11th JAPAN- FRANCE JOINT SEMINAR ON BATTERIES

Island of Versailles, Nantes

September 20-22, 2016 - Nantes, France

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IMN
INSTITUT DES MATÉRIAUX
JEAN ROUXEL

11th JAPAN-FRANCE JOINT SEMINAR ON BATTERIES

Sept. 20 - 22, 2016 - Nantes, France

BIENVENUE AU
11th JAPAN-FRANCE JOINT SEMINAR ON BATTERIES

It is our great pleasure and honor to welcome you to the 11th Japan-France Joint Seminar on Batteries at IMN, Nantes, France.

The first Japan-France joint seminar on lithium battery has been organized in 1997 in P.M. Curie University in Paris followed by others alternatively in Japan and in France. The 5th Japan-France Joint Seminar on Lithium Batteries has been organized by us in 2004 in Batz-sur-Mer in France. The present joint seminar follows the meeting held in 2014 in Hakone area in Japan, organized by Prof. Kanamura.

The purpose of the 11th Japan-France Joint Seminar on Batteries is to provide a forum for presentation and discussion of recent developments related to next-generation batteries for the French and Japanese researchers. This seminar focuses on advanced Li-ion batteries, all solid state batteries, air-batteries, Na-ion batteries, multi-valent ion batteries, supercapacitors, and new electrochemical energy storage devices. Developments on positive and negative electrodes, electrolytes, and in-situ/operando techniques are addressed as well. The program schedules both invited oral presentations and posters sessions.

We gratefully thank our sponsors, the University of Nantes, Polytech'Nantes and the IMN. The organization of this event would not have been possible without their support.

We do thank you very much for attending the 11th Japan-France Joint Seminar on Batteries and we sincerely hope that you will have a most joyful conference with rewarding exchange of ideas with colleagues, enabling you to set up new collaborative projects. And do not miss to enjoy the beautiful city of Nantes and the marvelous area close to the Loire river and the Atlantic ocean.

Once again: Bienvenue à Nantes!

The Organizing Committee : T. Brousse, N. Dupré, D. Guyomard

Committees

International Advisory Committee for the 11th Japan-France Seminar, September 20-22, 2016

- Prof. Thierry Brousse, IMN, University of Nantes, France

- Prof. Henri Groult, PHENIX, University of Paris VI, France

- Dr. Dominique Guyomard, IMN, University of Nantes, France

- Prof. Kiyoshi Kanamura, Tokyo Metropolitan University, Japan

- Prof. Naoaki Kumagai, Iwate University, Japan

- Dr. Jean-Pierre Pereira-Ramos, ICMPE, University of Paris Est Creteil, Thiais, France

- Prof. Masataka Wakihara, Tokyo Institute of Technology, Japan

Local Organizing Committee

- Prof. Thierry Brousse

- Dr. Nicolas Dupré

- Dr. Dominique Guyomard

SOCIAL ACTIVITIES

Château des Ducs de Bretagne

REGISTRATION & WELCOME BUFFET
Tuesday sept. 20
7.00 to 9.00 pm

RIVER CRUISE BANQUET
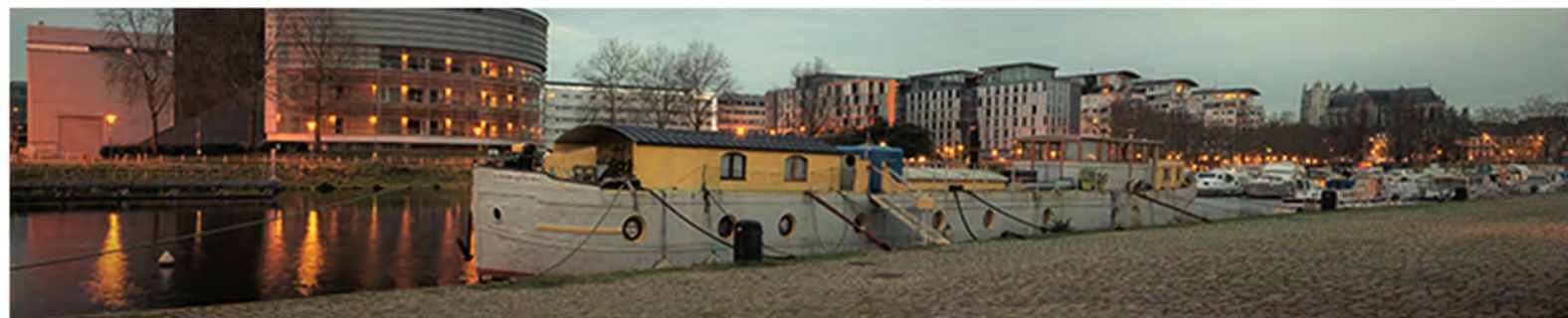## Wednesday sept. 21
8.30 pm

Château de la Gascherie

Château de la Desnerie

DINNER
Thursday sept. 22
7.30 pm

Program
of oral presentations

11th JAPAN-FRANCE JOINT SEMINAR ON BATTERIES

Sept. 20 - 22, 2016 - Nantes, France

IMN INSTITUT DES MATÉRIAUX JEAN ROUXEL · CNRS · UNIVERSITÉ DE NANTES

Tuesday, September 20th, 2016

19:00	**Registration & Welcome party** **Château des Ducs de Bretagne**

Wednesday, September 21st, 2016

08:45 **Introduction** by the director of the IMN and D. Guyomard

SESSION 1	*Next Battery Generation*	*Chairperson :* *Naoaki KUMAGAI*

09:00	O1	*In-situ FT-IR analysis of deposition and dissolution of Mg in tetrahydrofuran containing Grignard reagents* **Kiyoshi KANAMURA**, Tokyo Metropolitan University, Japan
09:25	O2	*Si anode failure mechanism in full Li-ion cells using advanced characterization tools* **Dominique GUYOMARD**, IMN Nantes, France
09:45	O3	*Lithium insertion properties of α'-NaV$_2$O$_5$ prepared by electrochemistry* **Jean-Pierre PEREIRA-RAMOS**, GESMAT Thiais, France
10:05	O4	*All-solid polymer lithium ion battery at higher temperatures* **Masataka WAKIHARA**, Tokyo Institute of Technology, Japan

10:30 COFFEE BREAK

SESSION 2	*Li and Na-Based Materials*	*Chairperson :* *Jean-Pierre PEREIRA-RAMOS*

11:00	O5	*A detailed analysis of methylated silicon as an improved electrode material for lithium batteries* **Michel ROSSO**, LPMC Palaiseau, France
11:20	O6	*High capacity layered oxides as positive electrode materials for Na-ion batteries* **Patrick ROZIER**, CIRIMAT Toulouse, France
11:40	O7	*Production and characterization of FePO$_4$ electrode material from sewage sludge incineration ash and Iron ion-containing acidic wastewater* **Naoaki KUMAGAI**, Tokyo Institute of Technology, Japan
12:05	O8	*New Tavorite-type compositions as positive electrode materials for lithium-ion batteries* **Laurence CROGUENNEC**, ICMCB Bordeaux, France

12:25 LUNCH & POSTER SESSION 1

SESSION 3	Characterization	Chairperson : Thierry BROUSSE

14:20	O9	*The contribution of the dielectric spectroscopy to the study of the electrode materials* **Jean-Claude BADOT**, ENSCP Paris, France
14:40	O10	*Contribution of XPS (X-Ray Photoelectron Spectroscopy) and AES (Auger Electron Spectroscopy) to the knowledge of solid electrode/electrolyte interfaces (SEI)* **Hervé MARTINEZ**, IPREM Pau, France
15:05	O11	*Full characterization of all-solid-state lithium microbatteries by Electrochemical Impedance Spectroscopy* **Sylvain FRANGER**, ICMMO Orsay, France
15:25	O12	*Nuclear Magnetic Resonance for the characterization of battery materials* **Michaël DESCHAMPS**, CEMHTI Orléans, France

15:45 COFFEE BREAK

SESSION 4	Electrolytes and Negatives	Chairperson : Kiyoshi KANAMURA

16:15	O13	*Transport phenomena of high concentrated nonaqueous electrolyte solutions : a comparison between Li- and Na-system* **Kentarou KURATANI**, National Institute of Advanced Industrial Science and Technology, Japan
16:40	O14	*Lithium imidazolide (LiTDI) as a challenger for $LiPF_6$ in lithium batteries* **Daniel LEMORDANT**, PCM2E-Université de Tours, France
17:00	O15	*Relaxation effects of the negative electrode TiSnSb using ^{119}Sn Mössbauer and ^{7}Li MAS NMR spectroscopies* **Nicolas DUPRE**, IMN Nantes, France
17:20	O16	*Superconcentrated electrolytes for electrochemically stable and fast-charging lithium-ion batteries : first-principles molecular dynamics study* **Keitarou SODEYAMA**, National Institute for Materials Science, Japan

20:00	**Cruise Banquet Dinner on the Erdre river**

Thursday, September 22nd, 2016

SESSION 5	Beyond Li-ion	Chairperson : Masataka WAKIHARA

09:00 — **O17**
Hard carbons for Li-, Na-, and K-ion batteries
Shinichi KOMABA, Tokyo University of Science, Japan

09:25 — **O18**
Solid state electrochemistry : a tool for synthesis and characterization of solids
Claude DELMAS, ICMCB Bordeaux, France

09:45 — **O19**
A new high performance V_2O_5- based cathode for sodium-ion batteries
Rita BADDOUR-HADJEAN, GESMAT Thiais, France

10:05 — **O20**
Role of cationic vacancies on the electrochemical storage properties of hydroxy-fluorinated TiO_2 Anatase
Damien DAMBOURNET, UPMC Paris, France

10:30 COFFEE BREAK

SESSION 6	Solid State Batteries	Chairperson : Laurence CROGUENNEC

11:00 — **O21**
Fabrication of $LiCoO_2$ composite electrode on $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ solid electrolyte by aerosol deposition method
Hirokazu MUNAKATA, Tokyo Metropolitan University, Japan

11:20 — **O22**
High-throughput cathode materials exploration by combinatorial technology
Kenjiro FUJIMOTO, Tokyo University of Science, Japan

11:40 — **O23**
Solid-state redox reaction of oxide ions for rechargeable batteries
Naoaki YABUUCHI, Tokyo Denki University, Japan

12:05 — **O24**
Atomic layer deposition of thin films materials for 3D solid state Li-ion microbattery
Christophe LETHIEN, IEMN-IRCICA Lille, France

12:25 LUNCH & POSTER SESSION 2

SESSION 7	Next Battery Generation	Chairperson : Shinichi KOMABA

14:20 | **O25** — *Spark Plasma Sintering : an efficient route to design energy storage devices*
Vincent SEZNEC, LRCS Amiens, France

14:40 | **O26** — *All-solid-state lithium-ion batteries using oxide solid electrolyte assembled by Spark Plasma Sintering*
Toyoki OKUMURA, National Institute of Advanced Industrial Science and Technology, Japan

15:05 | **O27** — *Electrochemical mechanism of M_xSb ($0{\leq}x{\leq}0.5$, M=Sn, Bi, Fe) phases in Na batteries*
Laure MONCONDUIT, ICG Montpellier, France

15:25 | **O28** — *Lithium/Sulfur batteries upon cycling : application of electrochemical impedance spectroscopy, in situ X-Ray Diffraction and tomography*
Fanny ALLOIN, LEPMI Grenoble, France

15:45 | **O29** — *Highlights on latest battery technology achievements & challenges*
Sébastien PATOUX, LITEN-CEA Grenoble, France

16:05 **Closing remarks**

16:25 COFFEE BREAK

18:00 GET TOGETHER DOWNTOWN

19:00 **Dinner at Nantes downtown**

Program
of poster presentations

List of Posters

P1   *LiTDI and LiFSI as substitutes for LiPF$_6$ in Li-ion batteries electrolytes*
Christopher L. Berhaut, Université François Rabelais de Tours, France

P2   *Study of 5V cathode materials, role of protective oxide layer*
Philippe Dumaz, LEPMI Grenoble, France

P3   *Redox organic materials for low cost sodium aqueous batteries and non-aqueous supercapacitors*
Joël Gaubicher, IMN Nantes, France

P4   *Multiscale charge transport characterization in composite electrode for lithium-ion batteries*
Nicolas Gauthier, Université Paris Sud/Paris-Saclay, Orsay & UPMC Gif-sur-Yvette, France

P5   *Electrochemical Performance of K$_x$CoO$_2$ in Non-Aqueous K Cell*
Yuya Hironaka, Tokyo University of Science, Japan

P6   *In operando ATR-FTIR analysis of silicon anodes for Li-ion batteries*
Bon-Min Koo, Ecole Polytechnique Palaiseau, France

P7   *Phase Transition and Stacking Faults in Na-Extracted Layered Oxides*
Kei Kubota, Tokyo University of Science, Japan

P8   *Improvement of solid polymer electrolyte in low temperature lithium metal polymer batteries*
Adrien Lassagne, LEPMI Grenoble, France

P9   *Analysis of electronic and ionic wiring limitations to power performance of composite electrodes by dielectric spectroscopy and tomography*
Bernard Lestriez, IMN Nantes, France

P10 *Surface-fluorination for active electrode protection technology - a glance at fluorinated titanium dioxide materials... and more!*
Nicolas Louvain, Université de Montpellier et RS2E, France

P11 *Role of Solvents and Salts in Sb/Na Batteries: An XPS Analysis*
Lénaïc Madec, Université de Montpellier & Pau et RS2E, France

P12 *Inside the electrochemical magnesiation of intermetallic electrodes*
Laure Monconduit, Université de Montpellier et RS2E, France

P13 *Development of Li-rich layered oxides as concentration-gradient for high energy density lithium-ion batteries*
Ségolène Pajot, ICMCB Bordeaux, CEATech Aquitaine & Université de Grenoble, France

P14 *Development of positive electrode host materials for organic batteries*
Philippe Poizot, IMN Nantes, France

P15 *γ'-V$_2$O$_5$: a high voltage cathode material for lithium batteries*
Marianne Safrany Renard, ICMPE, Université Paris Est Créteil, Thiais, France

P16 *Preparation of SiO$_x$/C Composites with Na-Containing Polymer and Their Electrode Performance for Lithium-Ion Batteries*
Jun Sakamoto, Tokyo University of Science, Japan

P17 *FeNCN as new molecular negative electrode materials for Li- and Na-ion*
Moulay Sougrati, Université de Montpellier, France

P18 *P2- and P3-type Na$_x$Cr$_x$Ti$_{1-x}$O$_2$ Layered Oxides for Rechargeable Sodium Batteries*
Naoaki Yabuuchi, Tokyo Denki University, Japan

Abstracts
of oral presentations

In-situ FT-IR Analysis of Deposition and Dissolution of Mg

in Tetrahydrofuran Containing Grignard Reagents

Kiyoshi Kanamura, Hiroki Inoue, Yasuhiro Akita, Hirokazu Munakata

Department of Applied Chemistry, Graduate School of Urban Environmental Sciences

Tokyo Metropolitan University

Rechargeable Mg-metal batteries have been focused as post Li-based batteries since Mg-metal has a higher volumetric energy density than Li-metal. For efficient use of Mg-metal as anode in batteries, its electrochemical deposition and dissolution with high reversibility should be realized. So far, ether-based electrolyte solutions including Grignard reagents have been investigated due to a high coulombic efficiency of the deposition and dissolution of Mg-metal. However, the ether-based electrolyte solutions are easily oxidized at around 1.5 V vs. Mg^{2+}/Mg. Therefore, new electrolyte systems with high oxidation stability are strongly required. The investigation of reaction mechanisms of Mg deposition and dissolution in current Grignard reagent systems is expected to provide insights into the design of such new electrolyte systems. In this study, the dynamic behavior of Grignard reagents in tetrahydrofran (THF) during Mg deposition and dissolution was studied by in-situ FT-IR spectroscopy with an attenuated total reflection method, in which the behaviors of THF molecule coordinated with ethylmagnesium chloride (EtMgCl), phenylmagnesium chloride (PhMgCl) and ethylmagnesium bromide (EtMgBr) were mainly focused. In all the Grignard reagents, the solvation structure of THF molecule in the Mg deposition process was different from that in the dissolution process (Fig. 1), indicating that the solvated Mg^{2+} ions play an important role in the deposition and dissolution processes. Based on this detail discussion on the reaction mechanism, new electrolyte with high oxidation stability should be considered to realize highly reversible Mg deposition and dissolution with low over-potentials.
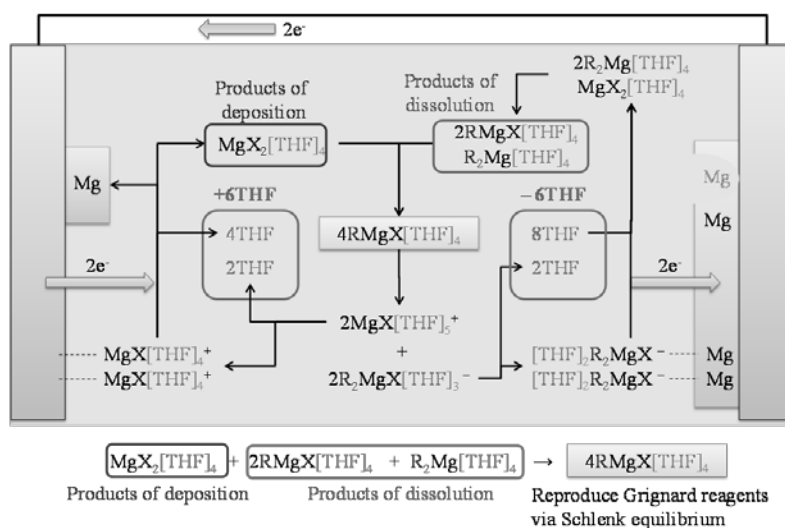

Figure 1 Grignard reagent-based species formed during Mg deposition/dissolution processes.

