LIVRE DES RÉSUMÉS
BOOK OF ABSTRACTS

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Title: **Tribute to Michel Armand**

Presenting Author: John B. Goodenough

Organization / Institution: Texas Materials Institute, University of Texas at Austin

Co-Author:

Type: Oral **Session:** O-1.03

Abstract Summary:

Michel Armand was a pioneer in the development of polymer electrolytes, and when we developed the olivine LiFePO4 as the cathode of a Li-ion battery, Michel immediately recognized it had a redox energy well-matched to a polymer electrolyte. He came immediately to Austin from Montreal with Michel Gautier to obtain for Hydro-Quebec an exclusive license to LiFePO4 and he participated in the development of the carbon coat to increase the capacity and rate capability so nicely exploited by the group of Karim Zaghib at Hydro Quebec. I report the development of polymer/inorganic-solid composite membranes as separators that may allow safe use of an alkali-metal as the anode.

Tribute to Michel Armand

John B. Goodenough
Texas Materials Institute, University of Texas at Austin

Abstract

Michel Armand was a pioneer in the development of polymer electrolytes, and when we developed the olivine $LiFePO_4$ as the cathode of a Li-ion battery, Michel immediately recognized it had a redox energy well-matched to a polymer electrolyte. He came immediately to Austin from Montreal with Michel Gautier to obtain for Hydro-Quebec an exclusive license to $LiFePO_4$ and he participated in the development of the carbon coat to increase the capacity and rate capability so nicely exploited by the group of Karim Zaghib at Hydro Quebec. I report the development of polymer/inorganic-solid composite membranes as separators that may allow safe use of an alkali-metal as the anode.

OREBA 1.0

Title: **"Lithium Batteries, Better Safe than Sorry"**

Presenting Author: Michel Armand

Organization / Institution: CIC energigune

Co-Author:

Type: Oral **Session:** O-1.04

Abstract Summary:

See PDF below

"Lithium Batteries, Better Safe than Sorry"

Michel Armand

CIC Energigune
C/Albert Einstein, 4801510 Miñano (Alava) Spain

Introduction:

It has been 42 years since the idea of intercalation was ushered. Even if it was realized later that both the $MnOOH/MnO_2$ (Lechanché) and $Ni(OH)_2/NiO_2$ (Ni/Cd) systems had to be read as H_xMnO_2 and $H_{2-y}NiO_2$, it remains one of the most successful concept in solid-state science and electrochemistry of the late XX^{th} Century. A justification is that the number of known intercalation compounds peaks with Li^+ as guest while H^+ ingress competes with host dissolution and Na^+ shows steric repulsion.

Though the ambition to dominate the EV market with at least an order of magnitude increase in sales volume is common to all systems now in competition, they keep their historical imprint. The lithium-ion was born out of failed attempts to use the lithium metal electrode with liquid electrolytes and the graphite electrode quite miraculously found free from co-intercalation with EC-based electrolytes. As it was designed initially for electronics, capacities were small, the safety concerns could be neglected and with the increase in performances, certainly worth the risk.

The shortcomings of the Li-ion are now more understood in terms of energy density, the weight devoted to the negative electrode is accentuated by the necessity of a copper current collector. The replacement of graphite by silicon will only increase marginally the specific capacity. Two strategies are presently followed: i) the use of high voltage positives ($LiNi_{0.5}Mn_{1.5}O_2$, "lithium-rich") though the classical carbonate electrolyte show signs of rapid degradation when trying to span a 5 V stability window especially at T > 40°C; ii) the re-emergence of the Li° electrode. It seems however doubtful that the two strategies can be combined in a near future as the electrolyte design (fluorination) to introduce oxidation stability limits its cathodic (Li°) stability.

Thus the philosophy of Li-ion remains basically the same, the quest for maximum voltage based on the finding of a proper SEI layer safeguarding the reactions of an electrolyte used well beyond is thermodynamic voltage, through additives. However, most of the new SEI-enhancing molecules are fluorinated organics, increasing the risk of HF release in case of fire and runaway reaction with C–F cleavage by Li. Besides, in order to decrease the electron density on the C–H bonds to make them more resistant to oxidation, sulfonate esters (instead of carbonate) are now proposed, and they are strongly carcinogenic alkylating agents.

On the other hand, some systems were typically designed at birth for large cells, including the Na/S system with β alumina. Safety and the cumbersome engineering for the maintenance a 300°C have relegated this system to load levelling where it is successful. The polymer electrolytes battery is another system that was designed from the beginning for the electric car market with minimal reliance on SEI. The main effort towards scaling-up to practical batteries was sustained with internal funding at Hydro-Québec from 1978 to 2000 totalling ≈ 10^9 $, and after a cascade of episodes, became commercial Bolloré's "pay & ride" Bluecar® system. It is the only system to date to use metallic lithium with apparently minimal safety problems. The technology allows using the metal (3× excess) as a current collector, a considerable gain in weight as compared to the copper/graphite tandem. The co-intercalation-free ingress of Li in graphite was known as early as 1978 (patent # F-78 32977), but it proved unnecessary with polymers.

The Li-ion and the polymer battery are left with a small advantage for the latter, @ 100 Wh/Kg vs. 85 of the full module in a car, but with the far greener LFP cathode instead of a mostly NMC cathode. $LiNi_{1/3}Mn_{1/3}Co_{1/3}$ is totally unsustainable for EV market if we consider that 30% of the "conflict mineral" cobalt production already goes into the small electronic market batteries and its safety is still borderline.

The main difficulty of the scientific community is to regain credibility after ridiculously exaggerated claims in the future progress of Li batteries ("500 miles range battery") in particular with the Li/air hype.

For the "post Lithium" electrochemical systems, Na is probably limited to ≈ 120 WH/kg, still very competitive for the electric grid market, but no conclusive safety test has been undertaken yet with hard carbons (-) or lamellar oxide (+). The embryonic Mg battery will not result in gains until two electrons system for the transition metal has been found, the best hope being for instance $MgMnSiO_4 \Leftrightarrow \square MnSiO_4$ but very slow.

Title:	**Lithium Metal Phosphates as Cathode Materials for Li-Ion Batteries Status and Future Perspectives**
Presenting Author:	Margret Wohlfahrt-Mehrens
Organization / Institution:	Zentrum für Sonnenenergie
Co-Author:	
Type:	Oral **Session:** O-2.01

Abstract Summary:

Lithium Metal Phosphates as Cathode Materials for Li-Ion Batteries
Status and Future Perspectives

Margret Wohlfahrt-Mehrens

ZSW - Zentrum für Sonnenenergie- und Wasserstoff-Forschung, Baden-Württemberg, D 89081Ulm, Germany,

Since the pioneering work of J. Goodenough et al. poly-anion materials with olivine related structures and the general formula LiMPO4 (M = Fe, Co, Mn, Ni) have attracted large attention as potential cathode materials for Lithium ion batteries. Especially LiFePO4 has been extensively studied in the last two decades due to its low toxicity, environmental benignity, high cyclability and low raw materials and production costs. Meanwhile cells using LiFePO4 as cathode material have been successfully introduced to the market. The most attractive key point of the poly anion materials can be seen in the strong P-O covalency which affects a decrease of the Fe-O covalency due to the inductive effect causing on one side a decrease of the redox potential in comparison to the oxides. On the other side the higher thermal stability of the phospho olivines and the low tendency to release oxygen is explained by the strong P-O covalency and the rigid PO_4-structure decreasing the thermal safety risks. An intrinsic feature of poly anion materials is their low electronic and ionic conductivity. The presentation will summarize the status of fundamental understanding of lithium insertion mechanism, strategies to improve ionic and electronic transport properties and dynamic properties of phase transitions. The presentation will start with a brief overview on synthesis and characterization and fundamental aspects of pure materials $LiFePO_4$, $LiMnPO_4$ and $LiCoPO_4$ and their properties. Common strategies to further improve these materials will be presented and discussed including their implications for future applications.

A. K. Padhi , K. S. Nanjundaswamy , J. B. Goodenough , *J. Electrochem. Soc.* **1997** , *144* , 1188 .

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K. S. Nanjundaswamya , A. K. Padhi , J. B. Goodenough , S. Okada , H. Ohtsuka , H. Araib , J. Yamaki , *Solid State Ionics* **1996,** *92,* 1

Title: **Development of High Energy Density LiCoPO4**

Presenting Author: Bin Li

Organization / Institution: Wildcat Discovery Technologies

Co-Author: Dee Strand, Wildcat Discovery Technologies
Steven Kaye, Wildcat Discovery Technologies

Type: Oral **Session:** O-2.02

Abstract Summary:

While LiFePO4 batteries exhibit improved safety over oxide based cells, their energy density is limited due to the relatively low operating potential of 3.6V. In contrast, LiCoPO4, with an olivine structure expected to have similar stability and safety to LiFePO4, has a high operating potential of 4.9V. The increase in voltage translates to a significant improvement in overall energy density. Wildcat Discovery Technologies has developed a LiCoPO4 (CM1) cathode material with specific capacity of over 140 mAh/g. The material has 95% capacity retention at 2C (relative to C/20), and has demonstrated over 1000 cycles when used in conjunction with Wildcat high voltage electrolyte. This presentation will discuss the material development process and progress on high voltage CM1.

Wildcat is a start-up company focused on the development of new materials for energy storage. Its unique high throughput workflow automates the entire discovery process, from reaction set-up, to material synthesis, formulation, assembly, and testing of cells and enabling the screening of >3000 cells/week. Wildcat's high throughput approach has been proven in multiple battery development projects, including the development of oxide and phosphate cathodes, and high voltage electrolytes for rechargeable batteries, high power carbon fluoride cathodes and electrolytes for primary batteries. The company has >60 collaborative research projects with large material suppliers, cell manufacturers, and OEMs and three DOE grants. In 2012, Wildcat was named one of the 50 most innovative companies by Technology Review.

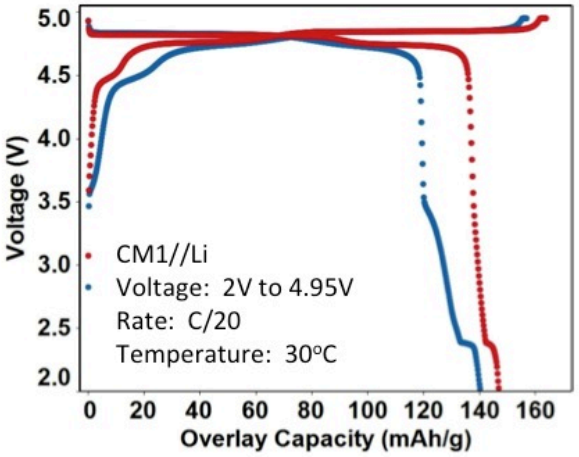

Figure 1. High specific capacity of Wildcat Gen3 CM1

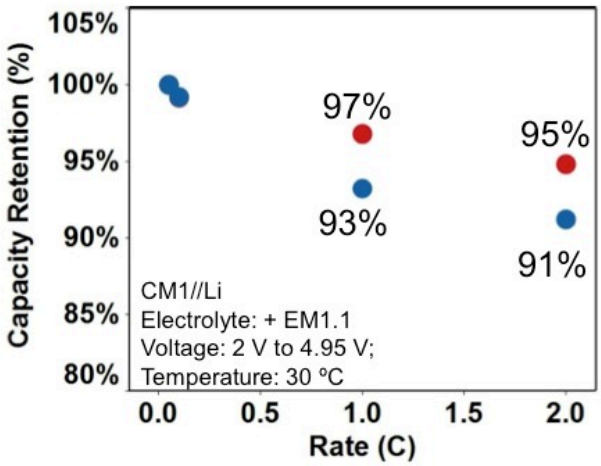

Figure 2. Wildcat CM1 demonstrates good rate performance

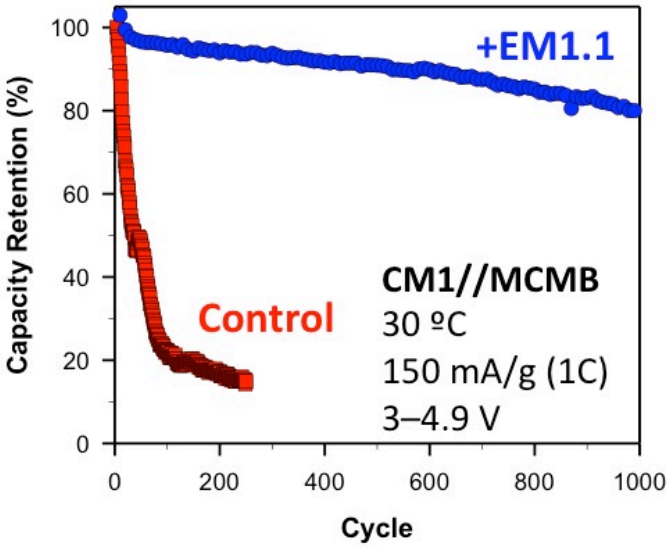

Figure 3. State of the art cycle life obtained for high voltage CM1 full cells

Title: **Carbon nanocoatings for LFP cathode material**

Presenting Author: Marcin Molenda

Organization / Institution: Jagiellonian University, Faculty of Chemistry, Kraków, Poland

Co-Author: Michał Świętosławski, Jagiellonian University, Faculty of Chemistry, Kraków, Poland
Roman Dziembaj, Jagiellonian University, Faculty of Chemistry, Kraków, Poland

Type: Oral **Session:** O-2.03

Abstract Summary:

Performance of Li-ion batteries based on LiFePO4 (LFP) cathode material may be significantly improved by downsizing of LFP grains, however this remains to create an optimal “wiring” in the composite. Conductive carbon nanocoatings (conductive carbon layers, CCL), derived from hydrophilic polymers in solvent-free water mediated process, fulfill the wiring requirements and provide additional advantages. They serve as conductive stress buffering matrix (against active material volume changes during electrochemical reaction) and assure optimal SEI formation. The nanocoatings formation conditions and its special properties related to coexistence of sp2 and sp3 carbon assure the best fit into active material surface and high chemical stability as well as high electrical conductivity of the nanocomposites. Moreover, the carbon nanocoatings reveal a unique pore structure with average pore size 3-4 nm, i.e. for easy lithium ions diffusion. The developed process of carbon nanocoatings formation, which has been already patented, is a scalable and versatile nanotechnology for Li-ion cathode and anode composites production accordingly to green chemistry rules.

Basing on the developed technology composite cathodes C/LiFePO4 were successfully prepared in simple and cheap process of wet impregnation of poly-N-vinylformamide (PNVF) based polymer carbon precursor followed by controlled pyrolysis. Formed carbon nanocoatings significantly improved electrical conductivity of LiFePO4 cathode material from ~10-9 S•cm-1 to the level of ~10-2 S•cm-1 @RT. Charge/discharge tests of the prepared cells showed that CCL nanocoatings improved capacity retention and overall cells electrochemical performance.

Carbon nanocoatings for LFP cathode material

M. Molenda[1,2,*], M. Świętosławski[1], J. Świder[1] and R. Dziembaj[1]

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Performance of Li-ion batteries based on $LiFePO_4$ (LFP) cathode material may be significantly improved by downsizing of LFP grains, however this remains to create an optimal "wiring" in the composite. Conductive carbon nanocoatings (conductive carbon layers, CCL), derived from hydrophilic polymers in solvent-free water mediated process, fulfill the wiring requirements and provide additional advantages. They serve as conductive stress buffering matrix (against active material volume changes during electrochemical reaction) and assure optimal SEI formation. The nanocoatings formation conditions and its special properties related to coexistence of sp^2 and sp^3 carbon assure the best fit into active material surface and high chemical stability as well as high electrical conductivity of the nanocomposites. Moreover, the carbon nanocoatings reveal a unique pore structure with average pore size 3-4 nm, i.e. for easy lithium ions diffusion. The developed process of carbon nanocoatings formation, which has been already patented, is a scalable and versatile nanotechnology for Li-ion cathode and anode composites production accordingly to green chemistry rules.

Basing on the developed technology composite cathodes $C/LiFePO_4$ were successfully prepared in simple and cheap process of wet impregnation of poly-N-vinylformamide (PNVF) based polymer carbon precursor followed by controlled pyrolysis. Formed carbon nanocoatings significantly improved electrical conductivity of $LiFePO_4$ cathode material from $\sim 10^{-9}$ $S \cdot cm^{-1}$ to the level of $\sim 10^{-2}$ $S \cdot cm^{-1}$ @RT. Charge/discharge tests of the prepared cells showed that CCL nanocoatings improved capacity retention and overall cells electrochemical performance.

Title: **Insights on the mechanism of Na Extraction/Insertion in NaFePO4/FePO4 cathode material**

Presenting Author: Montserrat Galceran Mestres

Organization / Institution: CIC EnergiGUNE

Co-Author: Damien Saurel, CIC EnergiGUNE
Montse Casas-Cabanas, CIC EnergiGUNE

Type: Oral **Session:** O-2.04

Abstract Summary:

Insights on the mechanism of Na Extraction/Insertion in NaFePO4/FePO4 cathode material

M. Galceran, D. Saurel, V. Roddatis, B. Acebedo, E. Martin, T. Rojo and M. Casas-Cabanas

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During the past two decades, the demand for the Electrical Energy Storage (EES) systems has increased for both portable applications and stationary applications, predominantly in the form of batteries. [1,2 ,3]. Owing to concerns over lithium cost and sustainability of resources, sodium-ion batteries are considered as promising candidates for both portable and stationary energy storage systems, since they could potentially be much less expensive, safer and environmentally benign.

Within this context, olivine-type NaFePO4 has recently been identified as a potential cathode material in Na-ion batteries. This material exhibits one of the highest reversible capacities reported up to date for a polyanionic Na-ion cathode material (154 mAh/g) [4] and maintains some of the exceptional features of its Li counterpart: reaction within a narrow voltage range inside the voltage stability window of the electrolyte, good stability and good cyclability. Since fundamental differences between the insertion of lithium versus insertion of sodium in the same host compound have been observed in several materials [5,6,7], understanding the reaction mechanisms of Na-ion electrode materials is key for the development of advanced electrode materials.

While Li insertion/extraction in FePO4 occurs through a symmetric 2-phase reaction at room temperature (with a certain Li solubility in the end members) that results in its characteristic flat voltage curve [8,9], the voltage-composition curve of NaFePO4 exhibits a clear asymmetry between charge and discharge, with a voltage drop at x≈0.7 visible only upon charge that has been shown to correspond to an intermediate phase that exhibits ordering of sodium and vacancies [4,10].

In this work we will present a thorough analysis of the crystal chemistry of the system and the reaction mechanism system through X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM). A detailed analysis of the reaction mechanism in NaFePO4/FePO4 system through in situ XRD has confirmed the asymmetry of the process and unveiled a complex mechanism with additional unexpected phenomena during the charge and discharge processes [11]. The different mechanism with respect to LiFePO4 is ascribed to the larger interface energy penalty that results from the cell mismatch between the different phases involved in the reaction and will be discussed during this presentation.

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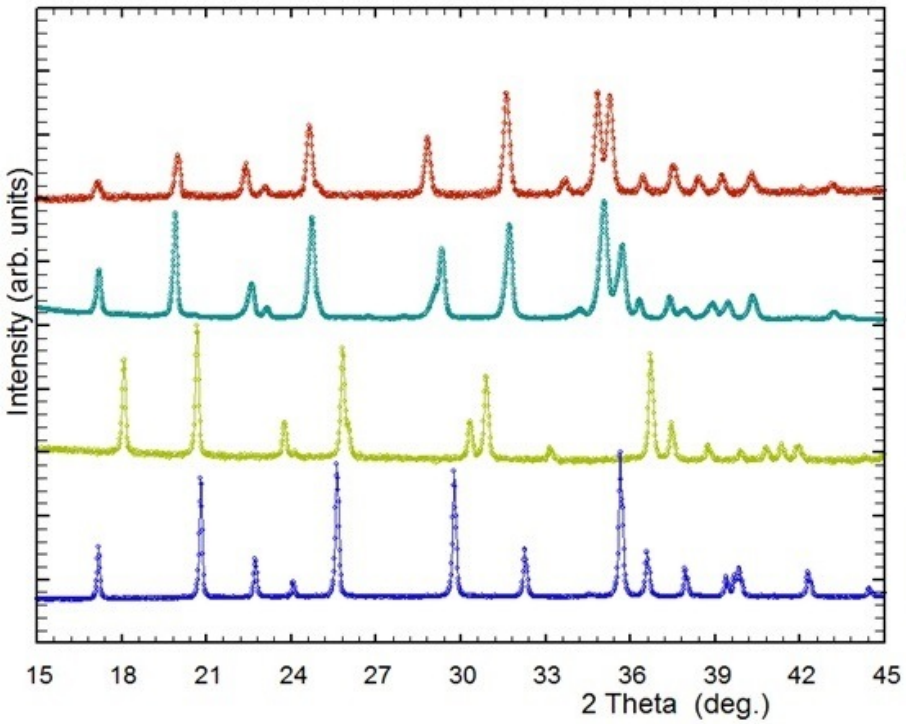

$NaFePO_4$
Pnma
a = 10.403 Å
b = 6.221 Å
c = 4.948 Å

$Na_{2/3}FePO_4$
Pnma
a = 10.274 Å
b = 6.076 Å
c = 4.936 Å

$FePO_4$
Pnma
a = 9.805 Å
b = 5.784 Å
c = 4.779 Å

$LiFePO_4$
Pnma
a = 10.312 Å
b = 5.998 Å
c = 4.687 Å

reduction — NaI

oxidation — NO_2BF_4

Title: **Exotic Redox Behaviors in Phosphates**

Presenting Author: Atsuo Yamada

Organization / Institution: The University of Tokyo

Co-Author:

Type: Oral **Session:** O-3.01

Abstract Summary:

The lithium ion battery is the most advanced energy storage system, which utilizes an electrode reaction involving reversible lithium intercalation into a solid matrix. The structural and transport properties of these battery materials have been extensively studied as a function of lithium content, and structural/electronic phase diagrams have been revealed for a wide variety of lithium intercalation compounds. In this discussion meeting, we try to shed new light to the intercalation system with an eye to the following 4 issues, focusing on two phosphates, Li1-xMPO4 and Li2-xMP2O7.

