 active redox couples [4]: Mn^{3+}/ Mn^{4+} (around 3.3V), Mn^{4+}/ Mn^{5+} and/or O^{2-}/ O^{-} (around 4.1V). In order to have a better insight of lithium deinsertion process, we used magnetic measurements at various charge states. We will show that magnetic measurements are perfect tools to access to the oxidation level of the material, and in agreement with the values obtained after iodometric redox titrations. We will namely show that this material is oxidized up to Mn^{5+} oxidation state with a competition of the oxygen oxidation [4].

In short, in this work are reported the first results of a new electrochemically active compound as positive electrode for Li-ion batteries, with the active participation of both redox centers: Manganese and Oxygen [5].

[1] B.L. Ellis, K. Tae Lee, L.F. Nazar, Chem. Mater. 22 (2010) 691-714
[2] H. Koga, L. Croguennec, M. Ménétrier, K. Douhil, S. Belin, L. Bourgeois, E. Suard, F. Weill, C. Delmas, J. Electrochem. Soc. 160 (2013) A786-A792
[3] Patent FR1258625
[4] M. Sathiya, G. Rousse, K. Ramesha, C. P. Laisa, H. Vezin, M. T. Sougrati, M-L. Doublet, D. Foix, D. Gonbeau, W. Walker, A. S. Prakash, M. Ben Hassine, L. Dupont, J-M. Tarascon, Nature Mat. 12 (2013) 827-835
[5] M. Freire, N.V. Kosova, C. Jordy, D. Chateigner, O.I. Lebedev, A. Maignan, V. Pralong, Nature Mat. in press (2015)

Fe_3O_4–CONTAINING MULTILAYER GRAPHENE FOR ENHANCED LITHIUM STORAGE CAPABILITY

Rinaldo Raccichini[a,b,c], Alberto Varzi[a,b], Venkata Sai Kiran Chakravadhanula[a,b,d],
Christian Kübel[a,b,d], Stefano Passerini[a,b]
[a] Helmholtz Institute Ulm (HIU), Helmholtzstrasse 11, D-89081 Ulm, Germany.
[b] Karlsruhe Institute of Technology (KIT), P.O. Box 3640, D-76021, Karlsruhe, Germany.
[c] Institute of Physical Chemistry, University of Muenster, Corrensstrasse 28/30, D-48149 Muenster, Germany.
[d] Karlsruhe Nano Micro Facility, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen 76344, Germany.

Email address of the presenting author: rinaldo.raccichini@kit.edu

Graphene is considered as replacement for graphite, the state-of-the-art material for lithium-ion battery (LIB) anodes [1]. However, it is not clear whether it can really outperform graphite in terms of delithiation voltage, cycling stability and volumetric capacity [1,2]. In this respect, we present a novel ionic liquid microwave-assisted synthesis of Fe_3O_4-containing multilayer graphene (hereinafter called MUG-Fe_3O_4) showing exceptional high rate performance due to the formation of metallic iron upon the 1st lithiation.

The characteristic structure and morphology of the composite has been investigated, through different physical and chemical analysis, in order to prove its peculiarity in terms of structural arrangement between the Fe_3O_4 nanoparticles and the multilayer graphene matrix (Fig. 1).

The use of MUG-Fe_3O_4, as LIB anode active material, and its comparison with the bare multilayer graphene (hereinafter called MUG) and commercial graphite, revealed the enhanced lithium ions storage properties of this material in the 0.005V-1V potential range. Indeed, especially at high currents (i.e., 5 A g^{-1}), improved rate capability, remarkable cycling stability, low average delithiation voltage (0.244 V) (Fig. 2 a,b) and a substantial increase of volumetric capacity with respect to commercial graphite (58.7 Ah L^{-1} vs. 9.5 Ah L^{-1}) are achieved (see Table).

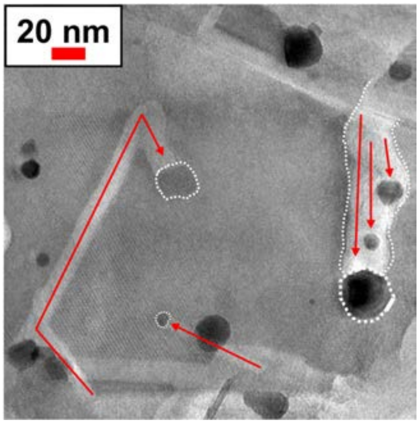
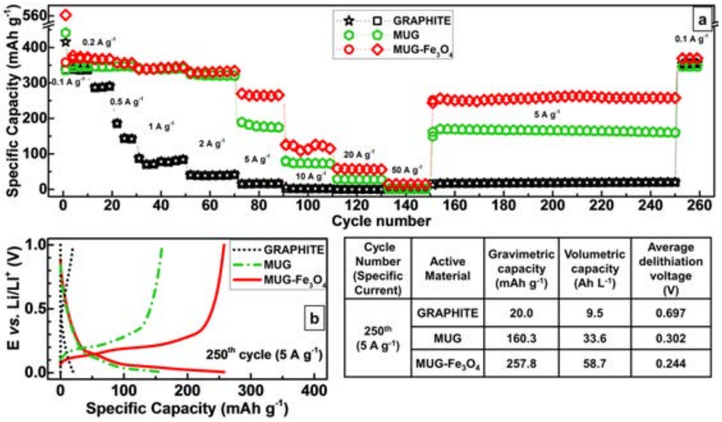


Figure 1: MUG-Fe_3O_4 TEM micrograph. Fe_3O_4 nanoparticles are outlined with white round dot dashes and, the carving paths, are indicated with red arrows



Cycle Number (Specific Current)	Active Material	Gravimetric capacity (mAh g^{-1})	Volumetric capacity (Ah L^{-1})	Average delithiation voltage (V)
250th (5 A g^{-1})	GRAPHITE	20.0	9.5	0.697
	MUG	160.3	33.6	0.302
	MUG-Fe_3O_4	257.8	58.7	0.244

Figure 2: Graphite, MUG and MUG-Fe_3O_4: (a) rate capability test comparison at different specific currents and (b) potential profiles of a selected cycle (250th) at 5 A g^{-1}.
Table: Comparison of the specific gravimetric and volumetric capacities and average delithiation voltages.

[1] R. Raccichini, A. Varzi, S. Passerini, B. Scrosati, Nat. Mater. 14 (2015) 271-279.
[2] M.N. Obrovac, V.L. Chevrier, Chem. Rev. 114 (2014) 11444-11502.

FAULTS, AN ACCESSIBLE PROGRAM FOR REFINING POWDER DIFFRACTION PATTERNS OF LAYERED STRUCTURES

Montse Casas-Cabanas[a], Marine Reynaud[a], Jokin Rikarte Ormazabal[a],
and Juan Rodríguez-Carvajal[b]

[a] *CIC Energigune, Parque Tecnológico de Álava, Calle Albert Einstein 48, Miñano, Spain.*
[b] *Institut Laue Langevin, 6 rue Jules Horowitz, Grenoble, France.*

mreynaud@cicenergigune.com

Layered systems include a large number of mineral families and synthetic compounds of great technological importance with, for instance, applications in the field of electrochemical energy storage. Their physical-chemical properties being directly related to their structural features, the microstructural characterization of these materials is of high importance and includes the determination of different kinds of defects, their amount and their locations.

So far, a widely used tool to interpret the diffraction data of one-dimensionally disordered systems was the program DIFFaX [1], which permits to simulate X-ray and Neutron powder diffraction patterns. In order to overtake the limitations of simple simulations, we have developed the FAULTS program [2-3], based on the DIFFaX code, which enables to refine experimental XRD and NPD patterns of crystal systems with any type of planar defects, such as twins and stacking faults. An improved version of this program, more performant and with additional features is now available within the FullProf suite of programs [4] or as an independent program [5].

FAULTS can read experimental XRD and NPD data from many different formats. Refinable parameters are provided by the user in a free-format input data file, in which the structure is described in terms of layers of atoms which are interconnected *via* stacking operations that occur with a certain probability. Refinements of all the parameters involved in the calculation of the diffracted intensities is carried out using the Levenberg-Marquard optimization algorithm, implemented in the Crystallographic Fortran Modules Library (CrysFML) [6].

Another major feature of FAULTS with respect to DIFFaX is the implementation of a more adequate isotropic size broadening treatment which takes into account the Gaussian (H_G) and Lorentzian (H_L) contributions to the FWHM in addition to the consideration of a finite number of layers per crystallite already present in DIFFaX. As these are refinable parameters, this treatment allows a successful description of the separate contributions to line broadening of instrumental features, the finite crystallite size and planar defects.

Our presentation will show the structure and operation of the program FAULTS, and some examples will be given.

[1] M.M. Treacy, J.M. Newsam, M.W. Deem, Proc. R. Soc. London Ser. A, 433 (1991) 499-520.
[2] M. Casas-Cabanas, J. Rodríguez-Carvajal, M.R. Palacín, Z. Kristallogr. Suppl., 23 (2006) 243-248.
[3] M. Casas-Cabanas, M. Reynaud, J. Rikarte, J. Rodríguez-Carvajal, submitted.
[4] J. Rodríguez-Carvajal, FullProf Suite. Available at http://www.ill.eu/sites/fullprof/index.html.
[5] M. Casas-Cabanas, M. Reynaud, J. Rikarte, J. Rodríguez-Carvajal, FAULTS. Available at http://www.cicenergigune.com/en/areas-investigacion/power-storage-batteries-and-supercaps/lineas-investigacion/li-ion/faults/
[6] J. Rodríguez-Carvajal and J. González-Platas, IUCr CompComm Newsletter, 1 (2003) 50-58. Available at http://www.iucr.org/iucr-top/comm/ccom/newsletters/. Repository available at: http://forge.epn-campus.eu/projects/crysfml/repository.

This work was supported by MINECO (Proyectos I+D, Retos 2013) reference number ENE2013-44330-R.

NMC Positive electrode materials with metal-site vacancies for Lithium-ion batteries

Ramesh Shunmugasundaram[a], Rajalakshmi Senthil Arumugam[b] , Kris J. Harris[c], Gillian R. Goward[c] and J.R. Dahn[a,b]
[a] *Dept. of Chemistry and* [b] *Dept. of Physics and Atmospheric Science,*
Dalhousie University, Halifax, NS, Canada, B3H 3J5
[c] *McMaster University, Department of Chemistry and Chemical Biology,*
1280 Main St. West, Hamilton, Canada, L8S 1H2

E-mail address of the presenting author: s.ramesh@dal.ca

One of the key issues with Li-rich NMC positive electrode materials is their high first-cycle irreversible capacity loss (IRC), which is usually around 20 % of their first charge capacity. Recently Li-rich positive electrode materials that can simultaneously exhibit low-IRC (~ 10 % or less) and high reversible capacity (> 240 mAh/g) have been reported [1]. The low-IRC materials were single phase layered materials that had inherent metal-site vacancies, determined by He pycnometry, in their pristine state. About 35 samples that can accommodate metal-site vacancies in their pristine state were synthesized and their IRCs were measured. Figure 1 shows a plot of % IRC and reversible capacity against the fraction of metal-site vacancies per formula unit. Low-IRC behaviour is well correlated to the concentration of metal-site vacancies of the studied materials [2]. ^{7}Li NMR experiments, which measure the distribution of Li between Li and transition metal layers, were performed on the pristine single-phase low-IRC materials. Correlations between the stoichiometry, vacancy content and the Li atom distribution allow a hypothesis for the mechanism behind low irreversible capacity to be developed.

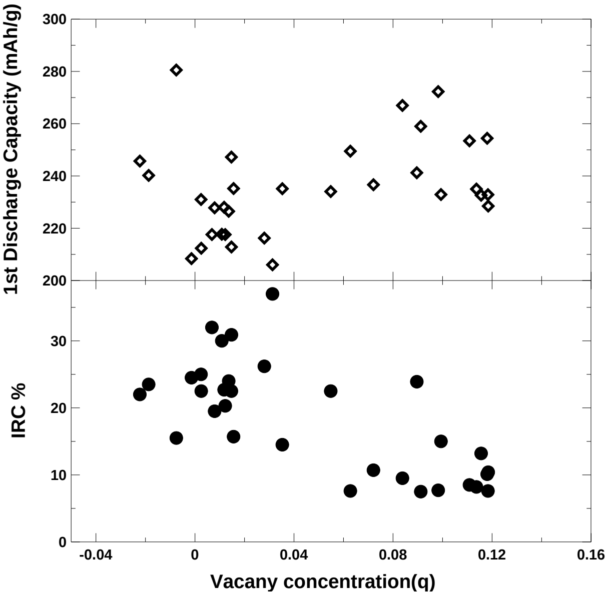


Figure 1. Reversible capacity (top panel) and fraction of irreversible capacity (bottom panel) of $Li_p\square_qNi_xMn_yCo_zO_2$ as function of vacancy content, q.

References:

[1] R. Shunmugasundaram, R. Senthil Arumugam, J. R. Dahn, Chem. Mater., **2015**, *27* (3), pp 757–767
[2] R. Shunmugasundaram, R. Senthil Arumugam, Kris Harris, Gillian Goward, J. R. Dahn submitted to Chem. Mater.

STUDY OF THE MORPHOLOGICAL EVOLUTION OF Si-BASED ELECTRODES BY MEANS OF IN-SITU X-RAY TOMOGRAPHY

Victor Vanpeene[a,b], Aurelien Etiemble[b], Eric Maire[b] Lionel Roué[a],
[a]*INRS-EMT, 1650 boulevard Lionel Boulet, Varennes, J3X 1S2, Canada*
[b]*MATEIS INSA Lyon, 7 Avenue Jean Capelle, 69621 Villeurbanne, France*
victor.vanpeene@emt.inrs.ca

The poor cycle life of Si-based electrodes is mainly due to their large volume variation upon cycling, inducing electrical disconnections and instability of the solid electrolyte interface (SEI). The study of the morphological variation of Si-based electrodes upon cycling is thus highly relevant to evaluate their degradation and to optimize their formulation and architecture. However, this is challenging considering their complex three-dimensional structure and their major evolution with cycling. Furthermore, samples are fragile and reactive and therefore difficult to prepare for bulk observations. In this context, X-ray tomography appears as an effective non-destructive and 3D observation tool.

In this communication, in-situ synchrotron X-ray tomography analyses are performed on Si-based electrodes prepared from a pH3 buffered slurry of ball-milled Si powder + carbon black + carboxymethylcellulose (CMC) (80/12/8) loaded into a carbon paper (AvCarb EP40) by impregnation. After an appropriate image reconstruction procedure, key morphological parameters of these Si-based electrodes and their evolution with cycling are determined such as the electrode thickness and the pore size distribution and pore volume fraction as shown in Fig. 1.

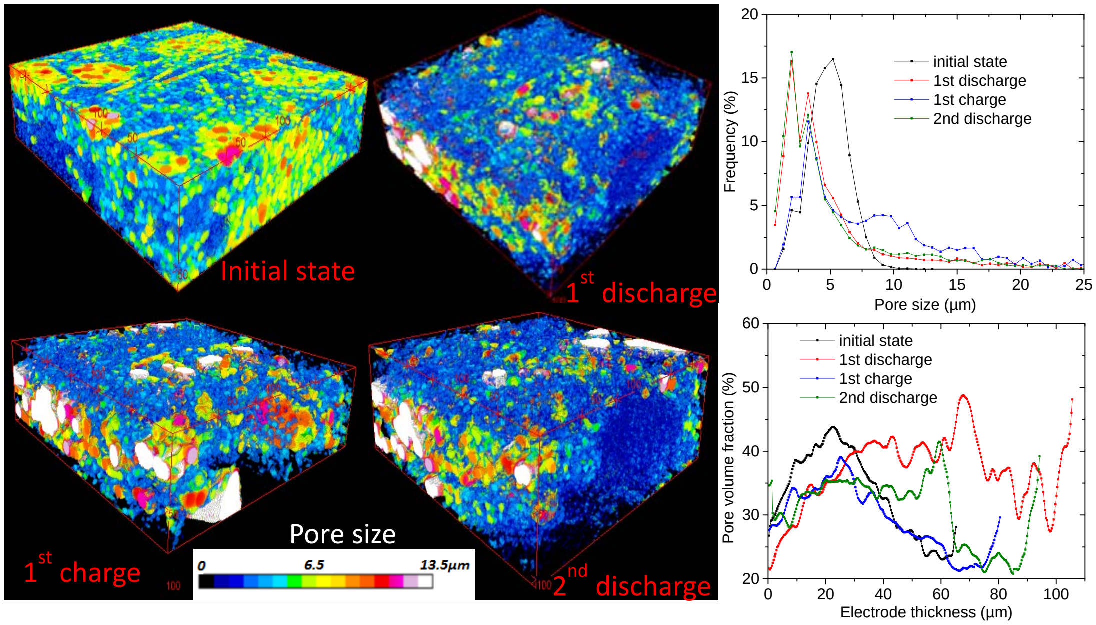


Fig. 1. Evolution with cycling of the pore size (3D view and distribution curve) and the pore volume fraction as a function of the electrode thickness for a Si-based electrode with carbon paper as 3D current collector. The initial thickness of the electrode is 85 µm and its Si loading is $1.4 mg_{Si}$/cm^2. Cycling was performed at a current density of 400 mA/g_{Si}, resulting in 1st discharge, 1st charge and 2nd discharge capacities of 1152, 766 and 852 mAh/g electrode, respectively.

Small change — great effect: Steep increase of Li ion dynamics in $Li_{4+x}Ti_5O_{12}$ at the early stages of chemical Li insertion ($x = 0.1$, $x = 0.3$)

Walter Schmidt and Martin Wilkening

Institute for Chemistry and Technology of Materials, and Christian Doppler Laboratory for Lithium Batteries, Graz University of Technology (member of NAWI Graz), 8010 Graz, Austria

w.schmidt@tugraz.at ; wilkening@tugraz.at

Polycrystalline $Li_{4+x}Ti_5O_{12}$ (LTO, $0 < x \leq 3$) is a well-known negative electrode material for lithium-ion batteries. It shows a flat Li insertion plateau of about 1.5 V vs. Li/Li^+; its theoretical specific capacity is approximately 175 mAh/g. The increased use of LTO, which is also commercially available, is due to various properties such as low cost, satisfactory safety and easy preparation. Most importantly, upon Li insertion, the expansion of the material is almost negligible favoring a long cycle life. In samples with $x = 0$, Li self-diffusion, which can be microscopically probed via Li nuclear magnetic resonance (NMR), is rather low. With increasing Li insertion, however, the diffusivity increases significantly. This is accompanied by a redistribution of Li ions across the 8a and 16c sites in the spinel structure [1].

While earlier ^{7}Li NMR studies put emphasis on samples with Li contents of $x > 1$ [2], there are, however, no information available from NMR answering the question of how Li self-diffusion changes when x is only slightly increased. The present study shows that even at $x = 0.1$ ^{7}Li NMR relaxometry, when performed in the so-called rotating frame of reference, reveals a drastic enhancement of Li diffusivity [3]. This enhancement, which points to the 8a – 16c – 8a migration pathway, is associated with a considerable reduction of the local hopping barrier. Thus, the largest increase in Li diffusivity is observed at the early stages of Li insertion [3]. Strong Coulomb repulsions caused by the simultaneous occupation of neighboring 8a and 16c sites might be considered to explain the enhanced Li diffusivity observed.

High resolution NMR was helpful to corroborate the findings from time-domain NMR. Via ^{6}Li MAS NMR is was possible to reveal the magnetically different Li sites in LTO (8a, 16c, 16d) and to calculate the site occupancies by evaluating the areas under the NMR lines. This enabled us to follow the change in site occupancy as a function of x. Site-specific (MAS) NMR spin-lattice relaxation times and ^{6}Li 2D NMR experiments point to rapid Li ion change between the 8a and 16c sites. This is in contrast to the Li ions residing in the 16d voids; obviously, they do not participate in the fast Li diffusion process that is relevant for battery applications.

[1] M. Wagemaker *et al.*, Adv. Mater. 2006, 18, 3169.

[2] M. Wilkening *et al.*, Phys Chem. Chem. Phys., 2007, 9, 6199.

[3] W. Schmidt *et al.*, Chem. Mater., 2015, 27, 1740.

Tuesday 22
Poster Session 2

Single-phase Na^+/Li^+ co-insertion mechanism within olivine $FePO_4$

Marie Lachal[a,b], Renaud Bouchet[a,b*], Charles Delacourt[c], Cécile Rossignol[a,b], Fannie Alloin[a,b], Saïd Obbade[a,b]
[a] *Université Grenoble Alpes, LEPMI, F-38000 Grenoble, France*
[b] *CNRS, LEPMI, F-38000 Grenoble, France*
[c] *Université de Picardie Jules Verne, LRCS, 80039 Amiens, France*
**marielachal@hotmail.fr*

Olivine $LiFePO_4$ (de)lithiation mechanism has been largely studied over the past 10 years and is usually observed and interpreted as a two-phase transition. However, recent publications demonstrated that the dynamic transformation from $LiFePO_4$ to $FePO_4$ (and reverse) would go through a metastable solid solution Li_xFePO_4, especially in the case nanoparticles at high charging rate [1-3]. Olivine $NaFePO_4$ (de)sodiation mechanism appears even more complex with the existence of the intermediate phase $Na_{2/3}FePO_4$, leading to two charging plateaus and extended solubility limits [4-6]. This work presents the peculiar (de)insertion mechanism during chemical delithiation and electrochemical sodiation observed by *operando* XRD. Firstly, *ex situ* XRD performed on partially chemically delithiated Li_xFePO_4 powders have shown a stabilized solid solution at equilibrium state, which is usually observed under dynamic conditions [3]. Secondly, the $Li_{0,6}FePO_4$ phase obtained by chemical delithiation has been electrochemically characterized in Na half-cell. Associated *operando* XRD displays a progressive shift of the diffraction peaks (Figure 1), revealing a Li^+/Na^+ co-insertion mechanism via a complete solid solution. These results, reported for the first time, bring new insights on Li^+/Na^+ insertion mechanisms within olivine $FePO_4$ structure.

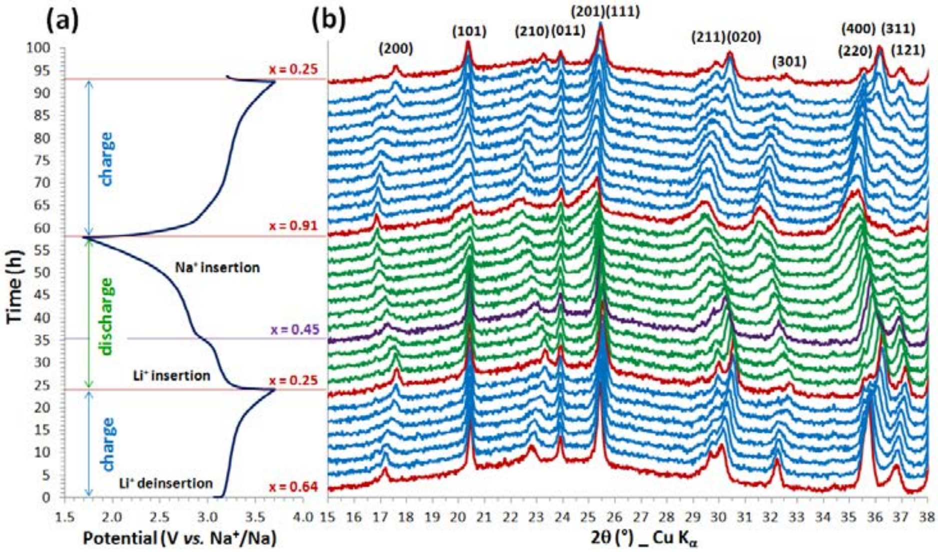


Figure 1: Electrochemical and structural characterizations of $Li_{0.6}FePO_4$ in Na half-cell : (a) Charge/discharge galvanostatic curve at C/60 rate, (b) *operando* XRD patterns at different states of charge/discharge.

[1] R. Malik, F. Zhou, G. Ceder, Nat. Mater. 10 (2011) 587–590.
[2] Y. Orikasa, et al. J. Am. Chem. Soc. 135 (2013) 5497–5500.
[3] H. Liu, et al. Science 344 (2014) 1252817.
[4] P. Moreau, D. Guyomard, J. Gaubicher, F. Boucher, Chem. Mater. 22 (2010) 4126–4128.
[5] M. Galceran et al. Phys. Chem. Chem. Phys. 16 (2014) 8837–8842.
[6] J. Gaubicher et al. Electrochem. Commun. 38 (2014) 104–106.

Polysulphides confined! New design of the separator for better Li–S cell performance

Joanna Conder, Lorenz Gubler, Petr Novák, Sigita Trabesinger
Electrochemistry Laboratory,Paul ScherrerInstitut,
CH-5232 Villigen PSI, Switzerland

joanna.conder@psi.ch

The lithium–sulphur (Li–S) battery can provide significantly higher specific energy in comparison to current battery technologies and thus lend itself to future applications in electric vehicles, grid-scale energy storage, and others[1]. This benefit largely comes from sulphur's high theoretical specific charge of 1672 mAh g^{-1} andresulting high theoretical specific energy of ca.2600 Wh kg^{-1}. While sulphur is environmentally friendly and inexpensive, a number of challenges have hampered commercialisation of Li–S electrochemical couple thus far. Most important drawbacks of sulphur are poor conductivity and generationof soluble polysulphide intermediates (Li_2S_n, $4 < n < 8$) upon discharge, which contribute to undesirable cyclic electron transfer reactions, a process known as the polysulphide shuttle[2].

To tacklethe latter challenge, we modified the surface of the polypropylene separator by introducing styrene sulphonate groups (SS) that repel the generated S_n^{2-} species. This new separatorin the form of an asymmetric membrane with cation-exchange SS functional groups (Figure 1) was synthesised by a one-step plasma-induced graft co-polymerisation. Both successful grafting and membrane asymmetry were confirmed by attenuated total reflectance Fourier transform infrared spectroscopy. Morphological changes as a function of the degree of modification were analysed using scanning electron microscopy. Many electrochemical techniques, such as galvanostatic cycling at different C-rates with and without potentiostatic step, and cycling voltammetry, were used to confirmthe benefitsof these materials in the Li–S cell. The reaction mechanism of the Li–S system with modified separatorwas further studied by means ofelectrochemical impedance spectroscopy and operando X-ray diffraction, and compared to the cell with Celgard 2400 reference separator.

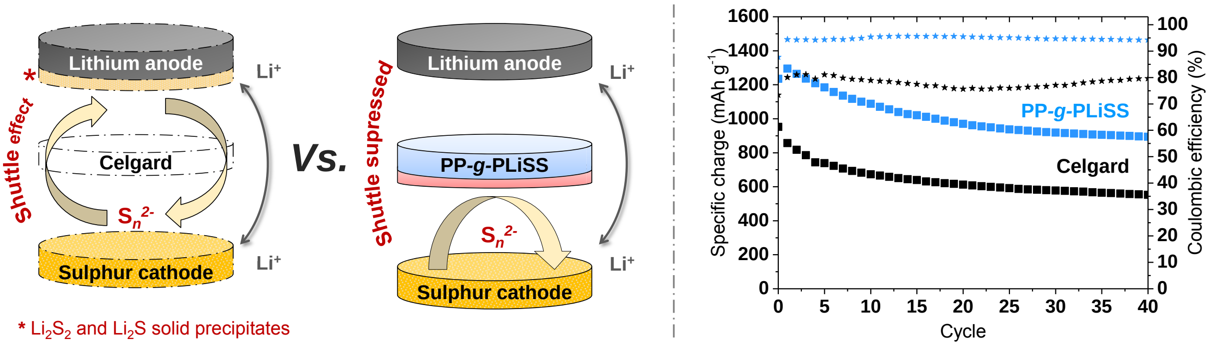


Figure 1 Configuration of Li–S cell assembly showingthe concept of the functionalisedseparator (left)[3]. Cyclingperformance of Li–S cells at C/20 with modified separator,in comparison to Celgard 2400(right).

References:
[1] G. Xu, B. Ding, J. Pan, P. Nie, L. Shenand X. Zhang, J. Mater.Chem. A 2 (2014) 12662–12676.
[2] S. S. Zhang, J. Power Sources 231 (2013) 153–162.
[3] J. Conder, S. Urbonaite, D. Streich, P.Novák, L. Gubler, RSCAdv. 5 (2015) 79654–79660.