Si anode failure mechanism in full Li-ion cells using advanced characterization tools

N. Dupré[1], P. Moreau[1], L. Quazuguel[1,2], E. De Vito[3], M. Boniface[2], B. Lestriez[1], A. Bordes[3,4], F. Rieutord[2], S. Lyonnard[2], P. Bayle-Guillemaud[2], D. Guyomard[1]

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The behavior of silicon electrode in half cell set-up (i.e. cycled vs lithium metal) is now well understood and methods to optimize its performance have been extensively described. In this configuration, the lithium supply is not limited, therefore failure mechanisms can be completely different from those obtained in full cell (Li-ion) set-up. As of today, a much faster aging of silicon anode in full cell has been observed but the failure mechanism has not been understood. In this work, silicon electrodes are cycled in full cell set-up *versus* $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ as the positive electrode that initially contains the cyclable lithium. A combination of techniques, such as ^7Li, ^{19}F MAS NMR, XPS, TOF-SIMS and STEM-EELS, provides an in-depth characterization of the SEI forming on the surface of silicon particles as well as its evolution upon cycling.

Upon cycling, heterogeneous thick patches of LiF and carbonates appear at the surface of the Si particles. The development of the inorganic part of the SEI mostly occurs during the early stages of cycling, while an incessant degradation of the organic solvents of the electrolyte occurs continuously. After extended cycling, all the lithium from the positive electrode is consumed either trapped in an intermediate part of the SEI or in the electrolyte. While the cell cannot function properly anymore, degradation of the organic electrolyte solvents goes on, leading to the formation of Li-free organic degradation products thickening the SEI. Such comprehensive work allows for a better study of the failure mechanisms of Si-based composite electrodes for Li-ion batteries cycled in a Li-ion configuration.

From these multiprobe and multiscale characterization results, the mechanism of SEI formation will be described, and our comprehension of the origin of the much faster aging of silicon anode in full cell *versus* half cell will be disclosed.

Lithium insertion properties of α'-NaV$_2$O$_5$ prepared by electrochemistry.

L.T.N. Huynh[1,2], D. Muller-Bouvet[1], R. Baddour-Hadjean[1], M.L.P. Le[2], J.P. Pereira-Ramos[1]

[1]*Institut de Chimie et des Matériaux Paris Est, ICMPE/GESMAT, UMR 7182CNRS-Université Paris Est Créteil, CNRS 2 rue Henri Dunant, 94320 Thiais, France*

[2]*VNU-HCM key Laboratory, Applied Physical Chemistry Laboratory (APCLAB), Vietnam National University, Ho Chi Minh City, Vietnam.*

V$_2$O$_5$ and its derivatives like M$_x$V$_2$O$_5$ mixed oxides and bronzes have received continued interest as host lattice for Li insertion reactions. Indeed the strategy of introducing another metallic cation in V$_2$O$_5$ structure leads to various 2D or 3D structures depending the cationic species (Li$^+$, Na$^+$, Ag$^+$, Ni^{2+}, Cr^{3+} etc..). Among them, the layered α'-NaV$_2$O$_5$ bronze has been little investigated as a possible cathodic material. Only a cursory analysis of the Li insertion properties α'-NaV$_2$O$_5$ has been performed but contradictory curves for the potential dependence vs. Li uptake are reported without any reliable structural investigation [1, 2]. α'-NaV$_2$O$_5$ is the highest member of the α'-Na$_x$V$_2$O$_5$ (0.7 ≤ x ≤ 1) sodium vanadium bronzes [3]. This compound is now mostly prepared by a hydrothermal process at 180-200°C but we recently reported the electrochemical formation of NaV$_2$O$_5$, isostructural to the high temperature α'-NaV$_2$O$_5$ orthorhombic bronze [4]. This recent finding combined with the lack of data on the Li insertion process α'-NaV$_2$O$_5$ prompted us to investigate in details this material towards Li insertion. Here we report the Li insertion properties of α'-NaV$_2$O$_5$ including cycling and kinetic data. In addition, the structural response of the host lattice studied by XRD and Raman spectroscopy allows to elucidate the Li insertion mechanism. We show a rechargeable behavior is achieved around 2V with a stable specific capacity of 120 mAh g^{-1} for 50 cycles at C/10. A ball milling process allows to optimize the capacity, the rate capability and cycle life with 200 mAh g^{-1} at C/5 and still 120 mAhg^{-1} at C rate.
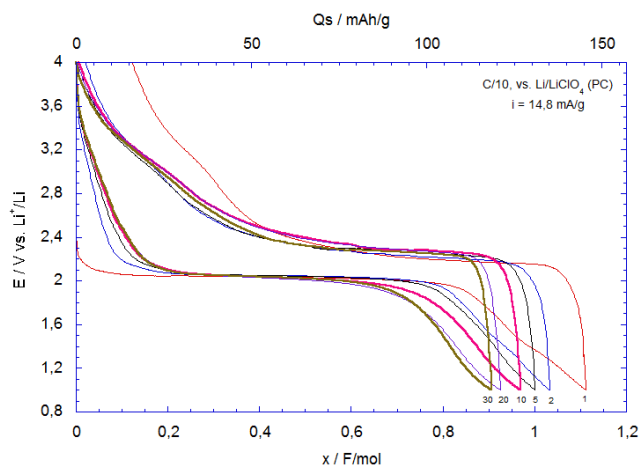
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4- D. Muller-Bouvet, R. Baddour-Hadjean, M. Tanabe, L.T.N. Huynh, , M.L.P. Le, J.P. Pereira-Ramos, Electrochim. Acta 176 (2015) 586-593

All-Solid Polymer Lithium Ion Battery at Higher Temperatures

M. Wakihara[1], H. Aoyagi[2], S. Murayama[2], H. Hiruta[2], T. Murata[2] and H. Shimamura[2]

1. Emeritus Professor of Tokyo Institute of Technology (Department of Applied Chemistry, Oookama, Meguro-ku, Tokyo 152-8552, Japan)
2. Nippon Nyukazai Co., Ltd. (Chidori-cho, Kawasaki-ku, Kawasaki-shi, 210-6805, Japan)

The rechargeable lithium ion battery (LIB) has crucial demands of our modern society, such as power source of various devices, EV and HEV. However, conventional LIB suffer from safety problems because they contain volatile and flammable organic solvents in the electrolyte solution. In order to improve the safety, alternative material systems for the electrolyte are urgently desired today. In this respect, there are many studies for developing (1) inorganic solid compound electrolytes, (2) ionic liquid electrolytes, (3) poly(ethylene oxide) (PEO) which has been known to be typically representative of the polymer matrix for all solid polymer electrolytes(SPEs). We thought that the selection of the PEO-based SPEs would be the fastest way for the realization of large-scale LIB with nonflammable property. While PEO-based SPEs containing supporting agent LITFSI have relatively low ionic conductivity (10^{-7} to 10^{-5} S cm^{-1}) at a room temperature. In our group, the addition of aluminate ester (Al-PEG) to monomer (poly(ethylene glycol) mono-methacrylate) (MPG-130MA) containing LITFSI has been tried for anticipating both the increase of the ionic conductivity from the effect of the Lewis acidity of Al in Al-PEG and of the nonflammable property. Al-PEG usually has three EO chains with each methyl end and works as a plasticizer. In other words, we expected the easier diffusion of lithium ion by adding Al-PEG at the first stage[1]. On the other hand, it is very important to maintain stable and continuous segmental motion of lithium ion in polymer matrix. Accordingly we tried that one of the methyl ends of Al-PEG was replaced by methacrylate ($-CO(CH_3)C=CH_2$) in the present study. It is considered that the C=C double bond in the monomer of both MPG-130MA and Al-PEG might react in each other during polymerization reaction by heating or irradiating UV and form stable polymer chain for keeping up good segmental motion of lithium ion conduction. The Al-PEG in the present study is no longer in the state of a plasticizer but has a roll of part of matrix polymer. In some of the SPEs, 20wt%of triglyme (DMTG) was added to monomer as a prasticizer to increase the ionic conductivity of lithium ion.

The ionic conductivity of obtained SPE containing 5wt% of Al-PEG showed 10^{-4} S cm^{-1} at 60 degree C and the value was a little higher than that of the SPE without Al-PEG ($10^{-4.7}$ S cm^{-1}). Also Cyclic voltammogram of the same SPE showed stable behavior in the voltage range between 2.0 V and 5.0 V at temperatures until 70 degree C.

We constructed laminate-type cell using the SPE containing 5wt% of Al-PEG. LiFePO$_4$ (LFP) and Li$_4$Ti$_5$O$_{12}$ (LTO) were selected as the cathode and the anode, respectively. Relatively high charge discharge performance was observed even at a high temperature 100 degree C. In this case, no prasticizer (DMTG) was added, because easier volatility happened at such higher temperatures.

Reference

1) M. Wakihara, Y. Kadoma, N. Kumagai, H. Mita, R. Araki, K. Ozawa and Y. Ozawa, J.Solid State Electrochem., 16, 847 (2012).

A detailed analysis of methylated silicon as an improved electrode material for lithium batteries

A. Cheriet[a,b,c], D.A. Dalla Corte[a], B.-M. Koo[a], L. Touahir[a], J.-N. Chazalviel[a], C. Henry de Villeneuve[a], F. Ozanam[a], M. Rosso[a], A. Keffous[b], N. Gabouze[b], C. Pereira-Nabais[d], J. Swiatowska[d], M. Cassir[d], P. Marcus[d], A. Gohier[e], P. Tran-Van[e]

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b) CRTSE, Division Couches Minces Surfaces et Interfaces, 2 Bd Franz Fanon, BP 140 Alger 7-Merveilles 16038, Algeria
c) Dept. of Physics, University of Setif, Algeria
d) IRCP, CNRS, Chimie ParisTech (UMR8247), Paris, France
e) Renault Research Department, Guyancourt, France

Silicon is an attractive anode material for Li-ion batteries due to its high theoretical charge capacity. However, a severe limitation of this material comes from the very large swelling accompanying the incorporation of Li ions.

Thin films of amorphous methylated silicon were shown to accommodate the volume changes due to lithiation / delithiation cycles more easily than pure-silicon ones, leading to a better cyclability of the negative electrodes based on this material [1].

We present a detailed study of the evolution of this material during lithiation/delithiation by complementary in situ and ex situ techniques : electrochemical measurements, IR, ToF-SIMS, optical microscopy, AFM. Our results give a detailed insight into the lithiation mechanisms involved in pure and methylated amorphous silicon.

[1]   L. Touahir et al., J. Power Sources 240 (2013) 551-557.

High capacity layered oxides as positive electrode materials for Na-ion batteries.

Patrick Rozier

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[3]Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459

The search for positive electrode material for Na-ion batteries started back to the 1980's in parallel to Li based systems underlining the expected similarities between these two alkaline species. Though the potentialities of Li based systems obscured researches dedicated to Na ones for more than 30 years, the renewal of interest since 2010 prompted fast growing of reported works in this field. Without surprises, most of investigated family of compounds reflects the one already studied for Li-ion systems among which the layered oxides Na_xMO_2 (M including at least one transition metal). Mainly two types of polymorph $P2-Na_{2/3}MO_2$ and $O3-Na_1MO_2$ differing by the oxygenated surrounding adopted by the Na cations (Prismatic or Octahedral) are easily prepared using conventional solid state reaction. The P-type structures exhibit better electrochemical performances than O-type essentially due to an easy diffusion of Na ions via face sharing prisms [1]. Unfortunately, P-type structure are Na deficient meaning that the capacity in full cell is restricted. To enhance the capacity of layered oxides we demonstrated the possibility to reach stoichiometric P-type Na_1MO_2 via the use of ball milling with metallic Na. The investigation of the electrochemical behavior of this latter compound shows that the reversible capacity in full cell is twice that of the pristine material and that the other characteristics such as the good capacity retention upon cycling and rate performances are maintained [2]. However, the nearly stoichiometric P-type Na_1MO_2 shows high sensitivity to moisture, which prevent an easy handling, in agreement with low voltage of the redox couple which limit the energy density that can be obtained. One way to enhance both capacity and energy density is to activate the anionic redox couple as demonstrated in Li-rich materials. We decided then to investigate the possibility of activating such anionic redox couple in Na-rich layered oxides. The study of the electrochemical behavior of different members of the $Na_2Ru_{1-y}Sn_yO_3$ solid solution shows that like their Li-analogue, they present capacities that exceed theoretical capacity calculated from the cationic redox species [3]. The high capacity was found, by means of XPS analysis, to be associated to the accumulation of both cationic (Ru^{5+}/Ru^{4+}) and anionic (O^{2-}/O_2^{n-}) redox processes. The structural evolutions during cycling have been followed using in situ XRD and found to be associated with the cation disordering and loss of crystallinity on cycling. Therefore, in contrast to the Li series, such a formation of oxygen species is followed, for the Sn rich samples, by the irreversible loss of O_2.

These works which shows for the first time the feasibility of synthesizing nearly stoichiometric P-type layered oxides and obtaining high capacities due the anionic redox activity contribution, open the way to design new positive electrode materials for Na-ion batteries with the possibility to exchange at high voltage more than 1 electron per transition metal. It now remains to chemically manipulate these layered compounds to enhance their cycling behavior and stability against moisture so that they could be handled in air.

References
[1] N. Yabuuchi, M. Kajiyama, J. Iwatate, H. Nishikawa, S. Hitomi, R. Okuyama, R. Usui, Y. Yamada, S. Komaba, Nature Mat. **11** 512 2012.
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[3] P. Rozier, M. Sathiya, A-R Paulraj, D. Foix, T. Desaunay, P-L Taberna, P Simon, J-M Tarascon, Electrochem. Com. **53** 29-32 2015

Production and characterization of FePO$_4$ electrode material from sewage sludge incineration ash and Iron ion-containing acidic wastewater

Naoaki KUMAGAI, Hitoshi YASHIRO, Masataka WAKIHARA and Teruhito SASAKI

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We have examined the extraction of phosphorus (P) component from a sewage sludge incineration ash with an alkaline wastewater followed by Fe ion-containing acidic wastewater for recovering a phosphate component, which was utilized for the manufacture of a phosphate fertilizer and FePO$_4$ cathode material. The major components of the ash were P (13 wt%), silicon, calcium, aluminum, iron, magnesium, barium, potassium, and sodium. The efficiency of P extraction by the alkaline wastewater (0.5～1.0 mol L^{-1}) was similar to that of extraction with a pure NaOH (also 0.5～1.0 mol L-1) at 70℃. The P component in the residue after treating with an alkaline wastewater was extracted with Fe ion containing acidic wastewater at pH=0.1~2.0 at a room temperature. The toxic heavy metals were scarcely present in the P fraction. Our researching results revealed an available method for the production of high-quality P fertilizer and FePO$_4$ electrode material from a sewage sludge and industrial wastewaters.