1. Electrochromism in correlation with static phase diagram1
2. Marcus-Hush kinetic analysis for polarons with visible optical absorption1
3. Non-equilibrium phase transition2
4. 4V Fe3+/Fe2+ generation and unusual thermal stability by diphosphates3,4

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Title: **Carbon composite LiFePO4 and the electrode structure for low cost and high performance lithium ion battery.**

Presenting Author: Kazuma Hanai

Organization / Institution: SEI corporation

Co-Author: Kazunori URAO, SEI corporation
Shinji SAITO, SEI corporation

Type: Oral **Session:** O-3.03

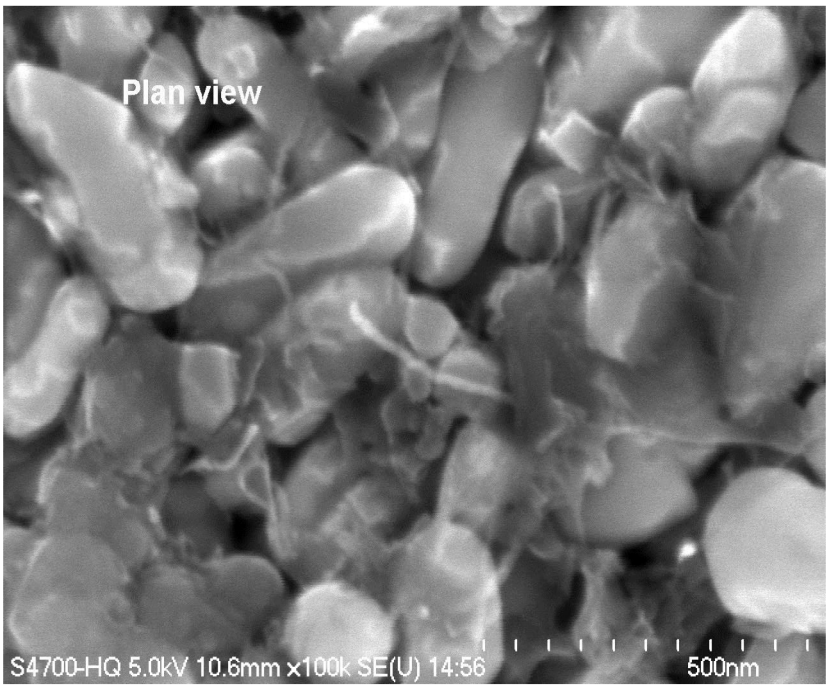
Abstract Summary:

The electrode performance was developed using carbon composite LFP and novel electrode structure for the cathode electrode. Conducting carbon black and carbon nano tube should be incorporated into the LFP cathode to decrease the cell resistance. However, typical CNT shows un-homogeneous distribution due to their particle size. The dispersion in suitable solvent is considered to a solution for nano particles. The CNF dispersion in organic solvent was prepared by surface modification to hydrophilic structure.

LFP is considered to promising candidate for the industrial LIBs. The electronic conduction on the electrode should be maintained during long cycle to use the advantage of LFP. The C-C bonding between conducting carbon additives and the surface carbon layer on the LFP particle is effective structure to overcome the detach point on the electrode. The surface modification includes negative effect for the electronic conductivity. Therefore, the composite LFP was prepared using the conducting carbon black, the CNT dispersion and the heat treatment under the inert atmosphere. The composite electrode showed lower resistance and long cycle life.

The electrode should be loaded thicker to improve the energy density on the LFP applications. However, the electrode resistance is increased with increasing the electrode thickness, and the electronic conductions between cathode material and the Al foil become more delicate for mechanical stress. The projection on the Al foil is considered to be a solution to improve the electronic conductivity and the adhesion. The projection affects to increase the conduction point and stabilized cathode material as the anchor. The in-line projection coating mechanism was developed to prevent the contamination of Al foil splinter and stabilized the projection shape.

The developed electrode using the composite LFP and the projection foil shows great enhanced electrochemical properties.


Plan view
S4700-HQ 5.0kV 10.6mm x100k SE(U) 14:56
500nm

Title: **Combining Mesograf with carbon coated LFP to create a novel carbonaceous composite**

Presenting Author: Gordon Chiu

Organization / Institution: Grafoid Inc.

Co-Author: Karim Zaghib, IREQ
Abdelbast Guerfi, IREQ

Type: Oral **Session:** O-3.04

Abstract Summary:

LiFePO4 is a low-cost olivine-type material for the use in rechargeable lithium-ion batteries. It is highly stable during electrochemical cycling, environmentally friendly and chosen as China's main cathode material. However, the poor electrical conductivity of LFP needs to be addressed either by doping or by carbon coating. We investigate using an inexpensive method to make few layer graphene as an additive to combine to form a unique composite.

Our process involves employing hexagonal layered mineral graphite rocks (HLM) as the electrodes itself and immersion into an electrolytic slurry that includes an organic solvent, metal ions. The electrolysis introduces the organic solvent and ions from the metal salt from the slurry into the interlayer spacings that separate the atomic interlayers of the HLM rock, thereby exfoliates directly and decomposes the HLM rock.

By combining few layer graphene (Mesograf) with carbon coated LFP to create a novel carbonaceous composite via mechanofusion. The low cost features in the production of few layer graphene, mechanofusion and LFP make this an interesting combination.

OREBA 1.0

Title: **Reaction distributions on LiFePO4 electrodes**

Presenting Author: Zempachi Ogumi

Organization / Institution: Society-Academia Collaboration for Innovation,Kyoto University

Co-Author: Yoshiharu Uchimoto, Graduate School of Human and Environmental Studies, Kyoto University
Hajime Arai, Society-Academia Collaboration for Innovation, Kyoto University

Type: Oral **Session:** O-4.01

Abstract Summary:

Reaction distributions on LiFePO4 electrodes

Zempachi Ogumi
Office of Society-Academia Collaboration for Innovation, Kyoto University,
Gokasho, Uji, Kyoto 611-0011, JAPAN

Olivine structure lithium iron phosphate (LiFePO4), which is widely used as a positive electrode material in LIBs, was examined in this study. Under charging and discharging, the material undergoes phase reactions between Li-rich Li1-□FePO4 (LFP) and Li-poor Li□FePO4 (FP) [1]. This system is expressed with a eutectoid-type binary phase diagram [2, 3]. In this work, we investigated the reaction distribution formation and relaxation behavior in LiFePO4 composite electrodes.

1) The Driving force for the Relaxation of Reaction Distribution in LiFePO4 Electrodes

Composite electrodes containing active materials, carbon and binder are widely used in Li-ion batteries and their morphology influences the electrochemical performance of batteries. A detailed observation of the reaction distribution in composite electrodes as well as their mechanism is important, because such distributions greatly influence the rate performance and long-life performance of Li-ion batteries. The relaxation of the reaction distribution in LiFePO4 electrodes was investigated by applying the micro XAFS technique. We herein discuss the driving force for the relaxation of reaction distribution by comparing two types of electrodes having different charge/discharge profiles.

The LiFePO4 electrode were charged under room temperature at 1C rate until the Li desorption degree approached 0.5 and 0.3, respectively. In order to observe the cross section, the dried electrodes were fabricated by a microtome. The micro XAFS measurements were performed at the beam line BL37XU at SPring-8, Japan. The beam size was 1.3 (H) x 0.8 (W) □m2.

Figure 1 shows the Fe K-edge X-ray absorption near edge structure (XANES) spectra of the surface and the inside of the LiFePO4 electrodes. The absorption edge energy of the surface was higher than that of the inside. This result indicates that Fe ions on the surface were more oxidized than that in the inside. This difference was not changed even after leaving 24 h in the cell. This means the distribution of the oxidation state was not relaxed. On the other hand, the behavior for LiCoO2 was different and no reaction distribution was observed after 24h. A major difference between LiFePO4 and LiCoO2 is evident in the charge/discharge potential profile. LiFePO4 cathode has an extremely flat charge/discharge potential profile [1]. This feature indicates that electrochemical potential of Li-ion in LFP is the same as that in FP. In contrast, the charge/discharge profile of LiCoO2 cathode does not exhibit a clear plateau and LiCoO2 cathode has an electrical potential gradient near a Li insertion nominal value of x = 0.7 in LixCoO2 [4]. The results of this study imply that the driving force for the relaxation of the reaction distribution depends on the gradient of electrochemical potential of Li-ion.

2) Investigation of Determination Factor of Reaction Distribution in LiFePO4 Composite Electrodes

There are a number of internal resistances inherent in the composite electrode (for instance, charge transfer resistance, ionic or electronic conductivity resistance, and solid-state diffusion resistance). Since the electrode reaction occurs preferentially in regions with lower resistance, reaction distribution is happened within the composite electrode. In this work, we investigated the relationship between the reaction distribution and ionic conductivity in composite electrodes.

LiFePO4-based composite electrodes were densified at various pressures to control their porosity. These electrodes were assembled in electrochemical flat cells with lithium metal as the counter electrode. The LiFePO4 electrodes were discharged under 25oC at 10 C rate. 2D-imaging XAFS measurements were performed at the beam line BL-4 at Ritsumeikan SR center, Japan. The beam size was 4 (H) x 4 (W) mm2. Fe K-edge XAS spectra of the LiFePO4 electrodes were collected in transmission mode. The ionic conductivity in composite electrodes is measured with the previously reported 6-probe method [5].

Average absorption energy from Fe-K edge XAFS as a function of distance from current collector for various pressed electrode is plotted in Fig. 2 (a). As the LiFePO4 electrode is discharged, the absorption energy edge of the Fe-Kedge X-ray absorption spectra decreases. When the porosities of the electrodes were less than 44% the absorption energy was higher at the top surface of the electrode than at the bottom. However, when the porosity of the electrode was 57% and 48 %, the energy was nearly constant in the vertical direction. These results imply that the reaction distribution is happened in lower porosity composite electrodes. The ionic conductivity in composite electrodes is shown in Fig. 2 (b). When the porosities of the electrodes are less than 47%, the ionic conductivity decreased. The decreased ionic conductivity causes the preferential reaction at the electrode surface. When the porosity is higher, however, the ionic conductivity is high. This results in the uniform discharge reaction at all depths in composite electrodes.

ACKNOWLEDGMENTS

This study was supported by the Research and Development Initiative for Scientific Innovation of New Generation Batteries (RISING) project of the New Energy and Industrial Technology Department Organization (NEDO) in Japan.

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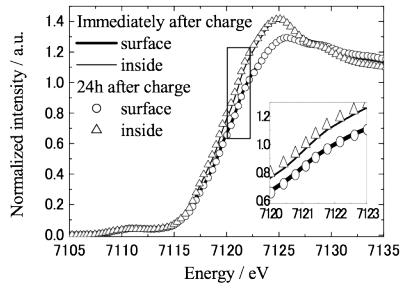

Fig.1 Fe *K*-edge XANES spectra of the surface and the inside of $LiFePO_4$ electrodes

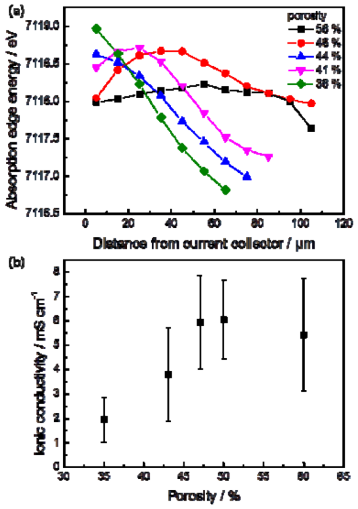

Fig.2 (a) Average absorption energy as a function of distance from current collector measured by the 2D-XAFS of various porosity composite electrode. (b) Effective ionic conductivity of various porosity composite electrode.

Title: **Development of LiFePO4/C cathode materials with improving the high temperature and C-rate performances**

Presenting Author: Chueh-Yu Ke

Organization / Institution: Tatung Fine Chemicals Co.

Co-Author: Mei-Chun Wu, Tatung Fine Chemicals Co.

Type: Oral **Session:** O-4.02

Abstract Summary:

Among the several materials under development for use as cathodes in lithium-ion batteries, lithium iron phosphate (LiFePO4) has been recognized as a promising candidate for the cathode of Li batteries due to the environmental benignity, cycling stability, safety and high theoretical capacity of 170 mAh g−1.[1-2] However, the poor conductivity, resulting from the low lithium-ion diffusion rate and low electrical conductivity in the olivine structure of LiMPO4, has posed a bottleneck for commercial applications. Improvements of poor conductivity have been achieved in two ways. One way is synthesizing small, monodispersed particle size, and forming electrically conductive coating on materials. Another way is doping some ions to improve conductivity.

Tatung Fine Chemicals Co.(TFC) synthesized precursor were prepared by the solution method.[3] The iron powder was immersed and dissolved in the aqueous solution containing phosphate, Lithium and carbon precursors. The precursors slurry mixture was atomized and dried into powders by the spray-dry method. These as-sprayed powders were subsequently calcined at different thermal treatment in a nitrogen atmosphere.

By adjusting the proportion of some precursors and manufacturing parameters, TFC can get the different electrochemical properties products. The P13 type has better low-temperature characteristics than P13F type. But P13F type has better high temperature and C-rate characteristics.

Acknowledges
The authors are indebted to the research analysis support of Tatung University.

Development of $LiFePO_4$/C cathode materials with improving the high temperature and C-rate performances.

Chueh-Yu Ke and Mei-Chun Wu

R&D Division, Tatung Fine Chemicals Co., Taipei, Taiwan

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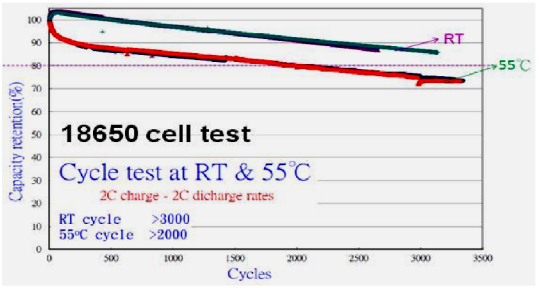

Fig 1. The P13F type was cycling test. The charge/discharge rate are 2C/2C at different temperatures by 18650 cell. At 30°C, the capacity remnant over 80% after 3,000 cycling. At 55°C, the capacity remnant over 80% after 2,000 cycling.

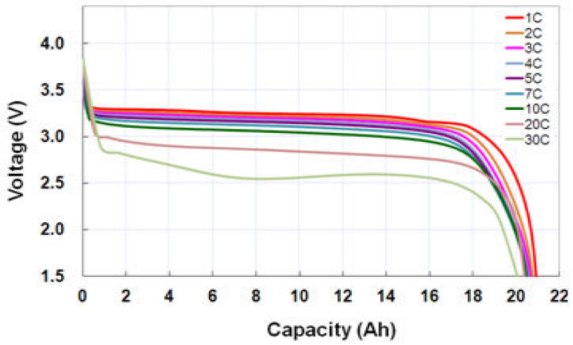

Fig 2. The P13F type was testing C-rate characteristics by 20Ah pouch cell. Charging was carried out at 1C and discharging at 1~30C. The 30C/1C capacity remnant about 95%.

Title: **Interactions of Carbon/LiFePO4**

Presenting Author: Andy Xueliang Sun

Organization / Institution: University of Western Ontario

Co-Author:

Type: Oral **Session:** O-4.03

Abstract Summary:

Interactions of Carbon/LiFePO4

Andy Xueliang Sun,1* Jiajun Wang1,3, Jinli Yang1, Songlan Yang1,4,, Yongji Tang1,4, Jian Liu1, YongZhang1, Guoxian Liang2, Michel Gauthier2, Yu-chen Karen Chen-Wiegart3,Mohammad Norouzi Banis1, Xifei Li1, Ruying Li1, Jun Wang3, T.K. Sham4

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Carbon coating is a meaningful approach to modify the low intrinsic electrical conductivity of LiFePO4.[1] Recently, a size-dependent surface phase change of LiFePO4 during carbon coating has been revealed [2]. As shown in Figure 1, the new phase (Fe2P2O7) can be formed during carbon coating. The impurities on the surface of LiFePO4 have been studied using an ingot sample with discernable Fe and P-rich phases. The catalytic effect of each phase on the carbon coating thickness has been investigated and the results show that Fe phase promotes the formation of carbon whereas P-rich phase inhibits carbon growth.[3-6] LiFePO4/graphene composites have been studied using stacked and unfolded graphene. It has been found that unfolded graphene enables better dispersion of LiFePO4 and restricts the LiFePO4 particle size at the nanoscale. Such structure can greatly enhance the electrical conductivity, thereby realizing the full potential of the active materials.[7-10]

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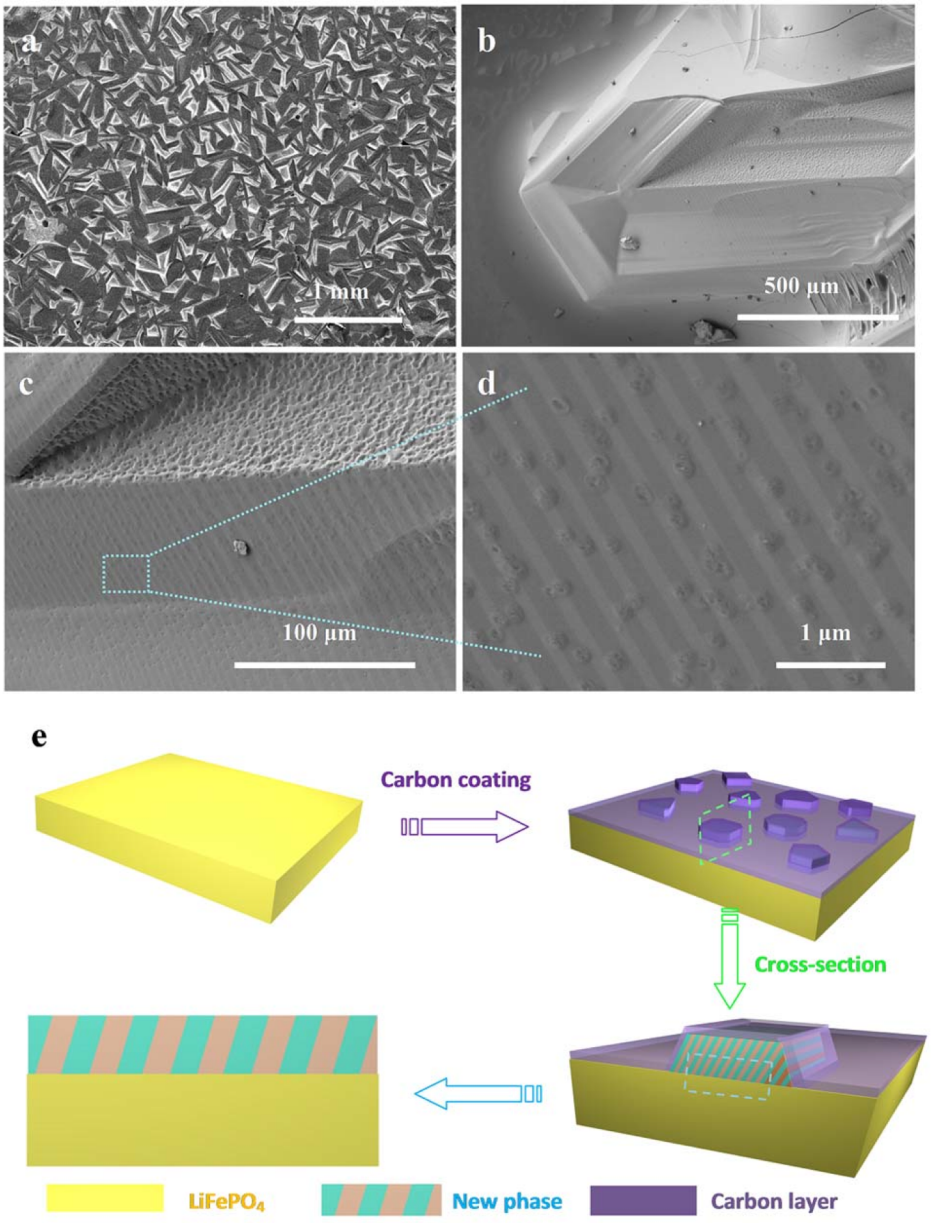
Figure 1. **Surface new phase formation**. (**a-d**) Scanning electron microscopy (SEM) image of surface phase formation on $LiFePO_4$ after carbon coating. (**e**) Schematic representation of surface phase formation on $LiFePO_4$.Scale bar, 1 mm (**a**), 500 µm (**b**), 100 µm (**c**) and 1 µm (**d**).