Improved Calculation of Li and Na Intercalation Properties in TiO_2 Polymorphs using the Screened Exchange Functional

James A. Dawson and John Robertson

Department of Engineering, University of Cambridge, Cambridge CB2 1PZ, United Kingdom

jad95@cam.ac.uk

There are numerous examples of density functional theory (DFT) and potential-based calculations of Li and Na intercalation in a wide variety of host materials, however, these methods are not without their shortcomings. While potential-based calculations are useful for very large or low symmetry systems, they are not appropriate for bulk systems with complex electronic or magnetic structures and there quality is fully dependant on the quality of the model used. Standard DFT calculations in such works nearly always use the local density approximation (LDA) or generalized gradient approximation (GGA), which have both been shown to underestimate intercalation energetics [1] and fail in reproducing several other structural and electronic properties of the host materials. They are also well-known for their severe band-gap underestimation and inaccuracies in the calculation of defect transition levels. While some of these errors can be reduced using post-DFT methods like the inclusion of the Hubbard *U* parameter, it is not clear whether they are sufficiently accurate in predicting defect levels [2].

To correct for the problems associated with local-density methods, we use the screened exchange (sX) functional for the calculation of Li and Na defect formation energies, charge transitions and electronic structures in various TiO_2 polymorphs (anatase, rutile and TiO_2(B)). The sX functional has the major advantage of replacing all LDA exchange with a Thomas-Fermi screened Coulombic exchange potential [2]. The local exchange and correlation functionals underlying the LDA and GGA cause spurious self-interaction which increases the energy of occupied states and decreases the energy of unoccupied states, whereas the exchange potential is self-interaction free. This results in more accurate defect formation energies and charge transition levels. The sX functional has successfully been applied to several cathode and anode materials [3-5].

By comparing our results to those calculated using GGA (both in this work and the literature), we report improved agreement with experiment in terms of local and electronic structure of the TiO_2 polymorphs and intercalation energetics. For rutile, sX and GGA calculated energetics are similar, while for anatase, sX shows a significant improvement on the GGA underestimated values. In agreement with the literature, all polymorphs are shown to readily incorporate Li, while for Na, the situation is more complicated with negative intercalation energies calculated for anatase and TiO_2(B), but not for rutile.

[1] F. Zhou, M. Cococcioni, C. A. Marianetti, D. Morgan and G. Ceder, Phys. Rev. B 70 (2004) 235121.

[2] S. J. Clark, J. Robertson, S. Lany and A. Zunger, Phys. Rev. B 81, (2010) 115311.

[3] J. A. Dawson, Y. Guo and J. Robertson, J. Appl. Phys. 107, (2015) 122110.

[4] H. Li, Y. Guo and J. Robertson, J. Phys. Chem. C 119, (2015) 18160-18166.

[5] S. J. Clark and J. Robertson, Phys. Rev. B 82, (2010) 085208.

Sol-gel routes to antimony electrodes for lithium and sodium batteries

Nicholas E. Drewett, Laurence J. Hardwick
Stephenson Institute for Renewable Energy, Department of Chemistry, University of Liverpool, Liverpool, L69 7ZD

email address of the presenting author: N.Drewett@liverpool.ac.uk

Antimony is of interest as a research material for use in battery anodes due to its attractive properties, such as its relatively high gravimetric capacity and the ability to insert both lithium and sodium into its structure. Relatively few synthetic routes to this material exist, with most studies characterising nanocomposites[1,2], bulk microcrystalline powders[3] or vacuum evaporated thin films[4]. While recent work has developed a colloidal synthesis to pure antimony nanoparticles[5], there is still a demand for a robust and easy route to produce antimony particles for use in battery anodes. Herein we present a one pot sol-gel synthetic route to making high-purity antimony particles. The ease of synthesis combined with the flexible nature of sol-gel techniques should allow for tailoring of the antimony particles to suit a range of requirements, such as particle size. The rate capability of one sol-gel material is presented in Figure 1, with the SEM data in the insert showing the antimony particle size in the region of 5-50 microns. The cycling data is consistent with expectations for antimony microparticles within this size distribution, with an initial capacity of 674 $mAhg^{-1}$ at C/10 (66 $mAg^{-1}Sb$) and capacities of 528, 455, 405, 345 and 272 $mAhg^{-1}$ at C/2, C, 2C, 4C and 8C respectively. We will present the synthesis and physical characterisation of a selection of antimony particles, along with a study into their electrochemical properties for both sodium and lithium insertion.

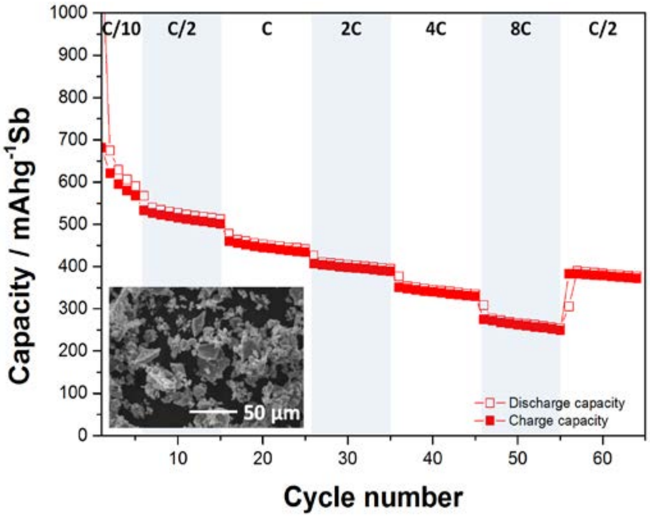


Figure 1. Cycling performance for antimony electrodes in lithium half cells (1C is taken as 660 mAg^{-1} Sb), inset SEM image of material. Antimony electrodes had the composition Sb(64%)/CB(21%)/CMC(15%), with a 1 M $LiPF_6$ in 1:1 w/w ethylene carbonate : dimethyl carbonate electrolyte.

[1] Á. Caballero, J. Morales, L. Sánchez, J. Power Sources 175 (2008) 553-557

[2] J. H. Sung, C.-M. Park, J. Electroanal. Chem., 700 (2013) 12-16

[3] A. Darwiche, C. Marino, M. T. Sougrati, B. Fraisse, L. Stievano, L. Monconduit, J. Am. Chem. Soc. 134 (2012) 20805–20811

[4] L. Baggetto, P. Ganesh, C.-N. Sun, R. A. Meisner, T. A. Zawodzinski, G. M. Veith, J. Mater. Chem. A 1 (2013) 7985-7994

[5] M. He, K. V. Kravchyk, M. Walter, M. V. Kovalenko, Nano Lett., 14 (2014) 1255-1262

Spray-drying synthesis of $Na_3V_2(PO_4)_2F_3$ as cathode material in hybrid-ion batteries

Nicolas Eshraghi, Sébastien Caes, Claude Karegeya, Caroline Piffet, Frédéric Boschini
LCIS/GREENMAT, Institute of Chemistry B6, Quartier Agora , University of Liège,
4000 Liège, Belgium

E-mail: neshraghi@ulg.ac.be

In recent years, fluorophosphates with the NASICON (Na Super-Ionic Conductor) type structure have been studied as cathode electrode materials. These fluorophosphates exhibit rich chemistry, attractive lithium/sodium insertion properties and thus offer promising electrochemical properties. Among them, $Na_3V_2(PO_4)_2F_3$ deserves attention because of promising electrochemical properties and ease of fabrication [1]. This material was reported by Song et al. in hybrid-ion batteries [2] and sodium ion batteries [1,3].

Here, $Na_3V_2(PO_4)_2F_3/C$ powder was synthesized for the first time by the spray-drying method. $Na_3V_2(PO_4)_2F_3/C$ contains 15% of carbon nanotubes (CNTs) added in situ to increase the electronic conductivity and connection between particles. In this method a solution/suspension is sprayed by air creating fine droplets in drying chamber with hot air flow (100–300 °C). These droplets are instantly dried, making it possible to harvest a homogeneous composition powder while avoiding thermal degradation of the compound (oxidation).

Structural and microstructural characterizations were carried out by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Study of firing and heat treatment influence on the powder purity and particle morphology showed that powders dried at 180 °C and fired at 600 °C have the best properties.

Electrochemical measurements were carried out in hybrid-ion batteries, using a potentiostat (BT-LAB) in the range of 1.6-4.6 V and 2-4.6 V vs. Li^+/Li^0 at different cycling rates. Addition of CNTs increased the conductivity and as a result the capacity. $Na_3V_2(PO_4)_2F_3/C$ samples cycled between 1.6-4.6 V vs. Li^+/Li° demonstrated specific capacities of 175 and 149 at C/15 and C/10-rate, respectively. These results are higher than the capacity of 147 $mAh.g^{-1}$ at 0.09C-rate reported by Song et al.[2].

Better cycling performance and capacity retention was observed when electrochemical cells were cycled between 2-4.6 V with capacities of 140, 128 and 102 $mAh.g^{-1}$ at C/15, C/10 and 1C-rate, respectively with 80% capacity retention over 300 cycles.

These preliminary results show that the spray-drying technique is suitable for obtaining complex powders with a very good homogeneity leading to very good electrochemical properties.

References:

[1] R. A. Shakoor, D. H. Seo, H. Kim, Y. U. Park, J. Kim, S. W. Kim, H. Gwon, S. Lee and K. Kang, J. Mater. Chem., 2012, 22, 20535.

[2] W. Song, X. Ji, J. Chen,Z. Wu,Y. Zhu, K. Ye, H. Hou, M. Jinga and C. E. Banks, Phys. Chem. Chem. Phys., 2015, 17,159.

[3] Bianchini, M., Brisset, N., Fauth, F., Weill, F., Elkaim, E., Suard, E., Masquelier, C., Croguennec, L., Na3V2(PO4)2F3 Revisited: A High Resolution Diffraction Study, Chem. Mater. 2014, 26, 4238−4247.

Electrode Materials for Organic Batteries: can Modelling Investigations take part to the Challenge?

Christine Frayret[a], Daniele Tomerini[a], Carlo Gatti[b],
Matthieu Becuwe[a], Franck Dolhem[c], Philippe Poizot[d]
[a] *LRCS-CNRS UMR 7314, Université de Picardie, 33, Rue Saint-Leu, 80039 Amiens, France*
[b] *CNR-ISTM, Istituto di Scienze e Tecnologie Molecolari, via Golgi 19, 20133, Milano, Italy*
[c] *LG2A-CNRS-FRE 3517, Université de Picardie, 10, Rue Baudeloque, 80039 Amiens, France*
[d] *IMN-CNRS UMR C 6502, Université de Nantes, 2, Rue de la Houssinière, 44322 Nantes, France*

email address of the presenting author: christine.frayret@u-picardie.fr

Improvement of success rates for innovation in the research field devoted to the organic battery development mainly relies on the ability to rationally design and fabricate novel functional electrode materials by exploiting the large modularity linked to their intrinsic nature. The emergence of strategies for lead candidates' identification requires an understanding of the incidence of functionalization/modulation of the molecular backbones or change in redox centres,... on electrochemical features for various sets of compounds. This supposes reaching full knowledge of the physical–chemical properties and of the role they are playing in the involved processes. Provided selection criteria and full comprehension can be extracted from such approaches, modelling investigations may play a key role on this emerging area, with the promise of guided research, greener design and faster advances.

A work of prospection can correspond to the initial and most significant milestone in designing advanced materials, especially if differentiation between compounds can be rationalized. Our simulation methodology is thus aimed at defining property-based guidelines within a few sets of modulation. It can be applied to both systematic screening of existing compounds and hypothetical novel candidates, both being modulated through various effects. This should progressively complete the database for the discovery of new/optimized organic electrodes with improved features. Spin density maps, electronic delocalization indices or energy stabilization decomposition, … clearly constitute powerful local indicators that enable to distinguish molecular compounds, especially regarding their ranking in terms of electrochemical features. In particular, fine dissection of these data can give the opportunity to discover subtleties regarding the role played by each parameter within various sets of combined effects of functionalization/heteroatom substitution/nature of backbone, … that could not be disentangled easily otherwise. Recent studies in this area outline lessons originating from the consideration of various families and modifications [see *e.g.* 1–3]. By exploring various invention possibilities, the ultimate goal of such investigations is to help experimentalists engineering a few potentially attracting new compounds.

[1] D. Tomerini, C. Gatti, C. Frayret, Phys. Chem. Chem. Phys. 17, (2015) 8604–8608.
[2] C. Frayret, D. Tomerini, C. Gatti, Y. Danten, M. Becuwe, F. Dolhem, P. Poizot, in Proceedings of *CIMTEC 2014, 13th International Conference on Modern Materials and Technologies – 6th Forum on New Materials*, Chapter 3: Batteries, Supercapacitors and Thermoelectrics, *Techna-Group Series Advances in Science and Technology,* June 16 – 19, 2014, Montecatini Terme, Italy, Part A, pp. 146-151.
[3] A.A. Franco, C. Frayret, in: C. Menictas, M. Skyllas-Kazacos, T.M. Lim (Eds.), Advances in batteries for medium– and large–scale energy storage, Woodhead Publishing, 2014, pp. 509–562.

Electrochemical performance of micro-sized Sn for Na-ion Battery

Mika Fukunishi[a], Kei Kubota[a, b], Mouad Dahbi[a, b], Satoshi Yasuno[c] , and Shinichi Komaba[a,b]
[a]Department of Applied Chemistry, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku, Tokyo 162-8601
[b]Unit of Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Katsura, Kyoto, 615-8520
[c]JASRI, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198

m.fukunishi@rs.tus.ac.jp

Electrode materials for Na-ion battery have been extensively studied to realize low-cost and high-energy battery. Hard carbon, which delivers 300 mAh g^{-1}, is one of the promising candidates as the negative electrode.[1] However, its reversible capacity (actually energy density) is not high enough compared to LIB. Therefore, materials with higher capacity are still required to high energy density Na-ion battery. We reported that nano-sized Sn electrode delivers a reversible capacity of ca. 600 mAh g^{-1} with a good capacity retention in a voltage range of 0.0 − 0.65 V, which corresponds to 70% of the theoretical capacity of 847 mAh g^{-1} for Sn / $Na_{15}Sn_4$ sodiattion.[2] In this research, the impact of the Sn particle size of electrochemical properties was examined for practical Na-ion battery and the current density on the electrode surface is discussed based on the results of surface analyses; secondary ion mass spectroscopy and soft and hard photoelectron spectroscopy.

To prepare the working electrode, 80 wt% Sn powder (<150 nm or 10 μm, Sigma-Aldrich Co., Ltd), 10 wt% sodium polyacrylate (PANa) and 10 wt% graphite were mixed with 10 vol% methanol aqueous solution, and the resultant slurry was pasted onto an Al foil. Na metal was used as the counter electrode and 1 mol dm^{-3} $NaPF_6$/EC:DEC:FEC (49:49:2 vol%) was used as the electrolyte. The charge/discharge measurements were carried out using coin-type cell with a sodiation/desodiation current density of 50/50 or 50/750 mA g^{-1}.

Nano-sized Sn delivers reversible capacity of ca. 600 mAh g^{-1} over 100 cycles at 50 mA g^{-1} (Fig. 1(a)). On the other hand, micro-sized Sn delivers reversible capacity of ca. 700 mAh g^{-1} for 10 cycles but it declines rapidly after 20 cycles as seen in Fig. 1(b). However, Figure 1(c) reveals that micro-sized Sn does demonstrate better capacity retention at a higher desodiation rate of 750 mA g^{-1}, which means it delivers ca. 600 mAh g^{-1} over 60 cycles. By comparing Figures 1(b) and 1(c), the desodiation plateau at 0.18 V disappears and that at 0.55 V shifts to 0.6 V. This means that the phase transition during desodiation depends on the current density, resulting in the different capacity retention. We will discuss the details of the difference between nano- and micro-sized Sn particles from surface analysis data.

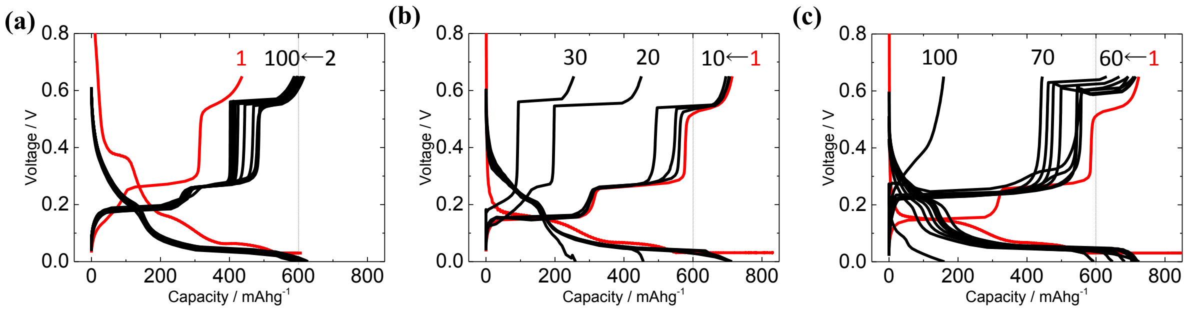


Fig. 1 Charge/discharge curves of Sn particle size of (a) φ150 nm at a desodiation current density of 50 mA g^{-1}, (b) φ10 μm at 50 mA g^{-1}, and (c) φ10 μm at 750 mA g^{-1} in Na cells.

[1] M. Dahbi, S. Komaba *et al.*, *Phys. Chem. Chem. Phys.*, **16**, 15007 (2014).
[2] M. Fukunishi, S. Komaba *et al.*, 2014 ECS / SMEQ Joint Meeting, Mexico, Abs. #94 (2014).

ORGANIC ELECTRODE MATERIALS, A NEW OPPORTUNITY FOR LOW COST AND SUSTAINABLE LITHIUM BATTERY ?

T.Gutel[a], A. Iordache[a], S.Solan[a], L.Picard[a], V.Maurel[b], S. Sadki[b], M. Bardet[b], L.Dubois[b]
[a] *CEA, LITEN, 17 rue des martyrs, 38054 Grenoble, France.*
[b] *CEA, INAC, 17 rue des martyrs, 38054 Grenoble, France.*

thibaut.gutel@cea.fr

Nowadays electrodes of lithium batteries are mainly constituted by inorganic compounds based on transition metals such as cobalt, nickel or manganese. Although their performances are satisfying, these materials present several important drawbacks. Indeed these compounds are expensive because they are prepared due to energy-consuming techniques from rare mineral precursors. Moreover, some metals are toxic and often hard to recycle. Eventually their reactivity leads to safety issues in abusive conditions.

Organic compounds such as nitroxide based polymers or quinones offer a cost-effective and environmental friendly alternative to conventional active materials for electrochemical storage.[1] Interestingly these products can be prepared from low cost precursors which can even come from biomass using classical organic and polymer chemistry techniques. Moreover these compounds are easy to recycle or reuse at their end of life. But until now, their use in electrodes is still challenging due to their high solubility in common electrolytes and their very low electronic conductivity.

On one hand, our work is focused on the synthesis and the grafting of nitroxide radical on a polymer backbone such as poly(2,2,6,6-tetramethyl-1-piperidinyloxy-4-ylmethacrylate) [PTMA] in order to develop organic radical battery (ORB) for high power application. But our team also develops new molecules such as thioquinone which are able to perform mutli-electron redox reaction leading to high specific capacity for high energy battery. On other hand, electrolyte compositions is also optimized in order to prevent the active materials from leaching into the solvent of electrolytes during cycling and our development of specific formulation allows us to implement these types of materials in electrodes of lithium batteries. Some impressive electrochemical performances have been obtained for high power but also high energy lithium battery.[2]

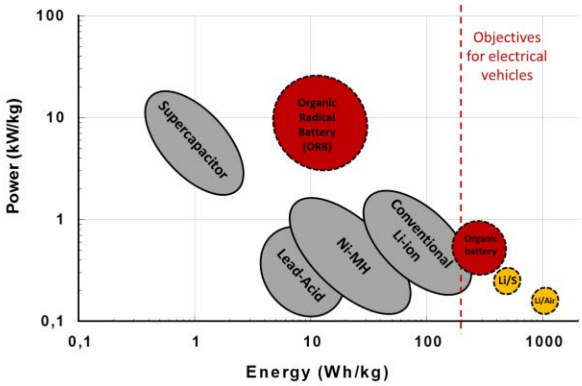


Fig1. Organic battery performances compared to conventional energy storage technologies

[1] P. Poizot *et al*, *Energy Environ. Sci.*, 4 (2011) 2003-2019 ; Y. Liang *et al.*, *Adv. Energy Mater.*, 2 (2012) 742-769
[2] Gutel *et al.*, Patent WO2013156899 (2012) ; Iordache *et al.*, *J. Power Sources*, 267 (2014) 553-559

Facile synthesis of Tin selenide (SnSe) nanoparticles on reduced graphene oxide (rGO) as promising anodes for Lithium-ion and Sodium-ion Batteries

Zhi Xiang Huang[a,b], Hui Ying Yang[a]
a. Pillar of Engineering Product Development, Singapore University of Technology and Design, 8 Somapah Road (S)487372, Singapore
b. Airbus Group Innovations, 110 Seletar Aerospace View (S)797562, Singapore
zhixiang.huang@airbus.com

Progress in technology requires the advancement of electrochemical energy storage to support a wide range of applications in different scales, from small portable electronics to electric vehicles and even large scale renewable energy harvesting. Recently, development of advanced lithium-ion batteries (LIB) have fueled the growth of hybrid and electric vehicles. Sodium-ion batteries (SIB) on the other hand has garnered renewed interest due its low cost and high abundance which is able to support grid scale energy storage. In these aspects, Sn-based anodes have been of great interest due to the high lithium storage capacity (Sn: 994 SnO: 875 SnS: 782 SnSe: 596 mAh/g).[1] Among these materials, there has only been a handful of reports on tin selenide (SnSe & $SnSe_2$). In 2011, Choi *et al* synthesized $SnSe_2$ nanoplates-graphene composites via colloidal approach for LIBs with reversible capacities of 640 mAh/g after 30 cycles.[2] Recently, Kim *et al* synthesized SnSe-C via ball milling for SIBs with high reversible capacities of 707 mAh/g after 50 cycles. [3] Herein, we present the synthesis of SnSe nanoparticles (NP) on rGO via facile hydrothermal reaction and annealing. This approach produces SnSe NP of 15-20 nm uniformly distributed on rGO (Fig 1a). When cycled as an anode in LIB, SnSe/rGO delivered 702, 592, 472, 376, and 311 mAh/g at current densities of 50, 200, 500, 800, and 1000 mA/g respectively (Fig 1b). After the increasing current density cycling, the electrode recovered 90% of its initial capacity when cycled at 50 mA/g. In terms of cycle life, SnSe/rGO delivered 545 mAh/g capacity after 150 stable charge-discharge cycles at 200 mA/g with 88% capacity retention. SIB cycling are in progress but preliminary results are promising. The morphology allows SnSe to be strongly anchored on rGO sheets which acts as a buffer to reduce volume changes during cycling and hence improve cycling stability. Furthermore, the small NP on rGO facilitate rapid lithium update and release hence improved rate cycling. Therefore, the improved cycling performance of SnSe/rGO will attract greater interest towards selenide based anode materials for both LIB and SIB applications.

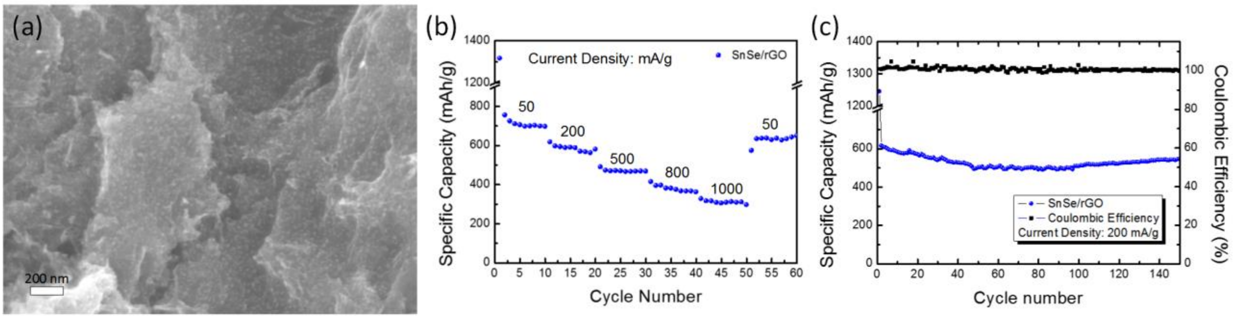


Fig 1 (a) SEM image of SnSe/rGO (b) Rate capability of SnSe/rGO (c) Cycling performance SnSe/rGO at current density of 200 mA/g and its corresponding coulombic efficiency

Reference to a journal publication:

[1] C. M. Park, J. H. Kim, H. Kim, H. J. Sohn, Chem. Soc. Rev. 39 (2010) 3115-3141.
[2] J. Choi, J. Jin, I. G. Jung, J. M. Kim, H. J. Kim, S. U. Son, Chem. Comm. 47(2011) 5241-5243.
[3] Y. Kim, Y. Kim, Y. Park, Y. N. Jo, Y. J. Kim, N. S. Choi, K. T. Lee, Chem. Comm. 51(2015) 50-53.

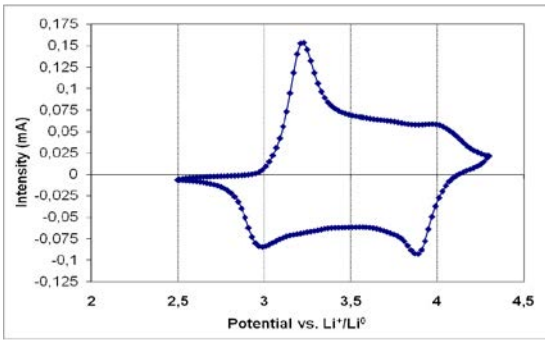
Properties of a lithium-doped state of polyaniline as an active material for lithium batteries

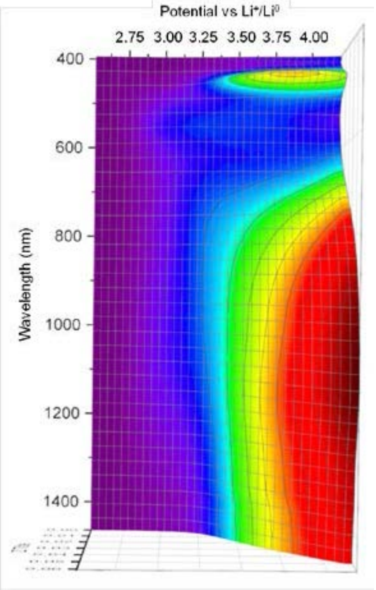
Pablo Jiménez[a], Bernard Lestriez[a], Eric Levillain[b], Olivier Aleveque[b], Dominique Guyomard[a] and Joël Gaubicher[a]
[a] *Institut des Matériaux Jean-Rouxel-(IMN), CNRS-UMR 6502, Université de Nantes – Campus Sciences 2 Rue de la Houssinière – 44322-Nantes-CEDEX-03 - France*
[b]*Laboratoire MOLTECH Anjou / UMR 6200 CNRS. Université d'Angers. 2, bd Lavoisier. 49045 ANGERS Cedex - FRANCE*

pablo.jimenez-manero@cnrs-imn.fr

Among the different types of organic compounds that have been tested as active materials for battery electrodes, conducting polymers offer the advantage of a low solubility and a high stability under repeated oxidation and reduction processes. Polyaniline (PANI) is known to be a robust and non expensive positive active material and it even had been incorporated as such in early commercial lithium-ion batteries [1]. Theoretical capacity of PANI in positive electrodes has always been assumed to be 143-145 mAh/g (related to mass of undoped PANI) corresponding to 1 electron per two aniline units in the polymer chain. This is because the second oxidation process in PANI (which would double the value of theoretical capacity) leads to an oxidation state of PANI (pernigraniline) of low stability towards degradation. So far the attempts to reach this second redox process involve the use of polyanions or special counteranions which reduce the practical specific capacity of PANI.

Here we present a chemically modified PANI which shows a higher capacity and a higher stability in a wider potential window than parent PANI. Our approach differs from that of the simple lithium salt doping of PANI, enabling the reversibility of the second redox process in PANI. Electrodes of this new Li-doped PANI with a low amount of carbon additive (5%) present a good rate capability and high reversible specific capacity (220 mAh/g_{PANI}) and energy density values (460 Wh/$kg_{electrode}$).





[1] Lan-Sheng, Y., Zhong-Qiang, S., Ye-Dong, L. (1991). *J. Power Sources*, *34*(2), 141-145; Nakajima, T., Kawagoe, T. 1989. *Synth. Met. 28*(1), 629-638.

[2] Jeon, J. W., Ma, Y., Mike, J. F., Shao, L., Balbuena, P. B., Lutkenhaus, J. L. (2013). *Phys. Chem. Chem. Phys.*, *15*(24), 9654-9662.

[3] European Patent n° EP14305254. P. Jimenez, J. Gaubicher, B. Lestriez, J.P. Bonnet, D. Guyomard.