New Tavorite-type Compositions as Positive Electrode Materials for Lithium-ion Batteries

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Polyanionic materials attract a strong interest in the field of Li-ion battery research. Tavorite-type compositions offer a very rich crystal chemistry, among which $LiVPO_4F$ has the highest theoretical energy density (i.e. 655 Wh/kg). New Tavorite-type compositions were obtained: $LiVPO_4OH$ and $LiVPO_4F_{1-y}O_y$, for these latter by direct syntheses or by aging upon oxidation in air. We will show how we can tailor the structure, the potential and the reaction mechanism involved, playing with the composition of the Tavorite-type phases. IR and NMR spectroscopies are obviously key characterization tools to identify the nature of the phase formed, with a clear signature for vanadyle and hydroxyl bonds, and to discriminate between defects and impurities. Electrochemical tests reveal original properties during the charge of $LiVPO_4OH$. Li^+ and H^+ are extracted from the structure at the same equilibrium potential (3.95 V vs Li^+/Li): the formation of the intermediate V^{4+}-rich phase is not observed whereas VPO_4O is obtained at the end of the charge. This system interestingly illustrates one possible track to follow to develop two-electron reactions at the same potential, playing with the stability of the antagonist bond in order to promote the concomitant and reversible extraction/reinsertion of two alkalis. In addition, we will also discuss how detrimental/positive the defects can be on the electrochemical properties of the mixed oxy-fluorophosphates $LiVPO_4F_{1-y}O_y$.

THE CONTRIBUTION OF THE DIELECTRIC SPECTROSCOPY

TO THE STUDY OF THE ELECTRODE MATERIALS

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The improvement of battery performance requires the rationale optimization of the composite electrode. The developments of new experimental techniques as well as methodologies are needed to understand the relationships between the composition, the architecture and the performance of composite electrodes. The fruitful contribution of Broadband Dielectric Spectroscopy (BDS) to study hierarchical materials applied to lithium ion and lithium metal batteries electrodes have been previously shown [1-4]. The results demonstrate that the broadband dielectric spectroscopy technique is very sensitive to the different scales of the electrode architecture involved in the electronic transport, from interatomic distances to macroscopic sizes, as well as to the morphology at these scales, coarse or fine distribution of the constituents. When the frequency increases, different kinds of polarizations appear from macroscopic sizes to interatomic distances and give rise to dielectric relaxations in the following order: (a) space-charge polarization (low-frequency range) due to the interface sample/current collector; (b) polarization of clusters (or agglomerates) of particles (micronic scale); (c) polarization of particles due to the existence of resistive junctions between them; (d) electronic transfers (at nanometric or at interatomic scale). The BDS measurement was up to now ex situ measurement, on dry electrode. They provide a fundamental insight into the conduction properties at all scales of the materials before being integrated in a real battery. An innovative device (measurement cell) has been developed to make synchronized BDS measurements and electrochemical cycling: the frequency range is about 10^2 - 10^{10} Hz. In this work, data acquisitions were made on dry electrodes (Active material / Carbon black / PVdF) and then on the same electrode wetted with an electrolyte. Short- and long-range motions of ions are evidenced in the low-frequency region. At higher frequencies, the study shows for the first time the influence of the ions of the electrolyte on the transfer of the electronic charges (and conversely) at the micronic and nanometric scales [4]. The new device opens thus important prospects to determine the evolutions of the multi-scales electrical properties during electrochemical cycling.

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Contribution of XPS (X-Ray Photoelectron Spectroscopy) and AES (Auger Electron Spectroscopy) to the knowledge of solid electrode/electrolyte interfaces (SEI)

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It is now generally admitted that the performance of all lithium ion or lithium batteries (including liquid or solid electrolyte) depends on the surface chemistry developed on the electrode / electrolyte interface system. This work presents a contribution to the knowledge of the solid electrolyte interface (SEI) from two different examples:

The first one concerns Spinel $Li_4Ti_5O_{12}$ (LTO) which is considered as a good alternative negative electrode material for Li-ion batteries due to its negligible change of lattice parameter during insertion/extraction of lithium ions, resulting in a very low capacity decrease upon cycling. The reactivity of LTO toward commons carbonates based electrolytes has been evidenced by surface analysis and an important gassing occurring at the electrode/electrolyte interface was reported. Therefore it is essential to better understand the interfacial phenomena. A precise understanding of the Spinel $Li_4Ti_5O_{12}$ (LTO) electrode/electrolyte interfaces in relation with batteries ($Li_4Ti_5O_{12}$/Li half-cells) electrochemical performances is presented. The influence of various parameters (cycling temperature, electrode and electrolyte composition, cycling potential window) upon the SEI formation and dissolution through the first cycle is investigated. The evolution of those interfaces after long cycling is also studied. Finally, $Li_4Ti_5O_{12}$/$LiMn_2O_4$ cells having potential assets in term of cost and safety will be investigated, in order to point out the changes in the SEI formation due to interactions between both electrodes. The samples are analyzed by X-ray Photoelectron Spectroscopy (XPS) and Scanning Auger Microscopy (SAM), two complementary extreme surface characterization techniques (analysis depth 5-10 nm), operating at different spatial resolutions.

The second example is related to the recent technological development of miniaturized systems which has induced a strong demand for developing compact power sources with high efficiency and small dimensions that are suitable for portable devices. Among these systems, the lithium microbattery may be relevant for a wide range of applications linked to the field of smart cards, implantable medical devices, MEMS (microelectromechanical systems) or other microelectronic devices. An all solid state battery $LiCoO_2$ / LiPON / Li is considered and more specifically the behaviour of the interface between the positive electrode and the solid electrolyte, studied by ion milling cross section / Auger Spectroscopy coupling.

Full characterization of all-solid-state lithium microbatteries by Electrochemical Impedance Spectroscopy

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The development of efficient principal or back-up energy storage for electronics devices is one of the most important issues for manufacturers. The miniaturization of microelectronics components paves the way to the development of smaller devices in which the integration of a conventional battery is no longer possible. All-solid-state thin film batteries have many advantages over conventional lithium cells. They are bendable, thin and safe with a long service lifetime and can be produced with a customizable shape for an optimized integration in advanced system designs. Finally, these microbatteries built without a liquid electrolyte comply with safety and environmental standards. The first applications planned for microbatteries are numerous: RFID tags, autonomous sensors for building and home automation, powered Smart Cards, wellness and sportswear microsystems. One of the major challenges to ensure mass production is to reduce the final testing time and its associated cost, whereas the common protocol implies to cycle the cells.

In this context, the use of Electrochemical Impedance Spectroscopy (EIS) is the most promising tool for a fast assessment of the production.

In this work, thin film batteries, composed of a stack of several active layers comprising a platinum current collector, a $LiCoO_2$ positive electrode, a LiPON vitreous solid electrolyte and a lithium negative electrode, were characterized by EIS. Three R//C contributions are observed (A, B, C) but only one (C), in the low frequency region, depends on potential step. The contribution (A) was the most obvious to assign and corresponds to the bulk solid electrolyte. Measurements on Pt/LiPON/Pt cells allowed confirming this assignation and to determine intrinsic electrolyte parameters: $\sigma = 2.10^{-6}$ S.cm^{-1} and $\varepsilon_r = 20$. The activation energy of ionic conductivity in LiPON was found to be close to 0.56 eV. The origin of contribution B was more difficult to clarify. This latter is not very important after the first charge of the microbattery but increases consistently after few months of storage at 100% SOC and is related to the geometry of the Li/LiPON interface and its chemical composition (pollution at the interface). Actually, a small part of transferred lithium no longer participates to the reversible capacity of the microbattery but we show here that a specific cycle can restore the interface quality. For the last contribution (C), we show, thanks to a scanning potentio-EIS protocol, that it corresponds to the charge transfer step of the microbattery [1].

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Nuclear Magnetic Resonance for the characterization of battery materials

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Nuclear Magnetic Resonance spectroscopy is especially useful for the characterization of the chemical nature of the environments of ^{7}Li spins. In materials like $LiVPO_4F$, the structure seems well ordered, as seen by XRD or TEM, however, ^{7}Li NMR spectroscopy shows that 10-20 % of the lithium content is in a different environment than the crystallographic site. Dipolar correlation experiments show that these lithium atoms are within a nanometer of the main site, and therefore are defects within the structure.

On the other hand, pulsed field gradients can also provide the positions of ^{7}Li spins in space. This feature is the key to the success of MRI of working batteries. Moreover, the spectra of the cathodes and anodes in a working battery can be separated in situ by PFG-NMR, and the power of spectroscopic imaging is demonstrated in a $LiCoO_2/Li_4Ti_5O_{12}$ battery. In favorable cases, the lithiation front can be observed in thick electrodes with a 100 μm resolution, highlighting the limitation in lithium transport in electrodes with porosity issues.

Transport Phenomena of High Concentrated Nonaqueous Electrolyte Solutions: A Comparison between Li- and Na-System

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In order to understand deeply the transport phenomena of the ions in electrolyte solutions at high concentrations, the solution density, viscosity and ionic conductivity of Li- and Na-TFSI dissolved in GBL and PC were measured at $0.1 \leq C/\text{mol}\cdot\text{dm}^{-3} \leq 2.0$ and $278 \leq T/\text{K} \leq 328$ (TFSI = bis(trifluoromethanesulfonyl)imide, GBL = γ-butyrolactone and PC = propylene carbonate). The partial molar volume of the solute, derived from the density, confirmed that the Na-systems occupy more volume in the electrolyte solutions than the Li-systems. On the other hand, the viscosity and ionic conductivity suggested that the Na-systems are more fluid and conductive than the Li-systems. The relative viscosity vs. the molarity follows a modified empirical Jones-Dole equation. The molar conductivity linearly decreased with respect to the cube-root of the molarity, which was analyzed by the pseudolattice model. The Raman spectroscopy revealed that, while the solvation number is comparable at 1-2 for either the Li- or Na-systems, Li^+ is more tightly bound to the solvent molecules than Na^+. The higher fluidity and conductivity of the Na-systems than those of the Li-systems result from the less occurrence of the solvent-shared ion pairs in the former than in the latter.

Lithium imidazolide (LiTDI) as a challenger for LiPF$_6$ in lithium batteries

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Lithium salts having an Hückel anion derived from imidazole such as lithium 4,5-dicyano-2-(trifluoromethyl) imidazolide **(LiTDI)** have been synthetized in 2008 by Leszek Niedzicki et Michel Armand and a patent has been deposited in 2009 [1,2]. Among all imidazole derived salts, LiTDI is probably the most promising and could be a challenger to LiPF$_6$ in the future. Unlike to LiPF6, this salt is not water sensitive and stable at high temperatures (200°C). As no HF is expected to be produced during battery cycling, corrosion of cathode material or metallic collector is avoided. LiTDI solutions in alkylcarbonate (AC) are able to form an adequate passivation layer on graphite and are compatible with high voltage cathodes up to 4.7V. Like LiPF$_6$, LiTDI based electrolytes are able to passivate aluminium collectors. The main drawback of LiTDI is the lower conductivity (6.8 mS.cm^{-1} à 1 mol.L^{-1} in EC/DMC à 25°C, Niedzicki et al.) as compared to LiPF$_6$ in the same AC solvent mixtures.
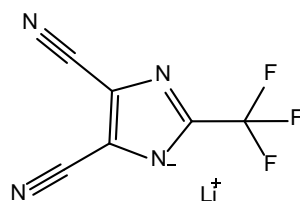
Structure of the TDI Hückel anion

In this work LiTDI is compared to competing salts like LiTFSI, LiFAP and LiPF$_6$ in a EC/DMC (50/50 wt%) mixture. Transport properties such as viscosity, Li+ and anion diffusivity and lithium transference number, were investigated and show the inadequacy of the EC/DMC mixture as only 36 % of the ion-pairs are dissociated.

Taking into account these results, a new solvent mixture (quoted as NSM in the following) has been designed. The LiTDI/NSM electrolyte has been tested and compared to the LiPF6/AC electrolyte in graphite (GR) and NMC half cells at different rates of discharge.

All results confirm that LiTDI/NSM could replace LiPF$_6$ as an electrolyte in many Li-ion batteries.

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Relaxation effects of the negative electrode TiSnSb using ^{119}Sn Mössbauer and ^{7}Li MAS NMR spectroscopies

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Lithium rechargeable batteries are considered the technology of choice for energy storage in portable electronic devices and zero emission vehicles. However, there are often limitations in the energy densities of the electrode materials, most commonly caused by weak capacities and limited electrode cycling life. Research is therefore underway to find new electrode materials capable of higher performance.

Conversion type materials have recently been considered as plausible alternatives to conventional electrode materials due to their large gravimetric and volumetric energy densities. The ternary alloy TiSnSb was recently proposed as a suitable negative electrode material due to its excellent electrochemical performance.[1,2] TiSnSb has been shown to reversibly take up more than five lithium per formula unit, leading to reversible capacities of 540 mA h/g or 4070 mA h/cm^3 at a rate of 2C.

During the first discharge, TiSnSb undergoes a conversion process, leading to the simultaneous formation of Li-Sb and Li-Sn intermetallic compounds. Using complementary in situ X-ray diffraction (XRD) and in situ 119Sn Mössbauer spectroscopy the phases Li$_3$Sb and Li$_7$Sn$_2$ were observed. The following electrochemical equation has been proposed for Li insertion:

$$TiSnSb + 6.5Li \rightarrow Ti + Li_3Sb + 0.5Li_7Sn_2$$

However, some ambiguities remain. Two distinct resonances are observed in the ^{7}Li solid-state NMR spectra obtained at the end of discharge. Contributions at 0, 3.5 and 8.5 ppm are tentatively assigned to the solid electrolyte interphase (SEI), Li$_3$Sb and Li$_7$Sn$_2$, respectively. A second group of resonances, composed of two distinct resonances, appear at approximately 20 ppm, which are tentatively assigned to Li$_7$Sn$_3$ (19.5 ppm) and a second Li-Sb phase (22 ppm).[3] It is noted that the phase Li$_7$Sn$_3$ has not been detected via ^{119}Sn Mössbauer spectroscopy during this or any previous studies of TiSnSb.

Distinct differences in chemical shift have been observed for Li$_3$Sb produced at the end of discharge of TiSnSb versus samples of Li$_3$Sb synthesised via solid state methods. The presence of additional elements at the end of lithiation appears to affect the chemical shift of Li$_3$Sb. To confirm if this is the case, additional 'model' compounds have been studied via NMR, including TiSb$_2$ and NbSb$_2$. Positive chemical shifts are observed for all model compounds, confirming the influence of the "inactive" elements in ternary alloys, e.g., Ti or Nb. The ternary alloy NbSnSb has also been investigated, as a direct comparison to TiSnSb, the results of which will be presented.

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Superconcentrated electrolytes for electrochemically stable and fast-charging lithium-ion batteries: first-principles molecular dynamics study

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Li-salt concentration has been recently proposed as an important control parameter of reduction stability of electrolytes and high ion conductivity in Lithium-ion batteries (LIBs)[1]. For example, highly concentrated (HC) $LiN(SO_2CF_3)_2$ (Li-TFSA) or $LiN(SO_2F)_2$ (Li-FSA) salt in acetonitrile (AN) electrolyte shows strong electrochemical stability against the reductive decomposition, though in low concentration (LC) solution AN is easily reduced and decomposed[1]. However, the atomistic origin of the improved reduction stability and high ion conductivity in HC system has been still an open question.

In this study, we investigated the mechanism of the improvement of the reduction stability and Li-ion diffusion mechanism depending on the salt concentration by using first-principles density functional theory (DFT) molecular dynamics (MD) calculations with explicit AN solvents[2]. We also calculated the diffusion coefficients of the Li-ions, anions, and solvents in the LC and HC electrolytes to elucidate how Li-ion diffusion was affected by concentration.