Title: **Localized Investigations of the Electrochemical Properties of Lithium Iron Phosphate Films using Micro-Pipets**

Presenting Author: Janine Mauzeroll
Organization / Institution: McGill
Co-Author: Steen Schougaard, UQAM
Micheal Snowden, McGill

Type: Oral **Session:** O-4.04

Abstract Summary:

Lithium ion batteries are a commercially successful method of portable electrical energy, demonstrated by their mass market use in portable electronics and growing interest as an alternative power source within the automotive industry1. For the lithium ion battery to rival fossil fuels as an automotive energy source, lithium ion batteries need to have improved capacity and charge/discharge rates. As new anode and cathode
materials are developed2 they are typically screened for advantageous properties by assembly into a working battery. This involves the fabrication of a film from a mixture of conductive material (e.g. carbon), a binder (e.g. polyvinylidene fluoride), and the active material of interest. The mixture is then cast onto a conductive material to form a thin film, before assembly within a coin cell. How the film is prepared, the ratio of the individual components of the film and the final assembly of the coin cell can significantly alter the performance of the battery.3,4 This could give misleading information about the effectiveness of a novel active material.

Here we present proof of principle measurements to demonstrate the suitability of micro-pipet measurements for probing lithium ion battery materials. Specifically, we probed lithium iron phosphate films to determine the working potentials of the film, and the charge capacity of the material. Lithium iron phosphate was a convenient test material, which provided stability under atmospheric conditions and was compatible
with water. Data obtained on candidate films by micro-pipet measurements were compared to conventional coin cell measurements, highlighting the suitability of this technique for future investigations of lithium ion battery materials.

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4) Ban, C.; Wu, Z.; Gillaspie, D. T.; Chen, L.; Yan, Y.; Blackburn, J. L.; Dillon A. C.; Adv. Mater. 2010, 22, E145–E149

Localized Investigations of the Electrochemical Properties of Lithium Iron Phosphate Films using Micro-Pipets

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Lithium ion batteries are a commercially successful method of portable electrical energy, demonstrated by their mass market use in portable electronics and growing interest as an alternative power source within the automotive industry.[1] For the lithium ion battery to rival fossil fuels as an automotive energy source, lithium ion batteries need to have improved capacity and charge/discharge rates. As new anode and cathode materials are developed[2] they are typically screened for advantageous properties by assembly into a working battery. This involves the fabrication of a film from a mixture of conductive material (*e.g.* carbon), a binder (*e.g.* polyvinylidene fluoride), and the active material of interest. The mixture is then cast onto a conductive material to form a thin film, before assembly within a coin cell. How the film is prepared, the ratio of the individual components of the film and the final assembly of the coin cell can significantly alter the performance of the battery.[3,4] This could give misleading information about the effectiveness of a novel active material.

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Title: **Ion Mobility in Layered, Tavorite and Olivine–type Alkali Metal Polyanion Materials**

Presenting Author: Linda F. Nazar

Organization / Institution: Department of Chemistry & Department of Physics and the Nanotechnology Research Centre, University of Waterloo

Co-Author: Xiaoqi Sun, Department of Chemistry & Department of Physics and the Nanotechnology Research Centre, University of Waterloo
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Guerman Popov, Department of Chemistry & Department of Physics and the Nanotechnology

Type: Oral **Session:** O-5.01

Abstract Summary:

Significant advances in the energy density and rate capability of Li-ion batteries have been witnessed in the past decade, with a wealth of new materials driving the research forward. Lithium metal phosphates saw their major development start with olivine $LiFePO_4$ in 1997. The fact that it has become a commercially viable electrode material despite its essentially electronically insulating nature has continued to drive new directions amongst researchers in this area. The combination of size control, functional conductive coatings, and variation in composition and structure has resulted in numerous new related materials that may vie with $LiFePO_4$ for future prominence. These include other layered and open framework structure-types containing fluorine as a network modifier, and the burgeoning Na-ion metal polyanion family. Synthetic approaches to new materials, and experimental/computational studies of their ion conduction properties will be presented.

Ion Mobility in Layered, Tavorite and Olivine–type Alkali Metal Polyanion Materials

Xiaoqi Sun,[a] Rajesh Tripathi,[a] Guerman Popov,[a] Stephen Wood,[b] M. S. Islam[b] and Linda F. Nazar[a]

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ABSTRACT

Significant advances in the energy density and rate capability of Li-ion batteries have been witnessed in the past decade, with a wealth of new materials driving the research forward. Lithium metal phosphates saw their major development start with olivine $LiFePO_4$ in 1997. The fact that it has become a commercially viable electrode material despite its essentially electronically insulating nature has continued to drive new directions amongst researchers in this area. The combination of size control, functional conductive coatings, and variation in composition and structure has resulted in numerous new related materials that may vie with $LiFePO_4$ for future prominence. These include other layered and open framework structure-types containing fluorine as a network modifier, and the burgeoning Na-ion metal polyanion family. Synthetic approaches to new materials, and experimental/computational studies of their ion conduction properties will be presented.

Title: **Quality Control of LiFePO4 Olivine Materials**

Presenting Author: Christian Julien

Organization / Institution: Sorbonne Universités, UPMC Univ. Paris 6

Co-Author:

Type: Oral **Session:** O-5.02

Abstract Summary:

See PDF below

Quality Control of $LiFePO_4$ Olivine Materials

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$LiFePO_4$ (LFP) has been reported to perform well in Li-ion batteries. This material has a relatively large theoretical capacity of 170 mAh g^{-1} compared with other iron-based compounds, good thermal stability in the fully charged state and little hygroscopicity, making it a candidate as cathode material for battery system applied to EVs and HEVs. This is because it has a well-developed crystalline structure with homogeneous particle size, purity and physical properties that greatly influence the electrochemical performance of the LFP material. The lithium battery cathode should be a mixed conductor of electrons and lithium ions. One of the key features of the olivine is its extremely flat charge/discharge profile categorized as typical of two-phase reaction while the serious problems as its polaronic insulator character and slow kinetics of ion movement can be overcome by particle-size minimization, carbon nanopainting or carbothermal formation of a surface conducting phase. Thus, it is obvious that severe quality control is requested for the use of LFP in high-power batteries.

In this paper, we investigate various tools that can be probe the main properties of LFP powders related to their electrochemical function in the view of mass production of the best active material with high gravimetric and volumetric capacities, rate capability and good cyclability as electrodes. For each experimental technique, several examples are given showing both the best product but also the compound having intrinsic defects or impurities penalizing its electrochemical performance.

First example: presence of the Li_3PO_4, Fe_2O_3 or $Fe(PO_4)$ phases with LFP particles. Such a defect can be easily detected by XRD or FTIR. Fig. 1 shows the typical XRD spectrum in the region 2θ=18-46°, where Bragg lines of parasitic elements are observed. The electrochemical features are significantly damaged by the $Fe^{\bullet}_{Li}$ defects that block the diffusion of Li ions along the corresponding 1D channel, while the Li_3PO_4 only acts as an inert mass.

Second example: presence of the Fe_2P clusters. Undesirable impurity like Fe_2P can be introduced during synthesis. It increases the electronic conductivity, but on the other hand it also decreases the ionic conductivity so that both the capacity and cycling rates are degraded with respect to C-LFP. The electrochemical charge-discharge profiles of Li//LFP cells cycled at room temperature with pure LFP and with Fe_2P-containing electrode material is shown in Fig. 2. It is obvious that at the rate 2C, the capacity retention decreases significantly for the material containing few% of Fe_2P.

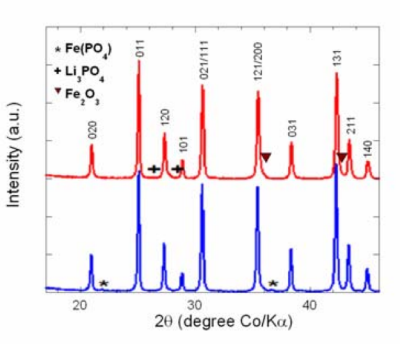

FIG. 1.

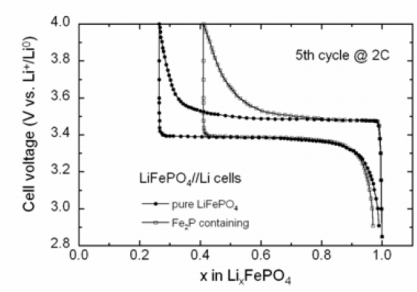

FIG. 2.

Third example: presence of a disordered layer (DSL) on the particle surface. For LFP nano-particles, the fraction (1-*y*) of iron ion, due to the Li vacancies in the DSL, is not negligible, magnetic measurements have shown that for uncoated particles Fe^{3+} ions are localized in the low spin state (S=1/2). Fig. 3 shows the TEM images of the surface of LFP particles before carbon coating (left) and after carbon coating (right). Note the granular aspect of DSL disappeared after carbon coating.

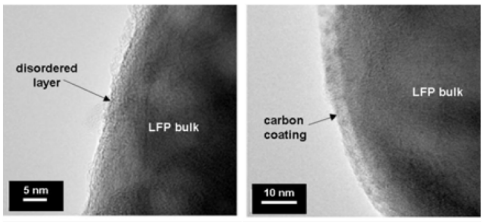

FIG. 3.

With optimized LFP//LTO electrodes a Li-ion 800 mAh battery has filled a gap in the performance in terms of safety, cycling life, which are key-issues in public transportation [JPS 196 (2011) 3949].

Title: **In situ Solvothermal Synthesis of Olivine Cathodes**

Presenting Author: Feng Wang

Organization / Institution: Brookhaven National Laboratory

Co-Author:

Type: Oral **Session:** O-5.03

Abstract Summary:

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For large-scale application of lithium-ion batteries in electric vehicles and grid-scale storage, it has been of great interest to develop cost-effective hydrothermal/solvothermal synthesis methods for preparing high-energy electrodes. But solution-based reactions are mostly carried out in a sealed autoclave and therefore the reactor is a black box – the inputs and outputs are known, but little is known about intermediate phases and reaction pathways. Real-time probing of synthesis reactions can provide the details of reaction process, elucidating intermediate phases and how temperature, pressure, time and the precursor concentration affect the reaction pathways, and eventually the final product. To this end, new in-situ reactors and relevant techniques have been developed and applied for studying solvothermal synthesis of olivine-type cathodes, LiFePO4, LiMnPO4 and solid solution (LiFexMn1-xPO4), using time-resolved synchrotron X-ray diffraction (XRD). Quantitative analysis of XRD patterns was performed via a rigorous Rietveld refinement procedure to extract the structural parameters, such as lattice constants, bond lengths and effective coordination numbers of crystalline phases, and their evolution as a function of reaction time and temperature. In addition, structural and electrochemical characterization were performed, via XRD, XAS and TEM-EELS, for gaining insights into lithium reaction mechanisms and possible limitations to the cycling stability of the synthesized electrodes. We show, the development of in-situ methods provides access to a wide range of solvothermal synthesis reactions, and in a combination with structure-property characterization of synthesized materials, eventually enables rational design and synthesis of battery electrodes of desired phases and material properties.

This work was supported by DOE-EERE under the Batteries for Advanced Transportation Technologies (BATT) Program, under Contract No. DE- AC02-98CH10886.

Title: **Nanostructure Characterization of Lithium Orthosilicate Cathode Materials**

Presenting Author: Raynald Gauvin

Organization / Institution: Department of Mining and Materials Engineering, McGill University

Co-Author: Nicolas Broduch, Department of Mining and Materials Engineering, McGill University
Hendrix Demers, Department of Mining and Materials Engineering, McGill University

Type: Oral **Session:** O-5.04

Abstract Summary:

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The development of next generation lithium-ion battery (LIB) nanostructured cathode materials needs cutting-edge collaborative research. The next generation LIB should be characterized by high energy density, fast charging rates, safety, long lifetime but also lower cost to meet the electric automotive industry needs. This work focuses on the characterization of a higher energy family of orthosilicate cathode materials, Li2MSiO4, where M=Fe, Mn, and Co. As part of this project Li2MSiO4 materials are hydrothermally synthesized built into electrodes/cells and subjected to extensive ex-situ and in-situ structural and phase evolution mechanisms characterizations and electrochemical performance analysis. The ex-situ and in-situ characterization studies are undertaken by taking advantage of the state-of-the-art electron microscopes at McGill University and Hydro-Québec's Institut de recherche d'Hydro-Québec (IREQ).

Ex-situ and in-situ transmission electron microscope (TEM) analysis are used to characterize the morphologies and crystal structures of the pristine Li orthosilicate cathode materials. IREQ Institute has a state-of-the art field emission scanning TEM (FE-STEM), the Hitachi HD-2700 equipped with a Cs aberration corrector giving a resolution of 0.06 nm and with an x-ray silicon-drift detector energy dispersive spectrometry (SDD-EDS) and an electron energy-loss spectrometry (EELS) system allowing Li detection. High-resolution imaging is used to monitor the structural changes at the atomic scale. Additionally, the HF-3000 Hitachi environmental TEM/STEM allows performing in-situ testing of Li battery materials in gaseous environments. This microscope has a serial EELS module which allows the mapping of the fine structure of Li-ion insertion materials, it can perform nano-diffraction and it has an x-ray SDD-EDS for quantitative microanalysis.

The state-of-the-art field emission scanning electron microscopes (FE-SEMs) SU-8000 and SU-8230 at McGill University are used ex-situ to characterize and to quantify (by x-ray microanalysis) the cathode materials. High-resolution imaging and quantitative x-ray microanalysis are performed. For improved spatial resolution, these materials will be characterized at low voltage (0.2 to 5 kV, LVSEM) for bulk materials as well as in the low voltage STEM (10 to 30 kV, LVSTEM) mode with electron transparent materials. Figure 1 shows ex-situ structural characterization of Li2CoSiO4 material. The morphological characterization using secondary electron (SE) in LVSEM with resolution around 1.5 nm and the bright field (BF) and dark field (DF), not shown, in LVSTEM with enhanced contrast and spatial resolution of 0.5-1 nm. Fast x-ray analysis with SDD-EDS technology was used for chemical mapping with high resolution (5 nm).

Li based phases are identified and characterized by diffraction information: electron diffraction in TEM and SEM and X-ray diffraction (XRD). This can be done with high spatial resolution in TEM using convergent beam electron diffraction (CBED) in the HF-3000 for in-situ characterization of batteries as well as with electron backscattered diffraction (EBSD) for bulk materials and thin films (transmitted electron forward scattered diffraction; t-EFSD) with the FE-SEM SU-8000. Also the x-ray diffraction (XRD) data collection is used to find crystal structure. Figure 2 shows an example of phase identification by t-EFSD in the FE-SEM of a lithium titanate oxide material. The same technique will be applied for phase identification of the orthosilicate cathode materials. Also, a unique surface preparation method, using broad ion milling was developed and was applied to pure Li sheet for characterization by EBSD. The microstructure information, grain size distribution, texture and orientation maps of the Li grains were obtained. Furthermore, unexpected impurity inclusion in the sheet was determined. This was the first EBSD work reported on this material, which is an achievement because pure Li is highly reactive with H, N and O species present in air. Since Li detection is a real challenge in materials science, these tools will improve our understanding of the new cathode materials.

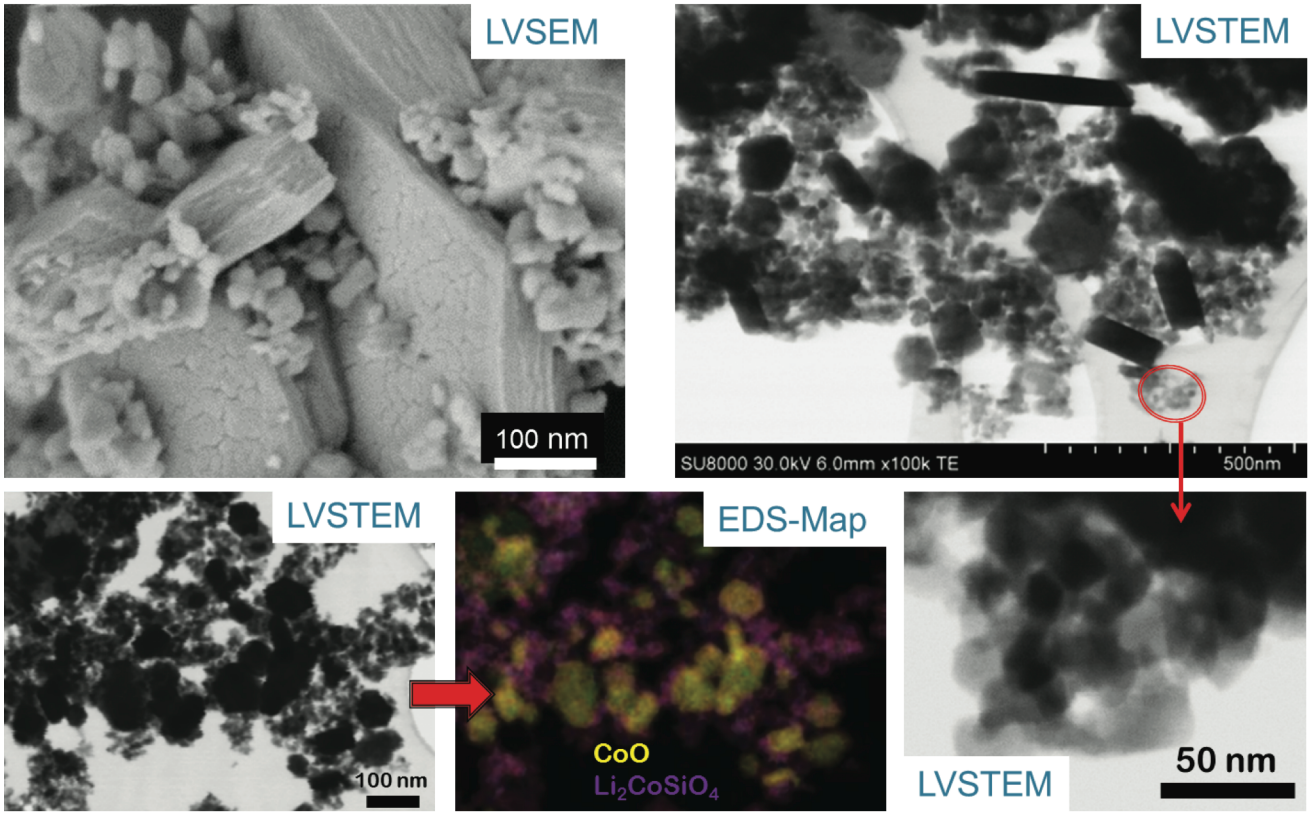


Figure 1

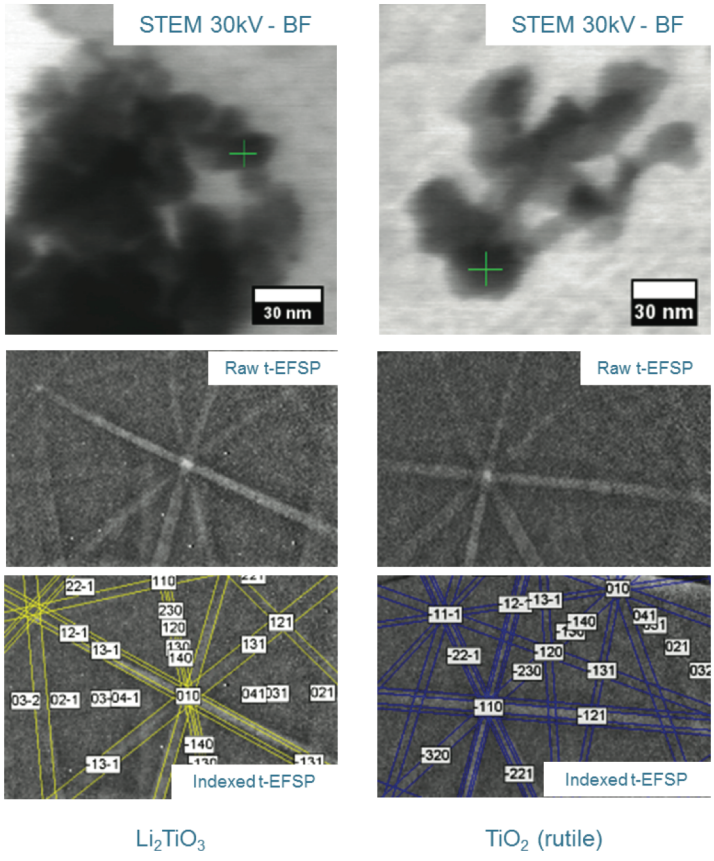


Figure 2

Title: **IR Far- and Near-Field Spectroscopy and Imaging of LixFePO4 Single Crystals**