Mixed Layered Cathode Material with Superior Performance for Application in Na-ion Batteries

Marlou Keller[a,b], Daniel Buchholz[a,b], Stefano Passerini[a,b]
[a] *Helmholtz Institute Ulm (HIU), Helmholtzstrasse 11, 89081 Ulm, Germany*
[b] *Karlsruhe Institute of Technology (KIT), P.O. Box 3640, 76021 Karlsruhe, Germany*

email address of the presenting author: marlou.keller@kit.edu

Sodium-ion batteries (SIBs) are considered as promising candidates for cost-efficient stationary energy storage systems. Sharing the working principle and design with the already commercialized lithium-ion battery facilitate their transfer into application. However, differences in cell chemistry request the investigation of new, high performance electrode materials.

In previous work, we have focused on the development and characterization of layered Na_xMO_2 (M= transition metal) materials[1–3]. The main target was to investigate abundant, low cost and environmentally friendly elements like iron (Fe), manganese (Mn) and magnesium (Mg) to replace the expensive and toxic cobalt (Co), thus underlining the philosophy of SIBs.

In this work, we present the synthesis and characterization of novel quaternary layered cathode materials of the type $Na_xMn_yNi_zFe_{0.1}Mg_{0.1}O_2$ ($0.67\leq x\leq 1.0$; $0.5\leq y\leq 0.7$; $0.1\leq z \leq 0.3$). By tuning the synthesis conditions, pure P2- and O3-type phases as well as a mixed P-/O-type material can be obtained as proven by X-ray diffraction (XRD) and scanning electron microscopy (SEM). All materials revealed good electrochemical performance but the mixed phase material, $Na_{0.76}Mn_{0.5}Ni_{0.3}Fe_{0.1}Mg_{0.1}O_2$, revealed extraordinary performance. The high average discharge potential (3.4 V vs Na/Na^+), high capacity (128 mAh g^{-1} at 0.1C) and extraordinary capacity retention (90.2 % after 600 cycles) in a narrow potential range (2.5-4.3 V), reveal its suitability for Na-ion cells using hard-carbon as negative electrode.

We propose that the superior performance is due to the co-existence of the O-type phase (enabling high (initial) specific capacities) and P-type phase (enabling improved high rate capability as well as high-voltage stability)[4]. Most important is that the synthesis was conducted under equilibrium conditions[5] resulting in the formation of P- & O-type phases, each in its most stable elemental composition.

Further investigations are needed to clarify and explain such outstanding electrochemical performance. In any case, the unexplored class of P-/O-type mixed phases introduces various new perspectives for the development of layered cathode materials and powerful Na-ion batteries.

[1] D. Buchholz, C. Vaalma, L.G. Chagas, S. Passerini, J. Power Sources. 282 (2015) 581–585.
[2] I. Hasa, D. Buchholz, S. Passerini, B. Scrosati, J. Hassoun, Adv. Energy Mater. 4 (2014) DOI 10.1002/aenm.201400083.
[3] I. Hasa, D. Buchholz, S. Passerini, J. Hassoun, ACS Appl. Mater. Interfaces. (2015).
[4] N. Yabuuchi, S. Komaba, Sci. Technol. Adv. Mater. 15 (2014) 043501.
[5] J.M. Paulsen, J.R. Dahn, Solid State Ion. 126 (1999) 3–24.

Structural, Electrochemical and Magnetic Properties of a Novel $KFeSO_4F$ Polymorph

Laura Lander[a,b], GwenaëlleRousse[a,b,c], Artem M. Abakumov[d], Moulay-TaharSougrati[e],
Gustaaf Van Tendeloo[d], Jean-Marie Tarascon[a,b,c]
[a]*Chimie du Solide et Energie, Collège de France, 11 Place Marcelin Berthelot, 75005 Paris, France*
[b]*Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, France*
[c]*Sorbonne Universités - UPMC Univ Paris 06, 4 Place Jussieu, 75005 Paris, France.*
[d]*EMAT, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium*
[e]*ICGM Institut Charles Gerhardt - Université Montpellier, Place Eugène Bataillon, 34095 Montpellier, France*

email address of the presenting author: laura.lander@college-de-france.fr

Since the discovery of the promising electrode material $LiFePO_4$, recent research has been focusing on the development of new iron-based polyanionic materials for next generations Li- and Na-ion batteries displaying better performances while still preserving cost and sustainability benefits.[1,2] On this quest, our group explored the wide family of sulfate-based compounds, where the most prominent members are monoclinic $Li_2Fe(SO_4)_2$ showing a potential of 3.83 V vs Li^+/Li^0 and $LiFeSO_4F$ crystallizing either in a *tavorite* or *triplite* crystal structure with the latter presenting a potential of 3.9 V vs Li^+/Li^0 .[3,4]

In order to further investigate the rich crystal chemistry offered by 3d-metal-basedfluorosulfates, we studied the effect of the replacement of Li by other alkali metals such as Na and K. One of the so discovered phases was $KFeSO_4F$, which crystallizes in the orthorhombic $Pna2_1$ space group and from which K^+ ions can be extracted in a complex electrochemical process.[5]

Knowing that sulfate-based compounds are prone to polymorphism, we recently unveiled a new low-temperature $KFeSO_4F$ polymorph.[6]Using combined synchrotron and neutron powder diffraction as well as electron diffraction, it was shown that the compound adopts a complex layered-like structure that crystallizes in a large monoclinic unit cell. Impedancemeasurements together with the Bond Valence Energy Landscape approachshow that the K^+ ions, which are located between the layers, are mobile within the structure and are electrochemically removed at an average potential of 3.7 V vs. Li^+/Li^0. Lastly, neutron diffraction experiments coupled with SQUID measurements reveal a long range antiferromagnetic ordering of the Fe^{2+} magnetic moments.These results confirm once more the richness of polymorphisms in sulfate-based materials and we hereby want to encourage the further exploration of their interesting electrochemical and physical properties.

[1] Padhi, A. K.; Nanjundaswamy, K. S.; Masquelier, C.; Goodenough, J. B. J. Electrochem. Soc.144 (1997)2581–2586.
[2] Masquelier, C.; Croguennec, L. Chem. Rev.113 (2013) 6552–6591.
[3] Reynaud, M.; Ati, M.; Melot, B. C.; Sougrati, M. T.; Rousse, G.; Chotard, J.-N.; Tarascon, J.-M. Electrochem. Commun.21 (2012) 77–80.
[4] Ati, M.; Melot, B. C.; Chotard, J.-N.; Rousse, G.; Reynaud, M.; Tarascon, J.-M. Electrochem. Commun.13 (2011) 1280–1283.
[5] Recham, N.; Rousse, G.; Sougrati, M. T.; Chotard, J.-N.; Frayret, C.; Sathiya, M.; Melot, B. C.; Jumas, J.-C.; Tarascon, J.-M. Chem. Mater.24 (2012)4363-4370.
[6] Lander, L.; Rousse, G.; Abakumov, A. M.; Sougrati, M.; van Tendeloo, G.; Tarascon, J.-M. J Mater Chem A(2015) Advanced Paper.

RECHARGEABLE LITHIUM METAL POLYMER (LMP) ORGANIC BATTERIES USING A COMMERCIAL POLYMER ELECTROLYTE

Margaud Lécuyer[a], Joël Gaubicher[b], Anne-Lise Barrès[b], Franck Dolhem[c,d], Marc Deschamps[a],
Dominique Guyomard[b], Philippe Poizot[b,e]

[a] *Blue Solutions, Odet, Ergué Gabéric, 29556 Quimper cedex 9, France*
[b] *Institut des Matériaux Jean Rouxel (IMN), UMR CNRS 6502, Université de Nantes, 2 rue de la Houssinière, B.P. 32229, 44322 Nantes cedex 3, France*
[c] *Laboratoire de Glycochimie, des Antimicrobiens et des Agroressources (LG2A), FRE CNRS 3517, Université de Picardie Jules Verne, 33 rue Saint-Leu, 80039 Amiens cedex, France*
[d] *Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, France*
[e] *Institut Universitaire de France (IUF), 103 bd Saint-Michel, 75005 Paris cedex 05, France*

Margaud.lecuyer@blue-solutions.fr

Bolloré group, through its branch BlueSolutions, invests in many electricity storage projects for diverse outlets. Most famous ones find applications in mobile solutions such as the well-known Bluecar® or electrified buses, visible for example in cities like Paris (Autolib), Bordeaux or Lyon and more recently Indianapolis. However, stationary applications are of prime importance, notably for the African market. Thus Bolloré group currently invests in countries such like Togo or Niger by developing railway lines that will be bordered by Bluezones. The latter consist in little cities (with school, free clinic center …) with autonomous energy supply thanks to the combination of solar PV with Lithium Metal Polymer (LMP) batteries. In this context, it urges to find innovative solutions to promote the stationary storage market. Whereas automotive applications require high volumetric energy densities, it is well known that low cost systems are required for stationary storage. Within this background, some organic electroactive compounds could be of significant interest due to their specific capacities, resource sustainability, environmental friendliness, structure diversity, and so on [1].

The presented work will focus on two different electroactive prototype compounds: tetramethoxy-*p*-benzoquinone (TMQ) as a representative of small (neutral) molecules and Indigo carmine as representative of redox-active organic salts. We have assessed these organic materials in place of $LiFePO_4$ in the composition of commercial LMP batteries by notably using a commercial dry polymer electrolyte. Interestingly, the as-obtained electrochemical behaviors depart from those already observed in regular carbonate-based liquid electrolytes. In particular, reversible two-plateau cycling curves were observed for indigo carmine that must be compared to a unique and sloping plateau measured in conventional liquid electrolytes as described by M. Yao and co-workers [2].

Moreover, very promising results were obtained with TMQ [3]. Basically, when carbonate-based electrolytes are used, this quinone exhibits quite poor electrochemical features such as a very limited depth of discharge (~50% of the theoretical capacity in the first cycle). Under LMP classical cycling conditions (100°C as operating temperature), TMQ reacts according to its theoretical two-electron process. With no optimization, the restored capacity represents 80% of the theoretical value (190 mAh/g) after 20 cycles operated at a C rate.

[1] P. Poizot, F. Dolhem, Energy Environ. Sci. 4 (2011) 2003–2019.
[2] M. Yao, M. Araki, H. Senoh, S.-i. Yamazaki, T. Sakai, K. Yasuda, Chem. Lett. 39 (2010) 950–952; M. Yao, K. Kuratani, T. Kojima, N. Takeichi, H. Senoh, T. Kiyobayashi, Sci. Rep. 4 (2014) 3650.
[3] M. Lécuyer, J. Gaubicher, A.-L. Barrès, F. Dolhem, M. Deschamps, D. Guyomard, P. Poizot, Electrochem. Comm. 55 (2015) 22–25.

A Li_2MnSiO_4@rGO composite with enhanced electrochemical performance as cathode material for lithium-ion batteries

Yujie Li*, Shuangke Liu, Chunman Zheng
College of Aerospace Science and Engineering, National University of Defense Technology, Changsha, 410073, China.

email address of the corresponding author: powerlyj@163.com

.Li_2MnSiO_4 cathode material has a high theoretical capacity of 332 mA h g^{-1}, much higher than commercial $LiCoO_2$ cathode[1].However, the low practical discharge capacities due to the low electric and ionic conductivities and rapid capacity fading due to the structural instability and manganese dissolution during cycles greatly hinder its development. Great efforts have been paid to improve its eletrochemical performance, including particle size tailoring, carbon coating, and ionic doping[2,3]. Recently, graphene has been used in Li_2MnSiO_4 cathode as conductive agent and showed enhanced electrochemical properties[4].

Herein, we designed a Li_2MnSiO_4@rGO composite with ultra-fine nanoparticles as a cathode material for lithium ion batteries. The ultra-fine SiO_2 nanoparticles were first anchered into the graphene oxide sheet via a stober methode, then Li, Mn salts and carbon precursors were added and milled finely, finally the mixture were sintered under Ar protection to obtain the Li_2MnSiO_4@rGO composite. The Li_2MnSiO_4 particles can be easily controlled by tailoring the SiO_2 particles that anchored on the graphene oxide, thus we could obtain the ultra-fine Li_2MnSiO_4 particle with diameter ~40 nm anchored graphene sheet composite. The ultra-fine Li_2MnSiO_4 nanoparticle and graphene protection could effectively improve its electrochemical reaction kinetics and structural stability.The Li_2MnSiO_4@rGO composite delivers a high discharge capacity of 175 $mAhg^{-1}$ and keeps a high capacity retention of 85.7% after 25 cycles at a current density of 10 mA g^{-1}.

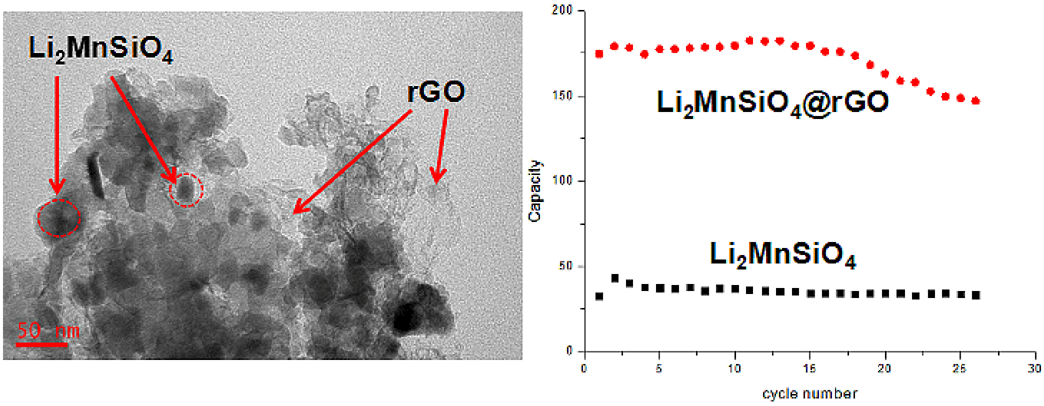


Fig.1 The TEM image and cycling performance of the Li_2MnSiO_4@rGO composite

Reference to a journal publication:
[1]A. Nyten, A. Abouimrane, M. Armand, T. Gustafsson, J.O. Thomas, Electrochem.Commun. 7 (2005) 156-160.
[2]S. Liu, J.Xu, D. Li, Y. Hu, X. Liu, K. Xie.Journal of Power Sources 232 (2013) 258-263
[3]Y.X. Li, Z.L. Gong, Y. Yang, J. Power Sources 174 (2007) 528-532.
[4]Z. Hu, K. Zhang, H. Gao, W. Duan, F. Cheng, J.Liang, J. Chen.J. Mater. Chem. A, 2013, 1, 12650

VANADIUM OXIDE AEROGEL - A FLEXIBLE MATERIAL FOR Li- AND Na-BATTERies

Arianna Moretti[a, b], Stefano Passerini[a,b]
[a]*Helmholtz Institute Ulm (HIU), Electrochemistry I, Helmholtzstrasse 11, 89081 Ulm, Germany;* [b] *Karlsruhe Institute of Technology (KIT), P.O. Box 3640, 76021 Karlsruhe, Germany*

arianna.moretti@kit.edu

There is a renewed interest on energy storage systems alternative to lithium-ion batteries. One of the main research stream, pushed by costs and safety benefits, regards the improvement of room temperature sodium-ion batteries for stationary applications. In this contest, taking advantage of the solid knowledge acquired over the years on Li-based systems, sensible efforts are ongoing to develop suitable electrode materials with high Na storage capability and satisfactory electrochemical performance. Among the others, vanadium oxides are particularly interesting due to the rich electrochemistry derived by various accessible oxidation states. Our interest is mainly focused on V_2O_5 layered amorphous compounds which demonstrated to reversibly host and release several cationic species [1]. Herein we present a V_2O_5 aerogel obtained via supercritical CO_2 extraction and its use as electrode material for lithium and sodium batteries. The aerogel is able to insert up to 2.3 eq. of Li^+ (that correspond to 340 $mAhg^{-1}$) and about 1 eq. of Na^+ (150 $mAhg^{-1}$) showing, in both cases, promising rate capabilities (Figure 1) [2]. The aerogel is additionally exploited as negative electrode for sodium-ion batteries possessing propitious electrochemical performance also in full cell configuration [3]. The use of ionic liquids based electrolytes in combination with the aerogel is also proposed. This overview of our recent findings highlights the versatility of V_2O_5 aerogel as one of the few "multipurpose" electrode materials suitable to be employed in different cell chemistries without major structural or chemical modifications.

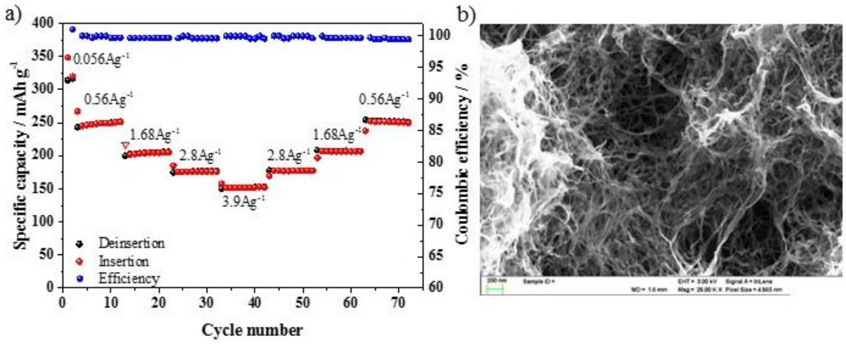


Figure 1. a) Electrochemical performance of V_2O_5 aerogel vs Lithium. b) Entangled ribbon network of V_2O_5 aerogel [2]

References:

[1] P.E. Tang, J.S. Sakamoto, E. Baudrin, B. Dunn, Journal of Non-Crystalline Solids, 350 (2004) 67-72
[2] A. Moretti, F. Maroni, I. Osada, F. Nobili, S. Passerini, ChemElectroChem, 2 (2015) 529-537
[3] A. Moretti, M. Secchiaroli, D. Buchholz, G. Giuli, R. Marassi, S. Passerini, Journal of the Electrochemical Society, 162 (2015) A1-A6

Acknowledgements:

This work was supported by BMBF within the project "MEET Hi-END - Materialien und Komponenten für Batterien mit hoher Energiedichte" (Förderkennzeichen: 03X4634A).

Disordered carbonaceous materials as high performance anode for Na-Ion Battery

B. Orayech and D. Saurel

CIC EnergiGUNE, Parque Tecnológico, C/Albert Einstein 48, 01510 Miñano, Spain
borayech@cicenergigune.com

Though Li-ion batteries (LIBs) have encountered enormous success, lithium extraction is expensive and most lithium reserves are found in geopolitically unstable regions of the world. Therefore interest has recently grown to look for alternatives to LIBs, such as Na/ion batteries (SIBs), which represent promising alternatives mainly due to the advantages of abundance of Na in the earth crust and the possibility to use aluminum current collector for the negative electrode.[1]

Although several candidate positive electrode materials have been reported to date for SIB, a limited amount of negative anode candidate have been encountered with low intercalation voltage, high first cycle coulombic efficiency and good cycle stability.[2,3] Graphite is considered as the standard LIB anode due to its cheap and easy production, its high reversibility and relatively good energy density due to its low insertion potential of about 100mV. However, due to the 0.3V difference between Na and Li, insertion of Na^+ into graphite would occur at negative voltages vs Na, prohibiting its use for SIB. Only disordered soft- and hard- carbon offer significant insertion above Na plating voltage, with the best reports in hard carbons with more than 300mAh/g. [4,5] Based on the use of SAXS it has been demonstrated by Stevens and Dahn that the mechanism of hard carbon is related to the presence of microporosity,[6] although Bommier et al recently demonstrated that microporosity probed by gas adsorption is detrimental to the performance of hard carbons.[4]

Herein, we will present and discuss our recent progress and perspective in the study of disordered carbons as negative electrodes for SIB. Various disordered carbonaceous materials have been explored, non-graphitic carbon or hard- carbons (HC) as well as soft carbons (SC). These highly disordered carbons do not contain long-range ordered “ABAB” stacking that is seen in graphite but comprise turbostratic structures with defects and structural voids, which enable them with good performance for Na-ion storage.

The microstructure and the morphology of these carbons have been studied by coupling gas adsorption, powder X-ray diffraction (in-situ and ex-situ PXRD) and Small Angle X-ray Scattering (SAXS) measurements, which, by correlating with their electrochemical performance, had led us to new insights into the mechanism of sodium insertion into disordered SC and HC and identifying key-microstructural features to be considered for best electrochemical performance.

[1] M. D. Slater et al. Adv. Funct. Mater. 2013, 23, 947-958.
[2] M. Schroeder et al. J. Power Sources, 2014, 266, 15, 250–258.
[3] S. Komaba et al. Adv. Funct. Mater. 2011, 21, 3859–3867.
[4] C. Bommier et al. Nano Lett., 2015, 15 (9), 5888–5892.
[5] A. Ponrouch et al. Electrochemistry Comm., 2015, 54, 51–54.
[6] D. A. Stevens and J. R. Dahn, J. Electrochem. Soc. 2001, 148, A803-A811.

REDOX BEHAVIORS OF P AND N TYPE COMPOUNDS AS NEGATIVE ELECTRODE MATERIALS FOR SODIUM AQUEOUS BATTERIES

Sofia Perticarari[a], Pablo Jimenez[a], Antonia Kotronia[a], Fabrice Odobel[b], Yann Pellegrin[b],

Errol Blart[b], Dominique Guyomard[a], Philippe Poizot[a] and Joel Gaubicher[a]

[a] *Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, 2 rue de la Houssini_ere, BP32229, 44322 Nantes Cedex 3, France.*

[b] *CEISAM, Chimie et Interdisciplinarité, Synthèse, Analyse, Modélisation, Faculté des Sciences et des Techniques, Université de Nantes, 2, rue de la Houssinière, BP 92208, 44322 NANTES Cedex 3 (France)*

sofia.perticarari@cnrs-imn.fr

The increasing importance of renewable energy sources like sunlight and wind power connected to the electrical grid has trigged the necessity of low cost energy storage systems. In this context, sodium aqueous electrolyte ion-batteries constitute a new promising technology, which reduces the cost, risk and environmental impact compared to other battery technologies. Today, the performances of these batteries are limited however, by low capacity negative electrodes. To address this issue, the electrochemical and physical behavior of several n and p type derivatives have been investigated in neutral Li, Na, K and Mg aqueous supporting electrolytes. The long term cyclability of diimide compounds involves close to one electron leading to high capacity values (approx. 90-100 mAh/g) at low voltage. Very interestingly, electrochemical activity shows singular features that unraveled a solid state disproportional mechanism favors by the unstability of the radical anion. Conversely, the extent of this reaction can be modulated according to the polarisability of the counter cation or the extent of the conjugated backbone. Results also enable to rationalize the capacity retention and the self discharge mechanisms of these materials based on both morphological and side reaction considerations. Our work also relates to soluble n type derivatives. Thanks to pi-staking interactions on a carbon based electrode such materials can be reversibly cycled in the adsorbed state at low potential. The electrochemical behavior as well as the long term stability on cycling will be presented.

DILITHIUM BENZENEDIPROPIOLATE: A SUPER-LITHIATED ORGANIC ELECTRODE MATERIAL

Stéven Renault[a], Viorica Alina Oltean[a], C. Moyses Araujo[b], Anton Grigoriev[b], Kristina Edström[a], Daniel Brandell[a]

[a] *Department of Chemistry - Ångström Laboratory, Uppsala University, Box 538, 751 21 Uppsala, Sweden*

[b] *Condensed Matter Theory Group, Department of Physics and Astronomy, Uppsala University, Box 516, 751 21 Uppsala, Sweden*

steven.renault@kemi.uu.se

Organic electrode materials (OEMs) for lithium-ion batteries (LIBs) constitute a very promising alternative to standard electrodes materials that are prepared from finite and non-renewable minerals resources, but instead being potentially environmental friendly, cheap, and abundant if derived from biomass via ecofriendly processes. However, their commercial use is currently held back due to primarily their poor energy density. High specific capacity OEMs are therefore of high scientific interest. During the last 3 years, OEMs with the ability of an unexpected reversible reduction of carbon-carbon double bonds have sporadically been reported [1]. As a consequence of this redox process – here coined 'superlithiation' – specific energy several times higher than commercial standards (graphite) and Li/C ratios of 1/1 have been reported.

A to-date never reported OEM, dilithium benzenedipropiolate, is here presented [2]. In addition to the expected reduction of its carbonyls, this material can reversibly reduce its unsaturated carbon-carbon bonds leading to a Li/C ratio of 1/1 and specific capacity as high as 1363 mAh g^{-1}: the highest ever reported for a lithium carboxylate. Density functional theory calculations suggest that the lithiation is preferential on the propiolate carbons. Due to that the sp hybridized carbons in this material are reacting according to the 'super-lithiation' mechanism, a path for design of OEMs able of Li/C ratios as high as 2/1 has been opened up.

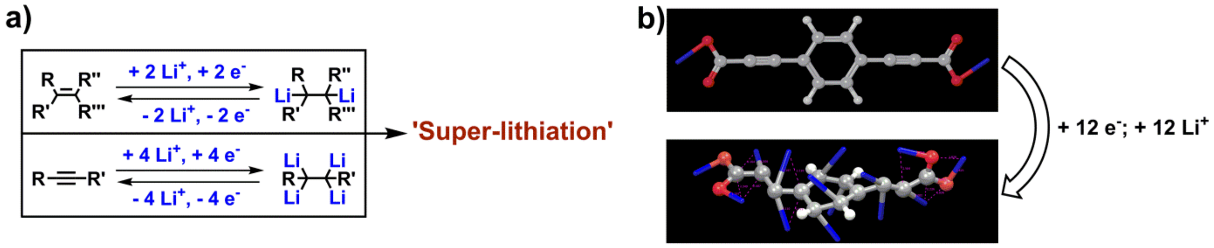


Fig. 1 a) 'Superlithiation' mechanism. b) Proposed lithium insertion mechanism in dilithium benzenedipropiolate.

[1] a) X. Han, G. Qing, J. Sun, T. Sun, Angew. Chem. Int. Ed., 51 (2012), 5147. b) W. Luo, M. Allen, V. Raju, X. Ji, Adv. Energy Mater., 4 (2014), 1400554. c) J. Wu, X. Rui, C. Wang, W.-B. Pei, R. Lau, Q. Yan, Q. Zhang, Adv. Enegy Mater., 5 (2015), 1402189. d) J. Wu, X. Rui, G. Long, W. Chen, Q. Yan, Q. Zhang, Angew. Chem. Int. Ed., 54 (2015), 7354.

[2] S. Renault, V.A. Oltean, C.M. Araujo, A. Grigoriev, K. Edström, D. Brandell, submitted.

STRUCTURE AND ELECTROCHEMISTRY OF $Na_{1+y}VPO_4F_{1+y}$ ($0 \leq y \leq 0.5$) FOR Na- AND Li-ION BATTERIES

Daria O. Rezepova[a], Arseny B. Sloboduyk[b], Nina V. Kosova[a]
[a]*Institute of Solid State Chemistry and Mechanochemistry SB RAS, 18 Kutateladze, 630128 Novosibirsk, Russia*
[b]*Institute of Chemistry, FEB RAS, 159 pr. Stoletiya Vladivostoka, 690022 Vladisvostok, Russia*

E-mail: rezepova_do@yahoo.com

$NaVPO_4F$ and $Na_3V_2(PO_4)_2F_3$ are interested for both sodium- and lithium-ion batteries application due to their ability to reversibly intercalate Na^+ and Li^+ ions in their structure [1-4]. $NaVPO_4F$, first proposed by Barker *et al.* [1], crystallizes in the tetragonal symmetry with the *I*4/*mmm* S.G. Meins *et al.* reported that $Na_3V_2(PO_4)_2F_3$ also exhibits the tetragonal symmetry with the $P4_2/mnm$ S.G. [2]. Barker *et al.* investigated its electrochemical properties [3]. Recently, Bianchini *el al.* using synchrotron radiation have identified $Na_3V_2(PO_4)_2F_3$ in another, orthorhombic structure with the *Amam* S.G. [4]. The structural and electrochemical behavior similarity of these two compounds allows one to assume that they belong to one and the same phase with some deviation from the stoichiometry.

In this study, a series of $Na_{1+y}VPO_4F_{1+y}$ ($0 \leq y \leq 0.5$) compositions was investigated in detail to establish structural similarity and distinctive features between $NaVPO_4F$ and $Na_3V_2(PO_4)_2F_3$ (or $Na_{1.5}VPO_4F_{1.5}$). $Na_{1+y}VPO_4F_{1+y}$ were prepared by mechanochemically assisted solid state synthesis. Composition, structure, morphology and electrochemistry of the materials were analyzed by XRD, SEM, EDX, FTIR, ^{23}Na and ^{31}P NMR spectroscopy, and galvanostatic cycling in Na^+ and Li^+ cells.