For the reduction stability, we found that TFSA anion sacrificially accepts reductive electron and decomposed in the HC systems, because specific chained network structure is formed and the electron affinity of the anion shifts lower. This indicates that the TFSA decomposed products can stack on the electrode surface, forming a sort of solid electrolyte interface (SEI). In fact, experimental XPS study confirmed the F-related species on the negative electrode.

For the diffusion mechanism, we confirmed that the calculated diffusion coefficients were on the same order of the experimental values. From the reliable trajectories, we confirmed that each Li-ion in the LC electrolytes is coordinated only by solvent molecules and diffuses with them. In the HC case, the Li-ions are coordinated both by solvent molecules and by anions arranged in a

Fig. 1. Solvent assisted Li-ion hopping in HC LiTFSA/AN system

specific network structure[2], which results in high viscosity. We analyzed the motions of individual Li ions, and found Li-ion hopping between the oxygen atoms of the anions in both FSA and TFSA anion systems (Fig.1). Additional DFT-MD calculations with different solvents also suggest the Li-ion hopping diffusion mechanism. We concluded that change of the diffusion mechanism can be an origin of the high Li-ion conductivity in the HC electrolytes.
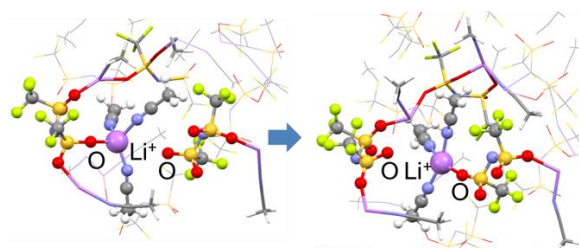
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Hard Carbons for Li-, Na-, and K-ion Batteries

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Non-graphitizable carbons (i.e. hard carbons) have been studied as a negative electrode material of Li-ion batteries used in high-power applications such as HEV. In 2001, electrochemical Na intercalation into hard carbon was first reported by Stevens and Dahn [1]. In 2009, our group succeeded in demonstration of the satisfactory practical performance for 3 volt Na-ion battery by using a commercially available hard carbon [1]. Now, hard carbon is regarded as a promising candidate for practical sodium-ion batteries. Furthermore, a first report on K insertion into hard carbon just appeared in 2016 [2], which follows our lead report on electrochemical reversible K insertion into graphite on Al current collector [3]. In this study, we prepared hard carbons at different carbonization temperature and investigate the temperature dependency on their structure and electrochemical performance in alkali-metal cells.

Hard carbons were prepared by carbonization of sucrose at 700 - 2000°C and tested in non-aqueous Li, Na, and K cells as seen in Figure 1. All of them show redox activity of alkali insertion in the voltage region between 0 and 1.5 V which would be acceptable for alkali-ion battery application. Because sodium hardly intercalates into graphene-stacked layers, sodium insertion into nano-sized pore is thought to be important. Due to the smallest atomic size of lithium, the larger specific capacity are observed whereas potential hysteresis appears as generally known. Potassium cells demonstrate about 250 mAh/g which is comparable to the graphite case to form KC_8. We will further discuss details structural and electrochemical properties of the hard carbon electrodes including functional binders.

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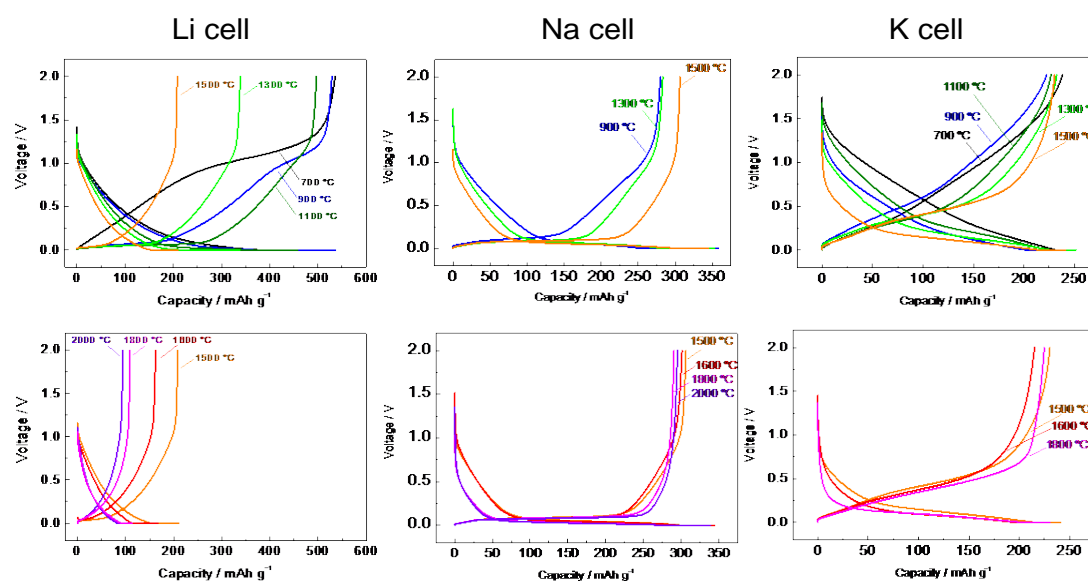[3] S. Komaba, *et al.*, *Electrochem. Commun.*, **60**, 172 (2015).

Figure 1. Second charge/discharge curves of hard carbons, prepared from sucrose at different carbonization temperatures, tested in Li/Na/K half-cells with 1 M LiPF$_6$/EC:DMC (1:1), 1 M NaPF$_6$/PC and 1 M KFSI/EC:DEC (1:1) electrolytes, respectively, at room temperature.

Solid state electrochemistry: a tool for synthesis and characterization of solids

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Researches on battery materials has considerably increased during the last 30 years due to the huge development of lithium-ion batteries for portable devices (laptops, cellular phones, …) and more recently with the need to store energy in order optimize its consumption. The next goal is the development of batteries for electric vehicles and their use into the grid. In most of the batteries, the intercalation (deintercalation) of monovalent cations (H^+, Li^+, Na^+) and electrons is the basic electrochemical reaction. The cell voltage is equal to the difference in Fermi level between the two electrodes. If one electrode exhibits a constant voltage it can acts as reference and therefore, the cell voltage reflects all structure modifications which occurs on the material upon intercalation. The change is cell voltage depends on: (i) the electronic band filling, (ii) the change in the band structure due to change in composition, (iii) the modification of the Magdelung energy. For the solid state chemist the studies of the electrochemical reaction using a battery open new possibility to determine phase diagram at RT, but also to synthesize new metastable phases from a precursor made by classical solid state chemistry.

In this presentation we report about the Na_xVO_2, and $Na_x(Fe,Mn)O_2$ systems with a special focus on the phase diagram. Depending on the composition and the experimental conditions O3 or P2 structures are obtained for the layered starting phases. The structures of all starting materials were determined by Rietveld refinement of their X-Ray diffraction patterns. As the transformation between O3 and P2 structural types would require M-O bond breaking, the O3 and P2 systems present different behaviors although they have the same chemical formulae

Three different phases were obtained for the $Na_{1/2}VO_2$ composition depending of the packing of the starting material. These phases exhibit very similar sodium ordering in the interslab space but very different vanadium ordering in the VO_2 slab. Depending on the oxygen packing the vanadium ions can be isolated or can form pairs or trimers within the VO_2 slab.

The study of the $Na_x(Fe,Mn)O_2$ systems for several Fe/Mn ratio leads either O3 to P2 type phases depending on the sodium amount and the on Fe/Mn Ratio. Depending on the compositions either the Mn^{3+}/Mn^{4+} or the Fe^{3+}/Fe^{4+} redox couples can be involved. The participation of iron has been proved by ex situ and in situ XAS and Mossbauer spectroscopy.

A general overview of the properties of these materials will be presented with a special focus on structures and properties.

A new high performance V_2O_5- based cathode for sodium-ion batteries.

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The growing interest in the Na-ion batteries is justified by cost and availability of sodium resources combined with an insertion chemistry close to the lithium one. While α-V_2O_5 was one of the first example of Li intercalation compounds only a few works report Na insertion into that layered host lattice. We recently reported sodium insertion into the so called α-V_2O_5 with a capacity of 120 mAh/g at a low voltage of 1.6V [1]. In this work a new sodium insertion compound is prepared by the chemical oxidation of the γ-LiV_2O_5 using NO_2BF_4 as oxidizing agent. One sodium ion per mole of γ'-V_2O_5 can be reversibly inserted at a remarkably high potential of 3.3V against 1.6V in the usual αV_2O_5. The γ'-V_2O_5 electrode can deliver a reversible and stable capacity of 110mAh/g at C/10 at room temperature (RT). A high capacity of 90 mAh/g is also available at higher 2C rate. An excellent capacity retention is also demonstrated at RT with 105 mAh/g recovered after 100 cycles at C/10. A two phases mechanism involving the γ'-V_2O_5 / γ-NaV_2O_5 system is evidenced from XRD and Raman spectroscopy experiments. The structural features of the fully sodiated γ-NaV_2O_5 phase with an usual expansion of the interlayer spacing (+2Å/compared to γ'-V_2O_5) are solved. These results reveal that the γ'-V_2O_5 constitutes a new competitive cathode material for the reversible intercalation of sodium ions.
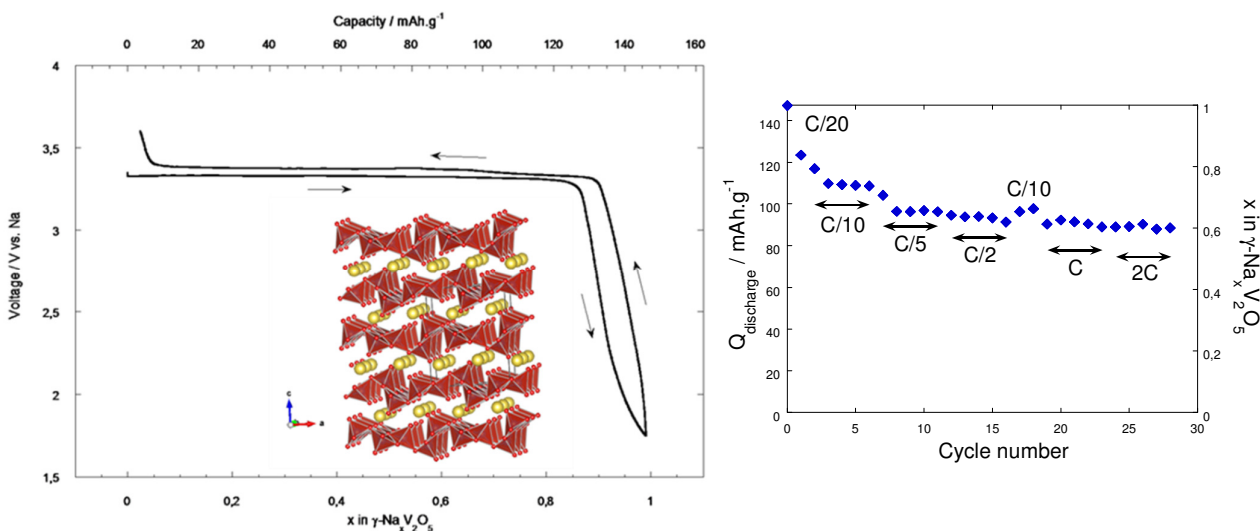

Figure1: Discharge-charge curves of γ'-V_2O_5 in a 1M NaClO4/PC electrolyte at 50°C (C/60). Right: Rate capability behavior at RT.

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Role of cationic vacancies on the electrochemical storage properties of Hydroxy-Fluorinated TiO$_2$ Anatase

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Introducing defects, particularly vacancies, into hosted intercalation compounds has been shown to be a viable way to modify the electrochemical properties of electrode materials. (1) The fundamental reasons for the improvement of the materials properties are particularly challenging since it's required a clear identification of the defects and a fine description of the local structural changes.

Recently, we reported on a novel methodology allowing modifying the chemical composition of titanium dioxide anatase, one of the polymorph of TiO$_2$, yielding the stabilization of cationic vacancies. (2) The latter were induced by the partial substitution of divalent oxides by monovalent fluorides and hydroxyl groups yielding the general chemical formula Ti$_{1-x-y}$□$_{x+y}$O$_{2-4(x+y)}$F$_{4x}$(OH)$_{4y}$, where □ represents a cationic vacancy. The concentration of the cationic vacancies can be synthetically controlled by tuning the reaction temperature, reaching an unprecedented deviation of the chemical composition respecting to the pure TiO$_2$ anatase. Indeed, up to 22% of cationic vacancies can be generated yielding Ti$_{0.78}$□$_{0.22}$O$_{1.12}$F$_{0.4}$(OH)$_{0.48}$.

Here, we propose to discuss the impact of cationic vacancies on the insertion properties of Ti$_{0.78}$□$_{0.22}$O$_{1.12}$F$_{0.4}$(OH)$_{0.48}$ with respect to Li$^+$ and Mg^{2+} ions.

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Fabrication of $LiCoO_2$ Composite Electrode on $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ Solid Electrolyte by Aerosol Deposition Method

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All-solid-state rechargeable lithium batteries using non-flammable ceramic solid electrolytes are promising as next-generation batteries with high safety. In general, high temperature sintering is carried out for those batteries to form an electrochemical interface since both electrode and electrolyte are solid. However, the high temperature heat treatment limits the combination of electrode and electrolyte materials because of a formation of impurities through their chemical reactions at high temperatures. Aerosol deposition (AD) method is one of new dry processes which can form a ceramic layer on a substrate without high temperature heat treatment. In this study, we tried to optimize AD conditions to obtain a thick $LiCoO_2$ layer on a $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ (LLZ) solid electrolyte for all-solid-state rechargeable lithium batteries. In addition to $LiCoO_2$ particles, its composite particles with Li^+-conducting Li_3BO_3 were synthesized and tested. Fig. 1 shows the cross-sectional SEM images of electrodes formed using $LiCoO_2$ particles and $LiCoO_2/Li_3BO_3$ (7/3 in weight) composite particles. They indicate that soft Li_3BO_3 works like binder to provide a thick electrode. Fig. 2 shows the charge-discharge curves of $LiCoO_2$ electrode and $LiCoO_2/Li_3BO_3$ composite electrode on LLZ pellets at 60 °C. The initial discharge capacity and utilization of $LiCoO_2$ were estimated to be 12.8 mA h g^{-1} and 9.3 % in the $LiCoO_2$ electrode, 55.5 mA h g^{-1} and 40.1 % in the $LiCoO_2/Li_3BO_3$ composite electrode, respectively. This result indicates that Li_3BO_3 works as not only binder but also Li^+-conducting pathways to improve the utilization of $LiCoO_2$. However, the obtained electrochemical performance was still low. Thus, the optimization of Li_3BO_3 content, electrode densification and so on are now underway for further improvement of $LiCoO_2$ utilization.
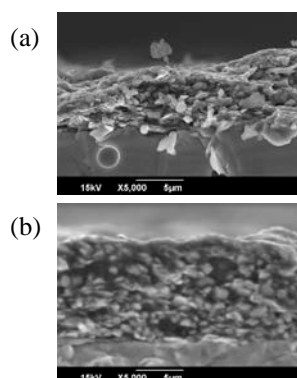

Fig.1 Cross-sectional SEM images of (a) $LiCoO_2$ electrode and (b) $LiCoO_2/Li_3BO_3$ composite electrode formed on LLZ pellets by AD method.
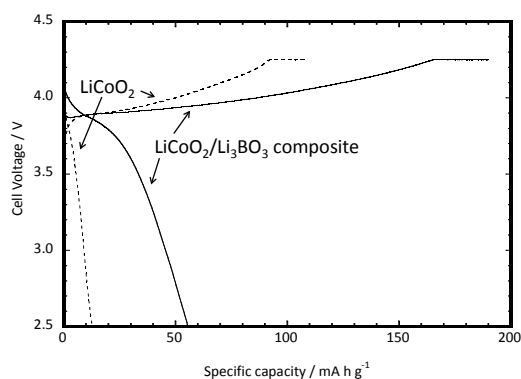

Fig.2 1st charge-discharge curves of (a) $LiCoO_2$ electrode and (b) $LiCoO_2/Li_3BO_3$ composite electrode on LLZ pellets, measured at 60 °C and 0.1 C-rate.