Presenting Author: Robert Kostecki

Organization / Institution: LBNL

Co-Author: Ivan Lucas, Alex McLeod

Type: Oral **Session:** O-6.01

Abstract Summary:

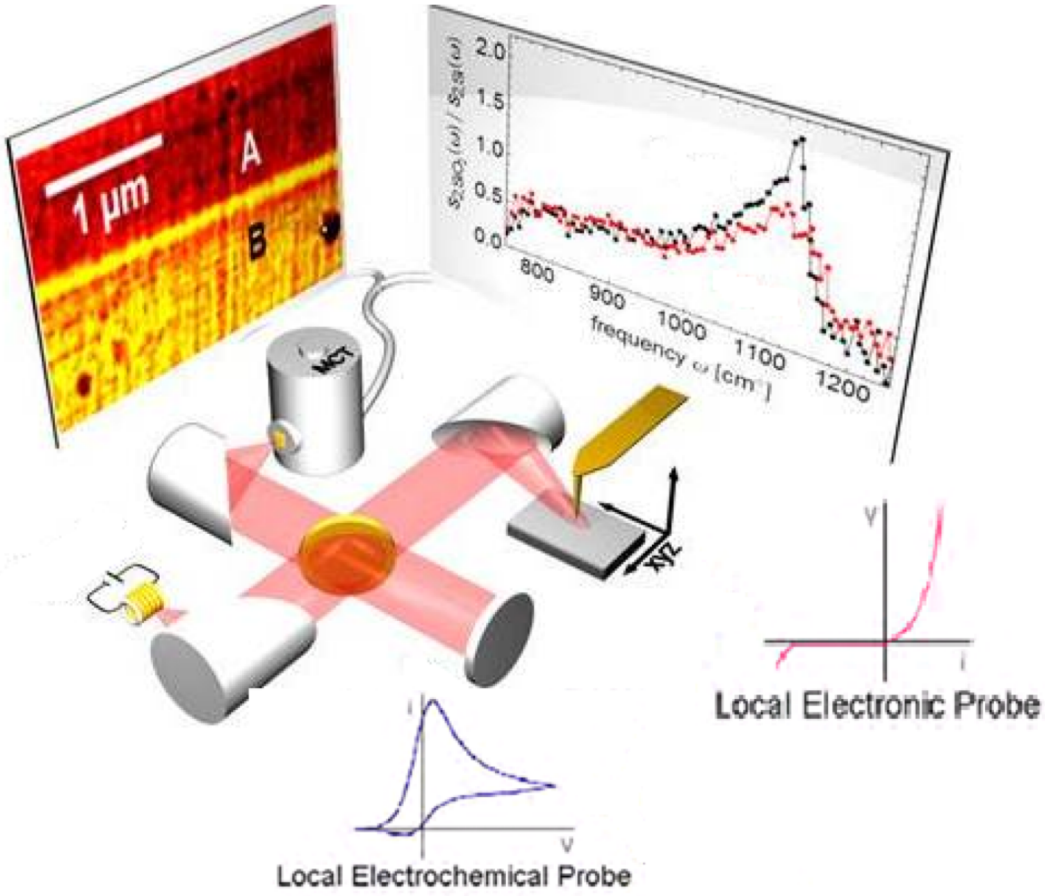
The present study demonstrates the high potential of IR ANSOM imaging and broadband nano-spectroscopy (nano-FTIR) for chemical and structural characterization of LixFePO4 single particles with unparalleled sensitivity and specificity. Most conventional analytical techniques employed to study fine changes in the local composition of LixFePO4 single particles offer limited insight into the reaction mechanism. Vibrational spectroscopies sensitive to lattice vibrations are of particular interest since the IR/Raman spectral signatures of LiFePO4, FePO4 and their meta-stable intermediates Li0.34FePO4 and Li0.60FePO4 provide excellent chemical contrast. However, the diffraction-limited spatial resolution of conventional far-field optical techniques presents a serious barrier to studying the structure and chemical composition of sub-micrometer specimens, used in commercial batteries.

IR ANSOM is an emerging near-field imaging and spectroscopic techniques which theory and practice undergo rapid and promising development. Recent technical improvements including lock-in detection of the optical signal, effective far-field background suppression schemes, and powerful quantum cascade or pulsed broadband IR laser light sources have enabled characterization of well-defined organic and inorganic nano-materials with unprecedented sensitivity and specificity and at comparable temporal resolutions..

The experimentally measured spectra of functional electrochemical materials are invariably convoluted, defying interpretation based on measured fingerprints, so that theoretical approaches to simulate and interpret these spectra are also vital. In this pioneering fundamental study we employ the infrared apertureless near-field scanning optical microscopy (IR ANSOM), augmented with nano-scale Fourier transform IR spectroscopy (nano-FTIR) and computational simulation to reveal 3-D distribution of charged and discharged phases within individual partially delithiated LixFePO4 microparticles.

Infrared near-field nanoscopy combined with Fourier transform infrared (FTIR) spectroscopy enables non-destructive characterization of well-defined samples at the nanoscale in ambient conditions. We demonstrate this unique capability by mapping phase distributions in microcrystals of LixFePO4, a burgeoning electrode material for Li-ion batteries. Ex situ nano-scale IR imaging provides direct evidence for the coexistence of pure LiFePO4 and FePO4 phases in single partially delithiated crystal microparticles. Furthermore, a quantitative 3-D tomographic reconstruction of the phase distribution within a single microcrystal provides new insights into the phase transformation and/or relaxation mechanism, revealing a FePO4 shell surrounding a diamond-shaped LiFePO4 inner core, gradually shrinking in size and vanishing upon delithiation of the crystal. This novel phase propagation pattern supports recent functional models of LFP operation relating electrochemical performance to material design.

The direct observation of 3-D phase distribution in LFP, heretofore unresolved experimentally, provides a new invaluable input into the ongoing debate about the operation mechanism of electrochemical energy storage materials. These results also demonstrate for the first time the extraordinary potential of near-field optical techniques for the characterization of electrochemical materials and interfaces.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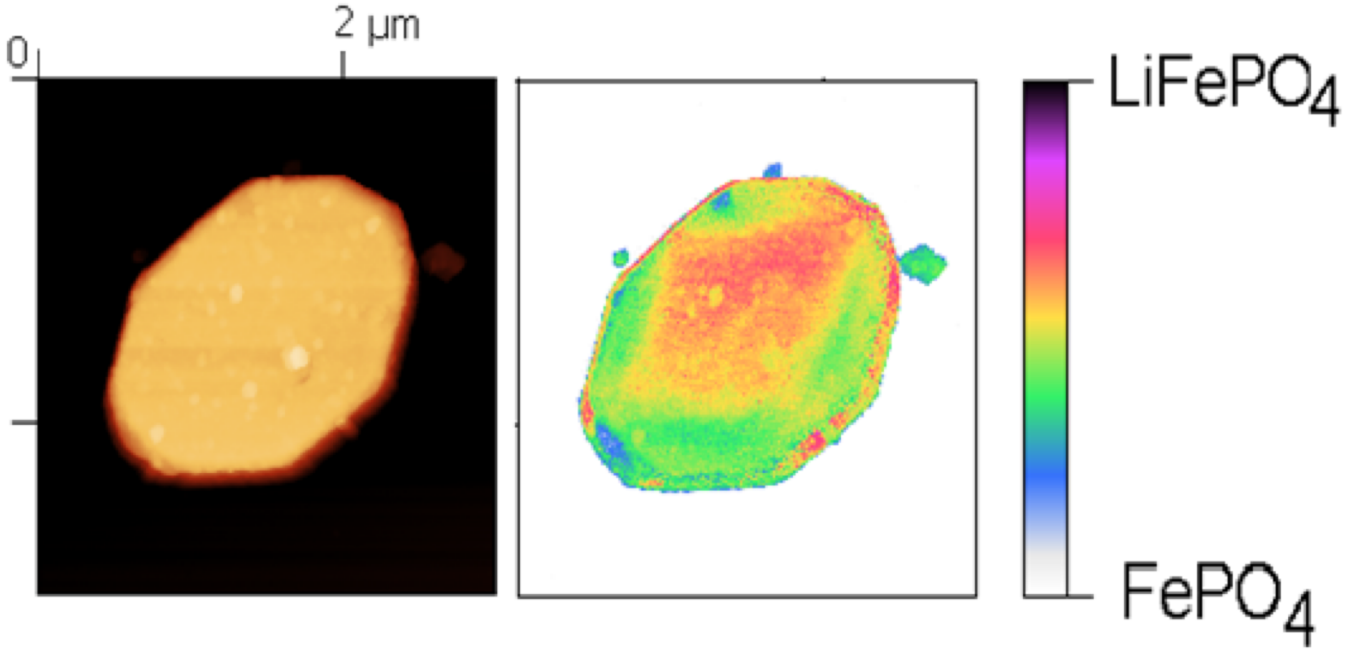
0
2 µm
LiFePO4
FePO4

Title: **Chemical modification of LiFePO4**

Presenting Author: Daniel Bélanger

Organization / Institution: UQAM

Co-Author:

Type: Oral **Session:** O-6.02

Abstract Summary:

Lithium iron phosphate, LiFePO4, with olivine structure has become of great interest as a cathode for the next generation lithium-ion batteries, particularly for hybrid electric vehicle applications, because of its high energy density, low cost, safety and environmental compatibility. The Li+ ion can be extracted/inserted from/into LiFePO4 at the electrode potential of 3.5 V versus Li/Li+, and the theoretical discharge capacity is 170 mA.h.g-1. On the other hand, the major drawback of LiFePO4 is the decrease of capacity with increasing charge/discharge current density, associated with its fundamentally low electronic and ionic conductivity. An attempt to overcome this problem involved the deposition of conductive carbon coating.

About two decades ago, the electrochemical modification of carbon electrode by the diazonium chemistry has been reported. The reduction of aryl diazonium salts at the surface of a carbon electrode generates radicals at the solution-electrode interface that eventually form a covalent carbon-carbon bond with the surface. Hence, a variety of organics functions could be grafted on the surface simply by changing the substituent of the aryl diazonium salt. It should be noted that in addition to the electrochemical approach, the spontaneous modification of carbons, without any electrochemical assistance, has been also reported.

Thus, this chemical grafting method was used to modify the surface and electrochemical properties of LiFePO4/C powder. This method allows the attachment of various substituted aryl groups with a strongly C-C bond in order to change the surface properties. The reduction of in situ generated diazonium cations in organic media leads to the functionalization of the carbon coating of LiFePO4/C.
This presentation will focus on the description of the diazonium chemistry for the surface modification of LiFePO4/C cathode for Li-ion batteries.

Chemical modification of $LiFePO_4$

Nicolas Delaporte[1], Alexis Perea[1], Ruhul Amin[1], Karim Zaghib[2#] and Daniel Bélanger[1]*

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2. Institut de Recherche d'Hydro-Québec (IREQ), 1800 Boulevard Lionel Boulet, Varennes, QC, Canada J3X 1S1

zaghib.karim@ireq.ca; *belanger.daniel@uqam.ca

Lithium iron phosphate, $LiFePO_4$, with olivine structure has become of great interest as a cathode for the next generation lithium-ion batteries, particularly for hybrid electric vehicle applications, because of its high energy density, low cost, safety and environmental compatibility. The Li^+ ion can be extracted/inserted from/into $LiFePO_4$ at the electrode potential of 3.5 V versus Li/Li^+, and the theoretical discharge capacity is 170 $mA.h.g^{-1}$. On the other hand, the major drawback of $LiFePO_4$ is the decrease of capacity with increasing charge/discharge current density, associated with its fundamentally low electronic and ionic conductivity. An attempt to overcome this problem involved the deposition of conductive carbon coating.

About two decades ago, the electrochemical modification of carbon electrode by the diazonium chemistry has been reported. The reduction of aryl diazonium salts at the surface of a carbon electrode generates radicals at the solution-electrode interface that eventually form a covalent carbon-carbon bond with the surface. Hence, a variety of organics functions could be grafted on the surface simply by changing the substituent of the aryl diazonium salt. It should be noted that in addition to the electrochemical approach, the spontaneous modification of carbons, without any electrochemical assistance, has been also reported.

Thus, this chemical grafting method was used to modify the surface and electrochemical properties of $LiFePO_4$/C powder. This method allows the attachment of various substituted aryl groups with a strongly C-C bond in order to change the surface properties. The reduction of *in situ* generated diazonium cations in organic media leads to the functionalization of the carbon coating of $LiFePO_4$/C.

This presentation will focus on the description of the diazonium chemistry for the surface modification of $LiFePO_4$/C cathode for Li-ion batteries.

Title: **High Voltage Li-ion Cathode Based on Substituted LiCoPO4**

Presenting Author: T. Richard Jow

Organization / Institution: U.S. Army Research Laboratory

Co-Author: Jan Allen

Type: Oral **Session:** O-6.03

Abstract Summary:

See PDF below

High Voltage Li-ion Cathode Based on Substituted $LiCoPO_4$

T. Richard Jow, Jan L. Allen, Joshua L. Allen, Samuel A. Delp, Jeff Wolfenstine

U.S. Army Research Laboratory, Adelphi, MD 20783, U.S.A.

To further increase the energy density of the state-of-the-art safe 3.4 V olivine lithium iron phosphate (LFP) based Li-ion batteries, 4.8 V lithium cobalt phosphate (LCP)[1] has been explored and studied. The structure of $LiCoPO_4$ is shown in Fig. 1 and a comparison of the discharge voltage of $LiCoPO_4$ to the discharge voltage of the isostructural $LiFePO_4$ is shown in Fig. 2. However, LCP suffers from lower conductivity than LFP. Furthermore, the voltage of LCP is higher than the oxidation stability limit of the state-of-the-art electrolyte made of $LiPF_6$ in ethylene carbonate (EC) and ethylmethyl carbonate (EMC) mixtures.

Initial results on LCP showed low capacity utilization and a severe loss of discharge capacity upon multiple charge-discharge cycles. For example, Amine et al.[1] observed a capacity utilization of 0.42 Li per LCP and Wolfenstine et al.[2] observed a capacity utilization of 0.6 Li. Tadanga et al.[3] observed a 10th cycle discharge capacity of ~52% of the initial capacity, Bramnik et al.[4] reported ~59% and Wolfenstine et al.[5] reported ~53% capacity retention (This has been attributed to irreversible structural changes or amorphization of the charged, low–lithium content material and electrolyte degradation.

Using Fe substitutionally-modified LCP (Fe-LCP)[6], the capacity utilization was improved to 0.7 Li and the capacity retention was substantially improved in conjunction with an electrolyte additive[7] that improves the electrolyte stability at high voltage as we reported recently. With further substitution as designated as Gen2 s-LCP, we further improved the capacity utilization to 0.78 Li and rate capability. Our Gen3 s-LCP shows further improvement in coulombic efficiency at >99% cycling as shown in Fig. 3.

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2. J. Wolfenstine, U. Lee, B. Poese and J.L. Allen, J. Power Sources, 2005, 144, 226.
3. K. Tadanaga, F. Mizuno, A. Hayashi, T. Minami and M. Tatsumisago, *Electrochemistry*,2003, **71, 1192**.
4. N.N. Bramnik, K.G.Bramnik, T. Buhrmester, C. Baehtz, H. Ehrenberg and H. Fuess, *J. Solid State Electrochem.* 2004, **8,** 558.
5. J. Wolfenstine, U. Lee, B. Poese and J.L. Allen, *J. Power Sources,* 2005, **144,** 226.
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7. A. v. Cresce, K. Xu, *J. Electrochem. Soc.* 2011, **158**, A337.

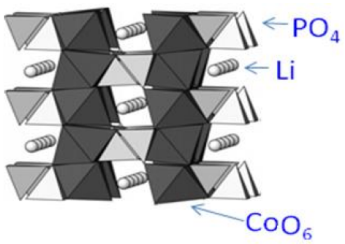


Figure 1: Structure of $LiCoPO_4$

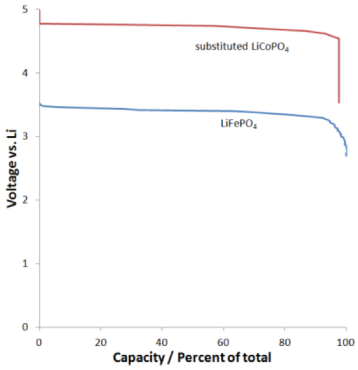


Figure 2. Illustration of the voltage difference between $LiFePO_4$ and and substituted $LiCoPO_4$.

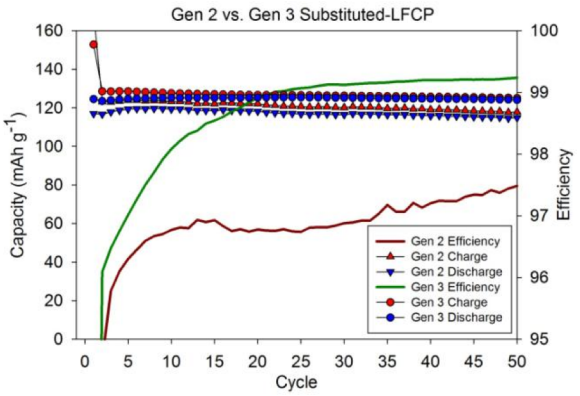


Figure 3 Capacity and coulombic efficiency of Gen2 and Gen 3 s-LCPs.

Title: **Electronic structure and transport properties of LiCoPO4 Li-ion Cathode Material**

Presenting Author: Jan Allen

Organization / Institution: US Army Research Laboratory

Co-Author: Richard Jow, US Army Research Laboratory

Type: Oral **Session:** O-6.04

Abstract Summary:

See PDF below

Electronic structure and transport properties of $LiCoPO_4$ Li-ion Cathode Material

Jan L. Allen[1], Jeff Wolfenstine[1], Michelle Johannes[2], Khang Hoang[2],
Travis Thompson[3], Jeff Sakamoto[3] T. Richard Jow[1]

[1]US Army Research Laboratory
[2]Naval Research Laboratory
[3]Michigan State University

$LiCoPO_4$ is of interest as a Li-ion cathode owing to its high energy (up to ~800 Wh / kg) and the potential for enhanced abuse tolerance owing to the strong covalent bonding of the PO_4 network. Its commercialization has been hindered by the lack of suitable electrolytes that can operate near 5 V and its capacity fade which results from structure deterioration [1-3]. Recent advances in electrolyte [4] and substitutions that enhance the stability of the material [5] have increased interest in this material as a next generation, high energy, high voltage (~4.8V) cathode material.

This paper will focus on the basic electronic structure of $LiCoPO_4$ compared to other olivines [6] based on an combined first principle calculations and experimental XPS measurements as well as transport (Li ion and electronic) properties of $LiCoPO_4$ and Fe-substituted $LiCoPO_4$ [7].

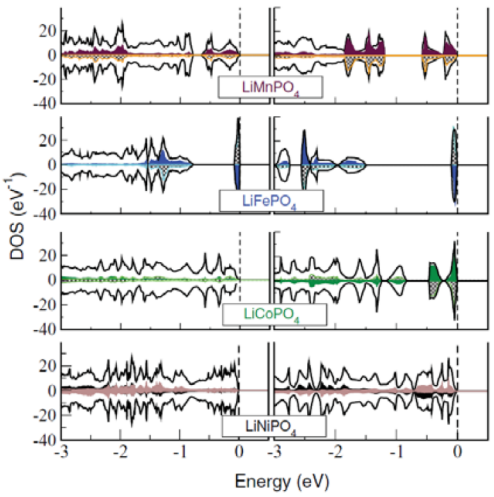
The olivine structured $LiFePO_4$ is a commercialized cathode material with excellent safety under abuse conditions. It has a relatively low energy density owing to its relatively low voltage of Li insertion. It is desirable to commercialize the manganese, cobalt or nickel based $LiMPO_4$ olivines with cell voltages of 4.1, 4.8 and 5.1V, respectively, in order to obtain a higher energy cathode with a similar safety profile.