XRD analysis showed that the as-prepared products are well-crystallized single-phase materials. The Rietveld refinement using TOPAS software and two models $P4_2/mnm$ and *Amam* revealed that the experimental data are better described with the orthorhombic *Amam* S.G. ^{23}Na and ^{31}P NMR spectra of $Na_{1+y}VPO_4F_{1+y}$ are very similar to each other. The ^{23}Na NMR spectra exhibit resonance at 170-180 ppm, while ^{31}P spectra exhibit two intense resonances at ~6700 and 5000 ppm in addition to a series of weaker resonances at lower frequencies. The presence of antisite defects has been proposed in $Na_{1+y}VPO_4F_{1+y}$. The smallest structural disorder and the best electrochemical performance was observed for the sample with y=0.25 both in Na^+ and Li^+ cells. Voltage profile of charge-discharge curves was similar for all the samples. *Ex situ* XRD and EDX studies were carried out to control the phase transformations and Na^+/Li^+ ion exchange upon cycling of $Na_{1+y}VPO_4F_{1+y}$ in Li cells.

[1] J. Barker, M.Y. Saidi, J.L. Swoyer, Electrochem. Solid-State Lett. 6 (2003) A1-A4.
[2] J.M. Le Meins, M.P. Crosnier-Lopez, A. Hemon-Ribaud, G. Courbion, J. Solid State Chem. 148 (1999) 260-277.
[3] J. Barker, R.K.B. Gover, P. Burns, A.J. Bryan, Electrochem. Solid-State Letters 9 (2006) A190 - A192.
[4] M. Bianchini, N. Brisset, F. Fauth, F. Weill, E. Elkaim, E. Suard, C. Masquelier, L. Croguennec. Chem. Mater. 26 (2014) 4238-4247.

Li_2S particle size influence on the first charge working mechanism of Li_2S-based Li-ion batteries

Alice Robba[a,b], Renaud Bouchet[a,c], Céline Barchasz[b], Jean-François Colin[b], Fannie Alloin[a,c]
[a] *Université Grenoble Alpes, LEPMI, F-38000 Grenoble, France.*
[b] *CEA, LITEN, 17 rue des Martyrs, 38054 Grenoble, France.*
[c] *CNRS, LEPMI, F-38000 Grenoble, France.*

email address of the presenting author: alice.robba@lepmi.grenoble-inp.fr

With their high theoretical energy density (~2600 $Wh.kg^{-1}$), lithium/sulfur (Li/S) batteries are highly promising, but these systems are still poorly understood due to the complex mechanisms/equilibria involved. Replacing S_8 by Li_2S as the active material allows the use of safer negative electrode, like silicon, instead of lithium metal. S_8 and Li_2S have different conductivity and solubility properties, resulting in a profoundly changed activation process during the first cycle. Particularly, during the first charge a high polarization and a lack of reproducibility between tests are observed [1] (Figure 1a). Differences observed between raw Li_2S material (micron-sized) and that electrochemically produced in a battery (nano-sized) may indicate that the electrochemical process depends on the particle size [2].

Then the major focus of the presented work is to deepen the understanding of the Li_2S material charge mechanism, and more precisely to characterize the effect of the initial Li_2S particle size. To do so, Li_2S nanoparticles were synthetized according to two ways: a liquid path synthesis [3] and a dissolution in ethanol, allowing Li_2S nanoparticles/carbon composites to be made [4]. Electrochemical tests show that starting with Li_2S nanoparticles could effectively suppress the high initial polarization (Figure 1b). Then X-Ray Diffraction (XRD) and Electrochemical Impedance Spectroscopy both applied *via* an *operando* mode will be presented in order to interpret this observation.

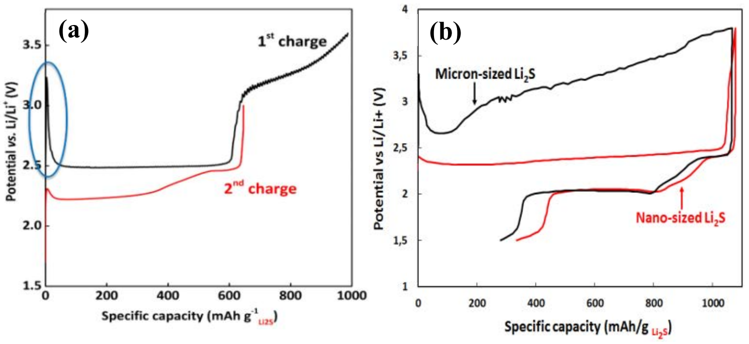


Figure 1: *(a) Typical voltage profiles of two first charges of a Li_2S-based cell* [1] *and (b) comparison of voltage profiles between micro and nano-sized Li_2S particles-based cell.*

[1] S. Waluś, C. Barchasz, R. Bouchet, J.-F. Martin, J.-C. Leprêtre, and F. Alloin, *Electrochim. Acta* 180 (2015) 178–186.
[2] S. Waluś, C. Barchasz, R. Bouchet, J.-C. Leprêtre, J.-F. Colin, J.-F. Martin, E. Elkaïm, C. Baehtz, and F. Alloin, *Adv. Energy Mater.* (2015).
[3] G. J.A, K. Wong, and S. Jick, *J.C.S Chem. Comm* (1978) 6–7.
[4] F. Wu, H. Kim, A. Magasinski, J. T. Lee, H.-T. Lin, and G. Yushin, *Adv. Energy Mater.* 4 (2014).

LITHIUM IRON METHYLENE DIPHOSPHONATE, A NEW ORGANIC-INORGANIC HYBRID MATERIAL FOR LI-ION BATTERIES.

Sébastien Sallard[a], Sebastian Schmidt[a], Denis Sheptyakov[b], Petr Novák[a], Claire Villevieille[a]
[a]Electrochemistry Laboratory, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland
[b]Laboratory for Neutron Scattering and Imaging, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland
sebastien.sallard@psi.ch

The research on positive electrode materials for Li-ion batteries has generally been focused on inorganic compounds. Introducing an organic component into the inorganic framework would open various new synthetic possibilities and might allow to adjust the electrochemical properties of the metal ions by the influence of neighboring organic groups. $[Fe(III)(OH)_{0.8}F_{0.2}(bdc)]\cdot H_2O$ is the first hybrid organic-inorganic materials reported to be active in positive electrode for Li-ion batteries,[1] and so far only few more examples of such electroactive hybrid materials are known in the literature.

To introduce a new class of organic-inorganic hybrid materials for Li-ion batteries with versatile organic parts, we chose to investigate transition metal diphosphonates. The material lithium iron methylene diphosphonate (LFMD) was selected as reference material as proof of concept for hybrid materials for positive electrode in Li-ion batteries. LFMD was synthesized by a simple hydrothermal route, yielding a material with a new crystalline phase. In a half-cell configuration, it exhibits a specific charge of 90 mAh/g upon lithiation, which remains stable for more than 100 cycles (Figure 1). The specific charge even continuously increases after 60 cycles to reach a value of 118 mAh/g after 160 cycles. The large irreversibility of the first and the second cycle with a different potential profile is assumed to originate from the removal of residual H^+ in the structure upon delithiation, leading to enhanced electrolyte decomposition. The consecutive delithiation steps do not any longer show this feature, thereby increasing the coulombic efficiency drastically from very low in the first cycle (~ 40%) to a more reasonable value (> 90%) after 10 cycles, reaching a stable value of 97% after 50 cycles. *Operando* XANES confirmed the oxidation and reduction of iron during the cycling.

The results obtained provide a basis for investigations on the influence of different heteroatoms or organic entities substituted to the diphosphonate on the electrochemistry of the hybrid material, which is the focus of our future research.

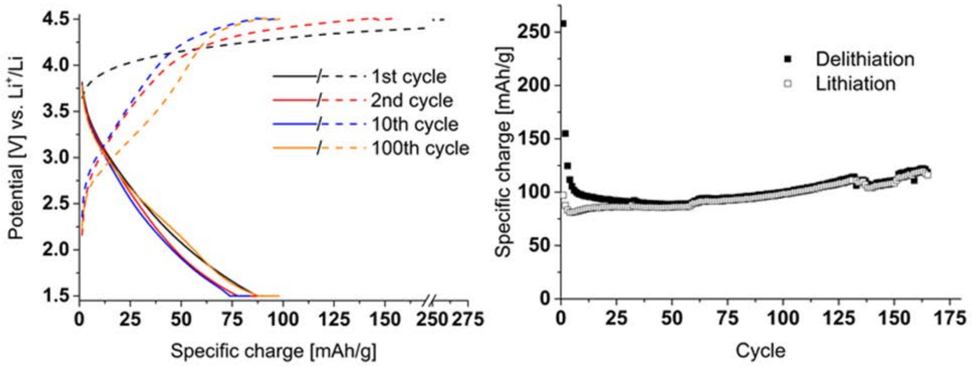


Figure 1 left: Galvanostatic profile of LFMD cycled in a half-cell configuration. After each half-cycle, a 1 h potentiostatic step was implemented. **Right:** The corresponding evolution of the specific charge during cycling of LFMD.

[1] G. Férey, F. Millange, M. Morcrette, C. Serre, M.-L. Doublet, J.-M. Grenèche, J.-M. Tarascon, J.-M. Angew. Chem. Int. Ed. 46 (2007) 3259-3263.

New insights into the kinetics of Na insertion and extraction into the $FePO_4/NaFePO_4$ system

D. Saurel [a], H. Anne [a], M. Galcerán Mestres [a], B. Acebedo [a], M. Lepoitevin [a], T. Rojo [a,b] and M. Casas Cabanas [a]

[a] *CIC Energigune - Parque Tecnológico, C/Albert Einstein 48, 01510 Miñano, Spain*
[b] *Departamento de Química Inorgánica, Facultad de Ciencia y Tecnología, Universidad del País Vasco, 48080 Bilbao, Spain*

dsaurel@cicenergigune.com

Sodium-ion batteries (SIB), which were studied in parallel to Li-ion batteries (LIB) in the early days of the research on insertion secondary batteries, are subject to a renewed interest in recent years as a potential lower cost alternative to LIB [1]. Similarly to LIB, in SIB Na^+ ions are shuttled between the positive and negative electrodes during charging and discharging, with an electrolyte acting as the transportation medium for those ions. Fundamental differences related to phase stability, volume expansion, ionic diffusivity or voltage between the insertion of lithium versus insertion of sodium in the same host compound have been observed in several materials, resulting in successive phase transitions that are less common in the lithium counterparts [2].

A material that well illustrates these differences is olivine $NaFePO_4$. This (meta)stable material under normal operation conditions can reversibly insert/extract Na ions with a theoretical capacity of 154 mAh/g at an average voltage of 2.9V [3]. This material presents intriguing differences with its Li-ion counterpart. Indeed, contrary to $LiFePO_4$ which presents a reversible biphasic transformation [4-5], distinct phase transformation mechanisms are observed during Na insertion and extraction into $NaFePO_4$ [6-8]. Moreover, the cell polarization is significantly higher in the case of sodium which suggests a less favourable kinetics of Na diffusion compared to Li, confirmed by larger diffusion coefficient for lithium as deduced from impedance spectroscopy performed at $x=0.9$ [9]. However, to our knowledge the diffusion coefficient remains unknown for intermediate sodium compositions. Furthermore, a discrepancy is observed in the theoretical predictions of activation energy of ionic diffusion in the end members,[10-11] while to our knowledge no experimental value has been yet reported.

Using ex-situ and in operando X-ray diffraction, galvanostatic intermittent titration technique and electrochemical impedance spectroscopy we have been able to follow the kinetics of phase transformation and ion/vacancies diffusion during charge and discharge and contrast the differences between the two types of ions inserting and extracting into/from the same host structure.

References:

[1] Palomares et al., Energy Environ. Sci. 5, 5884 (2012); Yabuuchi et al., Chem. Rev. 114, 11636 (2014)
[2] Ma et al., J. Electrochem. Soc. 158, A1307 (2011) Berthelot et al., Nature Materials 10, 74 (2011)
[3] Moreau et al., Chem. Mater. 22, 4126 (2010)
[4] Padhi et al., J. Electrochem. Soc. 144, 1188 (1997)
[5] Malik et al., J. Electrochem Soc., 160 (5), A3179-A3197, (2013)
[6] Casas-Cabanas et al., J. Mater. Chem. 22, 17421 (2012)
[7] Galceran et al., Phys. Chem. Chem. Phys., 16, 8837-8842, (2014)
[8] Gaubicher et al., Electrochem. Comm., 38, 104-106, (2014)
[9] Zhu et al., Nanoscale, 5, 780, (2013)
[10] Tripathi et al., Energy Environ. Sci, 6, 2257 (2013)
[11] Ong et al., Energy Environ. Sci., 4, 3680 (2011)

EXPLORATION OF NEW BORATE BASED CATHODE MATERIALS FOR LITHIUM- AND SODIUM ION BATTERIES

Florian Strauss[a,b,c], Gwenaëlle Rousse[a,c,f], Mohamed Ben Hassine[d],Mingxue Tang[e,f], Hervé Vezin[e,f], Daniel Dalla Corte[a,f], Robert Dominko[b,c], Jean-Marie Tarascon[a,c,f]

[a]Collège de France, "Chimie du Solide et Energie", 11 Place Marcelin Berthelot, 75005 Paris, France
[b]National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia
[c]ALISTORE - EuropeanResearch Institute, FR CNRS 3104, 80039 Amiens, France
[d]Laboratoire SPMS, École centrale paris, Grande voie des Vignes 92295 CHATENAY-MALABRY, France
[e]Université Lille Nord de France, CNRS, UMR 8516—LASIR, F-59655 Villeneuve d'Ascq, France
[f]Reseau sur le Stockage Electrochimique de l'Energie (RS2E),33 rue Saint Leu, 80039 Amiens, France
email address of the presenting author: florian.strauss@ki.si

In the search for new polyanionic cathode materials for Li- and Na-ion batteries, borate based materials could lead to increased capacities since the borate anionBO_3^{3-}presents the lightest group among all polyanions. However, so far only materials consisting of an *ortho* borate BO_3^{3-}polyanionic framework have been considered as potential positive electrode materials.[1,2]Becausethe borate BO_3^{3-} group has a weak inductive effect on the transition metal, the redox voltage is rather low compared to other common polyanionic cathode materialslike $LiFePO_4$or$LiFeSO_4F$.[2]
One strategy to increase the redox potential versus lithium or even sodium for a polyanionic material, containing the same transition metal, has been shown for $LiFePO_4$ and its counterpart $Li_2FeP_2O_7$. Replacing the *ortho*-phosphate PO_4^{3-} by a *di*- or *pyro*- phosphate group $P_2O_7^{4-}$which is more electron withdrawing,leadingto anelevated redox potential.[3]
So to combine the advantage of the light weight of borate groups and simultaneously increasethe redox potential of the transition metal, our approach is to apply this strategy of using condensed polyanionic groups, for instance moving from borate BO_3^{3-} to pyroborate $B_2O_5^{4-}$ or pentaborate$B_5O_{10}^{5-}$.
In this context we prepared a lithium copper pyrobrate$Li_6CuB_4O_{10}$ using ceramic synthesis and investigated its electrochemical and structural properties by a variety of in situ and ex situ XRD as well as galvanostatic electrochemical methods combined with TEM and EPR spectroscopy.This material shows a 4.0 V redox potential versus lithium and ana.c. conductivity around $10^{-2.5}$S/cm at temperatures higher than 300°C, determined by temperature controlled impedance measurements.
To further probe the electrochemical activity of new polyborate based materials, we successfully prepared a new group of sodium transition metal pentaborates $Na_3MB_5O_{10}$ (M = Mn, Fe, Co) by a ceramic process. Wesolved their crystal structure using synchrotron diffractionand characterized these materials in terms of magnetism, optical and electronic properties since their electrochemical activity versus sodium was rather small.
Finally we studiedthe reversible conversion reaction, of a bismuth oxyborate$Bi_4B_2O_9$ versus Li/ Na potential application as a high energy density cathode material. This material show amoderate capacity even at elevated C-rates and a good capacity retention rates (150 mAh/g at 1C over 20 cycles) with a small polarization (0.4 V). We studied the conversion mechanismand influence of different parameters like electrolyte, carbon content and milling time on the electrochemical behavior.

[1] V. Legagneur, Y. An, A. Mosbah, R. Portal, A. Le Gal La Salle, A. Verbaere, D. Guyomard, Y. Piffard, Solid State Ionics 139 (2001) 37-46.
[2] A. Yamada, N. Iwane, Y. Harada, S. Nishimura. Y. Koyama, I. Tanaka, Adv. Mater. 22 (2010) 3583-3587.
[3] S. Nishimura, M. Nakamura, R. Natsui, A. Yamada, J. Am. Chem. Soc. 132 (2010) 13596-13597.

SODIUM PYROPHOSPHATE CATHODE MATERIAL $Na_2FeP_2O_7$ FOR Na- AND Li-ION BATTERIES

Anna M. Tsapina[a,b], Arseny B. Slobodyuk[c], Sergei A. Petrov[b], Nina V. Kosova[b]
[a] *Novosibirsk State University, 2 Pirogova, 630090 Novosibirsk, Russia*
[b] *Institute of Solid State Chemistry and Mechanochemistry, 18 Kutateladze, 630128 Novosibirsk, Russia*
[c] *Institute of Chemistry FEB RAS, 159 pr. Stoletiya Vladivostoka, 690022 Vladivostok, Russia*

E-mail: tsapina.a.m@gmail.com

Sodium-based insertion materials are interested for low-cost and large-scale Na- and Li-ion batteries. In 2012, Yamada *et al.* [1] proposed a new polyanion-based $Na_2FeP_2O_7$ cathode material. The $Na_2FeP_2O_7$ pyrophosphate has a theoretical capacity of 97 mAh/g, high operating voltage (3.0 V vs. Na/Na^+), three-dimensional channels for Na^+ diffusion and good thermal stability. Adopting a triclinic symmetry (S.G. *P*-1), the crystal structure of $Na_2FeP_2O_7$ consists of the corner-sharing FeO_6 octahedra and the bridging pyrophosphate groups P_2O_7, thereby creating large tunnels along [100], [-110] and [01-1] directions for facile and fast Na^+ ion migration [1].

In the present study, we prepared $Na_2FeP_2O_7/C$ by mechanochemically assisted solid state synthesis using $FeC_2O_4·2H_2O$, Li_2CO_3 and $(NH_4)_2HPO_4$ as reagents and 5 wt% of carbon as a coating agent. Mechanochemical activation was performed using a high-energy AGO-2 planetary mill. The activated mixture was subsequently heat treated at 600 °C in Ar flow. Crystal and local structure, particle size and electrochemical properties of the as-prepared $Na_2FeP_2O_7$ material were analyzed by XRD with Rietveld refinement using GSAS software package, SEM, EDX, Mössbauer, ^{23}Na and ^{31}P MAS NMR spectroscopy, and galvanostatic cycling in Na^+ and Na^+/Li^+ cells.

The refined lattice parameters (a = 6.4163(3) Å, b = 9.4077(4) Å, c = 10.9786(5) Å, α = 64.468(2)°, β = 85.693(3)°, γ = 72.934(3)°, V = 570.63(5) Å^3, R_{wp} = 6.69 %) well correlate to the literature data [2]. According to Mössbauer spectroscopy, a majority of Fe^{2+} ions are in a high-spin state. The sample contains about 20% of Fe^{3+} impurities, indicating the presence of a large amount of structural distortion. The ^{23}Na MAS NMR spectrum of the $Na_2FeP_2O_7$ is presented by two components at -14 and 175 ppm overlapped with satellites, contrary to a broad line in the spectrum of $Li_2FeP_2O_7$ [3]. ^{31}P MAS NMR signal of $Na_2FeP_2O_7$ is located at ~0 ppm.

Galvanostatic cycling of $Na_2FeP_2O_7$ was performed in the 2.0–4.3 V range at C/20 rate and at room temperature starting with discharge. A sloping solid solution-like charge-discharge profile was observed. The discharge capacity was 87 mAh/g in Na-cell and 92 mAh/g in Li-cell. Electrochemical Na^+/Li^+ ion exchange was completed after the 4th cycle. Na^+/Li^+ non-oxidative chemical ion exchange was carried out in the solution of LiBr in acetonitrile for 24 h. According to EDX, only one Na^+ can be readily replaced for one Li^+ to produce the $NaLiFeP_2O_7$ composition with *P*-1 S.G.

[1] P. Barpanda, T. Ye, S. Nishimura, S. Chung, Y. Yamada, M. Okubo, H. Zhou, A. Yamada, Electrochem. Commun. 24 (2012) 116.
[2] T. Honma, A. Sato, N. Ito, T. Togashi, K. Shinozaki, T. Komatsu, J. Non-Cryst. Solids 404 (2014) 26.
[3] N.V. Kosova, A.M. Tsapina, A.B. Slobodyuk, S.A. Petrov, Electrochim. Acta 174 (2015) 1278.

UNDERSTANDING THE MECHANISMS LIMITING THE CONVERSION REACTION OF IRON OXIDE NANOSTRUCTURES IN LI- AND NA-ION BATTERIES

Mario Valvo[a], Bertrand Philippe[b], Fredrik Lindgren[a], Cheuk-Wai Tai[c], Kristina Edström[a]
[a] *Department of Chemistry – Ångström Laboratory, Uppsala University, Box 538, SE-75121, Uppsala, Sweden.*
[b]*Department of Physics and Astronomy, Uppsala University, Box 516, SE-75121, Uppsala, Sweden.*
[c]*Department of Materials and Environmental Chemistry – Arrhenius Laboratory, Stockholm University, SE-10691, Stockholm, Sweden.*

mario.valvo@kemi.uu.se

Na-ion batteries have attracted renewed interest during the last decades due their attractive features, which could establish this technology as a potential alternative to Li-ion cells for large-scale stationary storage of electrical energy. However, the route towards the development of effective Na-ion batteries runs into bigger challenges than those faced for Li-ions. Indeed, the noticeable differences in both mass and size between Li^+ and Na^+ ions severely influence the resulting electrochemical reactions. This fact limits the choice of suitable materials for Na-ion batteries, especially for negative electrodes, since graphite cannot be employed as reliable insertion host [1]. However, Na^+ incorporation via solvent co-intercalation phenomena [2] in graphite has been proposed as well. So far, the most promising materials for negative electrodes in Na-ion batteries are hard carbons [3], since they offer the best trade-off in terms of capacities, performances and cycle life. However, these aspects could be further improved and more abundant and cheaper materials, which can be easily fabricated at lower temperatures, have been proposed as well. Among these, iron oxide is certainly one of the most attractive and some preliminary studies in Na-half cells have been carried out [4-5]. The reaction pathway of iron oxide upon sodiation at first glance resembles that occurring upon lithiation. However, important differences do exist in the respective electrochemical processes, being the conversion reaction [6] of iron oxide into Fe and Na_2O clearly hindered compared to its analogue in presence of Li^+ ions [4, 7].

A careful comparative analysis via cyclic voltammetry on various types of iron oxide nanostructures (e.g. nanopowders, nanowires and thin-films) cycled in parallel in Li- and Na-half cells with analogous electrolytes will be presented, in order to clarify the different behaviours observed for these two electrochemical systems. The roles played by the characteristic structures, textures and their electrical wiring through the related electrode architectures will be highlighted. The limiting factors arising from the conversion of iron oxide upon lithiation and sodiation will be discussed and the related issues addressed.

References

[1] P. Ge, M. Fouletier, Sol. St. Ionics 28-30 (1988) 1172–1175.
[2] B. Jache, P. Adelhelm, Angew. Chem. Int. Ed. 53 (2014) 10169–10173.
[3] M. Dahbi, N. Yabuuchi, K. Kubota, K. Tokiwa, S. Komaba, Phys. Chem. Chem. Phys. 16 (2014) 15007–15014.
[4] M. Valvo, F. Lindgren, U. Lafont, F. Björefors, K. Edström, J. Power Sources 245 (2014) 967–978.
[5] B. Philippe, M. Valvo, F. Lindgren, H. Rensmo, K. Edström, Chem. Mater. 26 (2014) 5028–5041.
[6] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J.-M. Tarascon, Nature 407 (2000) 496–499.
[7] B. Huang, K. Tai, M. Zhang, Y. Xiao, S.J. Dillon, Electroch. Acta 118 (2014) 143–149.

MICROWAVE SYSNTHESIS OF NANOSTRUCTURED ELECTRODES FOR LI-ION BATTERIES

J. Vidal Laveda[a], M. Tucker[b], H. Playford[b], C. Murray[c], G. Paterson[d] and S. A. Corr[a]*
[a] *School of Chemistry, University of Glasgow, Glasgow, G12 8QQ, UK*
[b] *ISIS Pulsed Neutron and Muon Source, Didcot, OX11 0QX, UK*
[c] *Diamond Light Source, Didcot, Oxfordshire, OX11 0DE, UK*
[d] *School of Chemistry, University of Glasgow, Glasgow, G12 8QQ, UK*
j.vidal-laveda.1@research.gla.ac.uk

Nowadays, Li-ion batteries play a key role in the growing demand of portable electronics and hybrid electric vehicles (HEVs).[1] Fast and low temperature syntheses are highly desirable for the preparation of high quality functional inorganic nanoparticles. Microwave or ultrasonic treatment of metal alkoxides presents a rapid and low cost route to both anode and cathode nanomaterials for Li-ion battery applications.[2] Here, we demonstrate the significant reduction in processing times and energy consumption during the preparation of nanostructured battery materials when using single source metal alkoxides in comparison to commercial starting materials. In particular, we show the formation of olivine $LiMPO_4$ (M=Fe, Mn) and Mn_3O_4 hausmannite nanostructures *via* a simple and energy efficient route employing metal alkoxides, which affords electrode materials exhibiting excellent electrochemical performances.[3] Co-location of two transition metals in these metalorganic precursors is believed to bypass the need of diffusional mixing and allow the reactions to proceed faster and at lower temperatures generating highly crystalline materials. We also present neutron pair distribution function (PDF) analyses of some of our phases in an effort to examine the local structure and show that microwave processes produce highly crystalline materials. Finally, we also include cycling studies in order to probe the relationship between the synthetic route, composition and electrochemical performance.

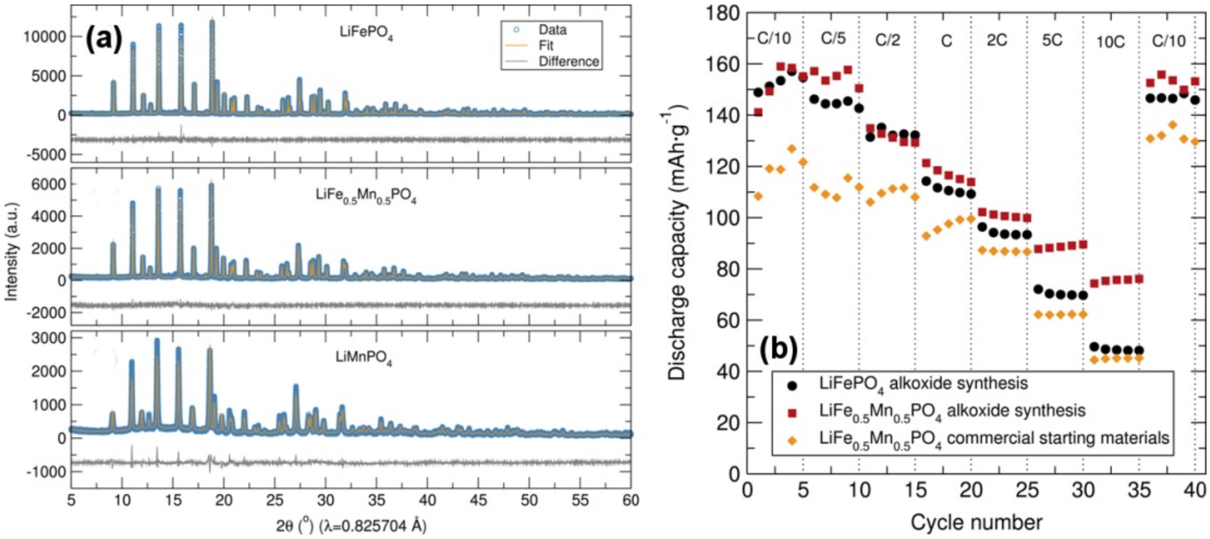


Figure 1. (a) High resolution powder x-ray diffraction of $LiFe_{1-x}Mn_xPO_4$ prepared from alkoxide precursors and **(b)** rate performance of $LiFePO_4$ and $LiFe_{0.5}Mn_{0.5}PO_4$ nanostructures.