# High-throughput cathode materials exploration by combinatorial technology

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Concept of combinatorial chemistry was proposed by Prof. Robert B. Merrifield who designed efficient solid phase peptide synthesis using polymer beads in 1960s. On the other hand, around the same time, J.J. Hanak, K. Kennedy et al. also reported the other concept of combinatorial metal and inorganic materials exploration using sputtering technique and so on. One of reasons why combinatorial metal and inorganic materials exploration didn't developed in 1960s was due to difficult to establish computer automation. From 1990s, however, many researcher tried to establish high-throughput materials exploration system since we could easily use personal computer.

Our research group (NIMS: 1999-2006, TUS: 2003-present) have hitherto developed combinatorial high-throughput preparation system based on solution processing. From the beginning, we are exploring various kinds of cathode materials for lithium ion secondary battery using our robot system. And, in order to accelerate materials exploration, we made not only the preparation system but also high-throughput powder X-ray diffractometer for phase identification and the combinatorial electrode array for obtaining 1st charge-discharge capacity.

As one example, multi-elements substituted layered-type $Li(Ni,Co,Ti)O_2$ were prepared using our exploration system. The following figure shows pseudo-ternary Li_2O-NiO-$CoO_{1.33}$-TiO_2 reaction phase diagram at 700°C under air atmospheric condition. From this diagram, it was found that the composition ratio of layered-type structure was Li : (Ni,Co,Ti) = 1:1. And, $Li(Ni,Co)_{0.9}Ti_{0.1}O_2$ compounds were better cycle performance than the other $Li(Ni,Co,Ti)O_2$. In this joint seminar, I will also show the other results of cathode materials exploration.
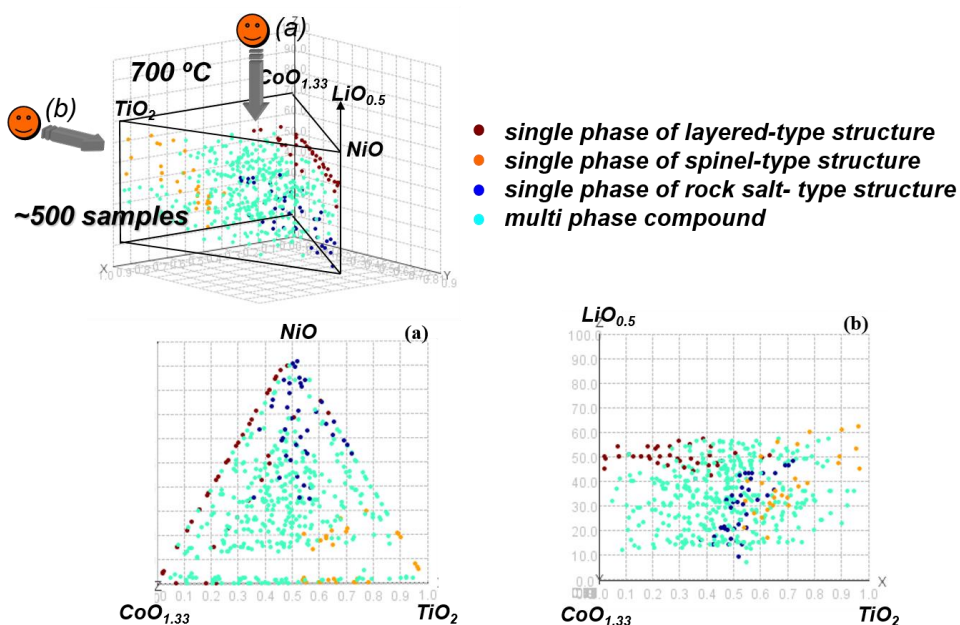
Solid-State Redox Reaction of Oxide Ions for Rechargeable Batteries

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The use of anion redox, especially oxide ions, is a crucial strategy to design and develop new electrode materials with high gravimetric/volumetric energy density for rechargeable lithium batteries. Reversible capacity of electrode materials is potentially further increased by the enrichment of lithium contents with less transition metals in the close-packed structure of oxide ions. Our group has reported that $Li_3Nb^{5+}O_4$[1] and $Li_4Mo^{6+}O_5$[2], which have higher lithium contents than that of Li_2MnO_3, are potentially utilized as host structures for a new series of high-capacity electrode materials. Recently, $Li_2Ti^{4+}O_3$ is also proposed as the host structure for high-capacity electrode materials with redox reaction of oxide ions.[3] Mn^{3+}-substituted sample, $0.5Li_2TiO_3 – 0.5LiMnO_2$ ($Li_{1.2}Ti_{0.4}Mn_{0.4}O_2$), delivers large reversible capacity of 300 mAh g^{-1} as shown in Figure 1a. Available energy density of $Li_{1.2-x}Ti_{0.4}Mn_{0.4}O_2$ exceeds 1,000 mWh g^{-1} as a positive electrode material. Moreover, charge compensation is realized by oxidation of oxide ions as evidenced by O K-edge X-ray absorption spectroscopy (Figure 1b) as a reversible process.

From these results, we will further discuss the possibility of high-capacity positive electrode materials, which effectively use the solid-state redox of oxide ions for the charge compensation, consisting of only 3d-transition metals.
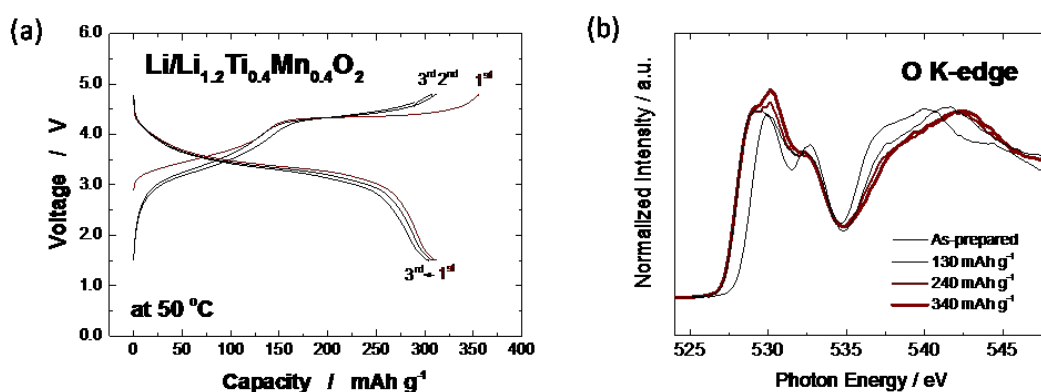

Figure 1. (a) Charge/discharge curves of ball-milled $Li_{1.2}Ti_{0.4}Mn_{0.4}O_2$ in the voltage range of 1.5 – 4.8 V at a rate of 5.0 mA g^{-1} at 50 °C, and (b) changes in O K-edge XAS spectra on charge for $Li_{1.2-x}Ti_{0.4}Mn_{0.4}O_2$.

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Acknowledgements

Atomic Layer deposition of thin films materials for 3D solid state Li-ion microbattery

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Nowadays, millimeter scale power sources are key devices for providing autonomy to smart, connected and miniaturized sensors. Planar solid state microbatteries do not exhibit a sufficient surface energy density. 3D microbatteries[1–3] appear therefore to be a good solution to improve the material mass loading while keeping small the footprint area. Nevertheless, the main technological barrier deals with the conformal deposition of unlithiated and lithiated thin films on 3D structures and Atomic Layer Deposition (ALD) technology seems to be a powerful technique to coat complex substrate. Silicon simple and double microtubes technology has been proposed as an original, robust and highly efficient 3D scaffold to significantly improve the geometrical surface of miniaturized 3D microbattery. Four functional layers composing the 3D lithium ion microbattery stacking has been successfully deposited. In depth X-Ray nanotomography and Transmission electron microscope analyses are performed to check the interfaces between each layer. For the first time, 3D anatase TiO_2 negative electrode is coated with a lithium phosphate thin film proposed as the 3D solid electrolyte. Li_3PO_4 low temperature form (from 10 up to 60 nm thick) exhibits a notably high ionic conductivity (# 6.2×10^{-7} S.cm^{-1}) for a solid electrolyte grown by ALD and an electrochemical stability window close to 4.2V. The specific area resistance has been found to be the lowest reported so far (# 3.8 Ω.cm^2). The deposited Li_3PO_4 is a pinhole free and step-conformal layer (100 %) on original, high aspect ratio (> 50:1) and highly robust 3D silicon scaffolds. The surface capacity of TiO_2 thin film electrodes, coated with the Li_3PO_4 solid electrolyte and evaluated as a part of a 3D all solid state Li-ion microbattery fabricated at the wafer level, is significantly increased by the proposed topology (high AEF – thick 3D layer), from 3.5 µAh/cm^2 for a planar layer up to 0.37 mAh/cm^2 for a 3D thin film (105 times higher).

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Spark Plasma Sintering: an efficient route to design energy storage devices

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Spark Plasma Sintering is a well-known sintering method involving the use of an electrical current added to the application of pressure. This technique presents some advantages over conventional methods such as pressureless sintering or hot pressing for example. These advantages include lower sintering temperature, shorter holding time (which may limit unexpected reactions) and marked improvements in the properties of materials consolidated by this method. For these reasons, we decided to use this technique to design devices for energy storage such as all solid state batteries or thick electrodes.

In a first part, an all-solid state symmetric monolithic sodium ion battery made by SPS and operating at 200 °C will be described, using NASICON-type electrodes and electrolyte. $Na_3V_2(PO_4)_3$ is used at both electrodes as the active material while $Na_3Zr_2Si_2PO_{12}$ plays the role of the Na^+ solid electrolyte. Both compositions present order-disorder phase transitions and present decent ionic conductivity properties, 1.5×10^{-3} S cm^{-1} and 1.9×10^{-4} S cm^{-1} at 200 °C for $Na_3Zr_2Si_2PO_{12}$ and $Na_3V_2(PO_4)_3$, respectively. The full battery (560 mm in thickness) was assembled in a 10' single step by spark plasma sintering at 900 °C. The electrochemical characteristics at high temperature (200 °C) were evaluated thanks to a new experimental set-up. The battery operates at 1.8 V with 85% of the theoretical capacity attained at C/10 with satisfactory capacity retention, for an overall energy density of 1.87×10^{-3} W h cm^{-2} and a capacity of 1.04 mA h cm^{-2}.

In the second part of the talk, some results concerning the preparation of thick porous sintered electrodes thanks to SPS will be presented. Indeed, SPS is a technique of choice which limits unwanted side chemical reactions thanks to the rapidity of the process. Our preliminary works carried out at LRCS have already shown the feasibility to manufacture thick porous composites electrodes by SPS. By incorporating a salt (NaCl) in the electrodes, it is possible to dissolve it after sintering and therefore to generate porosity within the electrode. The porosity (pore size and volume) can be easily controlled by its percentage in volume and the particle size of NaCl.

All-Solid-State Lithium-Ion Batteries Using Oxide Solid Electrolyte

Assembled by Spark Plasma Sintering

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To develop an all-solid-state lithium-ion battery (ASS-LIB) using oxide solid electrolyte for applications such as electric vehicles, the thicknesses of stacked electrode and electrolyte layers need to be curtailed to several ten to hundred μm order. This can be achieved through powder technology. In the ASS-LIB, the good contact interfaces should be prepared by a simple powder sintering process, and also produces little ion-blocking impurities. Well-known high lithium-ion conductive oxides possess of over 10^{-4} S cm^{-1}; however, these required sintering at high temperature beyond 1000 °C to facilitate good contact with the electrodes. In addition, most electrode materials produce impurities after sintering. To address these issues, the ASS-LIBs were assembled by the use of oxide solid electrolyte with low melting point ($Li_{2+x}C_{1-x}B_xO_3$)[1] and/or the use of spark plasma sintering (SPS)[2], which could be processed at low temperature.[3]

For assembling ASS-LIB, composite electrode powder was firstly prepared from a mixture of 70 wt% $LiCoO_2$ and 30 wt% $Li_{2.2}C_{0.8}B_{0.2}O_3$ electrolytes. Then, Au/composite electrode powder/ $Li_{2.2}C_{0.8}B_{0.2}O_3$ powder was assembled by SPS process at 450 °C for 1 min under 30 MPa of pressure. Lithium foil was used as a reference/counter electrode. A poly(ethylene oxide) -based polymer electrolyte film was inserted between the lithium foil and the $Li_{2.2}C_{0.8}B_{0.2}O_3$ electrolyte separator to reduce the interfacial resistance with adhesion as possible. Electrochemical charge-discharge test was performed at a constant current of 10 μA cm^{-2} at 60 °C. The ASS-LIB shows an initial charge-discharge profile which is similar to the liquid electrolyte case, and the discharge capacity is 118 mAh g^{-1}. No impurity peak was observed in the powder XRD pattern of the $LiCoO_2$-$Li_{2.2}C_{0.8}B_{0.2}O_3$ composite electrode after SPS process. Therefore, the reversible capacity of ASS-LIB could be measured in this study, thanks to the use of $Li_{2.2}C_{0.8}B_{0.2}O_3$ with low melting point and SPS process.

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Electrochemical mechanism of M$_x$Sb (0≤x≤0.5, M=Sn, Bi, Fe) phases in Na batteries.

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In the new exciting research on efficient electrode for Na-ion batteries, p-element-based electrodes have shown to be viable alternatives to hard carbon, providing very interesting performances with reversible capacities largely exceeding 400 mAh/g.[1-3] We have investigated several antimonides M$_x$Sb (0≤x≤0.5, M=Sn, Bi, Fe) (Figure 1) as electrode materials for Na batteries. The thorough investigation of both mechanism (through in situ XRD, NMR, and Mössbauer spectrometry) and performances will be presented.
 The role of the second element (Sn, Bi and Fe) on the good performance of these electrodes will be discussed. An XPS analysis will be presented to discuss about the solid electrolyte interphase (SEI) formed during the reversible sodiation in the Sb/Na batteries cycled in various electrolytes. [4, 5]
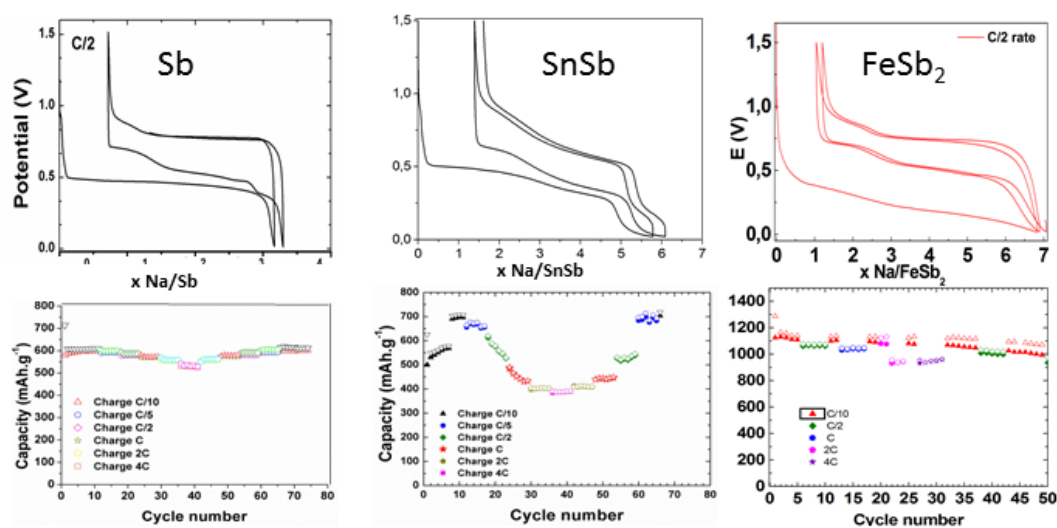

Fig. 1: above: Galvanostatic curves of M$_x$Sb (0≤x≤0.5, M=Sn, Fe) /Na, bottom: associated rate capability.

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Lithium/Sulfur Batteries upon cycling: Application of Electrochemical Impedance Spectroscopy, *in situ* X-Ray Diffraction and tomography.