Using a combination of experimental data (XPS) and first principle calculations we endeavored to understand the potential of the Mn, Co or Ni lithium phosphates to replace

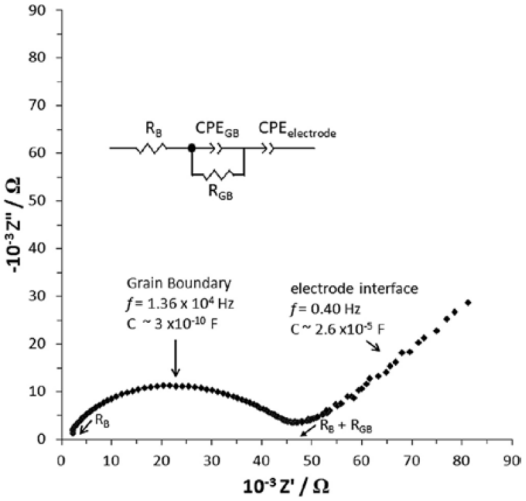
$LiFePO_4$ for higher energy applications. Computations show that polaron formation depends on the electronic structure near the valence band maximum (VBM). The results suggest that the electronic structure of $LiNiPO_4$ does not support the formation of polarons unlike the Fe, Mn and Co analogs. Polarons are the electron transport carriers of the olivine materials. A polaron is formed when Li is removed during charge creating a localized hole and contraction of the surrounding oxygen ions. The Ni compound has a too low percentage (~34%) of transition metal character (d orbital) at the VBM and $LiNiPO_4$ is therefore more likely to evolve oxygen during the charge process than undergo a redox reaction from Ni^{2+} to Ni^{3+}. The transition metal character at the VBM for $LiFePO_4$, $LiCoPO_4$ and $LiMnPO_4$ are 89, 78 and 60%, respectively which is sufficient for polaron formation. For these materials, the polaron mobility is shown to be of the order, $LiFePO_4$ > $LiCoPO_4$ >>$LiMnPO_4$. The mobility of the polaron in Mn olivine is considerably reduced owing to the distortion to the lattice caused by the Jahn-Teller Mn^{3+}. Thus, computations suggest that $LiCoPO_4$ is the most favorable candidate from a performance standpoint to replace $LiFePO_4$ for high energy applications. However, $LiCoPO_4$ is known to fade rapidly when cycled. To counter this challenge, we have developed Fe-substituted $LiCoPO_4$ which when used in conjunction with a high voltage electrolyte has dramatically improved cycle life and improved rate capability [5].

Transport measurements were used understand the Li-ion and electronic conductivity of $LiCoPO_4$ and Fe-substituted $LiCoPO_4$ in order to gain insight into means to further improve the performance of substituted $LiCoPO_4$. Hotpressed discs were prepared in order to enable the discrimination of bulk lattice conductivity from the total Li-ion conductivity. The electronic conductivities were measured via DC polarization curves. Both $LiCoPO_4$ and Fe-substituted

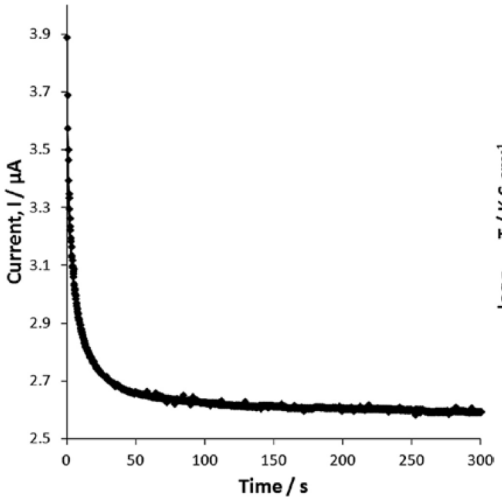
$LiCoPO_4$ were found to have relatively good bulk ionic conductivities of 4 x 10^{-6} and 1 x 10^{-6} S cm^{-1} and relatively poor electronic conductivities of 8 x 10^{-16} and 2 x 10^{-12} S cm^{-1}, respectively. Thus, suggesting that $LiCoPO_4$ or Fe-substituted $LiCoPO_4$ can function well as a Li-ion cathode as long as the poor electronic conductivity is addressed through carbon coatings [8].



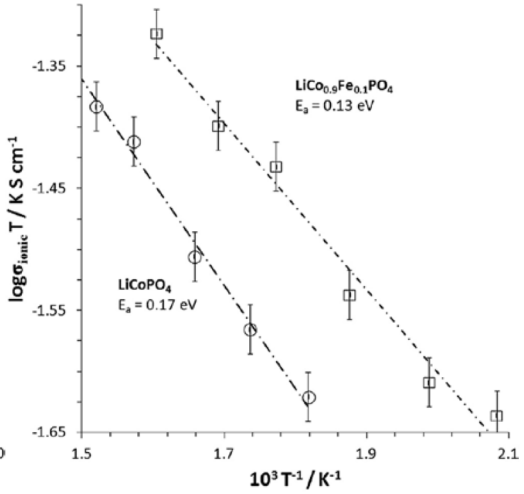
DOS plots for $LiMPO_4$



Impedance plot of $LiCoPO_4$ and equivalent circuit



DC polarization measurement



Temperature and bulk Li-ion conductivity

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4. A. V. Cresce and K. Xu, *J. Electrochem. Soc*. **158**, A337 (2011).

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Title:	**Current LFP market in Asia: opportunities and challenges**
Presenting Author:	Kevin Tu
Organization / Institution:	Advanced Lithium Electrochemistry
Co-Author:	
Type:	Oral **Session:** O-7.01

Abstract Summary:

LFP Market in Asia, Opportunities and Challenges

Mr. Kevin Tu, President, Aleees Canada

In the last few years we saw large scale adaptation of LFP cathode material as primary chose, especially in one of
world's largest market China, billions of dollars has been invested by government as well as private sector, creating a
very competitive market. Aleees has been operating in this market for the last 9 years, with a long list of customers in
the Asia market, there are quite a few observations obtained from operating in this challenging market place.

The presentation will discuss the many opportunities the current market provides as well as the many challenges the LFP
producer faces currently and will face in the near future. the purpose of the presentation is more toward provide
observations about the China market and share about Aleees approach to promote LFP cathode material in the this market.

Title:	**Characterization of the interaction of sputtered LiFePO4 thin-films with aluminum and titanium current collectors**
Presenting Author:	Aiko Bünting
Organization / Institution:	Forschungszentrum Jülich, Institute of Energy and Climate Research
Co-Author:	
Type:	Oral **Session:** O-7.02

Abstract Summary:

Characterization of the interaction of sputtered LiFePO4 thin-films with aluminum and titanium current collectors

Aiko Bünting, Christian Dellen, Sven Uhlenbruck, Chih-Long Tsai, Martin Finsterbusch, Doris Sebold, Robert Vaßen, Hans Peter Buchkremer

Institute of Energy and Climate Research
Forschungszentrum Jülich
Leo-Brandt-Str. 1, 52428 Jülich, Germany

A suitable cathode material for all-solid-state lithium-ion batteries might be LiFePO4. In all-solid-state batteries conventional liquid organic electrolytes are replaced by a less reactive and nonflammable solid electrolyte. Therefore, all-solid-state batteries gained much attention due to their good cycling stability, longer lifetime, and higher intrinsic safety.
In contrast to liquid electrolytes, solid electrolytes have a lower ionic conductivity and thus leading to a lower rate capability. The lower rate capability can be compensated by using a thin film approach, in which all components like current collectors, electrodes and electrolyte consist only of thin layers in the nanometer or micrometer range.
Such thin layers can be fabricated by using magnetron-sputtering processes. In many cases, non-metallic films like cathode materials must be sputtered at high temperatures or need a subsequent annealing step to get the desired crystalline structure. These high temperatures or subsequent annealing step can cause an interdiffusion between the single layers and thus influence properties like morphology and electrochemical performance.
The aim of this work is to characterize the interdiffusion behavior of magnetron-sputtered and post-annealed LiFePO4 thin-films on aluminum and titanium current collectors. Aluminum and titanium are promising candidates for the application in all solid-state-batteries because they are non-expensive and light-weight. Moreover, it is analyzed how a possible interdiffusion affects the electrochemical performance of thin-film LFP cathodes.
LiFePO4 has been deposited by an unbalanced radiofrequency-(RF)-magnetron sputtering process on aluminum and titanium substrates at room temperature. In a subsequent annealing step the as-deposited amorphous LiFePO4 thin-films were crystallized at 500 °C. The interaction as well as the interdiffusion between the LFP and the substrates is characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and secondary ion mass spectrometry (SIMS). Furthermore, the electrochemical performance of the LFP thin films is analyzed by cyclic voltammetry and charge/discharge measurements. As a main result it is shown that the interdiffusion of titanium into LiFePO4 strongly influences the resulting morphology and electrochemical performance.

Title: **Atomistic modeling of the olivine LiFePO4 and FePO4 systems.**

Presenting Author: Steen Schougaard

Organization / Institution: Université du Québec à Montréal

Co-Author: Christian Kuss, Université du Québec à Montréal
Guoxian Liang, Clariant Canada inc.

Type: Oral **Session:** O-7.03

Abstract Summary:

The olivine LiFePO4 system is the first phosphate to truly meet with widespread commercial success as the positive electrode material in lithium ion batteries. Its virtues of unprecedented chemical stability and fast redox chemistry make it useful in devices where power and long term performance are more important than energy density. Surprisingly and in spite of more than a decade of high-level research, the exact mechanism of lithium insertion and extraction is still a subject of discussion.
One of the puzzling questions is to what extend site exchange defects play a role in the observed difference in performance of samples that appear to be identical. I. e. to what extend does Fe in the one dimensional lithium diffusion channel obstruct the Li-ion transport.
In this talk we will present our most recent efforts towards an understanding of the role of Fe-Li site exchange. To this end we employ atomistic modeling rather than quantum mechanical approaches since it allows for modeling of a much larger number of atoms at much lower computational cost. The difficulty is however that a reliable set of force-field parameters must be developed. Our work therefore represents the first force-field parameters set, that reliably model the olivine LiFePO4 and the heterosite FePO4 structures both at and around the equilibrium structures. This tool has enabled us to model the behavior of lithium in an iron site and iron in a lithium site during redox cycling, which has entailed some surprising conclusions

OREBA 1.0

Title: **2020 cathode materials cost competition for large scale applications and promising LFP best-in-class performer in term of price per kWh**

Presenting Author: Fabrice Renard

Organization / Institution: Prayon

Co-Author:

Type: Oral **Session:** O-8.01

Abstract Summary:

See PDF below

2020 cathode materials cost competition for large scale applications and promising LFP best-in-class performer in term of price per kWh

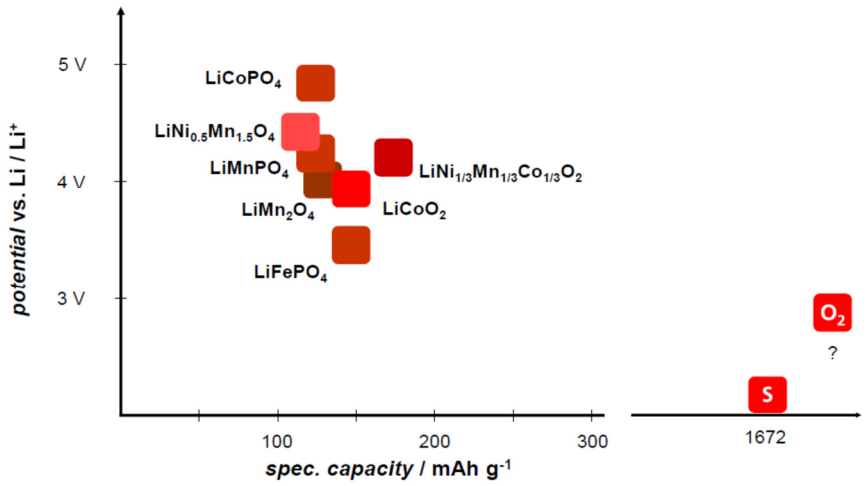
1. Introduction

The goal of this paper is to compare the cost structure of the Lithium Iron Phosphate cathode material in its position in terms of price/cost performance for mass industrialization in regard with other current cathode materials used for EV or ESS: LMO, NCA and NMC. The study integrates also LCO cathode although this material is not used for EV or ESS but, due to its massive usage in portable electronics, this material is still a reference cathode material for LIB to make a comparative study.

2. LIB cathode materials - State of the art

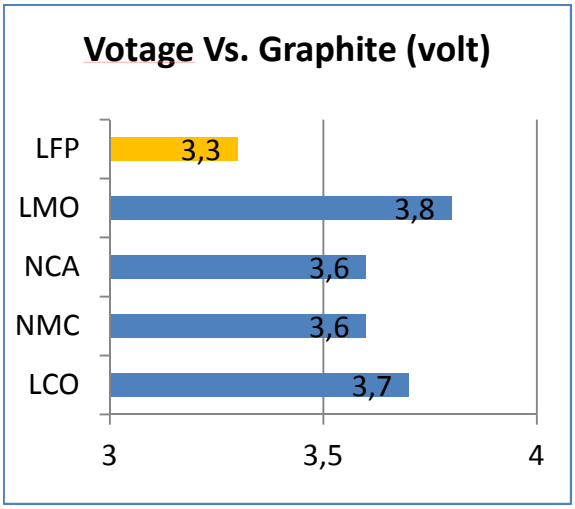
2.1. Performance of materials

Promising and existing cathode materials are mapped below in terms of voltage and specific capacity.

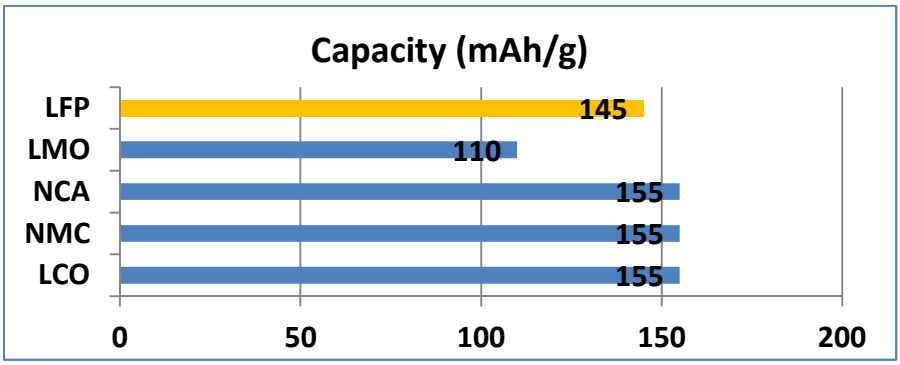


Source : Franhaufer

To highlight electrochemical performance in application, real potential and specific capacity of the five selected materials for this study are defined below :



Source : beLife



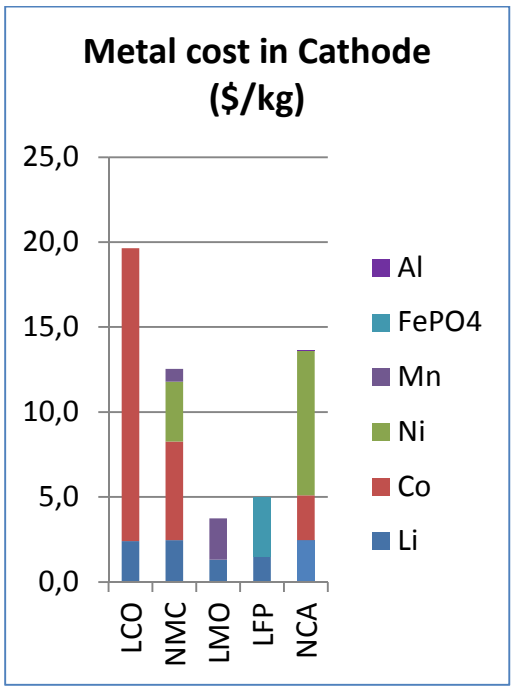
Source : beLife

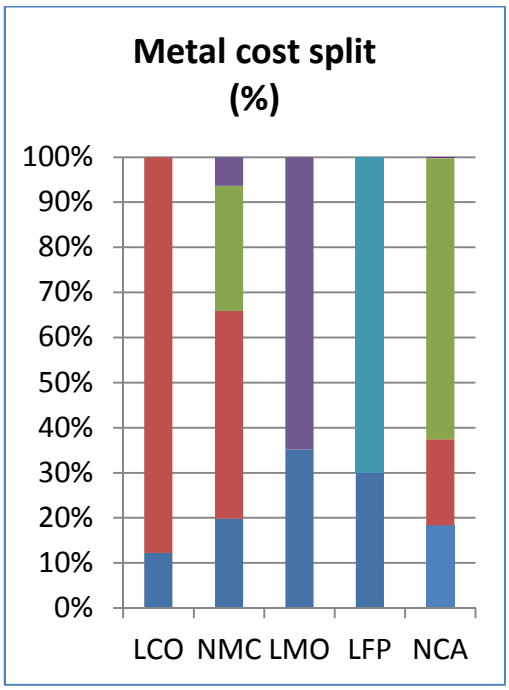
At cathode material level, NMC and NCA has a significant advantage in terms of kg/kWh for EV or ESS applications. They show a benefit of 17 % compared to LFP and 34% to LMO.

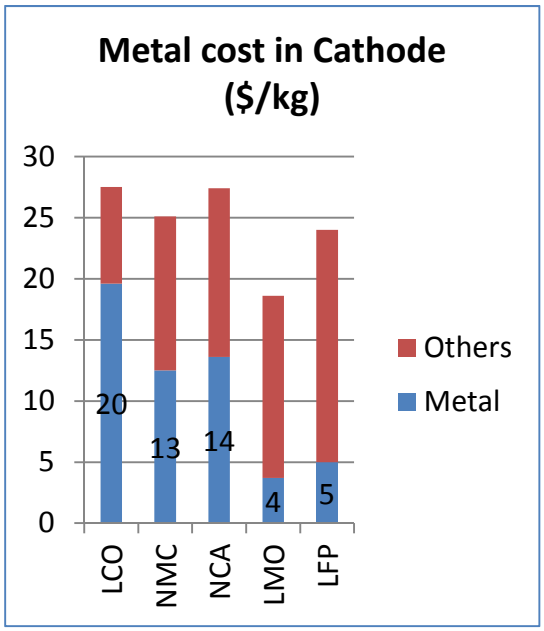
	mAh/g	Volts	**kg/kWh**
LCO	155	3,7	1,74
NMC	155	3,6	1,79
NCA	155	3,6	1,79
LMO	110	3,8	2,39
LFP	145	3,3	2,09

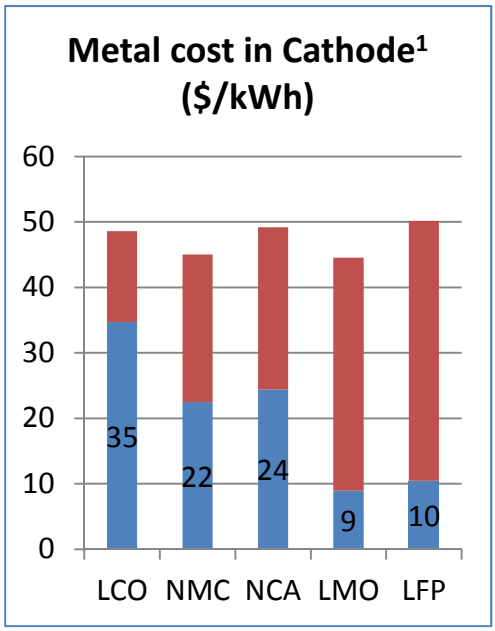
2.2. Metal cost in cathode (H2 2012)

Nota bene : Phosphorus is not a metal even if in this report the term metal includes all chemical elements constituting cathode materials : lithium, cobalt, nickel, manganese, iron but also phosphate