[1] J.-M. Tarascon and M. Armand, Nat. 414 (2001) 359-367

[2] T. E. Ashton. J. Vidal Laveda, D. A. MacLaren, P. J. Baker, A. Porch, M. O. Jones and S. A. Corr, J. Mater. Chem. A, 2 (2014) 623

[3] J. Vidal Laveda, V. Chandhok, C. A. Murray, G. W. Paterson, S. E. Corr, *Chem. Commun.* (2015) Accepted

MSb$_X$S$_Y$FAMILIES USED AS NEGATIVE ELECTRODE FOR X$^+$-ION BATTERIES (X=Li$^+$, Na$^+$)

Cyril Marino, Claire Villevieille
Paul ScherrerInstitut, Electrochemistry Laboratory, CH-5232 Villigen PSI, Switzerland

claire.villevieille@psi.ch

Li-ion batteries are starting to reach their limits in terms of energy density, cost and abundance, and progress is slower than expected. Thus, researchers are currently re-investigating other alkali metals as Li substitutes, mainly focusing on Na. This system has been considered to be purely academic, and no real applications or prototypes have been developed to investigate its viability or possible commercialization, the only exception being the high temperature Na-S system, which was commercialized in the 1960s.Recently however, the amount of research and number of papers devoted to the development of active materials for Na-ion batteries has increased exponentially, leading the community to consider the commercialization of Na-ion batteries in the near future. To achieve commercialization, suitable anodes and cathodes must be developed and studied in depth as the Na-system is often not analogous to the Li-system.

Recently, we have developed a new type of anode material, MSnS$_2$ (M = Fe, Cu), that is able to cycle in both lithium-ion and lithium- sulphur batteries. By tuning the potential window, we attained specific charges greater than 750 mAh/g and 500 mAh/g for the Li–S and Li–ion system,respectively, after 400 cycles [1].

We decided to apply the same approach to new negative electrode materials Sb-based such as Sb$_2$S$_3$ and CuSbS$_2$. As can be seen from the Figure 1, we tested them versus lithium (for Li-ion batteries) and versus sodium (for Na-ion batteries). Without any electrode engineering and with a high loading (ca. 5 mg/cm^2) we manage to cycle both materials in both systems (Li/Na) with a specific charge higher than 700 mAh/g for the Li system and about 600 mAh/g for the Na system.

Advanced electrochemistry results such as CV, different galvanostatic rates and influence of potentiostaticstep will be discussed to assess their performances in both systems.

For the reaction mechanisms, operando X-ray diffraction coupled with XAS measurements and postmortem surface analyses such as XPS and SEMwill be presented and the difference in the reaction mechanisms between the reaction with Li and the reaction of Na will be elucidated.

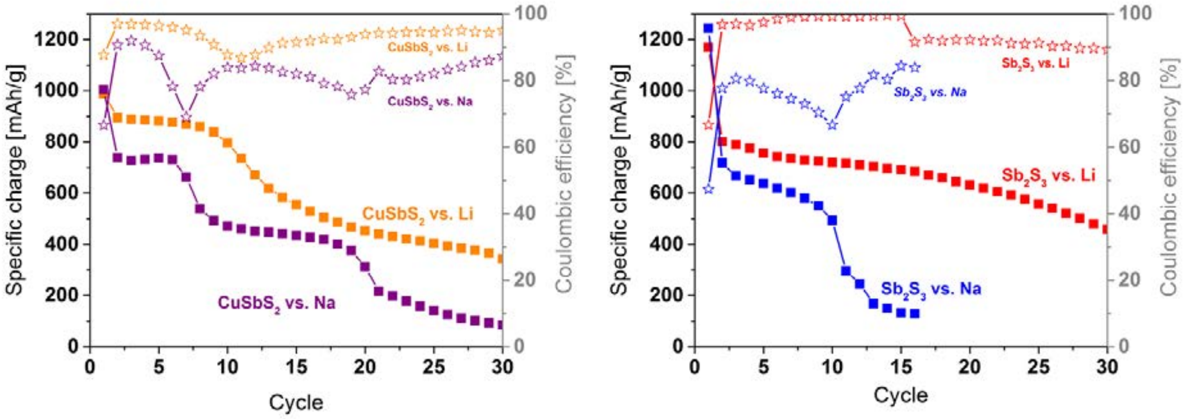


Figure 1.Specific charge obtained from the cycling at C/10 of left) CuSbS$_2$. Right) Sb$_2$S$_3$ as negative electrode for Li or Na-ion batteries.

[1] C. Villevieille, P.Novák, J. Electroch. Soc. 162 (2015) A284-A287.

Acknowledgment: This work was performed within the Swiss Competence Center of Energy Research Heat and Storage (SCCER) framework.

Lithium/electrolyte interface in Li/S_8 batteries conditions: passivation and dendritic growth

V. Vinci[a,b], R. Bouchet[a,b],V. Nourri[a,b], A. Benayad[c], F. Alloin[a,b]
[a] *Univ. Grenoble Alpes, LEPMI, F-38000 Grenoble, France*
[b] *CNRS, LEPMI, F-38000 Grenoble, France*
[c] *CEA, LITEN F-38054 Grenoble, France*
email address of the presenting author: *valentin.vinci@lepmi.grenoble-inp.fr*

Ecofriendly, cheap and widely available, sulfur allows to reach high theoretical energy density (~2600 Wh.kg-1)[1] when it faces to lithium. Li/S is therefore a very promising technology in the perspective of replacement of classical Li-Ion batteries, especially for the large markets of electric transport and stationary applications.

Beside the very complex discharge mechanism[1] of the positive sulfur electrode, which focuses most of the research, the dendritic growth of the lithium at the negative electrode during charging is one of the stumbling blocks of this technology. However, the electrodeposition of lithium is still little studied even though the high current densities involved in this technology would lead to an exacerbation of this phenomenon. The mitigation of dendritic growth would be a great step forward in the development of safe and reliable Li/S_8 batteries.

Therefore, the aim of this work is the study of the lithium metal/electrolyte interface both in equilibrium and under current conditions.

First, the lithium passivation and ageing is monitored in Li/El/Li symmetric cell by impedance spectroscopy and correlated to chemical surface analysis by XPS measurement. Then, the dendritic growth is systematically studied in galvanostatic experiments as function of both the current densities and electrolyte additives (Polysulfides Li_2Sx and $LiNO_3$). The morphology of the dendrites is determined by *post-mortem* SEM imaging (cf. figure 1). Eventually, to separate dendrites nucleation and growth processes, we performed *operando* optical analysis. Our methodology allows determining unambiguously the impact of the different additives that are classically used in this technology.

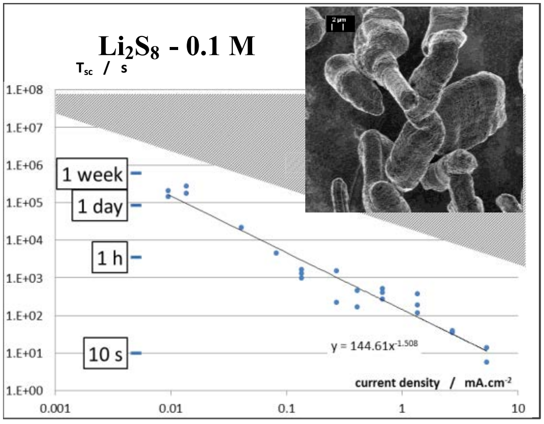


Figure 1 : two ways to understand dendrites : the time of short-circuit plotted in function of the current density and SEM images of dendrites (the hatched area represents the part of the graph that is beyond the total capacity of the Li° electrode)

Furthermore, our results are analyzed in the framework of classical models for dendrite formation (Yamaki, Chazalviel, Newman…)[2], [3], [4].

[1] C. Barchasz, F. Molton, C. Duboc, J.-C. Leprêtre, S. Patoux, and F. Alloin, "Lithium/sulfur cell discharge mechanism: an original approach for intermediate species identification.," *Analytical chemistry*, vol. 84, **May 2012**, no. 9, pp. 3973–80.

[2] J. Yamaki, S. Tobishima, K. Hayashi, and K. Saito, "A consideration of the morphology of electrochemically deposited lithium in an organic electrolyte," *Journal of Power Sources*, **1998**, vol. 74, pp. 219–227.

[3] C. Brissot, M. Rosso, J. Chazalviel, P. Baudry, and S. Lascaud, "In situ study of dendritic growth in lithium / PEO-salt / lithium cells," *Electrochemica Acta*, vol. **1998**, 43, pp. 1569–1574.

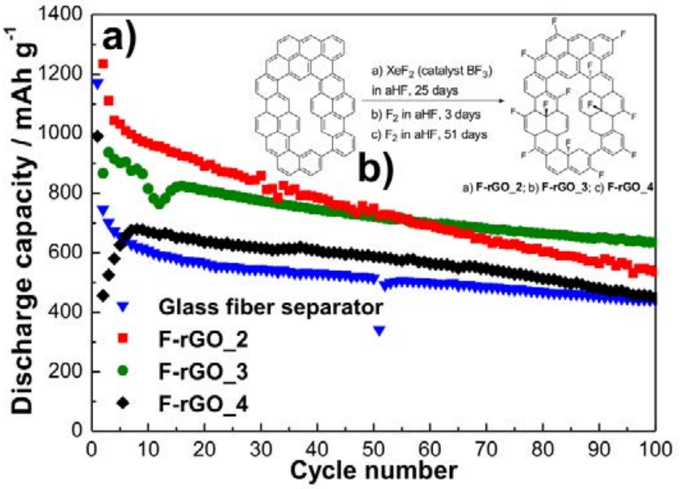
[4] C. Monroe and J. Newman, "Dendrite Growth in Lithium/Polymer Systems," *Journal of The Electrochemical Society*, **2003**, vol. 150, no. 10, p. A1377.

FLUORINATED REDUCED GRAPHENE OXIDE AND ITS APPLICATION IN Li-S BATTERIES

Alen Vizintin[a], Matic Lozinsek[b], Rajesh K. Chellappan[c], Dominique Foix[c], Andraz Kranjc[a], Gregor Mali[a], Goran Drazic[a], Bostjan Genorio[d], Rémi Dedryvère[c], Robert Dominko[a]
[a] *National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia*
[b] *Jozef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia*
[c] *IPREM-ECP (UMR 5254 CNRS), University of Pau, Hélioparc, 2 av. Pierre Angot, 64053 Pau CEDEX 9, France*
[d] *Faculty of Chemistry and Chemical Technology, Vecna pot 113, 1000 Ljubljana, Slovenia*

alen.vizintin@ki.si

Li-S batteries are expected to be the first post Li-ion battery technology in the commercial use. Their drawback is mainly connected with a capacity degradation, which involves a complicated reaction mechanism with different soluble lithium poylsulfides [1]. Among different strategies to stabilize the capacity degradation, the possible solution is a use of an ion-selective membrane or an interlayer [2] that can limit or stop the polysulfide diffusion/migration towards the anode side. Graphene and its derivatives are due to their properties, materials of the future electronic and energy storage applications and they can be used for an enhancement of electronic conductivity or as an insulating layer. We prepared separator interlayers based on fluorinated reduced graphene oxide (F-rGO). Formation of C–F bonds was confirmed by HAADF-STEM and solid-state NMR measurements. The introduced hydrophobic interlayer improved the cycling stability of the battery, compared to only glass fiber separator. X-ray Photoelectron Spectroscopy (XPS) studies have shown a direct effect on the amount of Li_2S and polysulfides found on the surface of lithium electrode, and demonstrated a better reversibility of reduction/oxidation mechanisms of sulfur at the cathode upon discharge/charge.



Discharge capacity of the fluorinated rGO interlayers (F-rGO_2, F-rGO_3 and F-rGO_4) and glass fiber separator (a) and reaction scheme of the rGO fluorination (b)

References:

[1] R. Dominko, M.U.M. Patel, V. Lapornik, A. Vizintin, M. Koželj, N.N. Tušar, I. Arčon, L. Stievano, G. Aquilanti J. Phys. Chem. C. 119 (2015) 19001–19010.

[2] A. Vizintin, M.U.M. Patel, B. Genorio, R. Dominko ChemElectroChem. 1 (2014) 1040–1045.

Nontopotactic Conversion Reaction in Highly Reversible Sodium Storage of Ultrathin Co_9Se_8/r-GO Nanosheets

Xianfen Wang, Zhi Xiang Huang, Ye Wang, Hui Ying Yang
Pillar of Engineering Product Development, Singapore University of Technology and Design, 8 Somapah Road, 487372, Singapore

xianfen_wang@sutd.edu.sg

Na-ion batteries have recently experienced renewed interest as a potential energy storage alternative to Li-ion battery system due to the natural abundance and wider distribution of Na resources. Though many cathode materials have emerged as promising candidate in terms of energy density and electrochemical performance, one main obstacle to the commercialization of NIB is the limited choice of anode that can provide suitable stability and rate performance. [1-2]

We report Co_9Se_8 as anode materials for sodium ion battery. Co_9Se_8 was assembled via a modified solvent-induced oriented attachment method through controlling the ratio of precursors to graphene oxide. The obtained Co_9Se_8 anode delivers a highly reversible capacity of ~420 mAh g^{-1} showing evident plateau around 1.7 and 1.2 V respectively. The shift of the potential plateau after initial cycle can be related with the formation of SEI, which also induces large capacity fade. The rate performance of Co_9Se_8 anode is also promising (298 mAh g^{-1} at 5 A g^{-1}) compared with other anode materials. [3-5] Impressively the rate capacity of Co_9Se_8 is higher than that of any carbonaceous materials such as hard carbon and expanded graphite at any current rate. While its performance is also good compared with other transition metal selenides such as Cu_2Se. The excellent performance can be attributed to the following aspect: (1) the redox process may involve a nontopotactic reaction as shown in the Figure 1(e) during sodiation/de-sodiation that the materials break down to facilitate complete reduction of redox-active metal ion to elemental metal, therefore allowing for highly reversible capacity. (2) rGO may not only provides suitable site for oriented attachment growth of the candidate Co_9Se_8 but also prevent the stacking of nanosheets. (3) In addition, the active materials take the advantage of graphene nanosheets as an elastic and conductive matrix to effectively accommodate the volume strain during charge/discharge. (4) the unique feature of Co_9Se_8 such as excellent conductivity and large surface area make a promising candidate as anode for sodium-ion battery.

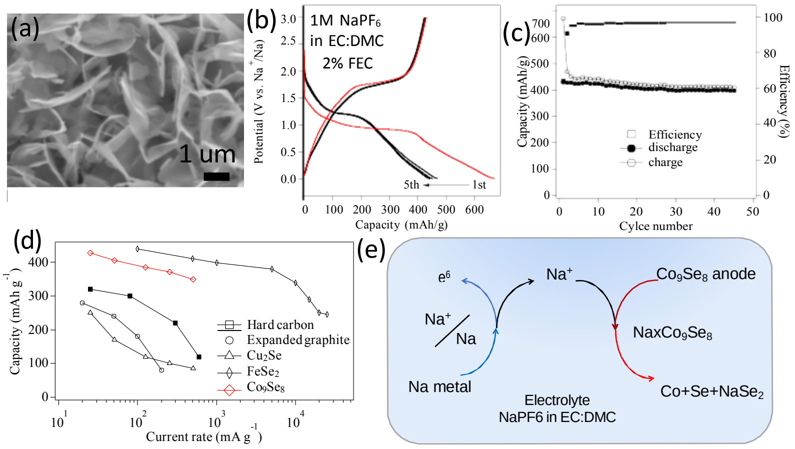


Figure 1. Morphology and electrochemical performance of Co_9Se_8/rGO as anode materials for NIB. (a) SEM image, (b) charge/discharge curves and (c) capacity retention performance at 50 mA g^{-1}, (d) rate performance comparison and (e) schematic illustration of non-topotactic reversible reaction in NIB.

Reference:

[1] S. W. Kim, D. H. Seo, X. Ma, G. Ceder, K. Kang, Adv. Energy Mater. 2 (2012) 710-721.
[2] N. Yabuuchi, K. Kubata, M. Dahbi, S. Komaba, Chem. Rev. 23 (2014) 11636-82
[3] Y. Wen, C. Wang, Nat. Commun. 5 (2014) 4033-4043.
[4] J. Yue, Q. Sun, Z. Fu, Chem Commun. 49 (2013) 5868-5870.
[5] K. Zhang, Z. Hu, Z. Tao. J. Chen. Adv. Mater. (2015). DOI: 10.1002/adma.201500196.

Wednesday 23
Poster Session 3

Bifunctional Electrocatalytic Effect for Oxygen Reduction and Evolution in Li-O_2 Batteries: RRDE and DEMS Insights

Hatem M.A. Amin, Christoph Molls, Mohammed Soltani, Helmut Baltruschat
University of Bonn
Roemerstrasse 164, 53117 Bonn
hatem@pc.uni-bonn.de, baltruschat@uni-bonn.de

Alkaline Li-air batteries could make a major breakthrough in battery technology. However, a key challenge is the development of a bifunctional catalyst which enhances the sluggish kinetics of both ORR and OER. In alkaline solution, Ag is known to be the best non-precious electrocatalyst for oxygen reduction. However, Ag is not catalyzing oxygen evolution. Spinels such as Co_3O_4 and various Perovskites have been shown to be good catalysts for oxygen evolution but are not very good for oxygen reduction. We have recently reported that a particular carbon-free mixture of a Ag catalyst with Co_3O_4 nanoparticles leads to a catalyst which not only combines the good performance of Ag for the ORR with that of Co_3O_4 for the OER, but shows a better activity than its components with good stability.[1, 2]

Here, we will present further insights and demonstrate that this effect is also observed for various perovskites. The synergistic effect is also observed when Co_3O_4 or the perovskites are deposited on smooth Ag and Au electrodes. We determined the free Ag surface area by Pb-underpotential deposition. XPS analysis has shown that the presence of Ag^+ in contact with Co_3O_4 facilitates the redox switching of Co_3O_4. This could be the reason for the enhanced catalytic activity of the mixture.

Using differential electrochemical mass spectrometry (DEMS) and ^{18}O- isotope labeling it has shown in our previous work that the lattice oxygen is participating in the OER at oxides.[3-6] This procedure is applied to Co_3O_4 and the mixed catalyst as well and showed higher amount of oxygen exchange at the mixed catalyst.

Cycling performance in DMSO at gold has been quantitatively studied.[7] Here, investigations of OER and ORR in an aprotic electrolyte based on a blend of tetraglyme and DMSO at gold electrode has been done using RRDE and DEMS techniques. Insights into the mechanism has also been considered.

Acknowledgement: Funding of this project by the BMBF (LuLi - project 03X4624A) is gratefully acknowledged.

References:

[1] H.M.A. Amin, H. Baltruschat, D. Wittmaier, K.A. Friedrich, Electrochimica Acta 151 (2015) 332-339.
[2] D. Wittmaier, N. Wagner, K.A. Friedrich, H.M.A. Amin, H. Baltruschat, Journal of Power Sources 265 (2014) 299-308.
[3] M. Wohlfahrt-Mehrens, J. Heitbaum, Journal of Electroanalytical Chemistry 237 (1987) 251-260.
[4] K. Macounova, M. Makarova, P. Krtil, Electrochemistry Communications 11 (2009) 1865-1868.
[5] S. Fierro, T. Nagel, H. Baltruschat, C. Comninellis, Electrochemical and Solid State Letters 11 (2008) E20-E23.
[6] S. Fierro, T. Nagel, H. Baltruschat, C. Comninellis, Electrochemistry Communications 9 (2007) 1969-1974.
[7] C. Bondue, P. Reinsberg, A.-E.-A.A. Abd-El-Latif, H. Baltruschat, Physical Chemistry Chemical Physics (2015) DOI: 10.1039/c1035cp04356e.

QUANTIFICATION OF LITHIUM PLATING IN COMMERCIAL LI-ION BATTERIES VIA IN SITU TECHNIQUES

David Anseán[a], Víctor M. García[a,b], Manuela González[a], Juan C. Viera[a], Cecilio Blanco[a]
[a]*Battery Research Laboratory, Department of Electrical Engineering and*
[b]*Department of Physical and Analytical Chemistry.*
University of Oviedo, Gijón, Asturias, 33204, Spain

email address of the presenting author: anseandavid.uo@uniovi.es

Lithium plating (Li plating) is considered one of the most detrimental phenomenon in lithium ion batteries (LIB) [1–3]. The effects of Li plating can lead to an increase of lithium consumption within the electrode-electrolyte interface due to side reactions [3,4], loss of active material and may also cause safety deterioration [1,5,6]. In addition, Li plating is considered one of the most complex phenomena to analyze in LIBs. Due to its importance, recent studies [3,7–10] have focused on the topic of Li plating on LIBs, aiming to further elucidate its effects and, most importantly, to detect it. However, to our best knowledge, an advanced, *in situ* and cost-effective technique to detect and quantify Li plating still remains lacking.

In this study, we will show an analysis to estimate Li plating via *in situ* techniques on a commercial high power $LiFePO_4$ cell under stressful, long-term testing conditions. Fig. 1a shows the evolution with cycle of the incremental capacity (IC) curves at C/25 for the tested cell. The use of IC curves allowed us to identify the presence of Li plating, as Peak ⓿ emerged after cycle 600. In combination with the IC peak area (PA) analysis [11], we were also able to quantify the amount of capacity underneath Peak ⓿. To further quantify the effects of Li plating, we carried out computer simulations using *'Alawa* battery diagnosis and prognosis toolbox [12]. Additional analyses and computer iterations allowed us to estimate the effects of Li plating during operation (i.e. online). The outcomes of these analyses are shown in Fig. 1b, which reveals the effects that the degradation modes caused on each individual electrode throughout cycling. We observed that Li plating abruptly reduces the capacity retention by a factor of three. The results provided in this work could enhance the knowledge regarding *in situ* detection of Li plating, and its possible application for engineering control systems (i.e. battery management systems, BMS).

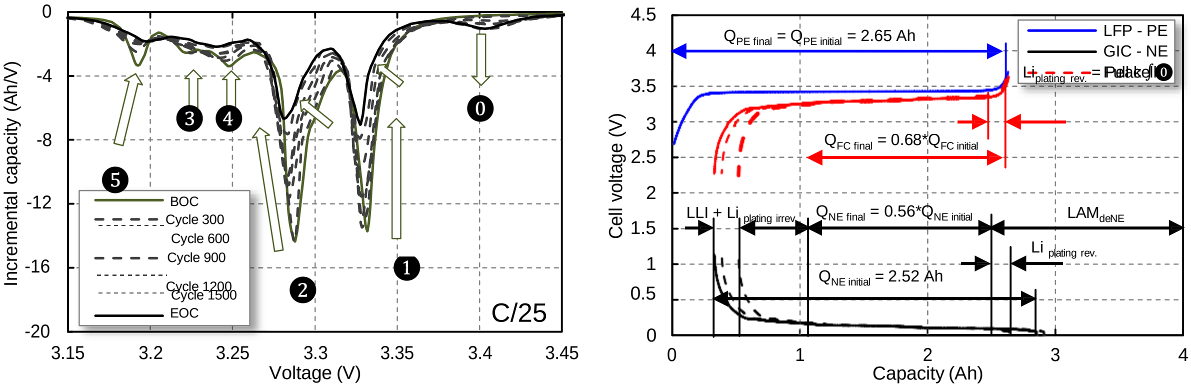


Fig. 1. Results from the GIC||LFP tested cell showing (a) experimental incremental capacity evolution at C/25 and (b) the simulated schematic representation of the evolution with cycling of the individual electrodes

References
[1] J. Vetter, P. Novák, M.R. Wagner, C. Veit, K.-C. Möller, J.O. Besenhard, M. Winter, M. Wohlfahrt-Mehrens, C. Vogler, A. Hammouche J. Power Sources 147 (2005) 269.
[2] M. Broussely, P. Biensan, F. Bonhomme, P. Blanchard, S. Herreyre, K. Nechev, R.J. Staniewicz, J. Power Sources 146 (2005) 90.
[3] M. Petzl, M.A. Danzer, J. Power Sources 254 (2014) 80.
[4] P. Arora, R. White, M. Doyle, J. Electrochem. Soc. 145 (1998) 3647.
[5] M.C. Smart, B.V. Ratnakumar, J. Electrochem. Soc. 158 (2011) A379.
[6] N. Legrand, B. Knosp, P. Desprez, F. Lapicque, S. Raël, J. Power Sources 245 (2014) 208.
[7] T. Waldmann, M. Kasper, M. Wohlfahrt-Mehrens, Electrochim. Acta 178 (2015) 525.
[8] M. Petzl, M. Kasper, M.A. Danzer, J. Power Sources 275 (2015) 799.
[9] J.C. Burns, D. a. Stevens, J.R. Dahn, J. Electrochem. Soc. 162 (2015) A959.
[10] C. Uhlmann, J. Illig, M. Ender, R. Schuster, E. Ivers-Tiffée, J. Power Sources 279 (2015) 428.
[11] M. Dubarry, C. Truchot, B.Y. Liaw, J. Power Sources 258 (2014) 408.
[12] M. Dubarry, C. Truchot, B.Y. Liaw, J. Power Sources 219 (2012) 204.

3D Microbatteries for Swarm Sensing

Muhammad Abdelhamid[a], Adam S. Best[b], Anand J. Bhatt[c], Mike Horne[a], Tony Hollenkamp[c],
Thuy Huynh[c], Chris Knight[c], Petar Liovic[d],Selim Mahbub[d]Andojo Ong[d], Theo Rodopoulos[a],
Thomas Rüther[c],Paulo de Souza[d], Jean-Pierre Veder[a]

[a]CSIROMineral Resources, Research Way, Clayton, VIC 3168, Australia
[b]CSIROManufacturing, Research Way, Clayton, VIC 3168, Australia
[c]CSIRO Energy, Research Way, Clayton, VIC 3168, Australia
[d]CSIROData61,College Rd, UNITAS,Sandy Bay, TAS 7005, Australia

adam.best@csiro.au

Small-scaled energy storage is a highly sought after technology for emerging miniaturised sensor systems. Yet despite the burgeoning interest in sensor miniaturisation, suitably small batteries that have sufficient energy to power these miniaturised sensor systems currently do not exist. The challenge facing current battery technologies is that the amount of energy that can be stored in a small-scaled battery is undesirably low. Reducing the size of a conventional battery has the undesirable effect of decreasing the energy available to the miniature sensor systems.Energy storage is thus considered to be a major roadblock in the trend towards sensor miniaturisation.

The development of miniaturised sensor systems is motivated by the potential implications in important application areas such as, but not limited to:

- Environmental monitoring – distributable autonomous and wireless sensors,
- Health monitoring – implantable micro-sensors,
- Security and defence – reconnaissance and surveillance (micro-drones).

CSIRO is developing such a miniaturised sensor system for swarm sensing. In this particular application insects are used as platforms to deploy thousands of miniature sensors. The technology has the potential to elucidate environmentally catastrophic events such as colony collapse disorder in honey bees and the incursion of fruit flies and other pest species. Environmental events such as these can have far-reaching implications for Australia’s local and global agricultural food supply and ultimately people’s livelihoods.

This presentation introduces the concept of swarm sensing and highlightsthe current research efforts that are focused on developing an innovative miniature batterythat iscapable of meeting the energy demands of the swarm sensing application. These miniature batteries overcome the problem of diminishing energy storage capacity for a reduced housing space or footprint by exploiting the use of complex 3D nanoarchitectured electrodes to dramatically increase energy storage capacity.Accordingly, these nanoarchitechtured batteries are referred to as 3D microbatteries.[1]

[1] J. F. M. Oudenhoven , L. Baggetto, P. H. L. Notten, Adv. Energy Mater. 1 (2011) 10–33.

Separating bulk from grain boundary Li ion conductivity in the sol-gel prepared solid electrolyte $Li_{1.5}Al_{0.5}Ti_{1.5}(PO_4)_3$

Stefan Breuer,*[,a] Denise Prutsch,[a] Qianli Ma,[b] Viktor Epp,[a] Florian Preishuber-Pflügl,[a]
Frank Tietz,[b,c] and Martin Wilkening*[,a]

[a] *Christian Doppler Laboratory for Lithium Batteries, and Institute for Chemistry and Technology of Materials, Graz University of Technology (NAWI Graz), Stremayrgasse 9, 8010 Graz, Austria*
[b] *Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, Materials Synthesis and Processing (IEK-1), 52425 Jülich, Germany*
[c] *Helmholtz Institute Münster, c/o Forschungszentrum Jülich GmbH, 52425 Jülich, Germany*

breuer@tugraz.at ; wilkening@tugraz.at

In terms of ionic conductivity lithium aluminium titanium phosphate (LATP) belongs to one of the most promising solid electrolytes. Besides sufficiently high electrochemical stability, its use in lithium-based all-solid-state batteries crucially depends on the ionic transport properties. While many impedance studies can be found in literature that report on *overall* or total ion conductivities, a discrimination of bulk and grain boundary electrical responses via conductivity spectroscopy has rarely been reported so far. Here, we took advantage of impedance measurements that were carried out at low temperatures to separate bulk contributions from the grain boundary responses. It turned out that bulk ion conductivity is by approximately three orders of magnitude higher than ion transport across the grain boundary regions. At temperatures well below ambient, long-range Li ion dynamics is governed by activation energies ranging from 0.26 to 0.29 eV depending on the sintering conditions. As an example, at temperatures as low as 173 K, the bulk ion conductivity, measured in N_2 inert gas atmosphere, is in the order of 8.1×10^{-6} S cm^{-1}. Extrapolating this value to room temperature yields ca. 3.4×10^{-3} S cm^{-1} at 293 K. Interestingly, exposing the dense pellets to air atmosphere over a long period of time causes a significant decrease of bulk ion transport. This process can be reversed if the phosphate is calcined at elevated temperatures again.