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Lithium/Sulfur batteries, due to their high theoretical values of gravimetric (2500 Wh kg^{-1}) and volumetric (2800 Wh L^{-1}) energy densities, became one of the most popular candidates for next-generation energy storage system[1]. However, the practical discharge capacity and cycle life of Li/S cells are still below expectation despite of many efforts which has been done during last three decades. The understanding of the working mechanism is an essential point in order to help to improve the electrochemical performances. This presentation will be an overview of our recent studies conducted in this goal.

It is well known that structural and morphological changes occur inside the Li/S cell upon cycling, since the redox reaction is accompanied by phase transformation of active material (solid/soluble phases), in that context, *in situ* and *operando* synchrotron-based XRD was applied, this investigation permitted us to define precisely the moment of liquid/soluble phase transitions and to propose electrochemical process[2,3]. In parallel, electrochemical impedance spectroscopy study was perform upon cycling and give complementary information on both transfer reactions, electrolyte conductivity evolution, electrode morphology and passivation layer formation.

Recently, coupled X-ray absorption and diffraction tomography preliminary results were obtained at ID15a at the ESRF. This powerful technic is used to characterize the batteries on length scales from the atomic to the microscopic. Sequential X-ray absorption tomography and X-ray diffraction measurements allowed different mechanisms within a Li/S cell to be observed, such as sulfur reduction/formation, polysulfide dissolution and Li$_2$S deposition/dissolution.

Another important issue of a Li-S cell lies in the fact of using metallic lithium as negative electrode, which leads to serious safety hazards (dendrites formation, reactivity). Some investigations have been focused on the development of lithium sulfide (Li$_2$S) positive electrode, as an alternative solution to sulfur electrodes, which could lead to metallic lithium-free Li-ion/S batteries. By applying GITT and *operando* XRD measurements, an electrochemical mechanism was proposed to explain the initial charge profile, in terms of equilibrium potential and polarization phenomenon[4].

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Highlights on latest battery technology achievements & challenges

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After introducing our battery activity, the presentation will focus on high energy density solutions. We will discuss how to push the limits of Li-ion batteries, and will detail the technologies offered to go further, with a specific attention to the Li/Sulfur technology. We will continue our journey through the batteries by considering the solutions to improve safety, cost, life,…

Firstly reported in the 80's, rechargeable lithium/sulfur (Li/S) batteries have received ever-increasing attention since 10 years. Indeed, elemental sulfur (S8) is a promising positive electrode material due to its high theoretical specific capacity of 1675 mAh.g^{-1}. Assuming full conversion of S8 to Li$_2$S, complete Li/S cells are expected to reach practical gravimetric energy densities from 300 up to 600 Wh.kg^{-1}. Those values, combined with low cost, non-toxicity and environmentally abundance of sulfur, make Li/S batteries one of the most promising candidates for next-generation energy storage systems. A review of the recent developments done in our laboratory will be presented, at different levels starting from the optimization of coin cell components up to assembly of prototypes, in addition to the last characterization methods that have been applied via *in situ* and *in operando* methods to allow deeper understanding of the Li/S technology.

Abstracts
of poster presentations

LiTDI and LiFSI as substitutes for LiPF$_6$ in Li-ion batteries electrolytes

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Most of the lithium-ion batteries (LiBs) used in electrical devices currently available contain lithium hexafluorophosphate (LiPF$_6$) dissolved in a mixture of alkylcarbonates as the electrolyte mainly because of [1] the high conductivity of LiPF$_6$ solutions, its help in the formation of a protective SEI on graphite and its ability to passivate aluminum, a low-cost metal used as current collector. Other important electrolyte properties include low viscosity and a large life-span without safety risks, especially when damaged. However, the thermodynamic instability and moisture sensitivity of LiPF$_6$ induce high risks of releasing HF and/or PF$_5$ via its thermal decomposition/hydrolysis in the presence of water. These drawbacks have been highly criticized justifying the importance in finding a replacement. Owing to (i) its high thermal stability, (ii) low sensitivity to the presence of water and (iii) its electrochemical stability [2], the lithium 4,5-dicyano-2-(trifluoromethyl)imidazol-1-ide (LiTDI) is seen as a promising substitute for LiPF$_6$ in LiBs.

In a previous study [3] the poor ion pair (IP) dissociation of LiTDI was discussed and found to be around 30 % in an ethylene carbonate/dimethyl carbonate (EC/DMC) mixture. This poor IP dissociation is not only responsible for the lower conductivity of LiTDI in EC/DMC as compared to LiPF$_6$ but also for the important capacity drops at higher C rates. In
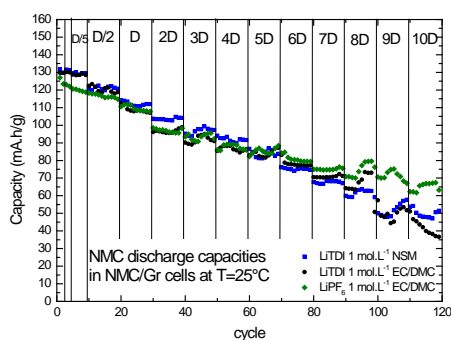
order to address these defects, a new thermally stable solvent mixture [4] (denoted NSM) allowing a better dissociation of the salt (37%), a higher conductivity (8.5 mS.cm^{-1} instead of 6.1 mS.cm^{-1} in EC/DMC at 25°C), a lower viscosity (2.4 mPa.s instead of 2.8 mPa.s in EC/DMC at 25°C) and good capacity retention at high C rates (up to 10C) in half-cells (graphite/Li and NMC/Li) as well as NMC/graphite cells has been found.

Another promising substitute for LiPF$_6$ is the lithium bis(fluorosulfonyl)imide (LiFSI) for its high conductivity, high thermal stability and its resistance to hydrolysis. In this work, transport properties (conductivity, viscosity, transference number and ion-pair dissociation) of LiTDI and LiFSI, their passivating properties (SEI and aluminum) and the cell capacities obtained while using them will be compared to that of several salts including LiPF$_6$.
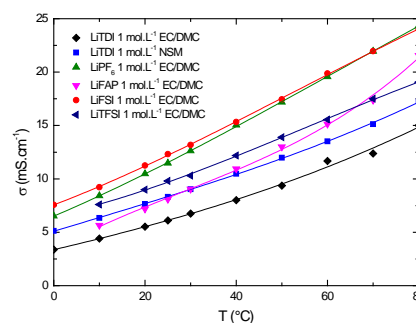
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Study of 5V cathode materials, role of protective oxide layer

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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 Al_2O_3, deposited by atomic layer deposition (ALD). The role of different oxides on LNMO's electrodes is discussed according to their chemical, physical and electrochemical properties.
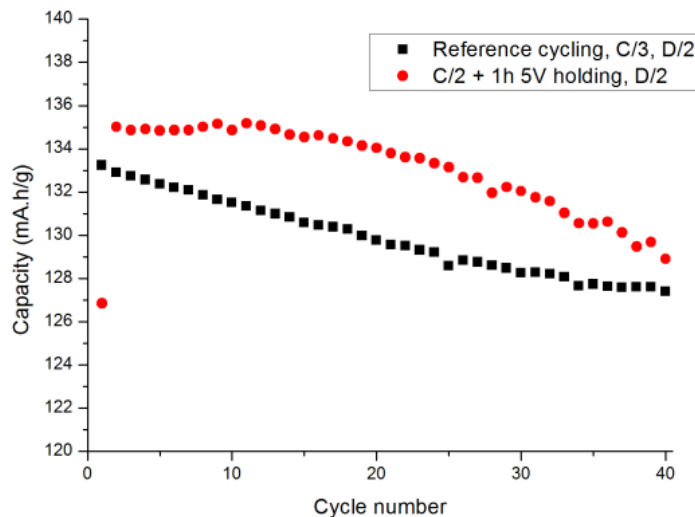

Figure 1 Capacity of LNMO spinel with different cycling parameters

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Redox organic materials for low cost sodium aqueous batteries

and non-aqueous supercapacitors

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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, redox organic materials constitute a promising source of active compounds. In this work, the interest of these organic materials is demonstrated through two approaches: one involving the development of low cost sodium aqueous batteries, the other one being devoted to that of pseudocapacitive supercapacitors based on grafted carbon electrodes.

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 and positive electrodes that are in addition associated with significant side reactions with the aqueous electrolyte. To address these issues, the electrochemical and physical behavior of n and p type derivatives have been investigated in various aqueous supporting electrolytes. Results allows to identify the key factors governing the long term stability on cycling. Capacity as high as 90 mAh/g for more than 200 cycles with a coulombic efficiency very close to 100% can be obtained even at slow rate.

We also report a facile method for grafting of 1-nitropyrene (Pyr-NO$_2$) onto highly graphitized carbon onion as electrodes for supercapacitors. This is achieved through lowering of the onset potential of the pyrene unit polymerization via in-situ reduction of the NO$_2$ group. The additional redox activity associated with the NO$_2$ redox activity allows to surpass the faradic capacity solely associated with the p-doping of the grafted pyrene backbone, as it is observed for the pyrene, 1-aminopyrene, and unreduced Pyr-NO2. Upon 20 wt % grafting of Pyr-NO2 the capacity of the electrode jumps from 20 mAh/g electrode to 38 mAh/g electrode which corresponds to 110 mAh/gPyr-NO2 per mass of Pyr-NO2. Altogether, this results in a striking increase of the energy density vs. the Li counter electrode by 90 % (29 to 55 Wh/Kg electrode), while the average potential is increased by 18 %. Very interestingly, such high performance comes together with outstanding retentions of both the initial capacity for more than 4000 cycles and power characteristics demonstrating the superior advantages of the present in-situ grafting technique. Lastly and most importantly, a full cell is demonstrated by combining Li-terephthalate/carbon as anode.

Multiscale charge transport characterization in composite electrode for lithium-ion batteries

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Despite the significant benefits that offer Li-ion batteries as an energy storage system, the electrode technology suffers of limitations with regard to the power and energy densities. As a result, 50% of batteries weight and volume are non-electroactive parts (collectors, separators, electrolyte). The limitations mainly originate from charge transport in these complex and hierarchical materials. The present study aims at better understand the strong interactions existing between the liquid electrolyte and the solid materials of the composite electrode. Our study presents the charge transport characterization at different scales, from electronic to ionic, by combining a high-frequency analysis performed by broadband dielectric spectroscopy (BDS, up to 10 GHz), with a low-frequency analysis performed by electrochemical impedance spectroscopy (EIS, down to 1 mHz). The electronic percolation threshold and the kinetics of impregnation by the electrolyte have been determined with respect to the carbon black content in the composite electrode (see Figure): the various contributions were attributed and modeled. In addition, the morphology as well as the porosity/tortuosity effects on the ionic mass transport will be discussed [3].
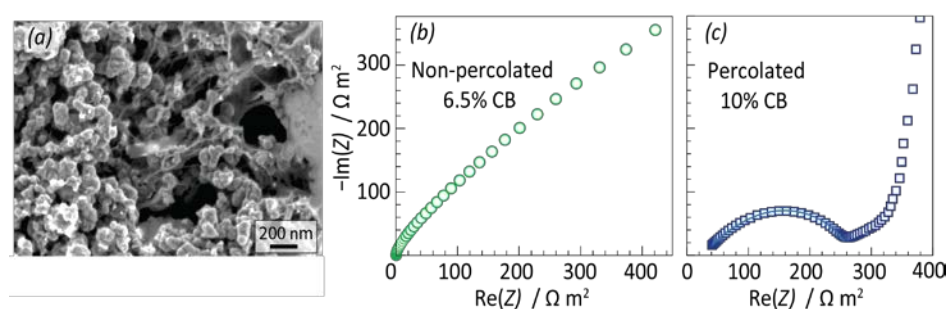

Figure : (a) SEM micrograph of a composite electrode.

Electrochemical impedance spectra for (b) 6.5% and (c) 10% carbon black.

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Electrochemical Performance of K_xCoO_2 in Non-Aqueous K Cell

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Reversible potassium insertion into graphite has been reported for a negative electrode material of potassium-ion batteries in 2015, and our group has demonstrated that the potassium half-cell delivers reversible capacity of ca. 250 mAh g^{-1} and exhibits an enormously high rate performance.[1] The findings have opened the door for realizing high-voltage potassium-ion batteries. However, further developments of the positive electrode materials are required. Electrochemical studies on Li-ion and Na-ion batteries started with $LiCoO_2$ and $NaCoO_2$, respectively, and potassium-containing layered cobalt oxides, K_xCoO_2 have been already reported by Delmas in 1975,[2] the electrode performance has been never reported to our knowledge. In this study, reversible potassium intercalation into the K_xCoO_2 and its phase evolution were investigated in potassium cells for the first time.

$K_{0.31}CoO_2$ with P2-type structure was prepared by a conventional solid-state reaction with starting materials of KOH and Co_3O_4. The structure and composition were confirmed using X-ray diffraction (XRD) and inductively coupled plasma-optical emission spectrometry (ICP-OES). Figure 1 shows charge/discharge curves and rate capability of $K_{0.31}CoO_2$ electrodes tested in aprotic K cells at room temperature. Reversible K extraction/insertion from/into $K_{0.31}CoO_2$ are observed in the voltage range of 2.0-3.9 V and the cell delivers reversible capacity of 57 mAh g^{-1} and good rate performance with stepwise voltage profile, which would be related to K/vacancy ordering. Phase transition will be presented and discussed with *operando* XRD and electrochemical data.
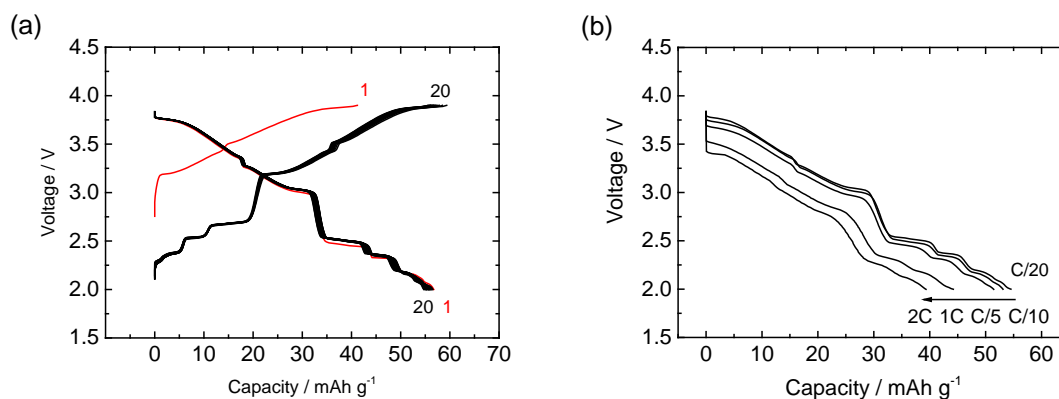

Figure 1. (a) Charge/discharge curves of $K//K_{0.31}CoO_2$ cell with 1 M KFSI EC:DEC at a current rate of 10.3mA g^{-1} in the voltage range of 2.0 – 3.9 V and (b) discharge curves at various C-rate of C/20 – 2C (1C = 236 mA g^{-1}).

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In operando ATR-FTIR analysis of silicon anodes for Li-ion batteries

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Attenuated Total Reflection Fourier Transform InfraRed spectroscopy (ATR-FTIR) allows for studying thin-film electrodes in situ and in operando, in conditions close to those used in Li-ion batteries. This technique was used to obtain quantitative information on the surface and bulk phenomena involved during electrochemical cycling of amorphous silicon and amorphous lithiated silicon electrodes [1].

Main results include a precise knowledge of the evolution of the solid|electrolyte interphase (SEI) composition and thickness, of the irreversible lithiation process and of the hydrogen content of the films. From our study we can also infer the lithiation mechanism and its dependence on the film composition.

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Phase Transition and Stacking Faults in Na-Extracted Layered Oxides

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Sodium-ion batteries are promising candidates for a stationary energy storage system because of abundant resources of sodium in the world. The electrode materials have been extensively studied and some companies have developed prototype full cells consisting of layered transition metal oxides and non-graphitizable carbon (hard carbon) as a positive and a negative electrode, respectively. Much efforts have been recently devoted to understand the reaction mechanism and further improve electrode performance. However, structure of the layered oxides, especially P2-type phases such as $Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$, at fully charged state is unclear and depends on the composition. In this study, phase transition caused by Na-extraction is examined using *ex-situ* synchrotron and *operando* X-ray diffraction (XRD) for P2-$Na_{2/3-x}Ni_{1/3}Mn_{2/3}O_2$ and its Cu-substituted phase.