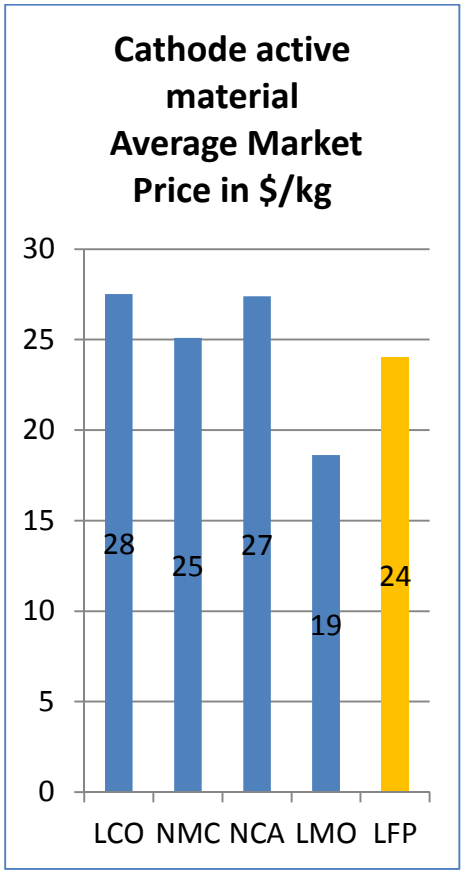


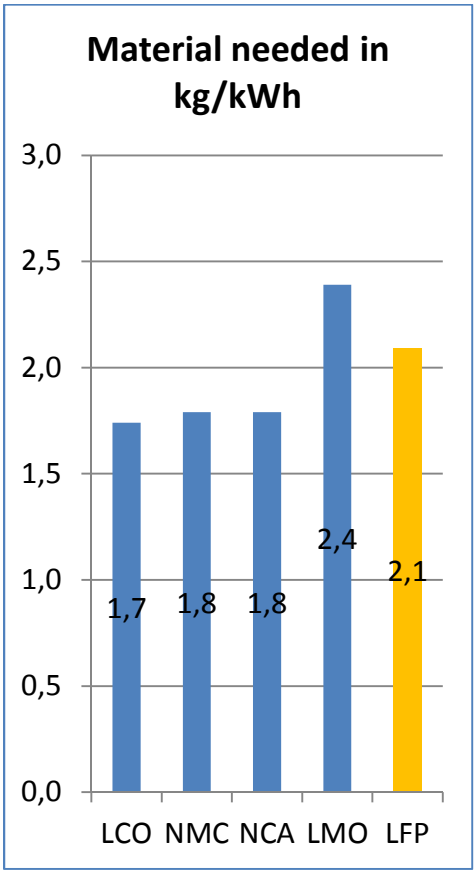




1- Before cell & pack process Yield

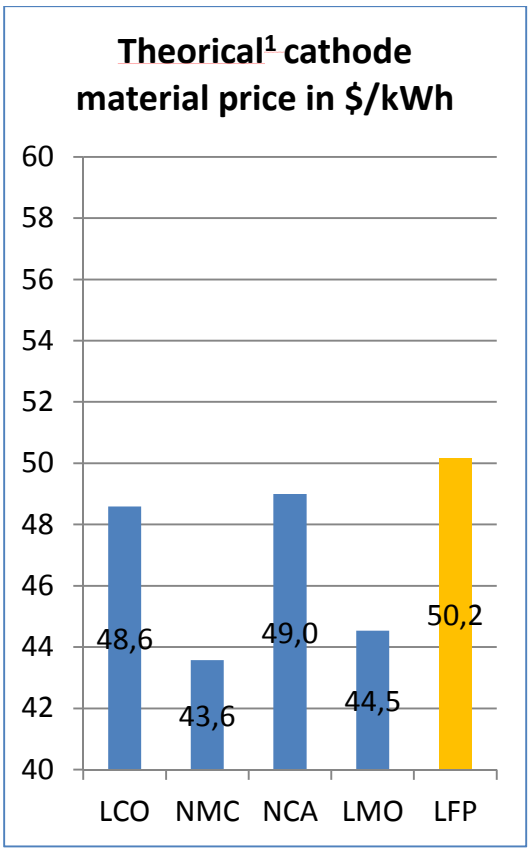
2.3. Cost of cathode materials (H2 2012)



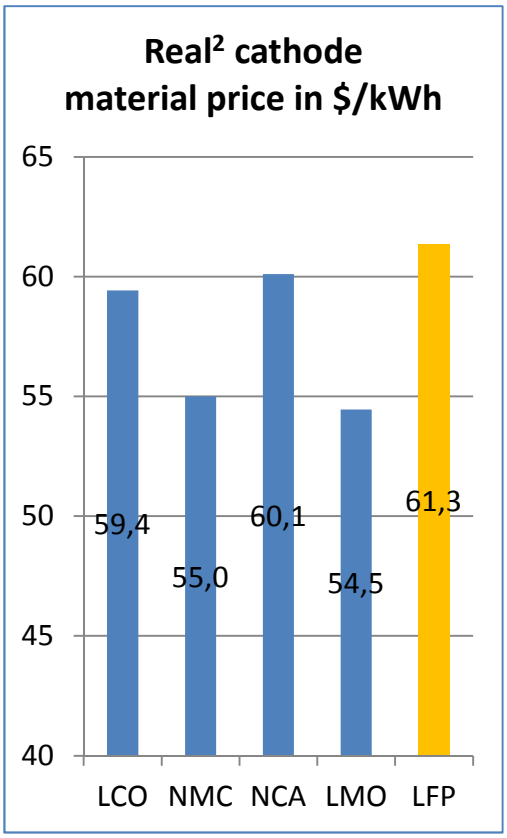


Actual average market price is directly linked with the technological maturity and the global worldwide available capacity for each cathode material and also largely driven by the level of competition.

Latecomers like LFP but also NMC subject to continuous improvements will become more and more competitive in comparison with LCO, NCA and LMO as shown later in the chapter describing prices forecast up to 2020.



1- Before cell & pack process Yield



2- After cell process yield (94%) and Pack process Yield (87%)

Only few mass productions for high quality LiFePO4+C AG patented LFP materials were up to the agenda in H2 2012.

Based on the above cathode competiting materials in $ per kWh, a full production cost below 20 $/kg is a first minimal target for LFP producers to move towards a competitive price under 50 $/kWh at pack level.

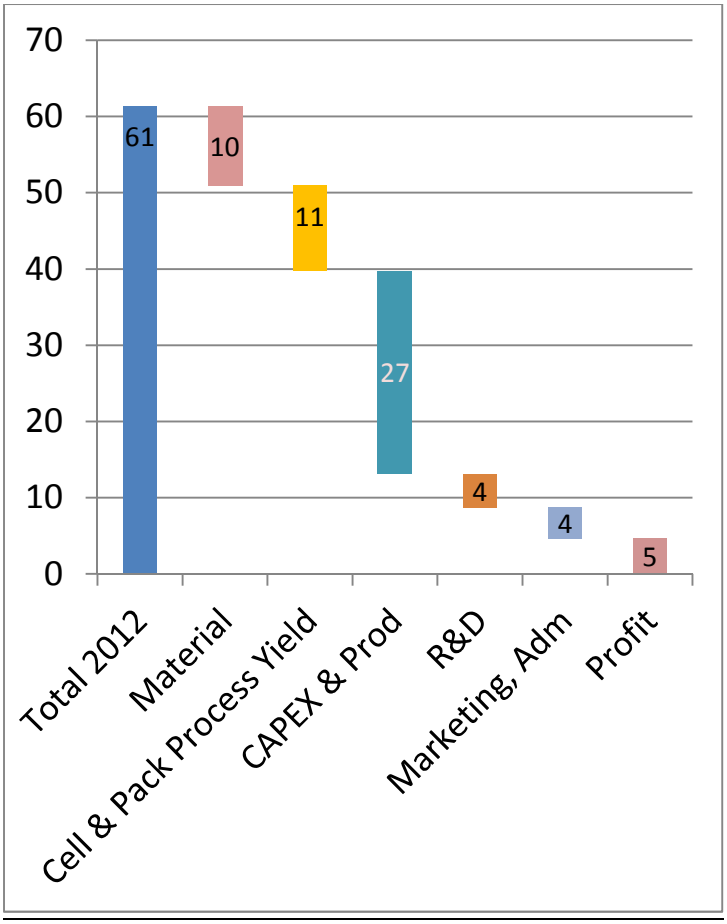
3. Detailed costs for LFP production end of 2012 – Gross Estimation

3.1. Rationales

- Assuming at least 1,000 tons per year of production
- Capacity: 140 mAh/g
- Voltage (Versus Graphite) : 3.3 volts
- Material costs:
  - Li_2CO_3: 6.4 $/kg
  - $FePO_4$: 3.5 $/kg
- R&D cost: 7%
- Marketing & Adm: 7%
- Profit: 7.5%
- Gross Margin: 21.5%

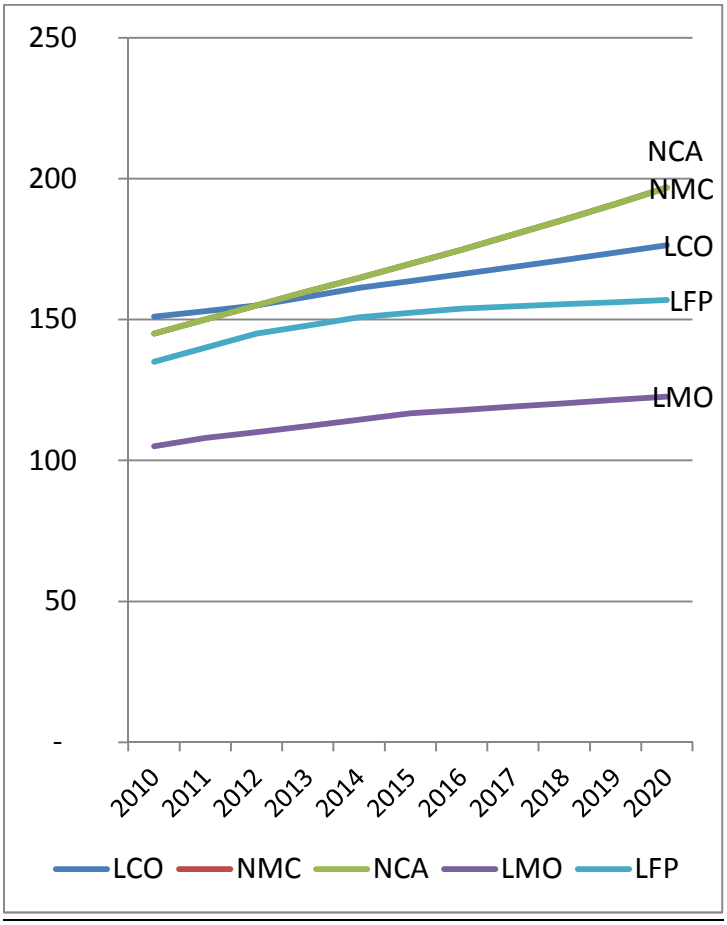
⇨ LFP cathode price ± 24 $/kg

3.2. LFP price in $/kWh at pack level (H2 2012)



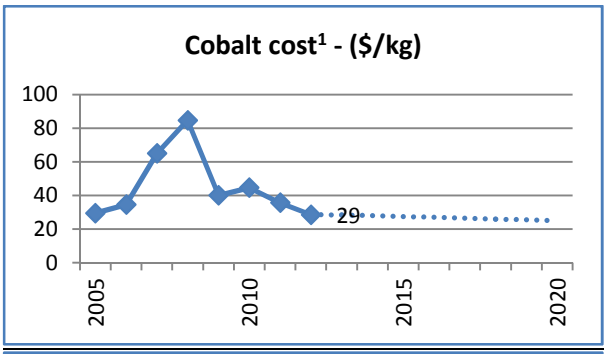
4. Cathode material price forecasts 2012 – 2020

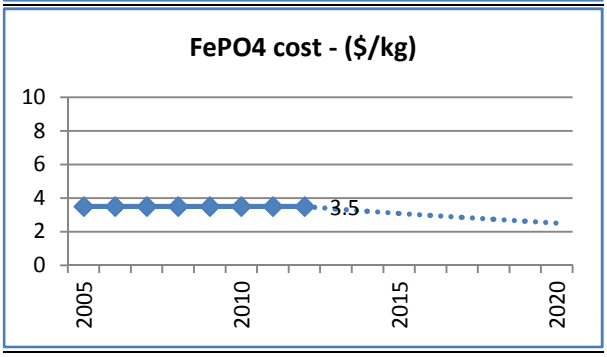
4.1. Specific energy increase in mAh/g

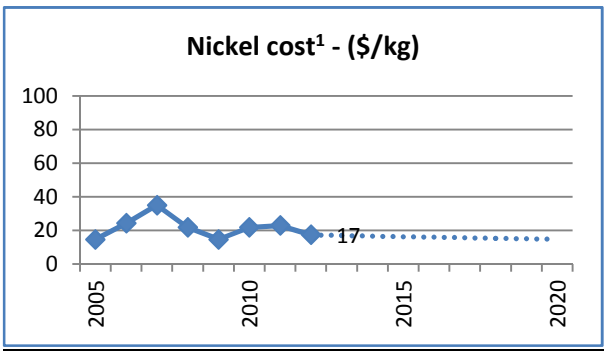


2012 – 2020 Average growth rate:
LCO: +1,7% - NMC: + 3%, - LMO: +1,4% - LFP: +1% - NCA: +3%

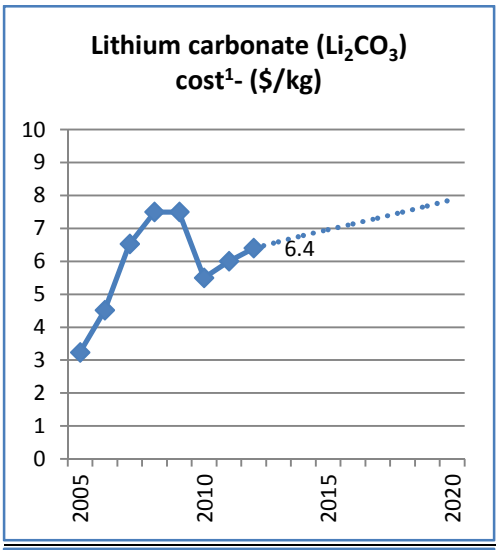
4.2. Raw materials

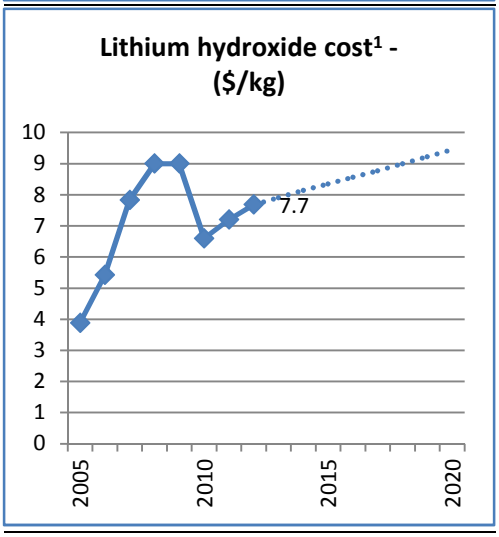






Source: LME, CDI, AVICENNE, Internal



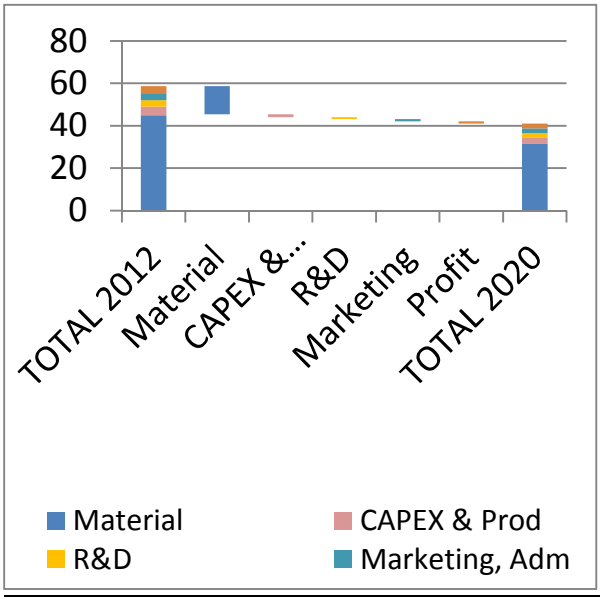


Source: FMC, Rockwood, SQM, Internal
Note: 1- Battery grade average

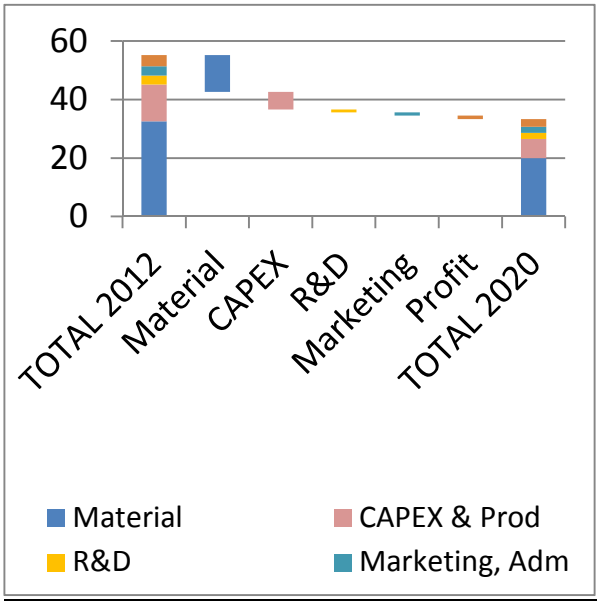
Manganese cost: stable at 4$/kg Mn over the concerned period.

4.3. Forecast 2020 in $/kWh at pack level per cathode material

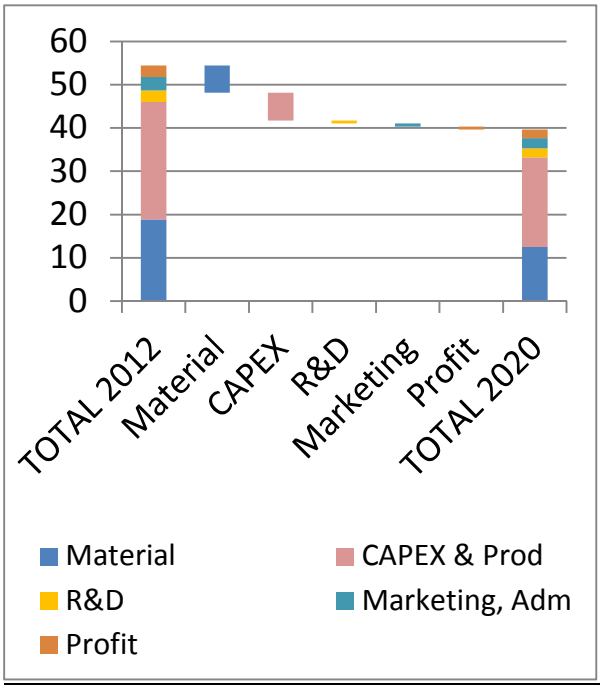
LCO forecast $/kWh at pack level



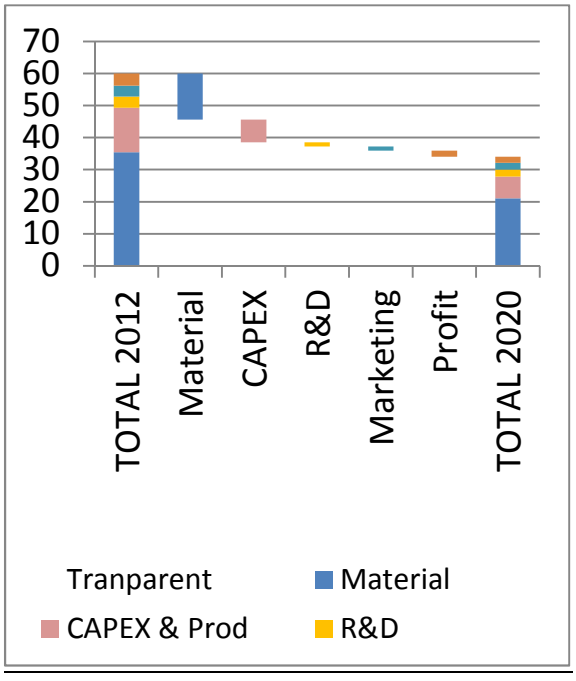
NMC forecast $/kWh at pack level



LMO forecast $/kWh at pack level



NCA forecast $/kWh at pack level

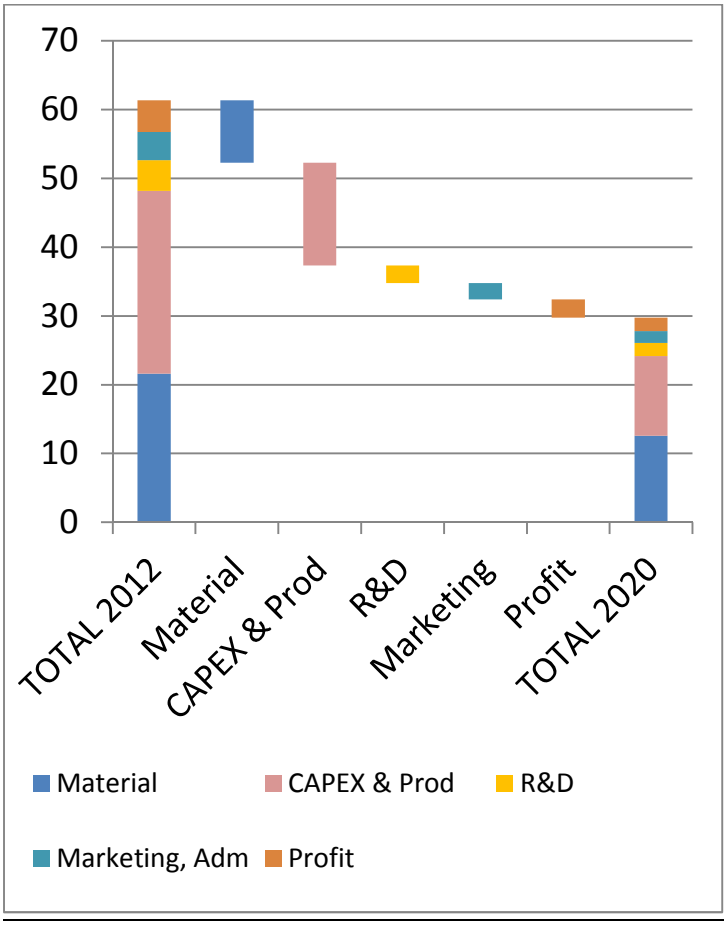


4.4. Forecast 2020 in $/kWh at pack level for LFP

4.4.1. Rationales

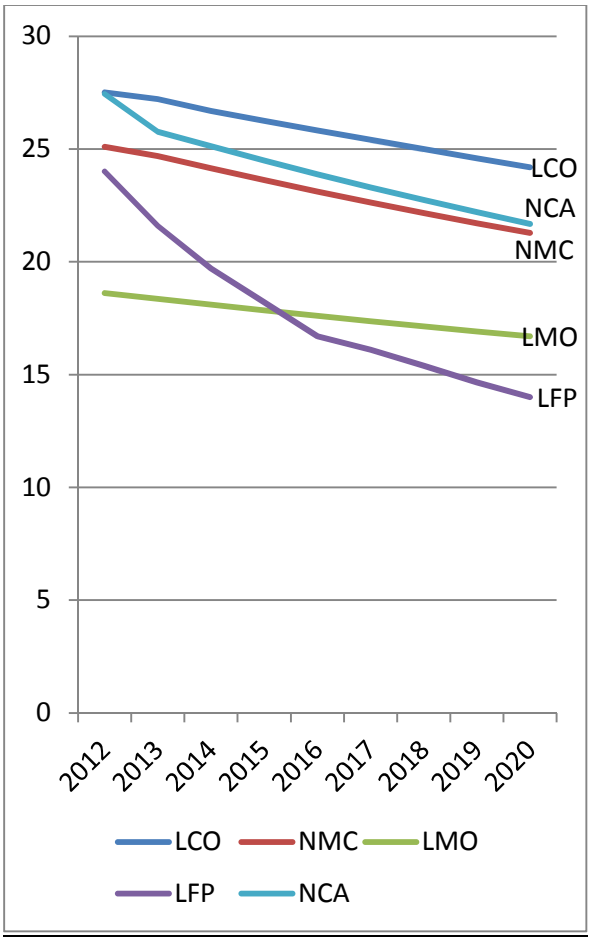
- Material price
  - Li: +3% per year from 2012 to 2020
  - Ni: -4% per year from 2012 to 2020
- Capacity: +1% per year from 2012 to 2020
- Capex & production cost: from 13$/kg to 6$/kg (-9% per year)
- Cell process yield: from 94% to 95%
- Pack process yield: from 87 to 95%