Facile Synthesis of Pd_3Co Bimetallic Hollow Nanospheres and Their Application for Rechargeable Li-O_2 Batteries.

Sung Man Cho, Jee Ho Yom, Sun Woo Hwang, Woo Young Yoon*
Department of Materials Science and Engineering, Korea University, 1, 5Ga, Anam-dong,
Sungbuk-Gu, Seoul, 136-701, Republic of Korea

email address of the presenting author: cho104401@korea.ac.kr

Lithium-oxygen (Li-O_2) batteries have attracted much attention due to their high theoretical specific energy and energy density compared to conventional lithium ion batteries, and are one of the most promising high-energy-storage systems for electric vehicles (EVs) and hybrid electric vehicles (HEVs). The theoretical specific energy and energy density of a Li–O_2 battery with the discharge reaction [$2Li + O_2 \rightarrow Li_2O_2$] are 3505 Wh kg^{-1} and 3436 Wh l^{-1}, respectively. However, their poor round-trip efficiency and low cycle life have limited their commercialization. The poor round-trip efficiency is the result of the sluggish reaction kinetics during cycling, which gives rise to a high overpotential. The carbon electrode also reacts with the discharge products (Li_2O_2) and promotes electrolyte decomposition during cycling in the Li–O_2 cell, which produces the side reaction products such as lithium carbonate (Li_2CO_3), lithium formate monohydrate (HCO_2Li), and lithium acetate (CH_3CO_2Li). This eventually leads to a much shorter cycle life than would be expected. Therefore, making the design of a carbon-free cathode with high catalytic catalysts and suitable pore structure is the key to enhance the performance of Li-O_2 batteries. In this work, for the first time, Pd_3Co bimetallic hollow nanospheres was investigated as a carbon-free cathode materials in Li-O_2 batteries. Pd_3Co hollow spheres were synthesized by simple polyol method and used for cathode materials. The resulting Li-O_2 cell demonstrated high energy efficiency and improved cycling stability, which were attributed to the high catalytic activity and pore structure of Pd_3Co hollow spheres.

Reference to a journal publication:

[1] P.G. Bruce, S.A. Freunberger, L.J. Hardwick, J.-M. Tarascon, Nat. Mater., 11 (2012) 19-29.
[2] B.M. Gallant, R.R. Mitchell, D.G. Kwabi, J. Zhou, L. Zuin, C.V. Thompson, Y. Shao-Horn, 116, J. Phys. Chem. C (2012) 20800-20805.

INK JET PRINTING AND PRINTABLE ELECTROLYTES FOR ALL-SOLID-STATE LITHIUM MICROBATTERIES

Pierre-Emmanuel Delannoy[a], Djamel Aidoud[a], Delphine Guy-Buissou[b], Benoit Riou[b],
Dominique Guyomard[a], Thierry Brousse[a], Jean Le Bideau[a], Bernard Lestriez[a]
[a] *Institut des Matériaux Jean Rouxel de Nantes (IMN)*
2 rue de la Houssinière B.P. 32229 44322 Nantes Cedex 3
[b] *ST Microelectronics, 10 Rue Thales de Millet, 3700 Tours*

pierre-emmanuel.delannoy@cnrs-imn.fr

Lithium battery is very effective system to store electrical energy for many applications, in particular for on board application. A promising market [1] is developing for microbatteries because of many new devices requiring some energy on board with drastic size limitation: RFID ship, medical or cosmetic devices (pace maker or nicotine patch), autonomous sensors, security (smart credit card)…

This poster presents our microbatteries development in regard with literature. Standard way of deposition is based on PVD process and use LiPON [2,3] as solid electrolyte with dense electrodes. This commercialized solution induces high cost and long time process. Other interesting ways use new 3D design to increase microbattery performance, in terms of energy or power density, or use easier way of deposition like printing to reduce process costs.

Our approach uses ink jet printing to deposit electrode and electrolyte. First, aqueous based electrode ink, compatible with ink jet printing, has been formulated to obtain homogeneous porous composite $LiFePO_4$ electrode [4]. Furthermore, photo-ionogel solid electrolyte has been obtained through UV-curing route with printed ionic liquid and monomers precursors. After the photo-polymerization of the deposited precursors, ionic liquid and lithium salt are confined into a polymeric matrix to form the photo-ionogel solid electrolyte. This printed photo-ionogel is compatible with porous composite electrode and has high solid electrolyte performances: high ionic conductivity, high electrochemical stability versus lithium and high thermal stability. Full lithium metal microbatteries incorporating photo-ionogel electrolyte have been printed and electrochemically tested.

Reference to a journal publication:

[1] Thin-Film and Printed Battery Markets. NanoMarkets, (2012).
[2] J.B. Bates, N.J. Dudney, G.R. Gruzalski, R.A. Zuhr, A. Choudhury, C.F. Luck, Solid State Ionics, 53-56, (1992), 647–654.
[3] X. Yu, J.B. Bates, G.E. Jellison, F.X. Hart, J. Electrochem. Soc.,144(2), (1997), 524–532.
[4] P.-E. Delannoy, B. Riou, T. Brousse, J. Le Bideau, D. Guyomard, B. Lestriez, J. Power Sources, 287, (2015), 261-268.

EV cell degradation under electric utility grid operations: Impact of calendar aging & vehicle to grid strategies

Arnaud Devie and Matthieu Dubarry
University of Hawaiʻi at Mānoa, Hawaiʻi Natural Energy Institute,
1680 East West Road POST109, Honolulu 96822 HI, USA

matthieu.dubarry@gmail.com

Battery degradation is extremely sensitive to usage and chemistry. Some batteries may be markedly sensitive to temperature, to state of charge, to both, or to some other factors. This raises concerns over battery durability in the rollout of electric vehicles (EVs) in hot climate. Additionally, with the integration of more and more intermittent renewable energy power plants on the grid, there is a push to use EV batteries as energy storage systems which may stress the batteries even more. In most studies on the techno-economical impact of EVs on the grid, the battery is often viewed as a black box and therefore there is no consensus on the actual long term impact of climate and/or vehicle-to-grid (V2G) and grid-to-vehicle (G2V) charging profiles on batteries. This work aims at assessing such impact.

Daily vehicle usage can be broken down into driving, charging and idling periods. In most cases, car batteries spend most of their time idling and it is therefore essential to understand the degradation associated with time, temperature and state of charge. Specifically, we studied the impact of driving on the cell degradation with or without V2G and G2V episodes. All the data was analyzed using HNEI's unique diagnosis and prognosis tools [1-3] to forecast the degradation over the battery warranty period and beyond. This research supports the goals of the Electric Vehicle Transportation Center.

[1] M. Dubarry, C. Truchot and B.Y. Liaw, J. Power Sources 219 (2012) 204-216
[2] M. Dubarry, A. Devie and B.Y. Liaw, J. Energy Power Sources 1(5) (2014) 242-249
[3] https://www.soest.hawaii.edu/HNEI/alawa/

Laboratory testing of LTO based cells for BESS applications

Arnaud Devie and Matthieu Dubarry
University of Hawai'i at Mānoa, Hawai'i Natural Energy Institute,
1680 East West Road POST109, Honolulu 96822 HI, USA

matthieu.dubarry@gmail.com

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.

The focus is to deploy, operate, and validate the performance of four grid-scale BESS for various ancillary service applications on grid systems across the state. Large scale battery energy storage systems will become an important part of the electric grid in the near future and it will be essential to ensure their reliability. The objective of this project is to understand the degradation of the individual batteries to anticipate failures. Laboratory testing of advanced Li-ion battery cells is performed to support life-time analysis of technologies targeted for large-scale grid energy storage applications.

HNEI's battery testing efforts have focused on grid scale deployment lithium ion titanate battery technology which is successfully being used for a variety of purposes including frequency and power regulation of large scale wind and solar energy generation. There is currently a lack of understanding of long term performance of battery technology in general, and specifically lithium ion titanate, used under large scale, grid conditions. This work aims to fill that gap in knowledge through laboratory scale battery testing and the development predictive lifetime models of performance of grid battery technology.

Accelerated testing of identical lithium ion titanate battery technology was performed in the laboratory and those results will be used to develop predictive performance models. This model will combine existing modules [1-4] that account for single cell asymmetric degradation, single cell heat generation, string imbalance, and cell paralleling. As real world data is collected from the grid batteries, the predictive models will be compared and assessed for accuracy and ability to predict performance. This work will present preliminary results.

[1] M. Dubarry, N. Vuillaume and B. Y. Liaw, J. Power Sources 186(2), (2009) 500-507.
[2] M. Dubarry, C. Truchot and B.Y. Liaw, J. Power Sources 219 (2012) 204-216.
[3] https://www.soest.hawaii.edu/HNEI/alawa/
[4] M. Dubarry, C. Truchot, A. Devie and B. Y. Liaw, J. Electrochem. Soc 162(6), (2015) A877-A884.

In-depth surface and reactivity investigation of Li – based electrolytes

Gebrekidan G. Eshetu[a, b,*], D. Thomas[c], S. Grugeon[d], S.Laruelle[d], R.J. Behm[c],
M. Armand[e], S.Passerini[a, b]

[a]*Helmholtz Institute of Ulm (HIU), Helmoltzstrasse 11, 89081 Ulm, Germany*
[b]*Karlsuruhe Institute of Technology (KIT), P.O.Box 3640, 76021 Karlsuruhe, Germany*[cc]*Dept. Surface*
[c]*Dept.Chemistry and Catalysis, University of Ulm, 89069, Ulm (Germany)*
[d]*Laboratoire de reactivite et Chimie des Solides, CNRS UMR7314, 33 rue Saint Leu, 80039 Amiens*
[e]*CIC Energigune, Parque Tecnologico de Alava, Albert Einstein 48, ED. CIC, 01510, Minano, Spain*
[*]Presenting author : gebrekidan.eshetu@kit.edu or tdashenek@yahoo.com

Abstract

In an electrochemical device, interfaces between electrolytes and highly reducing/oxidizing electrodes play an important role in governing the overall performance and safety of the systems. Ever since the inception of the SEI layer concept in 1979,[1] many investigations aiming at mastering the electrified interface at the vicinity of lithiated graphite and electrolyte materials have been conducted. However, the complete understanding and controlling of this passivation layer has remained as the least understood component of the LIB. Besides to its being a legitimate interface for charge transfer, the continuous decomposition and formation of the SEI layer also controls the reactivity of (de-) lithiated electrode materials, owing to the fact that all the cascading reactions in LIBs are initiated by the SEI cracking.[2,3]

In an effort to better understand the SEI and its accompanying role, a detailed comparative investigation on the reactivity and filming behavior of various new and state – of – the – art Li – based electrolytes was carried out using XPS, DSC and chemical simulation. The electrolytes investigated includes LiX (X = PF_6, TDI, FSI, TFSI and FTFSI), dissolved in EC/DMC (1/2, wt. %). The reactivity and SEI nature of the newly emerging imide (FSI-, and FTFSI-) and imidazole (LiTDI) - based electrolytes are evaluated and compared to the well - researched salts, mainly $LiPF_6$. Analysis of DSC traces indicates that the salt nature plays an important role in determining the reactivity of the LiX-EC/DMC electrolytes systems. For same state of charge (SOC), the reactivity of lithiated graphite (Li_xC_6) in the different electrolytes was found to be in the order of LiFSI > LiTDI > LiTFSI > LiFTFSI > $LiPF_6$ and LiTDI < LiTFSI < $LiPF_6$ < LiFTFSI < LiFSI in terms of increasing onset exothermic temperature and normalized total heat generated, respectively. Chemical simulation tests proved that FSI^- and $FTFSI^-$ anions readily get reduced by anthracene radical anion (≈ 1.0V vs. Li^+/Li^o), resulting in the formation of stable SEI layer components. On the contrary, $LiPF_6$, LiTDI and LiTFSI were found to be highly stable, even to lower potential reducing agent such as biphenyl (≈ 0.5V vs. Li^+/Li^o),enlisting the presence of predominance for salt and solvent reductions in the two categories.

Depth-profiling XPS analysis on both cycled and uncycled binder free half - cells was performed on the above-mentioned electrolyte formulations. The results provided insight into the differences and similarities of the SEI (composition, thickness, evolution etc.), resulting from the structure of the various anions.

References:

[1] E. Peled, *J. Electrochem. Soc.126 (1979)* 2047.
[2] G. G. Eshetu, S. Grugeon, G. Gachot, D. Mathiron, M. Armand, S. Laruelle, *Electrochim. Acta.102 (*2013) 133–141.
[3] Z. Chen, Y. Qin, Y. Ren, W. Lu, C. Orendorff, E. P. Roth, K. Amine, *Energy Environ. Sci.* 4 (2011) 4023.

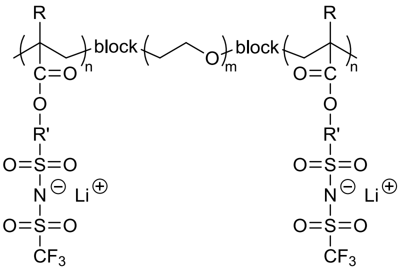
SYNTHESIS OF NEW SINGLE-ION COPOLYMER ELECTROLYTES FOR LITHIUM-METAL BATTERIES

Adèle Ferrand[a], Renaud Bouchet[b,c], Trang N.T.Phan[a], Sébastien Maria[a], Didier Gigmes[a]

[a] *Aix-Marseille Université, CNRS, Institut de Chimie Radicalaire, 13397 Marseille Cedex 20*
[b] *Université Grenoble Alpes, LEPMI, F-38000 Grenoble, France*
[c] *CNRS, LEPMI, F-38000 Grenoble, France*

email address of the presenting author: adele.ferrand@univ-amu.fr

Alternative mode of transportation such as fully-electric or hybrid vehicles are a matter of primary importance for a sustainable long-term development. In line with this societal context, the elaboration of cheap and safe batteries with high specific energy suitable for the mass-market of electric vehicles has been stimulating the scientific community for many years. Among different battery technologies, Lithium-Metal Batteries are very well-positioned[1] thanks to the high energy density of lithium. However, this technology presents several issues such as the use of liquid-based electrolytes that can lead to undesired leaks. But, the main concern of this technology is related to a possible lithium dendritic growth during charge/discharge cycles causing internal short-circuits possibly followed by dramatic explosion and fire. To overcome these drawbacks, solid polymer electrolytes (SPE) combining both high conductivity and suitable mechanical properties to prevent dendritic growth are perfect candidates. Recently, we demonstrated the remarkable potential of multifunctional single-ion block copolymers based on polystyrene derivatives and poly(ethylene oxide) as SPE for Lithium-Metal battery technology.[2-3] In order to constantly improve the SPE properties and to get a better insight of their mode of action, we present in this study the synthesis of new series of single-ion copolymer electrolytes based on anionic poly(meth)acrylate derivatives. (Fig.1)



R = H or CH_3
R'= alkyl group

Fig.1: Structure of single-ion block copolymer electrolyte

Various block copolymers with different compositions were synthesised using the Nitroxide-Mediated Polymerization technique. Their performance as SPE for ionic conduction was evaluated by electrochemical impedance spectroscopy.

[1] M. Armand, J-M. Tarascon, Nature. 451 (2008) 652–657.
[2] R. Bouchet, S. Maria, R. Meziane, A. Aboulaich, L. Lienafa, J-P. Bonnet, T.N.T. Phan, D. Bertin, D. Gigmes, D. Devaux, R. Denoyel, M. Armand, Nature Materials. 12 (2013) 452-457.
[3] R. Bouchet, T.N.T. Phan, E. Beaudoin, D. Devaux, P. Davidson, D. Bertin, R. Denoyel, Macromolecules. 47 (2014) 2659-2665.

Hierarchically Structured Materials for Supercapacitors and Batteries

Michael G. Fischer, Xiao Hua, Preston Sutton, Ullrich Steiner
Adolphe Merkle Institute, Chemin des Verdiers 4, 1700 Fribourg, Switzerland

email address of the presenting author: michael.fischer@unifr.ch

Amphiphilic block-copolymers are known to form well-ordered structures on the 10nm length-scale. Such nanostructures have been utilized to enhance the performances of solar cells[1] and supercapacitors[2] among other applications. By confining sol-gel chemistry to one of the blocks of the copolymer these structures can be transferred to various functional inorganic materials.

We synthesize and study nanostructured electrodes with different morphologies. The materials under investigation are either already used in lithium-ion batteries or supercapacitors, or considered as promising candidates for the next generation of energy materials. The obtained well-defined morphologies (cf. figure 1) provide large internal surface areas coated with carbon facilitating ionic and electronic conductivities.

We further aim to incorporate this synthesis approach into the fabrication of hierarchically structured materials. By blending the sol-gel precursor/block-copolymer mixture with a sacrificial homopolymer, macroporosity can be introduced into the electrode structure. Using this method, morphologies such as mesoporous microspheres, bicontinuous frameworks, and graded films can be obtained, which contain hierarchical pore networks. This particular structure is believed to be important to reduce the diffusion limitation of ion transport in the electrolyte to the intercalation sites of the material. In addition, a better understanding of the interplay between pore-volume and -interconnectivity will enable us to define an optimal ionic diffusivity for the electrodes, crucial for applications in consumer electronics, electromobility and large-scale energy storage.

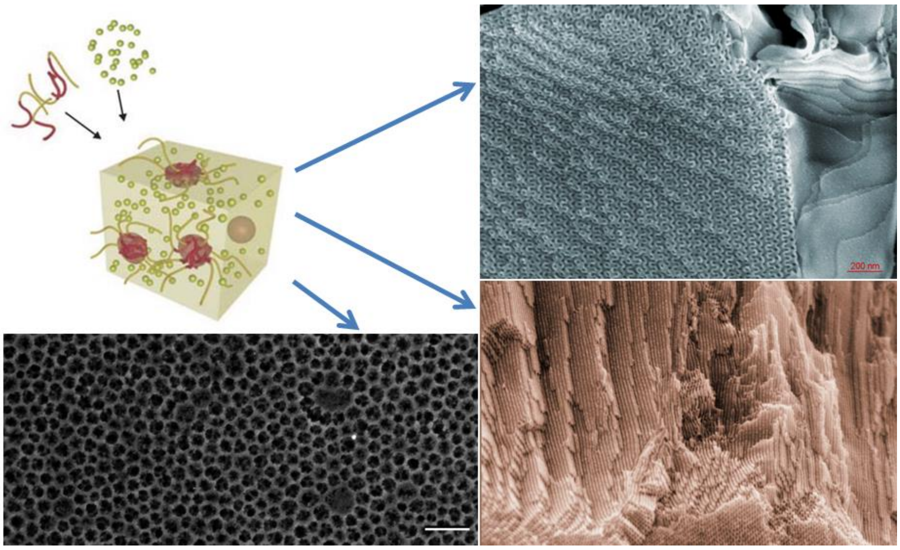


Fig. 1: Different ordered nanostructures of TiO2, obtained by combining sol-gel chemistry with block-copolymer self-assembly.

[1] E. Crossland et. al., Nano Letters 9 (2009) 2807–2812.
[2] D. Wei et. al., Nano Letters 12 (2012) 1857–1862.

POLYMER ELECROLYTES BASED ON SODIUM POLY [4-STYRENESULFONYL (TRIFLUOROMETHYLSULFONYL) IMIDE] FOR SODIUM ION BATTERIES

Oihane Garcia-Calvo[a], Asier Fernandez de Añastro[a], Nerea Lago[a], Teófilo Rojo[a,b] and Michel Armand[a]
[a] *CIC Energigune, Parque Tecnológico de Álava*
Albert Einstein, 48, ED.CIC, 01510 Miñano, Álava, (Spain)
[b] *Departamento de Química Inorgánica, Universidad del País Vasco UPV/EHU*
P.O.Box.644, 48080, Bilbao, (Spain).

ogarcia@cicenergigune.com

Sodium batteries are an incipient and competitive alternative of lithium batteries due to principally low-cost and abundance of sodium [1–4]. The development of safe and reliable sodium electrolytes is a critical factor needed for their success. The criteria for choosing an electrolyte in sodium batteries are: wide electrochemical window, stability against metallic sodium or low voltage intercalation anodes, and high ionic conductivity [5]. The main challenge to overcome in that field is the compatibility between electrodes and electrolytes that will lead in an efficient cycling. One strategy is to use solid electrolytes and, in particular, polymer electrolytes because they exhibit advantages against ceramics in terms of processability. Some solid polymer electrolyte designs contain a polymeric anionic framework, in which only the cations are capable of diffusion, being the transference number of these electrolytes close to the unity.

Taking into account the recent research based on the synthesis of sodium poly[(4-styrenesulfonyl)(trifluoromethylsulfonlyl)imide] (PSTFSI-Na) solid polymer electrolytes [6], here we describe an study of the electrochemical behavior of PEO (M_w $5 \cdot 10^6$)/PSTFSI-Na blends as polymer electrolytes for rechargeable Na-ion batteries.

The electrochemical characterization of these materials showed the highest ionic conductivity at operational temperature (70ºC) of 10^{-5} S cm^{-1} when the ratio [EO]/[Na] is about 17. Moreover, the cyclic voltammetry and galvanostatic cycling results showed that the PEO/PSTFSI-Na blends could work as the electrolyte in an all-solid-state sodium-ion battery.

---

[1] Kundu, D. Talaie, E. Duffort, V. Nazar, L. F. Angew. Chemie Int. Ed. 54 (2015) 3431–344.

[2] Ellis, B. L. Nazar, L. F. Curr. Opin. Solid State Mater. Sci. 16 (2012) 168–177.

[3] Slater, M. D. Kim, D. Lee, E. Johnson, C. S. Adv. Funct. Mater. 23 (2013) 947–958.

[4] Palomares, V. Serras, P. Villaluenga, I. Hueso, K. B. Carretero-González, J. Rojo, T. Energy Environ. Sci. 5 (2012) 5884.

[5] Hovington, P. Lagacé, M. Guerfi, A. Bouchard, P. Mauger, A. Julien, C. M. Armand, M. Zaghib, K. Nano Lett. 15 (2015) 2671–2678.

[6] Li, J. Zhu, H. Wang, X. Armand, M. MacFarlane, D.R. Forsyth, M. Electrochim. Acta 175 (2015) 232–239.

INTERFACE STUDIES OF ELECTRODES AND POLYMERS ELECTROLYTE BASED ON LI-CONDUCTIVE IMIDAZOLE SALTS

J.L. Gómez-Cámer[a], B. Acebedo[a], T. Trzeciak[b], M. Marcinek[b], M.A. Muñoz-Márquez[a]
[a] *CIC Energigune, Albert Einstein 48, 01510 - Miñano, Spain*
[b] *Department of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland*

email address of the presenting author: mamunoz@cicenergigune.com

The electrolyte is one of the most critical components in Li-ion batteries (LIBs) with regard to safety and ageing. Current LIBs are based on liquid electrolytes which derive from lithium salts dissolved in organic carbonates. Despite being the electrolytes of choice in the vast majority of LIBs, these liquid electrolytes show an undesired electrochemical instability along with a serious risk of leakage which is the last thing one would like to have when dealing with organic flammable solvents.

A LIB based on a solid polymer electrolyte (SPE) would overcome the safety and chemical stability problems of batteries based on liquid electrolytes. Moreover, the SPE would remove the necessity of using a separator in the LIB [1].

Despite SPEs offer improved properties, their conductivity at room temperature remains an issue. However, this can be turned into an advantage for high temperature applications since a LIB based in a SPE would provide an enhanced safety compared to batteries based on organic solvents.

One of the key factors to understand LIB battery operation is the solid electrolyte interface (SEI). Widely studied in LIBs based in liquid electrolytes, this layer is originated from the difference in the stability window of the electrolyte and the electrochemical potential of the electrodes. Typically, the SEI is formed during the first discharge cycle of the anode and it is mainly composed by degradation products of the electrolyte salt and species arising from the solvent reduction. The stability and composition of the SEI will seriously influence the rate capability, reversible capacity and safety of the batteries.

The importance of SEI formation in LIBs based on SPE has been recently shown [2]. In this presentation we will report the results of our latest investigations on the SEI composition in both electrodes of a SPE based C/Li cell. In this case we will show the superior performance of our SPE based on lithium conductive imidazole salts, as well as the characteristics of the SEI layers which have been analysed by means of X-ray Photoelectron Spectroscopy (XPS). The main differences of the SEI layer composition in conventional liquid electrolytes and solid polymer electrolytes will be discussed.

Acknowledgments

Support from EU FP7 program SIRBATT (contract no. 608502) is gratefully acknowledged. Juan de la Cierva Program from the Spanish Ministry of Economy and Competitiveness is also acknowledged.

[1] M. Armand and J.-M. Tarascon, Nature 451 (2008) 652.
[2] C. Xu, B. Sun, T. Gustafsson, K. Edström, D. Brandell and M. Hahlin, J. Mater. Chem. A 2 (2014) 7256.

Fabrication of flexible an all solid state thin film lithium battery with high volumetric energy density and safety

Chi-Hung Su*, Yuan-Ruei Jheng, Der-Jun Jan, Tien-Hsiang Hsueh, Yuh-Jeng Yu

Physics Division, Institute of Nuclear Energy Research, Taoyuan, 325 Taiwan

Email : chihung0927@iner.gov.tw

Wearable electronics have a market of $16.04 billion in 2013 and are expected to grow to over $80 billion by 2024. The growth of wearable electronics is towards the development of lightweight, slightness and being close to people life. Batteries used in wearable electronics require not only high energy density but also other characteristics such as cell size, safety, thickness and flexibility. However, the size and shape design of traditional Li batteries are limited because of their liquid electrolytes which are lithium salts in an organic solvent. In addition, liquid electrolytes have safety and health issues as they use flammable and corrosive liquids.

Flexible all-solid-state thin film lithium batteries (TFLB) are composed of solid materials and are assembled layer by layer. It is easy to make them thin and small size. Solid-state lithium batteries have high energy density and power density and are safety. In this study, we applied radio-frequency magnetron sputtering to produce flexible an all-solid-state TFLB on the flexible stainless steel substrates. Electrochemical characterization of this flexible TFLB revealed a discharge capacity of 570 μAh (or 47.3 μAh um^{-1} cm^{-2}) and the volumetric energy density was 177 μWhcm^{-2}μm^{-1}(or 1,770 Wh/L) between 3V and 4.3V. This TFLB has volumetric energy density three times higher than the traditional lithium battery. The maximum capacity retention in excess of 83 % was achieved after 50 charge-discharge cycles between 4.2V and 3V. During the folding, hitting, penetrating, or burning test, the TFLB was no vapor, no fire, and no explosion. Those tests can prove this TFLB has more safety.

Keywords: all solid state, thin film lithium battery, flexible, high volumetric energy density

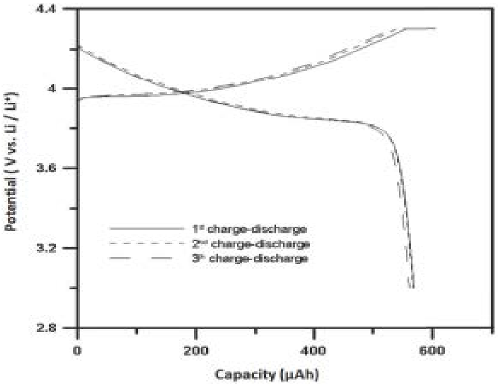
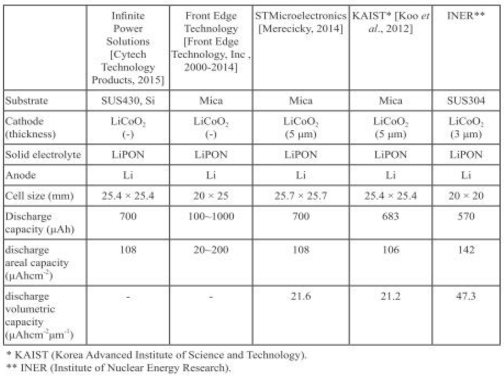


Figure 1. Charge and discharge behavior of a thin film all solid state lithium batteries at the first three cycles.

Table 1. Compare of the all solid state thin film lithium battery with international companies.