$Na_{2/3-x}Ni_{1/3}Mn_{2/3}O_2$ and $Na_{2/3}Cu_{1/12}Ni_{1/4}Mn_{2/3}O_2$ with P2-type structure were prepared by a conventional solid-state reaction. *Operando* X-ray diffraction was measured using an in-situ cell (Rigaku) with sample electrodes, 1 mol dm^{-3} NaPF$_6$/PC electrolyte and a counter electrode of Na metal. The XRD patterns for the electrodes revealed that structure of $Na_{2/3-x}Ni_{1/3}Mn_{2/3}O_2$ transformed from P2 into O2-type phase as a two-phase reaction by Na-extraction, while two- and single-phasic P2-OP4 transition was observed for $Na_{2/3-x}Cu_{1/12}Ni_{1/4}Mn_{2/3}O_2$. Furthermore, peak broadening of 10*l* reflection was observed at almost fully charged state for both samples, which is clearly seen in the *ex-situ* synchrotron XRD patterns for $Na_{2/3-x}Ni_{1/3}Mn_{2/3}O_2$ in Fig. 1a. According to study by Lu and Dahn, the peak broadening is assumed to be caused by stacking faults between two choices of O2-type structures (Fig. 1b).[1] The XRD pattern of O2-type phase with stacking faults, where the two choices were selected at random, was calculated using DIFFaX program. The simulated XRD pattern was similar to the observed one, suggesting formation of stacking faults with the two choices. Similarly, a calculated pattern of OP4-type phase with some stacking faults was also close to the observed XRD profile for $Na_{2/3-x}Cu_{1/12}Ni_{1/4}Mn_{2/3}O_2$ after charge to 4.5 V. Relationship between the phase transition accompanying stacking faults and electrode performance will be discussed.
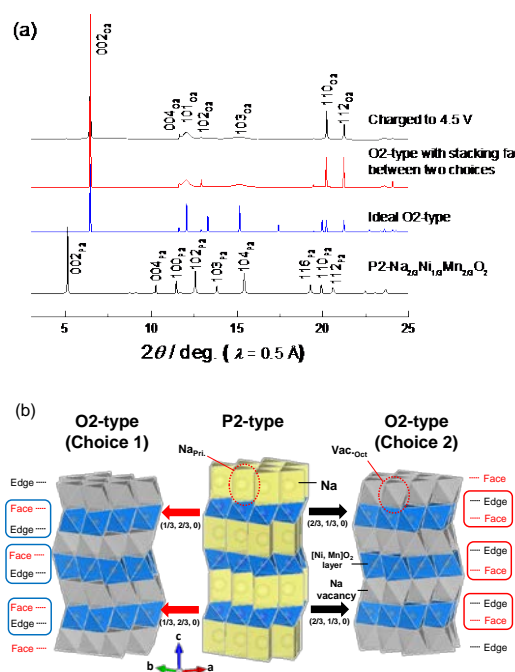

Figure 1. (a) Synchrotron *ex-situ* XRD patterns of $Na_{2/3-x}Ni_{1/3}Mn_{2/3}O_2$ and simulated ones for O2-type phase w/o stacking faults. (b) Schematic illustration of O2-type structure with two choices.

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Improvement of solid polymer electrolyte in low temperature lithium metal polymer batteries

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Nowadays, lithium-based batteries are widely used in electronic devices due to the Li-ion technology, and they are increasingly used in (hybrid) electric vehicles [1]. One major issue towards large-scale application concerns their safety, due to the volatility, flammability and low flash point of solvents used as electrolytes. With regard to the safety concerns, solvent free membranes are very attractive for solid polymer electrolytes (SPE) in particular, complexes of polyethyleneoxide (PEO) and lithium salt that is the most exploited polymer electrolyte system. PEO has been chosen for its outstanding ability to solvate lithium cation. However because of its high crystallinity, the ion conduction of this SPE is significantly lower than in liquid one. Better conductivities are provided by this complex above the PEO melting temperature, but at these temperatures the mechanical properties are very poor and dendrites formation was observed [2].

In order to combine, in a same material, the two antagonistic properties, i.e. high conductivity and good mechanical strength, block copolymer electrolytes (BCE) have recently been proposed as SPE [3-7]. The high performance of these functional materials is a consequence of their ability to self-assembly resulting to phase separated nanostructure and thus to a synergy of properties instead of average ones.

In this work we have designed a new BCE with a central block based on modified PEO, that is much more amorphous compared to linear PEO, and two lateral blocks of polystyrene.
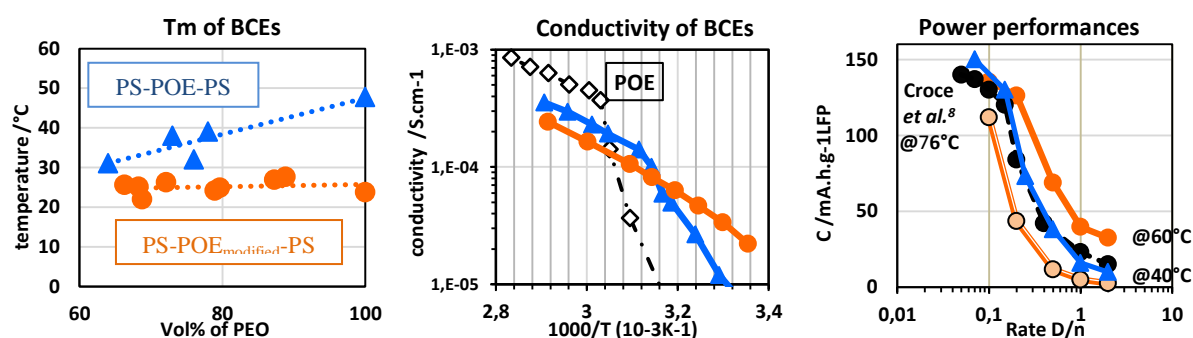
The proprieties of BCE were modulated by varying the lengths of PS. The impact of the ration between the two blocks on the mechanical strength, conductivity and lithium metal cell performances are deeply discussed in this work.

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Analysis of electronic and ionic wiring limitations to power performance of composite electrodes by dielectric spectroscopy and tomography

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A set of advanced techniques such as the broad band dielectric spectroscopy, X-Ray and FIB-SEM computed tomography, were used to study the multi-scale architecture and electrical properties of NMC- and LFP-based composite electrodes of surface capacities varying from 1.3 to 2.8 mAh cm^{-2} for lithium batteries.

Moreover, the discharge rate capability of these electrodes was also measured. The study as a function of the temperature allowed to identify which mechanism is dominating, charge transfer or diffusion, depending on the electrode composition, porosity, loading, and discharge rate.

This poster will describe which factor(s) (material properties, engineering parameters) mainly influence the rate discharging behavior of composite electrodes for lithium batteries.

Surface-fluorination for active electrode protection technology - a glance at fluorinated titanium dioxide materials… and more!

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In all domains, materials need protection: protection against corrosion, weathering, or scratches. Our objective is to provide protection to metal oxides in the field of energy storage. Used as electrode, metal oxides are extremely sensitive to their chemical environment.[1,2] For instance, in Li-ion batteries, metal oxides are slowly degraded by the electrolyte. Such degradation, coupled with other inherent problems of batteries, leads to what is tagged as irreversible capacity: a lost electrochemical capacity that cannot be brought back. We propose a solution to protect metal oxides materials by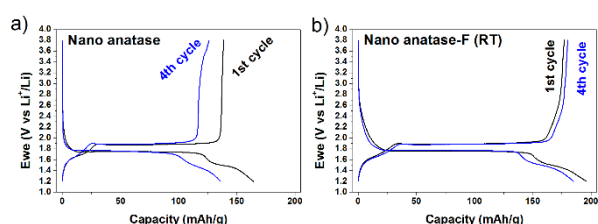 surface fluorination, an innovative concept applied to metal oxides. In Li-ion batteries, the surface fluorination of metal oxides will provide a surface protection against capacity fading by preventing its cause: the unwanted lithium consumption. The idea behind this is as simple as it seems: re-enforce the surface of TiO_2 electrode surface with fluorine, the same way toothpaste acts everyday on your own teeth!

Figure 1. Galvanostatic charge-discharge curves for TiO_2/Li (a) and TiO_2-F/Li (b) half-cells, at C/20 current density; electrolyte is $LiPF_6$ EC:PC:3DMC 1M.

The main objective is to study the influence of the surface fluorination (through molecular or atomic fluorine) on the electrochemical behaviour of TiO_2 electrodes under operating conditions. In Li-ion batteries, one of the main drawbacks for titanium oxides is the large irreversible capacity on the first charge/discharge cycle that is associated with surface reactions between the electrolyte and the electrode. Thus, surface fluorination is the key, as presented on Figure 1.[3]

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Role of Solvents and Salts in Sb/Na Batteries: An XPS Analysis

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Recent concern about critical resources of lithium and the increasing need for electrochemical energy storage technologies has recently renewed the interest of sodium-ion batteries.[1,2] Among the promising active materials identified within the last few years, alloy-based compounds such as Sb-based materials have shown unexpected electrochemical performance in Na-ion batteries (NIBs) compared to those in Li-ion batteries (LIBs).[3] Electrolyte degradation and SEI formation are, however, expected to be critical due to the large volume expansion of the alloy reaction and the large ionic radius of Na. Nonetheless, the higher working potential (versus NHE) of NIBs compared to LIBs could limit this electrolyte degradation. Despite the concern about the critical role of the SEI formation and evolution during cycling in NIBs, only few studies have been performed so far.[4]

In this work, the role of the salts and solvents in Sb/Na coin cells was investigated by correlating the electrochemical performance with an XPS analysis.[5] Three electrolyte blends were studied: 1 M $NaClO_4$ in PC + 5% FEC, 1 M $NaPF_6$ in PC + 5% FEC and 1 M $NaPF_6$ in EC:DMC + 5% FEC. XPS showed that the passivation layer formed during cycling is mainly constituted of carbonates, Na_2CO_3 and alkylcarbonates that appeared during discharge after the deposition of NaF from the degradation of FEC. A key role of the solvent on the SEI properties was observed and will be presented. Also, the best compromise in terms of performance, found for the $NaClO_4$/PC electrolyte despite its high solvent viscosity, will be discussed regarding the XPS analysis results.

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Inside the electrochemical magnesiation of intermetallic electrodes

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Investigating post-Li-ion systems such Mg-batteries is a promising challenge in the quest for high energy density. Mg offer theoretical capacities that compete with Li. However, in contact with conventional electrolytes, the passivation film limits the cationic diffusion. Compatible electrolytes are reported but show narrow electrochemical window.

Searching for alternative anode materials might help in developing performant Mg-batteries. In this presentation, we will focus on the electrochemical behavior of various electrode materials based on p-block elements such as bismuth (Bi), antimony (Sb), tin (Sn), *etc.* In our experimental screening, micrometric metallic powders are selected as active materials. Electrode materials are tested vs. magnesium electrode in "half-cell" configuration with organohaloaluminate-based electrolyte for evaluating their electrochemical behavior. An important focus is devoted to the investigation of the electrochemical mechanisms especially through *operando* X-ray diffraction.

The first part of this presentation deals with pure elements as electrode materials. Electrodes formulated from Bi powder exhibit the best performance.[1] The alloying reaction to form Mg_3Bi_2 occurs at a stable low potential and is highly reversible even at moderately fast current rates. In comparison, Sb- or Sn-based electrodes hardly alloy with magnesium. A reversible alloying reaction is also noticed when indium (In) powder. As In is lighter than Bi, the capacity significantly increases. However, a dramatic fading is observed upon cycling or with increasing current rates.[2]

In a second part, Bi is combined with lighter but less active elements in order to search for synergistic effects. Intermetallic InBi, solid-solution compositions $Bi_{1-x}Sb_x$, and composite Bi/Sn materials are obtained by mechanical alloying. Electrochemical mechanisms present unexpected pathways with intermediate phases and/or conversion-alloying process.[3]

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Development of Li-rich layered oxides as concentration-gradient for high energy density lithium-ion batteries

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The Li and Mn-rich layered oxides are currently attracting a strong interest from the scientific community, as being one of the most attractive class of positive electrode materials for Lithium-ion batteries. Indeed, the Li and Mn-rich layered oxides $Li_{1+x}M_{1-x}O_2$ (M = Mn, Co, Ni) exhibit very high reversible capacity at an affordable cost. A common feature for all the Li and Mn-rich layered oxides is their long voltage "plateau" (i.e. high capacity), observed only at the end of the first charge. This behavior has been explained by the reversible participation of oxygen anions in the redox processes. While it is clear that the largest advantage of the Li-rich layered oxides lies in their outstanding capacities, they suffer from a continuous voltage decay upon cycling. It is induced by irreversible structural modifications occurring at the outer part of the particles (that determines the potential measured) and inducing densification of the metal-oxygen framework.

One of the tracks we are following to modify the surface chemistry of the Li and Mn-rich layered oxides, and to stabilize reversible anion participation to the redox processes is the achievement of concentration gradients within the particles (aggregates). The goal is to promote the formation of the Li and Mn-rich layered oxides in the bulk and, moving to the surface, to enrich the layered oxides composition with Ni and Co: the target is to combine high energy density and chemical stability as it was reported for Ni-rich layered oxides.

The synthesis of carbonate precursors $Mn_{0.52}Ni_{0.29}Co_{0.19}CO_3$ showing a concentration gradient is achieved via a coprecipitation method and requests to adjust several synthesis parameters including the temperature, the pH, the feeding rate and the stirring speed. A thermal treatment is then performed with optimized Li/M ratios, lithium carbonate being the lithium precursor, and at different temperatures in order to promote lithium diffusion within the particles but also to maintain the concentration gradient after calcination. The average composition of the final lithiated oxide is $Li_{1.1}Mn_{0.47}Ni_{0.26}Co_{0.17}O_2$.

In-depth characterization of the composition and structure, from the surface to the core, was achieved combining X-ray diffraction, elemental chemical analyses by ICP, and different techniques of microscopy (EPMA, EDS and FIB-STEM). Electrochemical performances and the thermal stability in the charged state of the battery will be also discussed for this series of materials.

Development of positive electrode host materials for organic batteries

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Routine access to power sources is an essential factor towards the continuing progress of our technology-oriented society, and towards ensuring a better quality of life. In this context, due to the ever-increasing implementation of renewable energy sources, electrical energy storage systems are set to play a central and potentially critical role in the next-generation energy infrastructure. Accelerated progress and innovation in the development of new and potentially "greener" electrochemical storage devices is thus imperative. In this regard, and in parallel to research activities on regular inorganic-based electrode materials, the past decade has seen significant progress with respect to redox-active organic compounds, attracting much interest from the energy storage community. Indeed, organic chemistry provides great opportunities for discovering innovative electrode materials able to operate both in aqueous and nonaqueous electrolytes. Additionally, it must be pointed out that two types of electrochemical insertion mechanisms can be used in practice with either reversible uptake/release of cations or anions.

In this communication, we will present recent advances on new organic positive electrodes. In particular, we will report on 2,5-(dianilino)terephthalate derivatives as layered redox-active organic material belonging to low molecular weight aromatic amines, able to reversibly host anions even without a carbon additive, which is very unusual behavior for an organic electrode material.

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γ'-V$_2$O$_5$: a high voltage cathode material for lithium batteries

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In this work, we focused on a lithium insertion compound: the γ'-V$_2$O$_5$ phase. This polymorphic phase of α-V$_2$O$_5$ was synthetized for the first time by Cocciantelli et al. [1]. In this study, γ'-V$_2$O$_5$ is the product of the γ-LiV$_2$O$_5$ total delithiation by chemical oxidation using NO$_2$BF$_4$. Its main interest in comparison with the α-V$_2$O$_5$ phase is to present a large interlayer space that can facilitate the alkali ions insertion.