4.4.2. Forecast at pack level

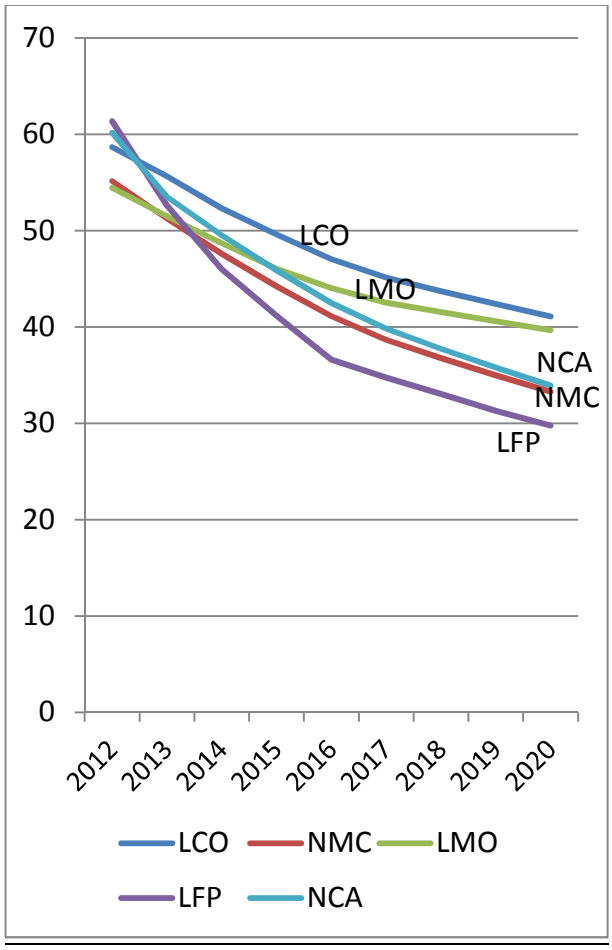


5. Conclusion

Cathode price forecast ($/kg)



Cathode price forecast ($/kWh) at pack level



Under usual reserve for long-term assumptions and in conclusion :

By 2020, LFP and its further evolutions will be comptetitive with the future generation NCM material specifically designed for full EV and probably become the bes-in-class in term of $/kWh but - linked with its lower specific energy capacity and voltage - will be more dedicated to large storage applications.

Conférence internationale sur les olivines pour batteries rechargeables
OREBA 1.0
International Conference on Olivines for Rechargeable Batteries

PRAYON

Acronyms:

LIB : Lithium Ion Battery
EV: Electrical Vehicle
ESS: Energy Storage System
LCO: LiCoO2
NMC: $Li(Ni_{0,33}Mn_{0,33}Co_{0,33})O_2$ or eq.
LMO: $LiMn_2O_4$
LFP: $LiFePO_4/C$ or eq.
NCA: $Li(Ni_{0,8}Co_{0,15}Al_{0,05})O_2$

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Title: **Preparation of olivine-based cathode materials from iron powder via a simple process**

Presenting Author: She-huang Wu

Organization / Institution: Tatung University

Co-Author:

Type: Oral **Session:** O-8.02

Abstract Summary:

Olivine-based cathode materials had been prepared successfully by a solution method with iron powder by mixing it with aqueous solution of lithium salt, phosphoric acid, salts of doped cations, citric acid, and conductive carbon source. After drying and heat-treating at 700-800o C under nitrogen atmosphere, carbon-coated powders with average primary particle size of 200nm and average secondary particle size of several microns were obtained. The process is easy for sample preparation in laboratory, but also very easy to scale-up for mass production. Carbon-coated composite LiFePO4/Li3V2(PO4)3 cathode materials had also been prepared via this process, they exhibit higher energy density than LiFePO4 and better cycling stability than Li3V2(PO4)3.

Preparation of olivine-based cathode materials from iron powder via a simple process

She-huang Wu, Kai-Mo Hsiao, Wei-hsin Ke, Chao-Jung Chien,
Je-Jang Shiu, Mao-Sung Chen
Department of Materials Engineering, Tatung University, Taipei 104, Taiwan

Olivine-based cathode materials had been prepared successfully by a solution method with iron powder by mixing it with aqueous solution of lithium salt, phosphoric acid, salts of doped cations, citric acid, and conductive carbon source. After drying and heat-treating at 700-800^{o}C under nitrogen atmosphere, carbon-coated powders with average primary particle size of 200nm and average secondary particle size of several microns were obtained. The process is easy for sample preparation in laboratory, but also very easy to scale-up for mass production. Carbon-coated composite $LiFePO_4/Li_3V_2(PO_4)_3$ cathode materials had also been prepared via this process, they exhibit higher energy density than $LiFePO_4$ and better cycling stability than $Li_3V_2(PO_4)_3$.

Title: **EMPHASIS ON PHOSPHATE LI-ION BATTERIES FROM TERRESTRIAL TO MORE ELECTRIC AIRCRAFTS APPLICATIONS**

Presenting Author: Florence Fusalba

Organization / Institution: CEA

Co-Author: Florence Fusalba, CEA

Type: Oral **Session:** O-8.03

Abstract Summary:

Due to their attractive performance characteristics, lithium-ion batteries have been identified as the battery chemistry of choice for a number of future applications, and especially those requesting high power pulse load operations. Electric power units will be only as good as their battery. It has always been the Achilles Heel of any more electric vehicle. Playing with technologies, ie. coupling various active materials at both the negative & positive electrodes, or using different sizing for components and cells give rise to a very versatile Li ion technology enabling improvements. Several routes are therefore possible, and in this paper the focus will be put on the so-called “safe” chemistries including phosphate materials coupled either with graphite or lithium titanates. Last results obtained at CEA on technologies integrating Lithium Iron Phosphate from cells to full battery systems using studies of cases to light targeted markets applications will be given and more electric aircrafts perspectives as for auxiliary power units or hybridization will be discussed.

OREBA 1.0

Title: **Is Doping Possible in LiFePO4?**

Presenting Author: Alain Mauger

Organization / Institution: Institut de Minéralogie, de Physique des Matériaux, et de Cosmochimie (IMPMC), UPMC Univ. Paris 6

Co-Author:

Type: Oral **Session:** O-9.01

Abstract Summary:

See PDF below

Is Doping Possible in $LiFePO_4$?

A. Mauger[1], C.M. Julien[2], K. Zaghib[3]

[1] Institut de Minéralogie, de Physique des Matériaux, et de Cosmochimie (IMPMC), UPMC Univ Paris 06, 4 place Jussieu, 75005 Paris, France

[2] Université Pierre et Marie Curie – Paris6, Physicochimie des Electrolytes et Nanosystèmes Interfaciaux (PHENIX), UMR 8234, 4 place Jussieu, 75005 Paris, France

[3] Energy Storage and Conversion, Research Institute of Hydro-Québec, Varennes, Québec, Canada J3X 1S1

$LiFePO_4$ has been selected as one of the positive electrode of batteries for electric vehicles, and more generally for high-power applications, owing to its thermal and structural stability, and its exceptional high-rate performance [1]. Since the material is a very poor electronic conductor, however, some treatment must be performed to make the $LiFePO_4$ powder conductive. Two different strategies were tried. One was to dope the material to make it conductive, by substitute Fe^{2+} ions for other transition-metal elements in a different valence state. Such attempts led to increase the conductivity by orders of magnitude [2], fostering the idea that it was possible [3]. However, it has been argued that this increase of conductivity was actually due to the formation of conductive surface films either because of formation of conductive carbon films, or metallic impurities such as Fe_2P, or simply precipitation of the metal dopant that cannot enter into the matrix, which have been observed by TEM experiments [4-6]. Neutron and XRD experiments have shown that the limit of solubility of the dopant such and Zr, Nb, Cr is very small, and that they are located primarily on Li sites, as expected from *ab initio* calculations [7], so that they reduce the diffusion of Li by obstruction of the channels, which degrades the electrochemical performance. The other strategy, which was the winning one, consists in coating $LiFePO_4$ with a conductive layer, usually carbon, although coating with a conductive polymer is also possible. In that case, the increase of the conductivity of the powder is due to the percolating metallic network that drives the electrons at the surface of any particle to the current collector, and the reduction of the particle size to limit the path of the electrons inside any particle to reach its surface. The very high rate performance achieved in [2] has been obtained by particles 90 nm thick covered with a 3 nm-thick carbon layer, which can be synthesized today at an industrial scale. The purpose of the present paper is to review how the study of the magnetic properties have given a major contribution to the understanding of the properties of $LiFePO_4$, starting with the electronic conduction process due to small magnetic polarons that preclude the possibility of any efficient doping, the role of the carbon coating and the surface modification that it generates due to the Fe-C affinity, which explains the outstanding performance of this material, and the identification of the impurities like Fe_2P that dissolve in the electrolyte.

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3. C.S. Sun, Z. Zhou, Z. G. Xu, D.G. Wang, J.P. Wei, X.K. Bian, J. Yan, *J. Power Sources* 193 (2009) 841.
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7. C.A. Fisher, V.M.H. Prieto, M.S. Islam, *Chem. Mater.* 20 (2008) 5907.

Title: **Introduction of nano-particles synthesizing technologies in Sumitomo Osaka Cement**

Presenting Author: Tetsuya Nakabeppu

Organization / Institution: Sumitomo Osaka Cement Co

Co-Author:

Type: Oral **Session:** O-9.02

Abstract Summary:

See PDF below

Introduction of nano-particles synthesizing technologies in SUMITOMO OSAKA CEMENT

T. Nakabeppu

New Technology Research Lab, Sumitomo Osaka Cement Co. LTD,
585, Toyotomi, Funabashi, Chiba 274-8601, Japan

Since 1980, we have been developing the nano-particles for the several fields and various functional materials were developed based on nano-technology.

Functional inks and film products generated by combination of dispersion and coating technology were widely used for ultraviolet ray cut, infrared ray cut, electromagnetic shield, antireflection, antistatic, antibacterial and deodorant. By the sintering and engineering technology, fine ceramic products were applied to semiconductor equipment and electronic devices.

Surface treated single-nano-zirconia particle with high refractive index and transparency were dispersed to form high refractive index and transparent composite resin. The dispersion were applied for the lens material and to miniaturize the lens unit.

Based on our nano-technology, we have developed lithium iron phosphate for the lithium ion battery cathode material. Since lithium iron phosphate is known as low electrical conductivity material, the fine and high crystallinity lithium iron phosphate particle was hydrothermal synthesized and carbon coated on to the surface of the particle.

The material consists of single phase $LiFePO_4$, with a primary particle size of 50-200 nm, and the particles were homogeneously coated with 2-3 nm thick carbon layer (see Fig. 1 and Fig. 2). The carbon content was 1 wt%. The specific surface areas were 9-11 m^2/g. The results of the rate capability at different discharge rates at 25°C are shown in Fig. 3.

The material was first adopted for the energy storage system battery and we've been doing mass production of the material since 2011. Recently, for its safe and long life characteristics, a number of works have been done to apply the material for the EV's. However, the improvement of the rate capability is still required for the several applications.

The recent development results to improve the rate capability of the lithium iron phosphate will also be reported at the meeting.

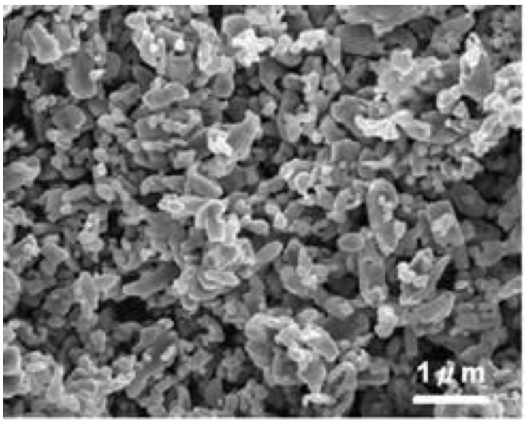

Fig. 1 SEM image of the carbon coated $LiFePO_4$

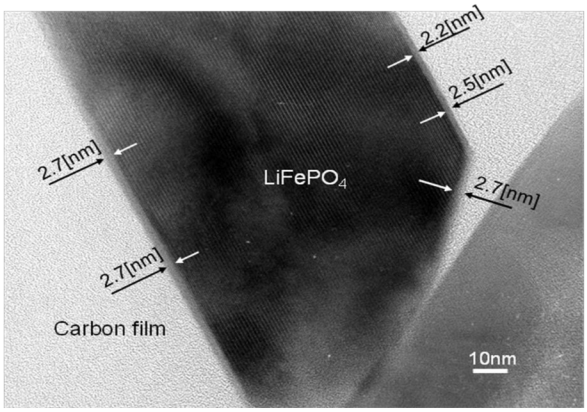

Fig. 2 TEM image of the carbon coated $LiFePO_4$

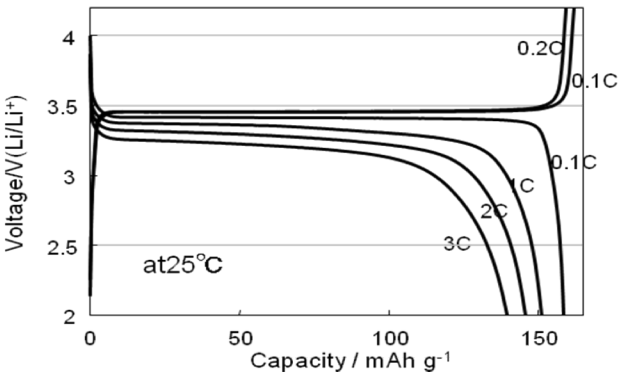

Fig. 3 Discharge curves of the carbon-coated $LiFePO_4$ at different rates (25°C).

Title:	**Polyol Synthesis Strategies for Olivine-structured Phosphate Nanoscale Electrode Materials**
Presenting Author:	Jaekook Kim
Organization / Institution:	Chonnam National University
Co-Author:	
Type:	Oral **Session:** O-9.03

Abstract Summary:

Polyol Synthesis Stategies for Olivine-structured Phosphate Nanoscale Electrode Materials
Jaekook Kim
Department of Materials Science and Engineering, Chonnam National University,
300 Yongbongdong, Bukgu, Gwangju 500-757, South Korea

Despite nanomaterials with unique properties playing a vital role in scientific and technological advancements of various fields including chemical and electrochemical applications, the scope for exploration of nano-scale applications is still wide open. The intimate correlation between materialistic properties and synthesis in combination with the urgency to enhance the empirical understanding of nanomaterial production demand the introduction of new strategies to develop promising nanomaterials. Herein we present a rapid polyol-based synthesis, performed under open-air conditions, to produce carbon wrapped olivine-structured nanocrystalline electrode materials. The versatile technique may facilitate the development of metal phosphates, in particular, with appreciable physicochemical properties beneficial for energy storage applications. The present strategy may present opportunities to develop “design rules” not only to realize cost-effective and simple nanomaterial production beyond lab-scale limits but also to produce nanomaterials suited for useful energy-related applications.

Title: **In-situ X-ray microscopy of a micro-sized battery cell with single-crystalline LiFePO4 as positive electrode**

Presenting Author: Nils Ohmer

Organization / Institution: Max Planck Institute for Solid State Research

Co-Author: Bernhard Fenk, Max Planck Institute for Solid State Research
Joachim Maier, Max Planck Institute for Solid State Research

Type: Oral **Session:** O-9.04

Abstract Summary:

Although LiFePO4 is already in use as a cathode material for Li ion batteries, the exact mechanism of (de)lithiation though is still under discussion. This is partly due to the lack of in-situ observations on a single particle level.
We use LiFePO4 single crystals grown via optical floating zone technique and thin film methods like molecular beam epitaxy (MBE) and thermal evaporation to build a micrometer-sized all-solid-state thin film battery cell with dimension 16x16x0.2 µm, exhibiting an oriented LiFePO4 single crystal as cathode material, using focused ion beam (FIB).
We present scanning transmission X-ray microscopy (STXM) measurements following the LiFePO4 transformation mechanism with a high spatial chemical resolution of 20 nm. We studied in-situ the phase boundary propagation within the LiFePO4 single crystal along the fast (010) orientation while electrochemically (de)lithiating the cathode material. The experiments allow us to study direction and homogeneity of the phase boundary motion. The results are discussed in terms of phase transformation and transport phenomena.

Title: **Synthesis and Characterization of Nanostructured Li Transition Metal Silicate (Li2MSiO4) Cathodes**

Presenting Author: George Demopoulos

Organization / Institution: McGill University

Co-Author: Xia Lu, McGill University
Karim Zaghib, Institut de recherche d'Hydro-Québec (IREQ)

Type: Oral **Session:** O-9.05

Abstract Summary:

Synthesis and Characterization of Nanostructured Li Transition Metal Silicate (Li2MSiO4) Cathodes

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Following the successful development-commercialization of the C-LiFePO4 (LFP) cathode by Hydro-Québec attention is directed towards the development of a higher specific energy polyoxyanion family of cathode materials, that of orthosilicates, Li2MSiO4, where M=Fe, Mn, Co, Ni. Orthosilicates are characterized by a theoretical specific capacity that is twice that of LiFePO4, namely 340 vs. 170 mAh/g, hence the great potential and opportunity. Hydro-Québec researchers led by Michel Armand were the first to identify orthosilicates as Li-ion cathode materials over 15 years ago [1 (a,b,c,d)]. Since then a number of studies have been reported in particular over the last few years as summarized in two recent reviews2,3. In this work, the synthesis of Li2MSiO4 (M = Fe, Mn),.using a combination of hydrothermal solution and reducing annealing treatment steps is studied4. From this routine, different polymorphs of silicates can be obtained that are structurally and composiotionally analyzed by XRD and TEM techniques before subjected to electrochemical characterization. In order to enhance the intrinsic poor electronic/ionic conductivity of the orthosilicate nanoparticles, they are coated in-situ with nitrogen-doped carbon5, which is characterized by Raman and XPS. Lastly, the atomic-scale Li ion storage and transport mechanisms are investigated by a via first-principle simulations.

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Title: **On the reactivity of Li7Ti5O12 and Pyr14TFSI towards molecular oxygen and its reduction products**

Presenting Author: Juan Herranz
Organization / Institution: Technische Universität München
Co-Author:

Type: Oral **Session:** O-9.06

Abstract Summary:

On the reactivity of Li7Ti5O12 and Pyr14TFSI towards molecular oxygen and its reduction products

Juan Herranz, K. Uta Schwenke, Michele Piana, and Hubert A. Gasteiger
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Despite the high gravimetric energy density envisaged for Li-O2 batteries, their practical applicability as energy storage and conversion devices remains uncertain owing to their poor round-trip efficiency, rate capability and cycle life [1]. The latter loss of capacity upon cycling is in terms related to the instability of the battery's cathode [2], electrolyte [3, 4] and anode [5] components. In an effort to circumvent this reactivity issues, we have studied the O2-stability of lithiated lithium-titanate oxide (Li7Ti5O12) and the ionic liquid 1-butyl-1-methylpyrrolidinium bis-(trifluoromethylsulfonyl)imide (Pyr14TFSI) as candidate Li-air battery anode and electrolyte solvent, respectively. Combining rotating ring-disc electrode voltammetry with UV-visible and nuclear magnetic resonance spectroscopies, our results point at the instability of both battery components. More precisely, the contact between molecular oxygen and Li7Ti5O12 causes the oxidation/delithiation of the anode material and the reduction of O2 to superoxide radical, which then reacts irreversibly with the Pyr14TFSI ionic liquid.