	Infinite Power Solutions [Cytech Technology Products, 2015]	Front Edge Technology [Front Edge Technology, Inc , 2000-2014]	STMicroelectronics [Merecicky, 2014]	KAIST* [Koo *et al.*, 2012]	INER**
Substrate	SUS430, Si	Mica	Mica	Mica	SUS304
Cathode (thickness)	$LiCoO_2$ (-)	$LiCoO_2$ (-)	$LiCoO_2$ (5 μm)	$LiCoO_2$ (5 μm)	$LiCoO_2$ (3 μm)
Solid electrolyte	LiPON	LiPON	LiPON	LiPON	LiPON
Anode	Li	Li	Li	Li	Li
Cell size (mm)	25.4 × 25.4	20 × 25	25.7 × 25.7	25.4 × 25.4	20 × 20
Discharge capacity (μAh)	700	100~1000	700	683	570
discharge areal capacity (μAhcm^{-2})	108	20~200	108	106	142
discharge volumetric capacity (μAhcm^{-2}μm^{-1})	-	-	21.6	21.2	47.3

* KAIST (Korea Advanced Institute of Science and Technology).
** INER (Institute of Nuclear Energy Research).

References

[1] M. Koo, K.I. Park, S. H. Lee, M. Suh , Nano Lett. 12 (2012) 4810 – 4816.
[2] Front Edge Technology, Inc , 2000-2014, form http://www.frontedgetechnology.com/
[3] Andrew Merecicky, June 23, 2014, form http://www.windpowerengineering.com/design/long-life-paper-thin-batteries-stmicroelectronics/
[4] Cytech Technology Products, 2015,form http://www.cytech.com/products-ips

Interfacial stability of Ni-rich layered oxide cathodes

Aude Hubaud[a], Fulya Dogan[a], Cameron Pebbles[a], Chen Liao[a], John Vaughey[a]
[a] *Chemical Science and Engineering Division*
Argonne National Laboratory (Argonne, IL USA)

aahubaud@anl.gov

Ni-rich NCM materials ($LiNi_xCo_yMn_zO_2$, $x \geq 0.5$) have been considered as some of the most promising alternative cathodes to $LiCoO_2$ for Li-ion batteries due to their higher capacity, lower cost and improved safety. However, the operation at high voltage required for high capacity results in rapid capacity fade.

We have been investigating the degradation mechanisms of selected Ni-rich NCM cathode materials at high voltage. The surface of the material appeared to suffer from an irreversible transformation with the formation of an ionically insulating rock salt phase. The presence of the rock salt phase could result in sluggish kinetics, thus causing the capacity fade. This suggests that preventing the surface degradation of NCM materials could help retaining high capacity during the operation at high voltage.

One approach to prevent the surface degradation of the cathode material is to change the surface properties by coating the particles. We have been developing a variety of ceramic coatings, as well as novel organic and composite coatings. We have been investigating the effect of the various coatings on the stability of the cathode surface as well as the effect on the electrochemical performance of the materials.

Fabrication of the random mixed Li-Cu structure to prevent dendrite growth for lithium metal battery.

Sun Woo Hwang[1], Jee Ho Yeom, Jae Won Lee, Sumg Man Cho and Woo Young Yoon*

Department of Materials Science and Engineering, Korea University, 1, 5Ga, Anam-dong, Sungbuk-Gu, Seoul 136-701, Republic of Korea., email adress: luffi778@gmail.com
**Corresponding author: E-mail address: wyyoon@korea.ac.kr; Tel.: +82 2 3290 3274; Fax: +82 2 928 3584*

The lithium (Li) metal is the most appropriate material for rechargeable Li metal battery (LMB) system by anode. It has enormous theoretical capacity at 3860 mAh g^{-1}, low pure density at 0.534 g cm^{-3} and lowest negative standard hydrogen electrode (SHE) at -3.045 V [1]. In this reasons Li metal anode is promised to applicate the post Li ion battery (LIB) industry such as electric vehicle (EV) and energy storage system (ESS). However usage of Li metal is restricted by dendrite growth of Li metal when Li ions are deposited on the Li surface. It makes loss of electrolyte and reducing safety of battery. To solve this problem we recommend the random structure which mixed the Li and Copper (Cu) powder.

We made the Li metal as the powder by droplet emulsion technique (DET), the average diameter of Li powder as 10 μm. The Li powder and Cu powder (< 20 μm) were mixed by the wye tube (Li: Cu = 2: 1 vol. %) and rotated 1,000 rpm at 24 hours. Afther mixing process we put the polyvinylidene fluoride (PVdF) binder and triethly phosphate (TEP) to fabricate the slurry. We casting the slurry on the Cu foil and heated the oven 12 hours.

The Li-Cu structure can block the dendrite growth when Li ion deposited on the Li metla surface. The Cu powder mixed with the Li powder which controlled the movement of Li ion. It makes Li ions stacked there origin sites when the battery charged. Also it makes available to increase the Li usage. The Cu structure can maintain there morpholgy in spite of battery cycling. Then Li can possibly stacked the vacancy site which located beside the Cu structure in stable. This characterstics make increase the energy density, life and safety of Li metal anode and suitable to applicate the post LIB system such as Li-S and Li-O_2 battery

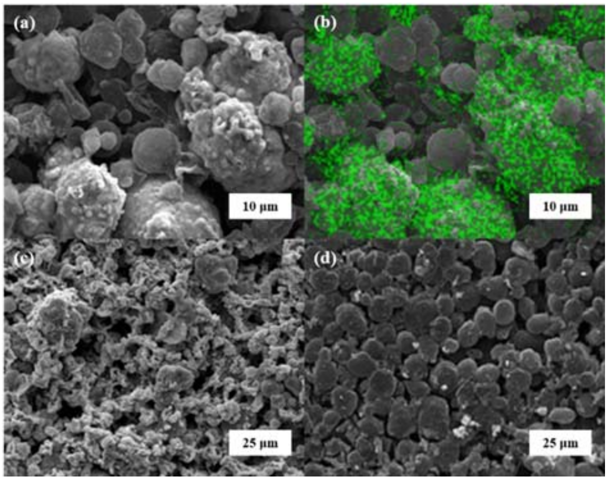


Figure 1. The SEM and EPMA images of Li-Cu structure. (a-b) SEM images of pure Li-Cu (green : Cu), (c) 100 cycles discharged (d) 100 cycles charged Li-Cu surface

Reference

[1 W. Xu, J. Wang, F. Ding, X. Chen, E. Nasybulin, Y. Zhang and J-G. Zhang, Energy Environ. Sci. 7 (2014) 513-537.

Synthesis and characterization of new single ion electrolytes for lithium metal polymer batteries

Adrien Lassagne[a,b], Renaud Bouchet[a,b], Cristina Iojoiu[a,b]
[a] *Université Grenoble Alpes, LEPMI, F-38000 Grenoble, France*
[b] *CNRS, LEPMI, F-38000 Grenoble, France*
Email address of the presenting author: adrien.lassagne@lepmi.grenoble-inp.fr

Due to their great success for portable electronic devices, lithium-based batteries are becoming increasingly important for (hybrid) electric vehicles[1]. One major issue towards large-scale applications concerns their safety.
The use of a solid polymer electrolyte (SPE), which is commonly a lithium salt associated with a polyethylene oxide (PEO) without organic solvents, could solve most of the safety issues encountered with liquid electrolytes. However, the development of SPE has been hampered by two hurdles: i) the inability to design a SPE with both: high ionic conductivity and good mechanical properties and ii) the low cationic transport number[2], which leads during battery operation to the formation of a strong concentration gradient with deleterious effects which favored dendritic growth[3] and limited power delivery.

In order to combine, in a same material, the two antagonistic properties (mechanical and conductivity), block copolymer electrolytes (BCE) have recently been proposed as SPE[4–8]. The interesting properties of these functional materials is a consequence of their self-assembly properties, which give rise to ordered structures and permits an addition of properties instead of average ones.
Recently, Bouchet et al.[9] synthetized triblock copolymers based on polystyrene bearing trifluoromethansulfonimide (PSSI) and PEO (PSSI-PEO-PSSI) and obtained a single-ion conductivity of 1.3 10^{-5} $S.cm^{-1}$ at 60° C.
In order to improve the electrolyte performances we synthesised new BCE in which the nature of anion was varied. The impact of anion nature, lengths of blocks, elaboration method on the mechanical strength, conductivity, cationic transference number and lithium metal cell performances are largely discussed in this work.

1. Armand, M. & Tarascon, Nature 451, (2008), 2–7
2. Devaux, D., Bouchet, R., Glé, D. & Denoyel, R. Solid State Ionics 227, (2012), 119–127
3. Chazalviel, J.-N. Phys. Rev. Lett. 42, (1990), 7355–7367
4. Ionescu-vasii, L. L., Garcia, B. & Armand, M. Solid State Ionics 177, (2006), 885–892
5. Singh, M. et al. Macromolecules, 40, (2007), 4578-4585
6. Young, N. P., Devaux, D., Khurana, R., Coates, G. W. & Balsara, N. P. Solid State Ionics, 263, (2014), 87-94
7. Bouchet, R. et al. Macromolecules, 47, (2014), 2420-2429
8. Beaudoin, E. et al. Langmuir, 29, (2013), 10874-10880
9. Bouchet, R. et al. Nat. Mater. (2013)

Nanoscale PEEM spectroscopy combined with XPS to elucidate the surface reaction mechanism of cycled electrodes

Daniela Leanza[a], Carlos A. F. Vaz[b], Alice Gillen[a], Petr Novàk[a], Mario El Kazzi[a]

[a] *Paul Scherrer Institute, Electrochemistry Laboratory, 5232 Villigen PSI, Switzerland*
[b] *Paul Scherrer Institute, Swiss Light Source, 5232 Villigen PSI, Switzerland*

Daniela.Leanza@psi.ch

For the first time we explore the potential and feasibility of X-ray PhotoEmission Electron Microscopy (PEEM) to investigate commercial-like battery electrodes and to study separately, at the nanoscale level, the surface layer chemistry evolution on the active materials and on the conductive carbon. Two types of electrodes are investigated, LiM (M=Mn, Ni, Co)O_2-Li_2MnO_3 (NCM) and $Li_4Ti_5O_{12}$ (LTO), as promising positive and negative electrodes, respectively, for Li-ion batteries. Thanks to the PEEM technique, we are able to overcome the limited spatial resolution and poor sensitivity to transition metals of conventional X-ray photoemission spectroscopy (XPS). Furthermore, both techniques probe the same range of depth (< 8nm). The elemental contrast images in Figure 1.I attest the high lateral resolution of PEEM and its ability to distinguish single particles of the active materials, NCM or LTO, from the conductive carbon in typical commercial-like electrodes, without the need of using model systems. The local XAS spectra (Figure 1.II) at the Ni-, Co-, Mn-L edges and C-K edge acquired on NCM particles allow us to monitor their oxidation states as well as the chemical species present on the surface without interference from the signal arising from the conductive carbon. By combining PEEM with XPS (Figure 1.III) during the early stage of cycling together with long cycling, we can obtain a better insight on the mechanism behind the surface layer formation on the positive and negative electrodes. Moreover, the origin of the surface layer present on LTO was elucidated, alongside the impact of the high potential on the NCM structure stability.

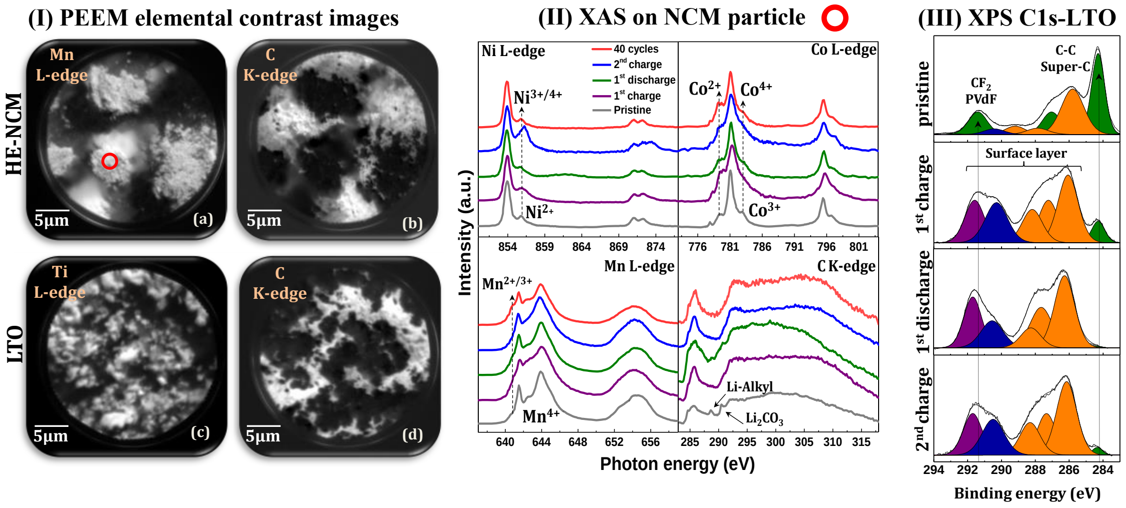

(I) PEEM elemental contrast images
(II) XAS on NCM particle
(III) XPS C1s-LTO

Figure 1: (I) Element-specific PEEM contrast images performed on NCM (a, b) and LTO (c, d) pristine electrodes. **(II)** XAS evolution of the transition metals oxidation states as well as the surface layer formation acquired on one single NCM particle. **(III)** LTO surface layer formation probed by XPS C1s core level.

A Systematic Study of Some Promising Electrolyte Additives in $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$/Graphite, $Li[Ni_{0.5}Mn_{0.3}Co_{0.2}]$/Graphite and $Li[Ni_{0.6}Mn_{0.2}Co_{0.2}]$/Graphite Pouch Cells

Lin Ma[a], Julian Self[a], Mengyun Nie[a] and J. R. Dahn[a]
[a]*Department of Physics and Atmospheric Science,*
Dalhousie University, Halifax, B3H 3J5, Canada

e-mail address of the presenting author: l.ma@dal.ca

$Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ (NMC111)/graphite, $Li[Ni_{0.5}Mn_{0.3}Co_{0.2}]O_2$ (NMC532)/graphite and $Li[Ni_{0.6}Mn_{0.2}Co_{0.2}O_2]$ (NMC622)/graphite pouch cells were examined with and without electrolyte additives using the ultra high precision charger (UHPC) at Dalhousie University, electrochemical impedance spectroscopy (EIS), gas evolution measurements and "cycle-store" tests. The electrolyte additives tested were vinylene carbonate (VC), prop-1-ene-1,3-sultone (PES), pyridine-boron trifluoride (PBF), 2% PES + 1% methylene methanedisulfonate (MMDS) + 1% tris(trimethylsilyl) phosphite (TTSPi) (PES211) and 0.5% pyrazine di-boron trifluoride (PRZ) + 1% MMDS. The charge end-point capacity slippage, capacity fade, columbic efficiency (CE), impedance change during cycling, gas evolution and voltage drop during "cycle-store" testing were compared to gain an understanding of the effects of these promising electrolyte additives or additive combinations on different NMC/graphite pouch cells.

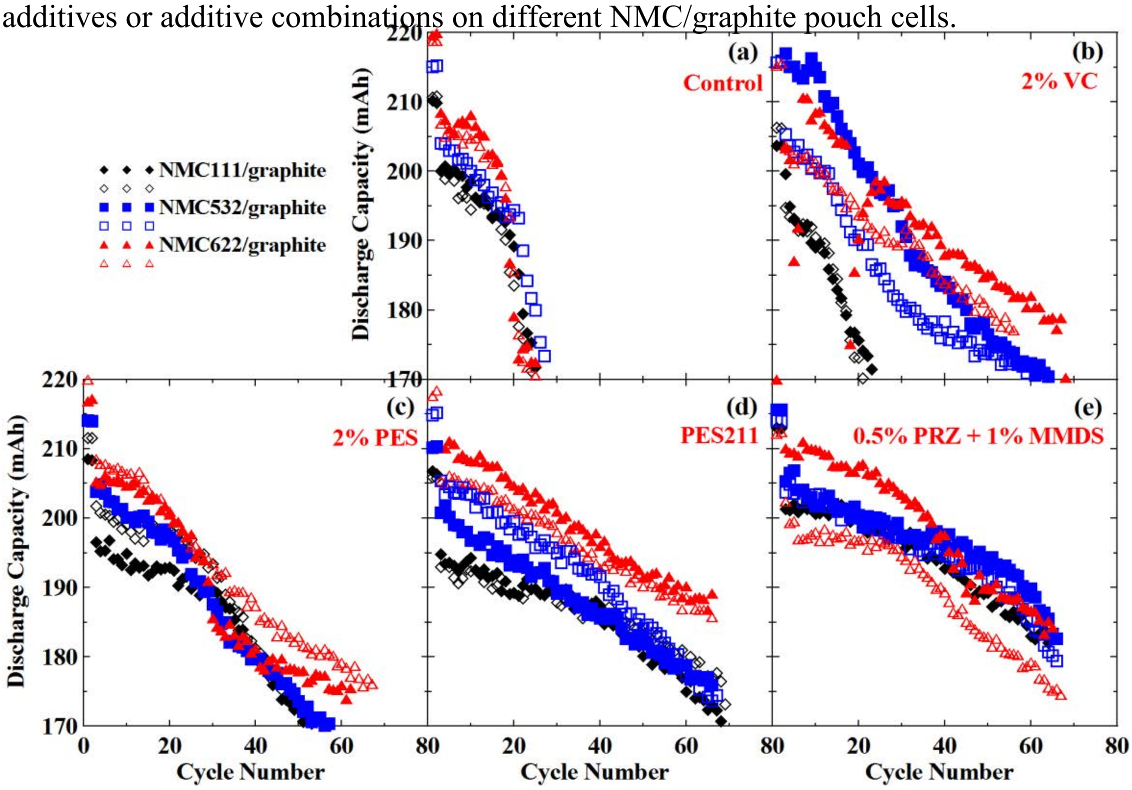


Figure 1. Capacity versus cycle number for NMC/graphite pouch cells with various electrolyte additives as indicated. Cells were charged and discharged between 2.8 and 4.4 V at 40°C at C/5. There was 24 h OCV period at the top of every charge. This is a very aggressive test. Notice that the electrolyte additive blends "PES211" and PRZ + MMDS are effective for every NMC grade while VC is only effective in this test for the highest Ni content grade (NMC622).

IMIDAZOLIUM-BASED MONO AND DICATIONIC IONIC LIQUID SODIUM ELECTROLYTES

Enrique Morales[a], Carmen del Río[a], Bernardo Herradón[b], Enrique Mann[b]
[a] *Instituto de Ciencia y Tecnología de Polímeros (CSIC), c/ Juan de la Cierva 3, 28006 Madrid (Spain)*
[b]*Instituto de Química Orgánica General (CSIC), c/ Juan de la Cierva 3, 28006 Madrid (Spain)*

email address: emorales@ictp.csic.es

Sodium and sodium-ion batteries have emerged as low-cost candidates for medium and large-scale stationary energy storage because of their safety, long-cycle life and versatile geometries. Is well known that apart of electrodes, the electrolyte play a fundamental role in terms of current (power) density, the time stability, and the safety of the battery. Inorganic and polymer electrolytes are commonly used in high temperature molten Na cells based on Na–S and Na–$NiCl_2$ [1], while liquid electrolytes are usually preferred for the room temperature ones [2].

Ionic liquids, known as molten salts at room temperature, have recently been of great interest for energy-storage applications due to their high electrochemical stability, high thermal stability, low volatility, non-flammability, and good contact/wetting properties, even their lower ionic conductivity and high viscosity compared to classical organic carbonate solvent electrolytes limit their use as high-performance electrolytes. In this present work, we report on the synthesis, thermal and electrochemical characterization of imidazolium-based mono and dicationic ionic liquids doped with sodium bis(trifluoromethylsulfonyl) imide (NaNTf2) as a potential electrolyte for sodium secondary batteries. All synthesized electrolytes are highly viscous liquids at room temperature, no melting or crystallization being detected even at temperatures as low as -150ºC, and stables up to temperatures well above the operation window, with ionic conductivity comparable to that of the corresponding lithium electrolytes.

Acknowledgment

Financial support from project MAT2014-54994-R is gratefully acknowledged.

References

[1] K.B. Hueso, M. Armand, T. Rojo, Energy Environ. Sci.,6(2013) 734-749.
[2] Monica Sawicki and Leon L. Shaw, RSC Adv., 5 (2015) 53129-53154.

Increase in the ionic conductivity of LiPON-type thin films electrolyte for lithium microbatteries

Antoine Munier[a], Lucie Le Van-Jodin[a] , Laurent Figuière[b]
[a] *CEA LETI/DCOS/SCPE/LMBE, 17 Rue des Martyrs, F-38054 Grenoble, France*
[b] *STMicroelectronics, Advanced Technologies R&D, IMS/ASD & IPAD division, 16 rue Pierre et Marie Curie, B.P.7155, F-37071 Tours Cedex 2, France*
antoine.munier@cea.fr

Introduction

With the development of portable electronic devices, thin films microbatteries are becoming an interesting alternative to button cells or supercapacitors [1]. The most useful electrolyte is the LiPON, proposed by Bates et al. [2]. The objective of this study is to increase the ionic conductivity of LiPON to reduce the internal resistance. The increase of the ionic conductivity with the increase of the Li content was studied. Correlation between stoichiometry and performance of the electrolyte were analyzed.

Experimental

The LiPON-type electrolyte films were deposited using radio-frequency magnetron sputtering. Power, pressure and N_2 flow rate were modified to optimized the electrolyte performances. The deposition rate, ionic conductivity, activation energy, electronic conductivity were determined by impedance spectroscopy and I(t) and the chemical composition by Inductive Coupling Plasma – Optical Emission Spectroscopy.

Results and discussion

With the variation of the deposition parameters, the ionic conductivity was almost doubled with an increase from $1{,}8.10^{-6}$ S/cm for standard LiPON films to $3{,}2.10^{-6}$ S/cm for LiPON-type films (Figure 1).

Conclusion

The new LiPON-type films developed in this study are suitable to be used as electrolyte in microbattery with a promising increase (almost doubled) of ionic conductivity and then a decrease of the internal resistance.

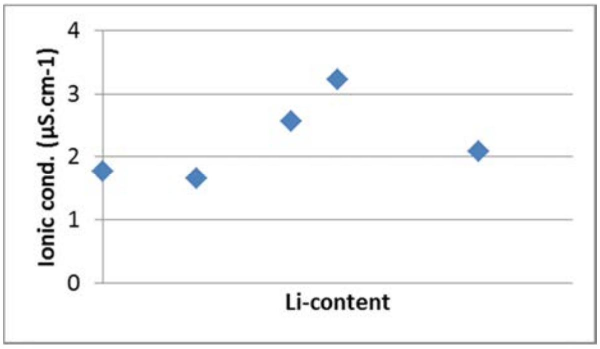


Figure 1 : Evolution of the ionic conductivity versus Li content

[1] B. Pecquenard, F. Le Cras, M. Martin, P. Vinatier, A. Levasseur, R. Salot, Techniques de l’ingénieur, J. Sci. Commun. 163 (2010) 51–59.
[2] J.B. Bates et al J. Power. Sources 43 (44) (1993) 103

SEI CHARACTERIZATION AND FAILURE MECHANISM OF SI ELECTRODES IN FULL LI-ION CELLS

Lucille Quazuguel[1], Nicolas Dupré[1], Philippe Moreau[1], Christian Rudish[1], Julien Danet[2],
Maxime Boniface[2], Eric De Vito[2], Sandrine Lyonnard[2], Pascale Bayle Guillemaud[2] and
Dominique Guyomard[1]
[1] Institut des matériaux Jean Rouxel (IMN), Université de Nantes-CNRS, 2 rue de la Houssinière, 44322 Nantes, France
[2] Commissariat à l'énergie atomique et aux énergies alternatives (CEA), INAC, F-38054 Grenoble 9, France

Corresponding e-mail: lucille.quazuguel@cnrs-imn.fr

Silicon-based electrodes are very attractive negative electrodes for lithium-ion batteries (LiB) compared to graphite due to their very high specific capacities (3572mAh g^{-1} vs 372mAh g^{-1}). However, a high cycling irreversibility appears on cycling due to 300 % volume expansion of the silicon particles, leading to cracks and decrepitation, creating new surfaces of silicon bound to react with the electrolyte. 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 [1].

This work takes part in the on-going European project Baccara (BAttery and superCapacitor ChARAacterization and testing) (http://project-baccara.eu/). Cells (nano-Si *vs* NMC) are cycled in carbonate electrolyte with a limited lithiation capacity of 1200mAh g^{-1} of silicon at a rate of one lithium in 2h in delithiation and lithiation of the silicon electrode (Figure 1a).

Classical and advanced techniques (NMR, XPS, TEM-EELS, FIB-TOFSIMS) are used to investigate and characterize silicon surface, Si/electrolyte interface, lithiated/non lithiated phases and explore and analyse their evolution upon aging/cycling of the full cell. Surface investigations show that a continuous SEI layer is formed during cycling, mainly composed of inorganic species such as LiF and organic species. The formation of the inorganic part of the SEI occurs during the early stage of cycling and this layer was found to not increase over the course of cycling (Figure 1b). Although the organic species produced by the degradation of organic solvents seem to be lithiated during the first part of the cycling, carbonate species found in the outer part of the SEI for an extended cycling are clearly not lithiated.

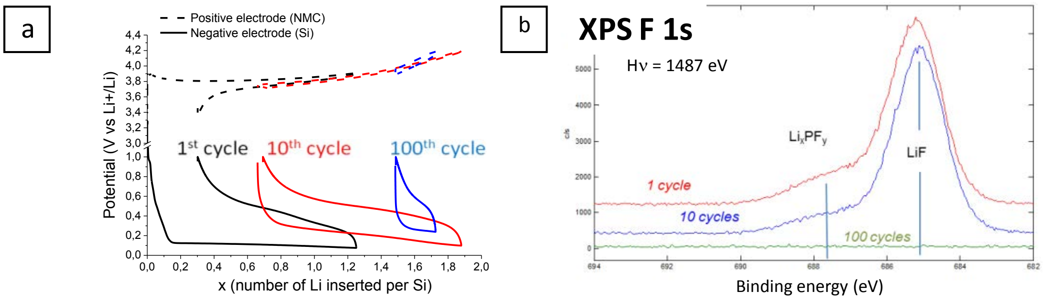


Figure 1 : a) Electrochemical behavior of negative and positive electrodes versus x, the lithium content at different cycles and b) F 1s XPS spectra of Si electrodes after 1st, 10th and 100th (end of lithiation)

References

1. Mazouzi, D.et al. J. Power Sources, 220, 180-184 (2012).
2. Obrovac, M. N., & Krause, L. J. J. Electrochem. Soc., 154, A103 (2007).
3. Mazouzi, D., Lestriez, B., Roué, L., & Guyomard, D. Electrochem. Solid-State Lett., 12 (11) (2009).

Novel electrolytes based on “Hindered glymes” - a strategy to prevent graphite exfoliation in Lithium secondary batteries

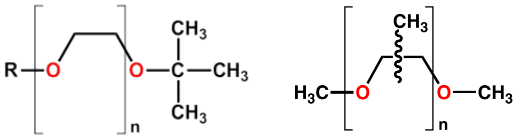
Devaraj Shanmukaraj[a], Sylvie Grugeon[b,c], Stephane Laruelle[b,c] and Michel Armand[a,b*]

[a]*CIC Energigune, Parque Tecnologico de Álava, Albert Einstein 48-ED.CIC 01510 Miñano, Spain*

[b]*Laboratoire de Réactivité et Chimie des Solides, CNRS UMR 7314, Université de Picardie Jules Verne, 33 rue Saint Leu, 80039 Amiens, France*

Email address of the presenting author: dshanmukaraj@cicenergigune.com

Commercial lithium batteries use as electrolytes, mixtures of at least one cyclic carbonate, the most common of which is ethylene carbonate (EC) to which various proportions of propylene carbonate (PC) can be optionally added. Since such cyclic carbonates are either solid (EC) at room temperature, or highly viscous (PC), co-solvents or thinners are usually added, the most common of which are dimethyl carbonate (DMC), diethyl carbonate (DEC) and ethyl-methylcarbonate (EMC). The solutes containing in the electrolyte compositions are usually selected from lithium salts with low lattice energy like $LiBF_4$, $LiCF_3SO_3$, $Li[CF_3SO_2)_2N]$, $LiPF_6$. In practice, $LiPF_6$ is almost exclusively used because of its high conductivity and beside does not corrode aluminum, the current collector, at potentials up to 4.5 V vs $Li^+/Li°$.The linear components (DMC, DEC, EMC) acting mainly as thinner of more viscous and high-melting EC, are however the least stable component and have low flash points that are serious handicaps for lifetime and safety. It thus makes it a critical requisite to reconsider the choice of the electrolyte, especially trying to get rid of the alkyl carbonate, fragile to reduction (RO^-, $RCO_2^{\bullet}$) [1], and with low flash points (dimethyl carbonate, DMC, Fp = 17 °C). On the other hand, poly ethers are a good alternative, Moreover ethers [2, 3] are also easily biodegradable solvents that are very stable to reduction and anodically withstand up to 3.9 V but all formerly known representatives solvates Li^+ strongly enough to co-intercalate in the graphite negative electrode and exfoliate it. We have put forward a new electrolyte composition comprising a polyether to which a bulky *Tert*-butyl group is appended (“hindered glyme”), totally preventing co-intercalation while keeping good conductivity. This alkyl carbonate-free electrolyte shows remarkable cycle efficiency of the graphite electrode, not only at RT, but also at 50 and 70°C with lithium bis(fluorosulfonimide) salt. The two-ethylene bridge “hindered glyme”[4] has higher boiling point and a flash point of 80°C, a considerable advantage for safety.