We demonstrate that one lithium per mole can be inserted reversibly into the host structure at a high potential of 3.6 V vs. Li$^+$/Li (against 3.4 V for α-V$_2$O$_5$ phase). It presents moreover a stable and reversible capacity of 140 mAh.g^{-1} with a high capacity retention (about 95% of Q$_{initial}$ at the 50th cycle) and a very high rate capability between C/10 and 5C.

It is furthermore possible to obtain in the extended 4 / 2.2 V potential range a lithium rich composition ζ-Li$_2$V$_2$O$_5$ with the insertion of two Li$^+$/mole (280 mAh.g^{-1}) in the structure.

A structural analysis by XRD and Raman spectroscopy confirmed the presence of three successive phases in the system in the 4 / 2.2 V potential range and clearly defined the limits of the biphasic domains.

The structure of the Li-rich ζ-Li$_2$V$_2$O$_5$ phase was resolved par Rietveld refinement and this phase shows moreover a completely new Raman fingerprint.
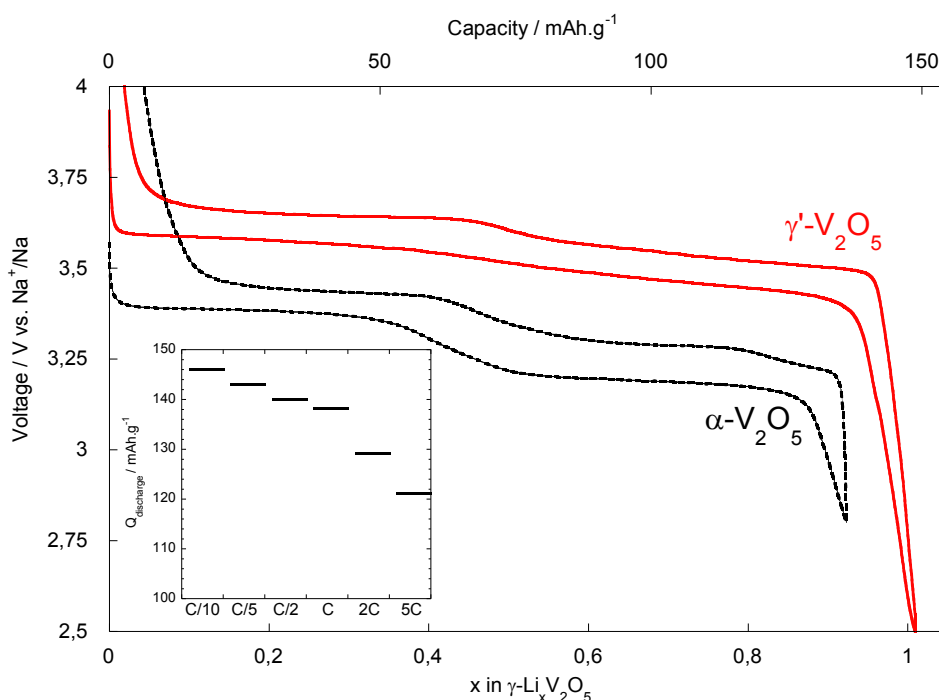
Discharge-charge curves of γ'-V$_2$O$_5$ and α-V$_2$O$_5$ in a LiClO$_4$/PC (1M) electrolyte at C/10.
In inset: Rate capability behavior at RT

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Preparation of SiO$_x$/C Composites with Na-Containing Polymer and Their Electrode Performance for Lithium-Ion Batteries

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1. Introduction

Silicon monoxide, SiO, is of interest for high-energy negative electrode materials for lithium-ion batteries since SiO has an advantage of better electrode performance due to suppressed volume expansion compared with Si during cycling. However, low initial coulombic efficiency is the challenge for commercially use. In a previous report, heat treatment higher than 1000ºC and carbon coating of SiO improve the initial coulombic efficiency [1]. In addition, heat treatment of mixture of SiO and sodium salt promotes disproportionation reaction of SiO and improves the cycle performance because nanocrystalline Si was uniformly dispersed within a porous SiO matrix after removing water-soluble sodium silicate [2]. Our laboratory reported the one step process of carbon coating and disproportionation by adding Na containing polymer [3]. In this study, we prepare SiO$_x$/C composites by using sodium alginate (AlgNa) not only as a carbon source but also as sodium source for the reaction promotion.

2. Results and discussion

Figure 1(a) showed the X-ray diffraction patterns of SiO$_x$/C composites prepared by heat-treating SiO and AlgNa in different weight ratios (SiO:AlgNa = 1:y) followed by washing the resultant product by water to remove water-soluble sodium silicate(s). The intensity of peaks assigned to SiO$_2$ and Si increased with increasing the amount of AlgNa. This shows promotion of disproportionation reaction of pristine SiO. Although the disproportionation temperature is required to set higher than 1000ºC in the previous work [2], addition of AlgNa successfully enables us to reduce the reaction temperature to 800ºC. In case of adding large amount of AlgNa (y = 1), undesired silicon carbide was produced.

Cycle stability of the composites was shown in Figure 1(b). In case of y = 0.167, the composite showed the best cycle stability to deliver more than 1000 mAh g^{-1} over 50 cycles. Furthermore, it is noteworthy that initial coulombic efficiency increased gently in y = 0 - 0.167, especially, the highest value of 70% is exhibited at y = 0.167, indicating the suitable carbon coating and formation of water-soluble sodium silicate(s) with AlgNa. On the other hand, adding larger amount of AlgNa, a remarkable decay of capacity was observed. It is likely due to inactive and insulating SiC and SiO$_2$ covering the particle surface, resulting in the deterioration of lithiation property. Based on these findings, we will further discuss the role of AlgNa as an advanced carbon source for preparation of the carbon composites.
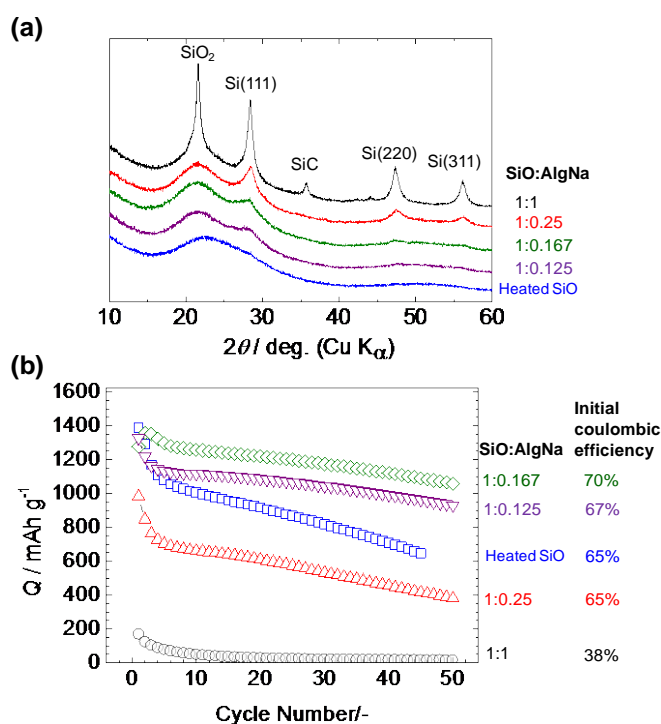

Fig. 1. (a) XRD patterns of SiO$_x$/C composites prepared with different amount of AlgNa as a carbon source. (b) Capacity retentions of SiO/C electrodes tested in Li cell with 1.0 M LiFF$_6$ EC:DEC at a rate of 100 mA g^{-1} in the range of 2.0 - 0.0 V vs. Li / Li$^+$.

3. References

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FeNCN as new molecular negative electrode materials for Li- and Na-ion

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We report evidence for the electrochemical activity of transition metal carbodiimides versus lithium and sodium[1]. In particular, the iron carbodiimide FeNCN can be efficiently used as a negative electrode material for alkali-metal-ion batteries (Li and Na), similarly to its oxide analogue FeO. Based on ^{57}Fe Mössbauer and infrared spectroscopy (IR) data, the electrochemical reaction mechanism can be explained by the reversible transformation of the Fe–NCN into Li/Na–NCN bonds during discharge and charge processes. These new electrode materials exhibit higher capacity compared to well-established negative electrode references such as graphite or hard carbon. Contrary to its oxide analogue, iron carbodiimide does not require heavy treatments (nanoscale tailoring, sophisticated textures, coating etc.) to obtain long cycle life with density current as high as 9 A/g for hundreds of charge/discharge cycles. Similar to the iron compound, several other transition metal carbodiimides (M_xNCN_y with M = Mn, Cr, Zn) can cycle successfully versus lithium and sodium. Their electrochemical activity and performances open the way to the design of a novel family of anode materials for both Li- and Na-ion batteries.
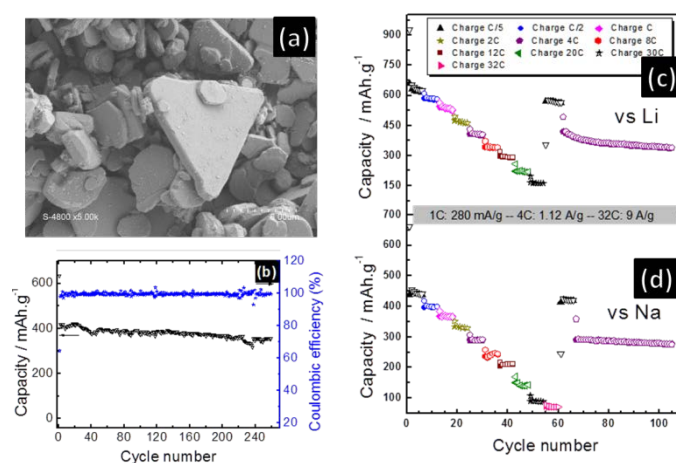

Fig. 1: SEM micrograph for FeNCN powder (a), cycle life of FeNCN/Na cell (b), capability rate vs Li (c) and Na (d)

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P2- and P3-type $Na_xCr_xTi_{1-x}O_2$ Layered Oxides for Rechargeable Sodium Batteries

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Rechargeable Na batteries are promising to realize sustainable energy development in the future because of the material abundance, and many electrode materials have been actively researched in the world. O3-type $NaCrO_2$[1, 2] is known to show excellent cycle performance and thermal stability[3]. Additionally, O3 $NaCrO_2$ shows second highest operating voltage among O3-type layered oxides, next to O3 $NaFeO_2$. In this study, to increase of the operating voltage of Cr^{3+}/Cr^{4+} redox by inductive effect, Ti^{4+} is substituted for Cr^{3+}, according to the formula of $Na_xCr_xTi_{1-x}O_2$ ($0.5 \leq x \leq 1$) and crystal structures and electrode performance are systematically examined as positive and negative electrode materials for rechargeable Na batteries.

After the survey on the Na-Cr-Ti-O ternary oxide system, three different phases were isolated in the range of $0.5 \leq x < 1$. For the sample of $x = 0.80$ at 950 ^{o}C, Na-deficient O3 phase, $Na_{0.8}Cr_{0.8}Ti_{0.2}O_2$, is found. For the sample of $x = 0.67$ at 1000 ^{o}C, P2-type phase, $Na_{2/3}Cr_{2/3}Ti_{1/3}O_2$, is observed. Similar to our work, P2 $Na_{0.6}Cr_{0.6}Ti_{0.4}O_2$ is also found in the literature.[4] Additionally, for the sample of $x = 0.58$ at 800 ^{o}C, Bragg diffraction lines of the sample, $Na_{0.58}Cr_{0.58}Ti_{0.42}O_2$, were assigned into P3-type layered structure. These samples with different layered stacking manners are used as both positive and negative electrodes. Especially, P2 $Na_{2/3}Cr_{2/3}Ti_{1/3}O_2$ as the positive electrode and P3 $Na_{0.58}Cr_{0.58}Ti_{0.42}O_2$ as the negative electrode shows excellent cyclability, and operating voltage of the P2 phase is much higher than that of O3 $NaCrO_2$. In addition, both samples show excellent rate capability as shown in Figure 1c, d. Large reversible capacities are observed for both samples even at >3,000 mA g^{-1}.

From these results, we will further discuss the impact of Ti^{4+}-substitution for Cr^{3+} on electrode performance and reaction mechanisms in Na cells for more details.
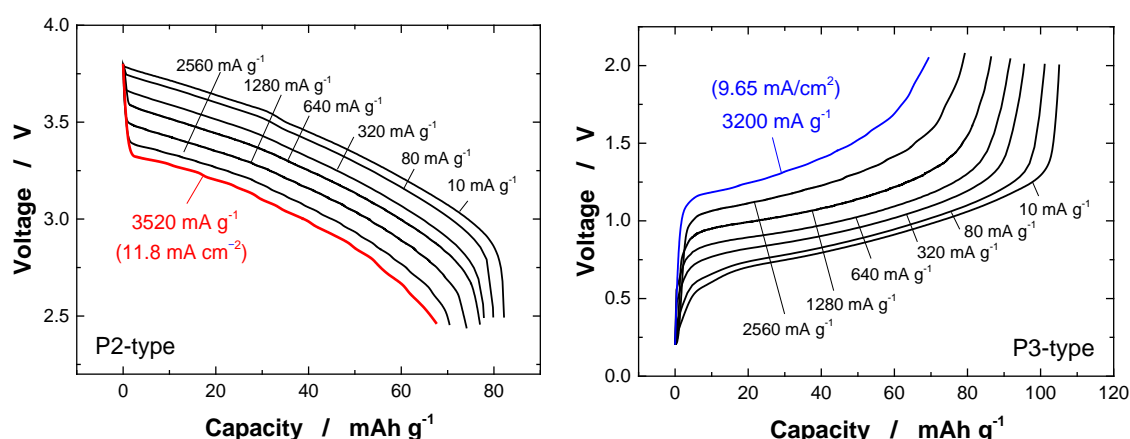

Figure 1. Rate capability of (left) P2 $Na_{2/3}Cr_{2/3}Ti_{1/3}O_2$ and (right) P3 $Na_{0.58}Cr_{0.58}Ti_{0.42}O_2$ in Na cells.

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11th JAPAN - FRANCE JOINT SEMINAR ON BATTERIES

Sept. 20 - 22, 2016 - Nantes, France

IMN — INSTITUT DES MATÉRIAUX JEAN ROUXEL
CNRS
UNIVERSITÉ DE NANTES

TUESDAY 09/20

19:00 - Registration & Welcome Party

WEDNESDAY 09/21

08:45		Introduction
		Session 1 - Next Battery Generation
09:00	O1	K. KANAMURA
09:25	O2	D. GUYOMARD
09:45	O3	J.P. PEREIRA-RAMOS
10:05	O4	M. WAKIHARA
10:30		Coffee break
		Session 2 - Li and Na-Based Materials
11:00	O5	M. ROSSO
11:20	O6	P. ROZIER
11:40	O7	N. KUMAGAI
12:05	O8	L. CROGUENNEC
12:25		Lunch & Poster session 1
		Session 3 - Characterization
14:20	O9	J.C. BADOT
14:40	O10	H. MARTINEZ
15:05	O11	S. FRANGER
15:25	O12	M. DESCHAMPS
15:45		Coffee break
		Session 4 - Electrolytes and Negatives
16:15	O13	K. KURATANI
16:40	O14	D. LEMORDANT
17:00	O15	N. DUPRE
17:20	O16	K. SODEYAMA
20:00		Banquet

THURSDAY 09/22

		Session 5 - Beyond Li-ion
09:00	O17	S. KOMABA
09:25	O18	C. DELMAS
09:45	O19	R. BADDOUR-HADJEAN
10:05	O20	D. DAMBOURNET
10:30		Coffee break
		Session 6 - Solid State Batteries
11:00	O21	H. MUNAKATA
11:20	O22	K. FUJIMOTO
11:40	O23	N. YABUUCHI
12:05	O24	C. LETHIEN
12:25		Lunch & Poster session 2
		Session 7 - Next Battery Generation
14:20	O25	V. SEZNEC
14:40	O26	T. OKUMURA
15:05	O27	L. MONCONDUIT
15:25	O28	F. ALLOIN
15:45	O29	S. PATOUX
16:05		Closing remarks
16:25		Coffee break
18:00		Get together
19:00		Dinner