Tert -G2: n = 2, R =Et   DP (n = 2)

Figure 1. Chemical structure of the glymes under study

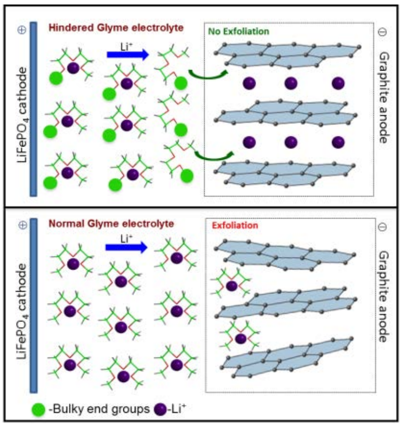


Figure 2. Concept of preventing solvent co- intercalation

1. D. Aurbach, B. Markovsky, I. Weissman, E. Levi, Y. Ein-Eli, *Electrochim. Acta* 45 (1999) 67-86.
2. D. Aurbach, E. Granot, *Electrochim. Acta* 42(1997) 697-718.
3. S. Tobishima, H. Morimoto, M. Aoki, Y. Saito, T. Inose, T. Fukumoto, T. Kuryu, *Electrochim. Acta* , 49 (2004) 979-978.
4. D. Shanmukaraj, S. Grugeon, S. Laruelle,M. Armand, *Chem Sus Chem,* 8(2015) 2691-269.

QUANTIFYING THE “ELECTROLYTE DECOMPOSITION REACTION” CONTRIBUTION TO FALSELY HIGH OBSERVED CAPACITIES IN Li_2FeSiO_4 USING MÖSSBAUER SPECTROSCOPY

Anti Liivat[a], Josh Thomas[a,*], Jianghuai Guo[b] & Yong Yang[b]

[a] Ångström Advanced Battery Centre (ÅABC), Department of Chemistry,
Uppsala University, Box 538, SE-751 21 Uppsala, Sweden.
[b] State Key Lab for the Physical Chemistry of Solid Surfaces,
Department of Chemistry, Xiamen University, Xiamen 361005, P. R. of China.

* josh.thomas@kemi.uu.se

Reversible cycling of two lithium ions (and two electrons) per transition-metal (TM) ion in a Li-ion battery is seen as a highly attractive way to increase the capacity of cathode materials to better match the higher capacities of today’s anode materials – typically graphite. Such a process is suggestively more likely to occur in polyanionic cathode materials, since simple TM-oxides tend to be less stable [1]. Low-cost Fe- or Mn-based silicates, such as lithium iron silicate (Li_2FeSiO_4) [2], are ideal candidate host materials in this context, provided they do not suffer from slow kinetics or structural volatility.

Highly reactive nano-composites of Li_2FeSiO_4 and carbon, further enhanced by the presence of a glassy network to facilitate Li-ion conductivity [3], have here been studied to probe the controversy surrounding the Fe^{3+}/Fe^{4+} redox couple, and the possibility of cycling a 2nd Li-ion in this material. To this end, *in situ* Mössbauer spectroscopy has been used to monitor the oxidation state of the Fe-ions in symmetric $Li_xFe^{3+}SiO_4$/1MLiPF$_6$ EC:DEC (1:1)/$Li_xFe^{3+}SiO_4$ ($x = 1$ and ≈ 0) cells cycled at RT and at low rate (C/20) over a wide voltage window. The de-intercalation reaction and electrolyte decomposition reaction(s) can be separated effectively by combining data from cycling these $x = 1$ and $x \approx 0$ type symmetric cells. Almost 0.6Li of the lithium in Li_xFeSiO_4 ($x = 1$) can be shown to cycle reversibly over 15 cycles, as seen from *in situ* Mössbauer spectra. However, electrolyte decomposition reaction(s) constitute a large fraction of the “cycled” Li above 4.6V. This explains the discrepancy between the cycled charge, as quantified from Mössbauer and electrochemical cycling data - and is further demonstrated with ultimate clarity when ~0.7 Li/f.u. can even be seen to “cycle” above 4.6V in $x \approx 0$ type symmetric cells, despite the fact that neither of the $FeSiO_4$ electrodes themselves actually contains any intrinsic lithium!

This work has been supported by the Swedish Energy Agency (VINNOVA) and the Swedish Science Research Council (VR).

References:

[1] A.K. Padhi *et al.*, *J. Electrochem. Soc.,* 144 (1997) 1188- 1194.
[2] A. Nytén *et al.*, *Electrochem. Commun.,* 7 (2005) 156-160.
[3] J. Bai *et al.*, *J. Mater. Chem.*, 22 (2012) 12128-12132.

Ageing studies on commercial 18650 batteries used in Tesla model S electric vehicles

Marlena Uitz[a], Michael Sternad[a], Thomas Traussnig[b], Corina Täubert[b], Volker Hennige[b] and Martin Wilkening[a]

[a] *Institute for Chemistry and Technology of Materials, and Christian Doppler Laboratory for Lithium Batteries, Graz University of Technology (member of NAWI Graz), 8010 Graz, Austria*

[b] *AVL List GmbH, Hans-List-Platz 1, 8020 Graz, Austria*

marlena.uitz@tugraz.at, wilkening@tugraz.at

Li-ion batteries will be attractive energy storage devices for years to come. They benefit from a high specific capacity combined with high cyclability. In order to advance in conventional lithium-ion technology it is necessary to develop new materials and to improve existing concepts. In particular, the latter includes ageing studies on, *e.g.*, commercially available batteries. Such studies help predict the lifetime of the batteries and assist in identifying the main failure mechanisms connected to lithium plating, passivating surface films, co-intercalation or dissolution of metal ions, for example.

In the present study commercial 18650 lithium-ion battery cells were used to perform fundamental cycle and calendar ageing studies. For this purpose systematic electrochemical tests were carried out at three different temperatures, viz. – 25 °C, 40 °C and 60 °C. The cells were charged and discharged via galvanostatic cycling at different C rates ranging from 0.3 C to 1 C. For comparison, calendar ageing was electrochemically monitored at four different SOCs (100%, 80%, 50% and 20%). After the various ageing steps the capacity fade and the increase in AC and DC impedance was determined.

It turned out that temperature has little effect on calendar ageing. The capacity fade (5% at most) increases with increasing SOC. In contrast to this behavior, during cycle ageing temperature has a much larger effect on capacity fade and DC impedances. As an example, after 500 cycles at 25 °C (or 40 °C) the capacity fade is approximately 12 % of the initial value while at 60 °C the fade has reached already 22%. DC impedances measured revealed the same trend. First post mortem analyses have shown that there are indications that ageing observed might be related to changes of the solid electrolyte interphase. Hence, the changes in electrochemical performance were correlated with the thickness and composition of the SEI formed. In particular, we quantitatively measured the formation of LiF via ion exchange chromatography.

MECHANISM IDENTIFICATION IN LITHIUM-OXYGEN BATTERIES BY IMPEDANCE SPECTROSCOPY

Nuria Vicente[a], Marta Haro, Germà Garcia-Belmonte[a]
[a] *Institute of Advanced Materials (INAM), Universitat Jaume I, ES-12006 Castelló, Spain.*

email address of the presenting author: vicenten@uji.es

Li-O_2 batteries are claimed to be one of the future energy storage technologies because of their high energy density in comparison to any other type of batteries. Here Li^+ ions and O_2 directly react with each other. To produce a practical Li-O_2 battery with energy density around its theoretical value, the thermodynamic and kinetic mechanisms, which govern and limit their functioning, must be deeply understood.[1] In this study, Li-O_2 discharge process in different cathodes has been monitored by electrochemical impedance spectroscopy (EIS) [2, 3], in the presence and absence of O_2. When impedance spectra are recording from 4.0 to 2.7 V vs Li/Li^+, show the same behavior with and without O_2: it is observed an extended electrochemical double layer capacitance (EDLC) made up of adsorbed Li^+, which depends on the carbon matrix surface area. As soon as oxygen reduction reaction (ORR) voltages (~2.6 V) are tested in presence of O_2, the electrode shows a low-frequency capacitance increment accompanied of EDLC reduction. This functioning evidences that exists a competition between Li^+ surface adsorption and its consumption when ORR starts. Three steps with their characteristic reaction time and resistance in the Li-O_2 discharge could be identified: (i) interfacial phenomena, (ii) EDLC, and (iii) chemical capacitance generated by ORR. Noticeably EDLC remains unaltered after cycling. This fact suggests that the ORR products (Li_2O_2 and Li_2CO_3) are not covering the internal electrode surface, but deposited on electrode-O_2 interface, hindering thereby the subsequent reaction.
In conclusion, an equivalent circuit model is proposed to study the Li-O_2 batteries (figure 1.a), which affords to monitor adsorbed Li^+ consumption and reveal the evidence of Li^+ desorption from the C surface when the ORR starts.[4]

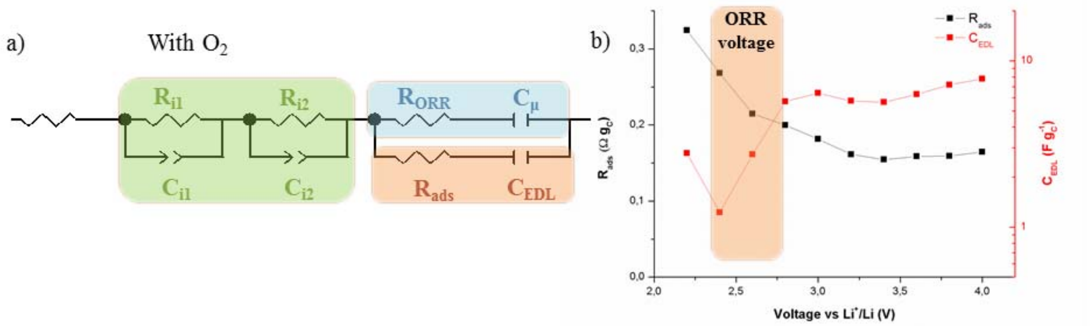


Figure 1. a) Equivalent circuit model for the system in presence of O_2: Green, interfacial phenomena; orange, EDLC; and blue, chemical capacitance ORR. b) Parameters determined during discharge process by the EIS fitting with the equivalent circuit model: resistance adsorbed Li^+, R_{ads}, and capacitance, C_{EDL}, associated to the formation of the EDL.

Reference to a journal publication:

[1] N. Imanishi, A. C. Luntz, P. Bruce The Lithium Air Battery: Fundamentals Springer (2013)J.
[2] Højberg, B. D. McCloskey, J. Hjelm, T. Vegge, K. Johansen, P. Norby, A. C. Luntz, ACS Appl. Mater. Interfaces 7, 4039 (2015)
[3] F. Martinez-Julian, A. Guerrero, M. Haro, J. Bisquert, D. Bresser, E. Paillard, S. Parrerini, G. Garcia-Belmonte J. Phys. Chem. C 118, 6069 (2014)
[4] Marta Haro, Nuria Vicente, Germà Garcia-Belmonte, Adv. Mater. Interfaces, DOI: 10.1002/admi.201500369 (2015)

NOVEL SURFACE MODIFICATION OF GRAPHITE WITH EXCELLENT PERFORMANCE FOR LITHIUM ION BATTERY

Yu-Ting Weng and Nae-Lih Wu
Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan

d96524013@ntu.edu.tw

Research in exploring alternative high-capacity lithium-ion battery (LIB) anodes in the past decades has predominantly focused on Li-alloying and conversion-reaction anodes. In spite of their potential high capacities, ranging from > 3000 mAh g^{-1} for Si anode to slight higher than 500 mAh g^{-1} for most metal-oxide conversion anodes, lithiation of these anodes involves formation of low-density lithiated products, resulting in tremendous volume expansion. The cyclic dimensional variations during charging-discharging cycles is known to result in pulverization of active-material particles and cracking and crumbling of electrode structure, leading to fast capacity fading and poor cycle life. On the contrary, graphite has an excellent cycle stability based on its theoretical lithiation capacity of 372 mAh g-1 with the potential plateau taking place well below 0.2 V (versus Li/Li). Composite anodes, therefore, comprising a limited amount of the alloying anodes, such as Si, to enhance the capacities of the graphite (G) anodes have been considered as attractive transient products for advanced high-energy LIBs before fully alloying anodes can be realized. In this paper, we report for the first time the use of thiophene-based conducting polymer blend, namely PEDOT-PSS, as a “capacity-amplifier” of several graphite-based anodes. PEDOT-PSS can be easily coated on the graphite surface by a conventional mixing-and-drying process and the electrode exhibits enhancing capacity (>700 mAh g^{-1}) and good cycle stability (>600 mAh g^{-1} after 300 cycles at 50 ^{o}C) without suffering from the volume expansion-induced capacity fading problem.

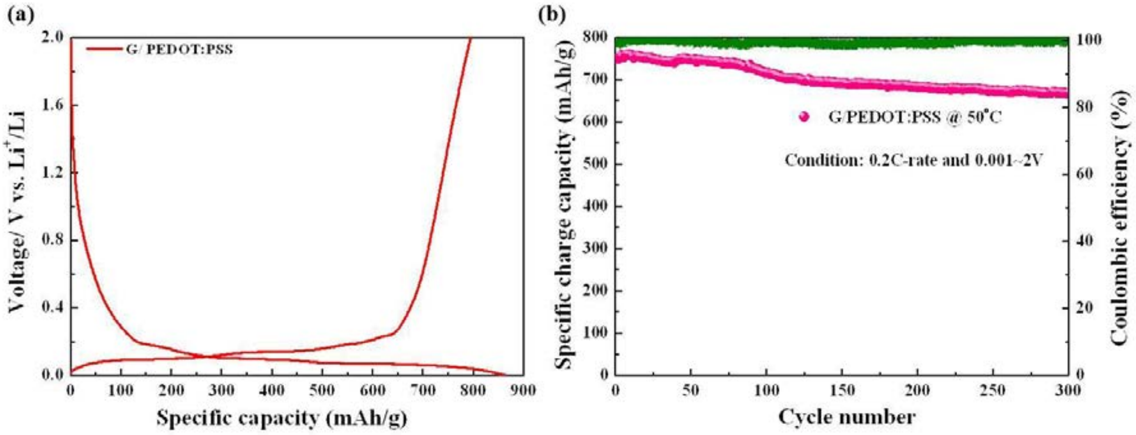


Figure 1(a) the second cycle charge–discharge voltage plots of G/ PEDOTPSS electrode acquired at 0.1 C-rate; (b) specific capacity versus cycle number of G/ PEDOTPSS electrode at a current density of 0.2 C-rate at 50 ^{O}C.

Electrolytes for High Voltage NMC Li-ion Cells

Jian Xia[a], Mengyun Nie[a], J. C. Burns[a], A. Xiao[b], W.M. Lamanna[b] and J. R. Dahn[a]*

a – Dept. of Physics and Atmospheric Science, Dalhousie University, Halifax, Nova Scotia, Canada B3H3J5
b – Electronic Materials Solutions Division, 3M Co., 3M Center, St. Paul, Mn., USA

Email address of the presenting author: jian.xia@dal.ca

Increasing the voltage of Li-ion batteries is one of the best ways to increase their energy density. However, there is no commercial electrolyte available for these high voltage cells since state-of-the-art electrolytes containing organic carbonates and typical salts are prone to decompose at high potentials. In this presentation, three electrolyte systems including ethylene carbonate (EC) – ethyl methyl carbonate (EMC), sulfolane (SL) – EMC and fluorinated carbonate mixtures composed of fluoroethylene carbonate (FEC) and bis(2,2,2-trifluoroethyl) carbonate (TFEC) with some selected additive blends were tested in high voltage $Li[Ni_{0.4}Mn_{0.4}Co_{0.2}]O_2$(NMC442)/graphite pouch cells. Figure 1a shows the voltage drop during storage at 40°C (500 h) as a function of initial open circuit voltage for the NMC442/graphite pouch cells with the three different electrolytes. Figure 1a shows that at 4.5 V or above, FEC:TFEC-based electrolytes have significantly smaller potential drops than EC:EMC-based or SL:EMC-based electrolytes, suggesting less electrolyte oxidation occurs in FEC-TFEC-based electrolytes at high potentials. Figure 1b shows the discharge capacity vs cycle number for NMC442/graphite pouch cells with the three different families of electrolytes. Figure 1c shows the difference between average charge and discharge voltage (ΔV) vs cycle number for the same cells shown in Figure 1b. Figures 1b and 1c show that cells using the FEC:TFEC-based electrolyte have the best capacity retention and least impedance growth during long term high-voltage cycling (to 4.5 V) at 40°C.

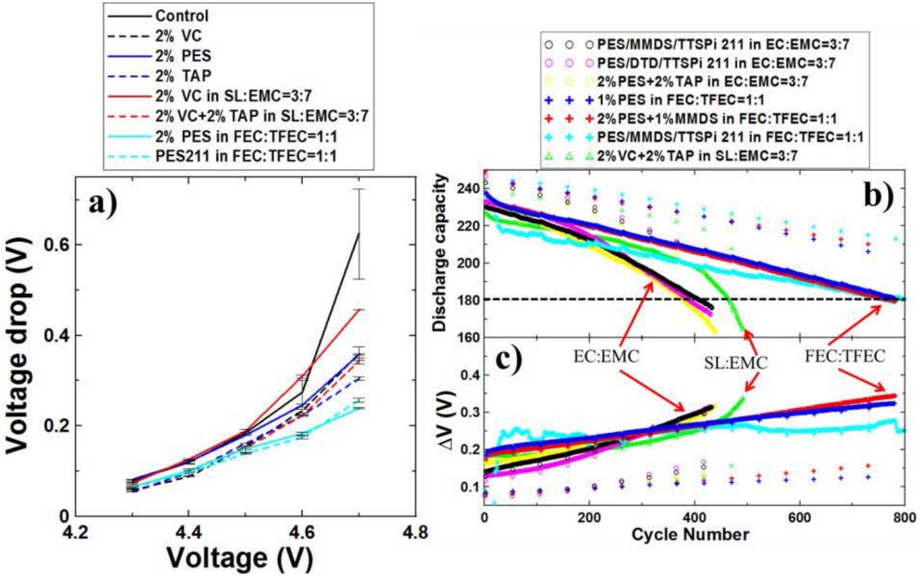


Figure 1. a) Voltage drop vs. initial open circuit voltage during storage at 40. ± 0.1ºC for 500 h, b) discharge capacity vs cycle number and c) ΔV vs cycle number for NMC442/graphite pouch cells containing EC:EMC, SL:EMC and FEC:TFEC electrolyte systems containing selected additive combinations. The long-term cycling is between 2.8 and 4.5 V at C/2.4 (100 mA) and 40C.

Understanding the surface modification mechanism of electrolyte additives on silicon anodes in Li-ion batteries

Chao Xu[a], Fredrik Lindgren[a], Nicolas Dupré[b], Bernard Lestriez[b], Dominique Guyomard[b], Kristina Edström[a], Torbjörn Gustafsson[a]
[a] *Ångström Advanced Battery Centre, Department of Chemistry-Ångström Laboratory, Uppsala University, SE-75121, Sweden*
[b] *Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, 2 rue de la Houssinière, BP 32229, 44322 Nantes Cedex 03, France*

Presenting author: chao.xu@kemi.uu.se

Silicon has been widely considered as the next generation anode material for lithium-ion batteries, due to its substantially higher capacity compared to conventionally used graphite. However, silicon-based electrodes suffer from problems such as poor capacity retention and low coulombic efficiency.[1-3] Significant amount of work has been devoted to improve the performance of silicon electrodes. Among all the efforts, electrolyte additives, fluoroethylene carbonate (FEC) and vinylene carbonate (VC) particularly, are found to be able to dramatically improve the electrochemical performance. In the present work, the decomposition mechanism of FEC as well as the surface modification of Si electrodes were investigated.[4] The FEC additive degrades prior to the other carbonate solvents at a higher reduction potential, and instantaneously a conformal solid electrolyte interphase (SEI) is formed on the silicon electrode. This stable SEI layer, which mainly consists of the decomposition products of FEC, sufficiently limits the emergence of large cracks and suppresses the additional SEI formation from the decomposition of other electrolyte components. These differences in SEI layer, formed with or without the presence of FEC, are schematically demonstrated in Fig 1. Besides, it was observed that the $LiPF_6$ decomposition can be influenced by the FEC additive, and this effect was further studied with a combination of X-ray photoelectron spectroscopy (XPS) and solid-state nuclear magnetic resonance (NMR) techniques.

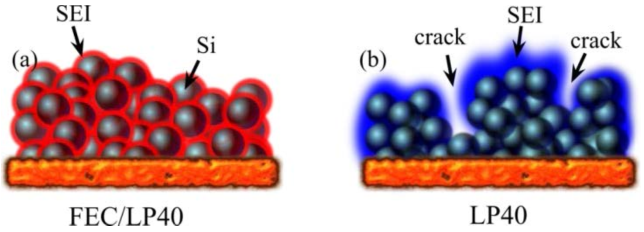


Fig 1. Schematic representation of the SEI formation on silicon anode with different electrolytes FEC/LP40 (a) and LP40 (b), respectively. The two SEI layers are different in compositions and highlighted with different colors. Reprinted with permission from ref4.

Moreover, we also demonstrated that by forming an effective SEI layer with the FEC and VC additives, the silicon electrodes with lithium 4,5-dicyano-2-(trifluoromethyl)imidazolide (LiTDI)-based electrolyte can be well functioning as the state-of-art $LiPF_6$-based electrolyte.

References:

[1] M. N. Obrovac, L. Christensen, *Electrochem. Solid-State Lett.* 7 (2004) A93-A96.
[2] V. Etacheri, R. Marom, R. Elazari, G. Salitra, D. Aurbach, *Energy Environ. Sci.* 4 (2011) 3243-3262.
[3] Y. Oumellal, N. Delpuech, D. Mazouzi, N. Dupré, J. Gaubicher, P. Moreau, P. Soudan, B. Lestriez, D. Guyomard, *J. Mater. Chem.* 21 (2011) 6201-6208.
[4] C. Xu, F. Lindgren, B. Philippe, M. Gorgoi, F. Björefors, K. Edström, T. Gustafsson, *Chem. Mater.* 27 (2015) 2591–2599.

Electrochemical analysis of irreversible behavior in silicon electrode for lithium ion battery.

Jee Ho Yom, Sun Woo Hwang, Sumg Man Cho and Woo Young Yoon*

Department of Materials Science and Engineering, Korea University, 1, 5Ga, Anam-dong, Sungbuk-Gu, Seoul 136-701, Republic of Korea
*Corresponding author: E-mail address: wyyoon@korea.ac.kr; Tel.: +82 2 3290 3274; Fax: +82 2 928 3584

This study focuses on the mechanism of irreversible behavior in silicon electrode at various C-rates (0.1, 0.05, and 0.01 C-rate). An irreversible capacity of silicon electrode was examined by electrochemical performance. In order to confirm the irreversible capacity, silicon electrode/lithium foil half cells (2032 coin cell) were assembled in a dry room. When the amount of Li inserted into silicon electrode was 1 mol per 1mol of silicon, the discharge capacity of silicon electrode cell was estimated 953 mAh g^{-1} and charge capacity is 706 mAh g^{-1} in 1st cycle at 0.1 C-rate. The irreversible capacity of silicon electrode was 247 mAh g^{-1}. The silicon electrodes at 0.05 and 0.01 C-rate showed irreversible capacities of 318 mAh g^{-1}, and 437 mAh g^{-1}, respectively. The irreversible capacity of silicon electrode decreased at high C-rate. This might indicate more lithium ion was trapped in the amorphous silicon phase at low C-rate [1]. Also more solid electrolyte interphase layer was being produced at 0.01 C-rate. The SEI layer and silicon phase at each C-rate were observed by SEM, XRD and TEM.

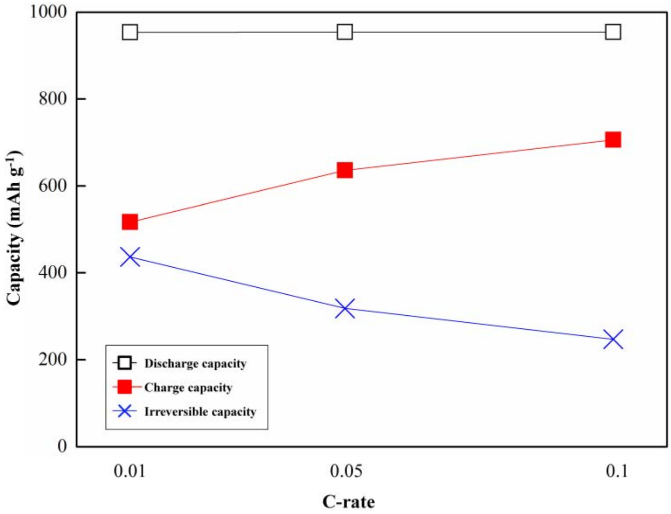


Figure 1. Voltage profiles after 1st cycle at a C-rate of 0.01, 0.05, and 0.1.

Reference

[1] M. N. Obrovac, L. J. Krause, J. Electrochem. Soc., 154(2), A103 (2007).

Development of Organic Ionic Plastic Crystal-Polymer Nanofibre Composites as Solid State Electrolytes

Yundong Zhou[a], Patrick C. Howlett[a], Jennifer M. Pringle[a]
[a]*Institute for Frontier Materials, Deakin University,*
Burwood, Victoria 3125, Australia.
zyund@deakin.edu.au

Organic ionic plastic crystals (OIPCs) are a class of solid-state electrolyte material with good thermal stability, non-flammability, non-volatility and good electrochemical stability. These materials deform easily under stress and can also allow fast transport of ions such as Li^+ through the rotational and translational motions of the matrix ions. Doping with lithium salts can increase the conductivity[1], and makes them increasingly promising for future application in lithium batteries[2]. However, waxy or powdery OIPCs cannot form a flexible membrane. Using electrospun polymer fibres as a matrix is a viable way of developing all-solid-state, free-standing and flexible electrolytes. We have recently reported that the plastic crystal *N*-ethyl-*N*-methylpyrrolidinium tetrafluoroborate ($[C_2mpyr][BF_4]$), doped with lithium tetrafluoroborate ($LiBF_4$) and combined with electrospun PVdF fibers can successfully support stable lithium cell cycling, with a capacity over 140 mAh g^{-1}. The conductivity was also enhanced with incorporation of the PVdF[3].

To further the development of such composite electrolytes, it's important to investigate the influence of polymer nanofibre on the thermal, structural, morphological, and electrochemical properties of OIPCs. Further, understanding the influence of composite composition on electrolyte parameters such as Li transference number, battery cycling performance and stability is key.

In this study, LiFSI doped $[C_2mpyr][FSI]$–PVdF electrospun nanofibers were developed as composite electrolyte membranes. The effects of PVdF incorporation on the plastic crystal were investigated by DSC, impedance spectroscopy, SEM, synchrotron XRD, and NMR. The optimized ratio was determined to be $[C_2mpyr][FSI]$–10wt%PVdF-10mol%LiFSI, and the transport number in this composite was determined to be 0.11.

This composite electrolyte supported more than 500 cycles of a lithium symmetric cell at a current density of 0.05mA/cm^2 at 50°C. Use of three layers of electrolyte membrane prevented shorting of the battery through dendrite formation. Thus, this composite is a promising solid state electrolyte for lithium batteries.

References:

[1]: M. Forsyth, J. Huang, D. R. MacFarlane, J. Mater. Chem. 10 (2000) 2259-2265.
[2]: L. Jin, P. C. Howlett, J. M. Pringle, J. Janikowshi, M. Armand, D. R. MacFarlane, M. Forsyth, Energy and Environ. Sci. 7 (2014) 3352-3361.
[3]: P. C. Howlett, F. Ponzio, J. Fang, T. Lin, L. Jin, N. Iranipour, J. Efthimiadis, Phys. Chem. Chem. Phys. 15 (2013) 13784-13789.