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Acknowledgments

Support of BASF SE in the framework of its Scientific Network on Electrochemistry and Batteries is acknowledged by TUM.

Title: **Size-Controlled Synthesis of LiFePO4/C Composites**

Presenting Author: Aishui Yu

Organization / Institution: Fudan Universsity

Co-Author: Hanjie Wang, Hangzhou Golden Horse Technology Company

Type: Oral **Session:** O-10.01

Abstract Summary:

Nano-micro-structured spherical LiFePO4/C composite was synthesized via a ball-milling-assisted spray-drying method. SEM characterization demonstrates that the primary and secondary particle sizes are on the order of several hundred nanometers and approximately fifteen microns. The primary particles were successfully controlled through homogenous milling with a narrow particle size distribution. Herein, LiFePO4/C composites with a primary particle (i.e., 200 nm and 400 nm in diameter) are prepared. The relationship between electrochemical performance and particle size was evaluated using both half- and full-cell tests. The results demonstrated that the 200 nm diameter sample has a better rate capability and low-temperature performance, whereas the 400 nm sample is better at cycling.

In a general synthesis, stoichiometric amounts of Fe2O3, LiH2PO4 and a certain quantity of sucrose were mixed in alcohol. A series of parameters were adjusted during the production process to control the sample particle size. The phase composition of the obtained compounds was characterized by X-ray diffraction (XRD) with Cu Ka radiation. Particle morphologies and size distribution were characterized by Malvern Laser Particle Size Analyzer, Scanning electron microscope (SEM) and a transmission electron microscope (TEM).

Control of primary particle sizes was realized by a sequential process. A ball-milling-assisted spray-drying method was introduced as first step to prepare precursors with the average primary particles diameter of 200 nm and 400 nm. And a sinter process followed to carbonize the sucrose and form a compact carbon layer surrounding the particles. The typical primary particle sizes of 200 nm and 400 nm-diameter samples are labeled as LFP-200 and LFP-400. X-ray diffraction patterns indicate high crystallizations of LFP-400 and LFP-200 samples without impurities. TEM images for LFP-400 and LFP-200 show that the primary LiFePO4 particles were well coated by a uniform and dense carbon layer with a thickness less than 10 nm.

An IFR26650-type full cell was assembled to investigate electrochemical performance of the electrode prepared with sized-controlled LiFePO4/C composites. The discharge specific capacities are 143.2mAh/g and 149.7mAh/g at 0.2 C for LFP-400 and LFP-200, respectively. In addition, the capacity retentions at 1C rate after 950 cycles for LFP-400 and LFP-200 were 93% and 86%, and capacity retentions at 3C rate were 97.6% and 99.3%. Electrochemical performance at low-temperature were tested in condition of -20 °C and 0.33 rate, which shows approximately 43% and 65% of static capacity (0.5 C at 25 °C) maintained for LFP-400 and LFP-200. The test results above suggest that the sample LFP-200 has better rate capability and better low-temperature performance than LFP-400, whereas the LFP-400 shows better performance in processing and cycling ability.

Title: **Structure Tuning of Olivine Cathode for Rechargeable Batteries**

Presenting Author: Li Wang

Organization / Institution: Tsinghua University

Co-Author: Zhongjia Dai, Tsinghua University
Xiankun Huang, Tsinghua University
Jian Gao, Tsinghua University
Yuming Shang, Tsinghua University
Xiangming He, Tsinghua University

Type: Oral **Session:** O-10.02

Abstract Summary:

Olivine LiMPO4 (M=Fe, Mn or their mixture) are promising cathode materials for lithium ion batteries, due to advantages in terms of low cost, environmental friendliness, high safety and cycling stability. Though they suffer from low electronic conductivity and slow lithium ion diffusion coefficient, combination of carbon coating, size reduction and cation doping have been proved to be effective resolutions. In particular, nanoparticles lead to low pack density and high specific area in the electrodes, resulting in low energy density and poor calendar life of the batteries, then to control the particle size in a reasonable range is of importance for application. Base on the fact that ion and electron transmission the olivine LiMPO4 materials are highly anisotropic, the crystal orientation, so resulting in particle morphology, is also a sensitive factor for LiFePO4 of good performances. Tuning the particle structure of olivine LiMPO4 with nanosize only in the direction of charge transfer may be a solution for large particle, high density, low specific area but fast kinetics. Moreover, hierarchical structured LiFePO4 is more beneficial to get apparently efficient particle-particle inter-connection, and is expected to enhance both electrochemical reaction and volume density.

In this report, olivine LiMPO4 with different morphology, size and secondary structure are prepared by solvothermal. Solvent, raw materials, precursor concentration, pH condition, temperature, feeding sequence are all take effects on the crystal formation and growth of the olivine LiMPO4 materials, while the feeding sequence determines the crystal orientation when using glycol as solvent. LiMPO4/C composites with flake morphology deliver both high capacity and high rate capability, while hierarchical LiMPO4/C spheres can conduct about 160 mAh/g at 0.1C rate with tap density of more than 1.5g/cm3. The research and development progress on technology and equipment for large-scale preparation will also be introduced.

Structure Tuning of Olivine Cathode for Rechargeable Batteries

Li Wang, Zhongjia Dai, Xiankun Huang, Jian Gao, Yuming Shang, Xiangming He*

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Olivine LiMPO$_4$ (M=Fe, Mn or their mixture) are promising cathode materials for lithium ion batteries, due to advantages in terms of low cost, environmental friendliness, high safety and cycling stability. Though they suffer from low electronic conductivity and slow lithium ion diffusion coefficient, combination of carbon coating, size reduction and cation doping have been proved to be effective resolutions. In particular, nanoparticles lead to low pack density and high specific area in the electrodes, resulting in low energy density and poor calendar life of the batteries, then to control the particle size in a reasonable range is of importance for application. Base on the fact that ion and electron transmission the olivine LiMPO$_4$ materials are highly anisotropic, the crystal orientation, so resulting in particle morphology, is also a sensitive factor for LiFePO$_4$ of good performances. Tuning the particle structure of olivine LiMPO$_4$ with nanosize only in the direction of charge transfer may be a solution for large particle, high density, low specific area but fast kinetics. Moreover, hierarchical structured LiFePO$_4$ is more beneficial to get apparently efficient particle-particle inter-connection, and is expected to enhance both electrochemical reaction and volume density.

In this report, olivine LiMPO$_4$ with different morphology, size and secondary structure are prepared by solvothermal. Solvent, raw materials, precursor concentration, pH condition, temperature, feeding sequence are all take effects on the crystal formation and growth of the olivine LiMPO$_4$ materials, while the feeding sequence determines the crystal orientation when using glycol as solvent. LiMPO$_4$/C composites with flake morphology deliver both high capacity and high rate capability, while hierarchical LiMPO$_4$/C spheres can conduct about 160 mAh/g at 0.1C rate with tap density of more than 1.5g/cm^3. The research and development progress on technology and equipment for large-scale preparation will also be introduced.

Title: **Mesoporous LiFePO4 Microspheres as High-rate Cathode material for Lithium-ion Batteries**

Presenting Author: Yuliang Cao

Organization / Institution: Wuhan University

Co-Author: Min Zhou Zhou, Wuhan University
Jiangfeng Qian, Wuhan University
Xinping Ai Wuhan University, Hanxi Yang, Wuhan University

Type: Oral **Session:** O-10.03

Abstract Summary:

LiFePO4 is now extensively investigated as a low cost cathode of Li-ion batteries for a variety of electric storage applications; however, its low tap density and rate capability bring about bring about difficulty and inconvenience to such applications. To overcome these problems, we tried to prepare mesoporous LiFePO4 microspheres (MMS-LFPs) with closely packed nanoparticles that form sufficient electrochemically favorable interfaces and abundant ionic channels. In this paper, we report a hydrothermal process for synthesis of the MMS-LFPs and describe the electrochemical performances of this material.

The MMS-LFP/C was synthesized by a hydrothermal route. The LiFePO4 precursor was prepared by dissolving stoichiometric amounts of LiOH•H2O, Fe(NO3)3•9H2O, NH4H2PO4, and citric acid (molar ratio:1:1:1:1) in distilled water to form a transparent solution (70 ml, corresponding to 0.4 M LiFePO4), and then transferring the solution into a 100 mL Teflon-lined stainless steel autoclave for hydrothermal treatment at 180 oC for 6 h. After the hydrothermal reaction, the reaction solution was evaporated at 80 °C under continuously stirring to obtain a light green spherical precursor. The precursor was calcined at 650 °C for 10 h under argon containing 5% H2 to obtain pure LiFePO4 microspheres. To coat with carbon, the precursor was impregnated in a sucrose solution (sucrose: LiFePO4 = 0.25:1 by wt.) and then dried and calcined in the same condition as mentioned above.

Figure 1 displays SEM and TEM images of the MMS-LFP and MMS-LFP/C. It is apparent that the sample shows a mesoporous microspherical structure and quite uniform distribution of particle size with average diameter of ~3 µm. Figure 1 c gives the SEM image of a carbon-coated LiFePO4 sphere (MMS-LFP/C). Apparently, the outer surface of the MMS-LiFePO4/C spheres is much smoothed and the porous structure on the spherical surface is hardly seen due to carbon coating.

Figure 2 shows the electrochemical performances of the MMS-LiFePO4/C materials at different rate. At low rate of 0.1 C (1C=170 mA g-1), the MMS-LFP/C delivered a discharge capacity of 157 mAh g-1, corresponding to 90% of the theoretical capacity of LiFePO4 (170 mAh g-1). The distinctive feature of this material is its excellent rate capability. The discharge capacity of the MMS-LFP/C was 97 mAhg-1 at high rate of 10 C (1700 mA g-1), which is considerably enough for the applications of EVs and energy storage.

In summary, LiFePO4/C with mesoporous microspherical structure was prepared simply by using a hydrothermal route. This material has an abundant open mesopores, which allow better irrigation of electrolyte and therefore provide huge electrochemically available surface for enhancing the rate capability of lithium insertion reaction. In addition, the closely packed microspherical structure of the carbon-coated LiFePO4 has high taping density for enhancing the volummetric energy density. Since the template-free hydrothermal method is facile, controllable, and cost-effective, it may be suitable for production of LiFePO4/C in battery applications.

Mesoporous $LiFePO_4$ Microspheres as High-rate Cathode material for Lithium-ion Batteries

Yuliang Cao, Min Zhou, Jiangfeng Qian, Xinping Ai and Hanxi Yang
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$LiFePO_4$ is now extensively investigated as a low cost cathode of Li-ion batteries for a variety of electric storage applications; however, its low tap density and rate capability bring about bring about difficulty and inconvenience to such applications. To overcome these problems, we tried to prepare mesoporous LiFePO4 microspheres (MMS-LFPs) with closely packed nanoparticles that form sufficient electrochemically favorable interfaces and abundant ionic channels. In this paper, we report a hydrothermal process for synthesis of the MMS-LFPs and describe the electrochemical performances of this material.

The MMS-LFP/C was synthesized by a hydrothermal route. The $LiFePO_4$ precursor was prepared by dissolving stoichiometric amounts of $LiOH{\cdot}H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $NH_4H_2PO_4$, and citric acid (molar ratio:1:1:1:1) in distilled water to form a transparent solution (70 ml, corresponding to 0.4 M $LiFePO_4$), and then transferring the solution into a 100 mL Teflon-lined stainless steel autoclave for hydrothermal treatment at 180 °C for 6 h. After the hydrothermal reaction, the reaction solution was evaporated at 80 °C under continuously stirring to obtain a light green spherical precursor. The precursor was calcined at 650 °C for 10 h under argon containing 5% H_2 to obtain pure $LiFePO_4$ microspheres. To coat with carbon, the precursor was impregnated in a sucrose solution (sucrose: $LiFePO_4$ = 0.25:1 by wt.) and then dried and calcined in the same condition as mentioned above.

Figure 1 displays SEM and TEM images of the MMS-LFP and MMS-LFP/C. It is apparent that the sample shows a mesoporous microspherical structure and quite uniform distribution of particle size with average diameter of ~3 μm. Figure 1 c gives the SEM image of a carbon-coated $LiFePO_4$ sphere (MMS-LFP/C). Apparently, the outer surface of the MMS-$LiFePO_4$/C spheres is much smoothed and the porous structure on the spherical surface is hardly seen due to carbon coating.

Figure 2 shows the electrochemical performances of the MMS-$LiFePO_4$/C materials at different rate. At low rate of 0.1 C (1C=170 mA g^{-1}), the MMS-LFP/C delivered a discharge capacity of 157 mAh g^{-1}, corresponding to 90% of the theoretical capacity of $LiFePO_4$ (170 mAh g^{-1}). The distinctive feature of this material is its excellent rate capability. The discharge capacity of the MMS-LFP/C was 97 $mAhg^{-1}$ at high rate of 10 C (1700 mA g^{-1}), which is considerably enough for the applications of EVs and energy storage.

In summary, $LiFePO_4$/C with mesoporous microspherical structure was prepared simply by using a hydrothermal route. This material has an abundant open mesopores, which allow better irrigation of electrolyte and therefore provide huge electrochemically available surface for enhancing the rate capability of lithium insertion reaction. In addition, the closely packed microspherical structure of the carbon-coated $LiFePO_4$ has high taping density for enhancing the volummetric energy density. Since the template-free hydrothermal method is facile, controllable, and cost-effective, it may be suitable for production of $LiFePO_4$/C in battery applications.

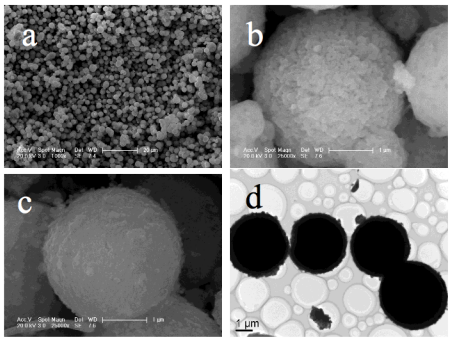

Figure 1. (a, b) SEM images of MMS-LFP without carbon coating. SEM (c) and TEM (d) image of MMS-LFP/C.

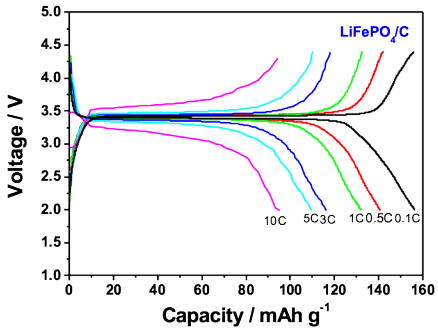

Figure 2. Charge/discharge profies of MMS-LFP/C at different rate.

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Acknowledgments: Financial support from the National Science Foundation of China (No. 21373155, 21333007) is gratefully acknowledged.

Title: **The Nanomicro Structure of LiFe0.98Mg0.02PO4/ Polyacene Composites**

Presenting Author: Hai-Ming Xie

Organization / Institution: Northeast Normal University

Co-Author: Li-Qun Sun, Northeast Normal University
Xing-Long Wu, Northeast Normal University
Jing-Ping Zhang, Northeast Normal University
Rong-Shun Wang, Northeast Normal University

Type: Oral **Session:** O-10.04

Abstract Summary:

We have designed a compound that consists of the nanomicro LiFePO4 with Mg2+ doping and a specific π-bond character planar polymer coating (polyacene, PAS). Nanomicro LiFe0.98Mg0.02PO4 particles were prepared by a FePO4•2H2O precursor. Fig.1 shows scanning electron microscopy (SEM) images of the LiFe0.98Mg0.02PO4/PAS particles.

Fig.1. SEM of LiFe0.98Mg0.02PO4/PAS (see attached document)

The nanosized primary LiFe0.98Mg0.02PO4 particles embedded in a nanosized PAS network forming porous micrometer-sized particles with a regular spherical shape. Nanosized primary particles work to shorten the lithium ion migration path in LiFe0.98Mg0.02PO4. Microsized secondary particles reduce the specific surface area of the particles in the sample, improving the processability of the cathode slurry.

The results show that the electronic conductivity, low-temperature properties, and the tap density of the as-prepared LiFe0.98Mg0.02PO4 /PAS composite were all rapidly improved simultaneously. The electronic conductivity of the LiFe0.98Mg0.02PO4/PAS composite can reach a magnitude of 101 S•cm-1. The LiFe0.98Mg0.02PO4 /PAS nanomicro composite exhibits a high discharge capacity of 161mAh•g-1.

Fig.2 shows the rate performance of the LiFe0.98Mg0.02PO4/ PAS at rates of up to 10 C. Superior performance of the PAS-coated composites is revealed. Specific reversible capacities of 145 and 135 mAh•g-1 were obtained at rates of 5 and 10 C, respectively.

Fig.2. Rate performances of LiFe0.98Mg0.02PO4/ PAS (see attached document)

12AH full cell was assembled further. The cell exhibits excellent cycle performance with capacity retention of 75% over 6000 cycles (Fig.3).The LiFe0.98Mg0.02PO4/PAS displayed a high discharge capacity, better rate performance and superior cycling stability. It can be used not only in the field of energy storage but also in the power battery.

Fig.3. Cycle performance of 12AH full cell (see attached document)

At present, the industrialization of the material has been realized. The scale is above a thousand tons of productivity yearly and the material shows the better consistency.

The Nanomicro Structure of $LiFe_{0.98}Mg_{0.02}PO_4$/ Polyacene Composites

Li-Qun Sun, Xing-Long Wu, Jing-Ping Zhang, Rong-Shun Wang, Hai-Ming Xie*

Department of Chemistry, National & Local United Engineering Laboratory for Power Batteries, Northeast Normal University, Changchun, Jilin 130024, PR China

We have designed a compound that consists of the nanomicro $LiFePO_4$ with Mg^{2+} doping and a specific π-bond character planar polymer coating (polyacene, PAS). Nanomicro $LiFe_{0.98}Mg_{0.02}PO_4$ particles were prepared by a $FePO_4 \cdot 2H_2O$

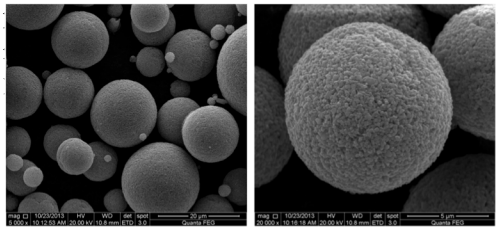

Fig.1. SEM of $LiFe_{0.98}Mg_{0.02}PO_4$/PAS

The nanosized primary $LiFe_{0.98}Mg_{0.02}PO_4$ particles embedded in a nanosized PAS network forming porous micrometer-sized particles with a regular spherical shape. Nanosized primary particles work to shorten the lithium ion migration path in $LiFe_{0.98}Mg_{0.02}PO_4$. Microsized secondary particles reduce the specific surface area of the particles in the sample, improving the processability of the cathode slurry.

The results show that the electronic conductivity, low-temperature properties, and the tap density of the as-prepared $LiFe_{0.98}Mg_{0.02}PO_4$ /PAS composite were all rapidly improved simultaneously. The electronic conductivity of the $LiFe_{0.98}Mg_{0.02}PO_4$/PAS composite can reach a magnitude of 10^1 $S \cdot cm^{-1}$. The $LiFe_{0.98}Mg_{0.02}PO_4$ /PAS nanomicro composite exhibits a high discharge capacity of 161mAh $\cdot g^{-1}$.

Fig.2 shows the rate performance of the $LiFe_{0.98}Mg_{0.02}PO_4$/ PAS at rates of up to 10 C. Superior performance of the PAS-coated composites is revealed. Specific reversible capacities of 145 and 135 mAh $\cdot g^{-1}$ were obtained at rates of 5 and 10 C, respectively.

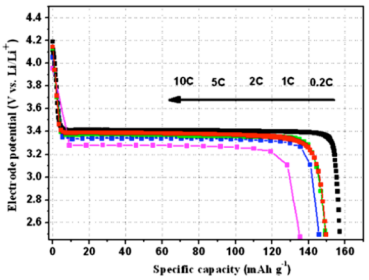

Fig.2. Rate performances of $LiFe_{0.98}Mg_{0.02}PO_4$/ PAS

12AH full cell was assembled further. The cell exhibits excellent cycle performance with capacity retention of 75% over 6000 cycles (Fig.3).The $LiFe_{0.98}Mg_{0.02}PO_4$/PAS displayed a high discharge capacity, better rate performance and superior cycling stability. It can be used not only in the field of energy storage but also in the power battery.

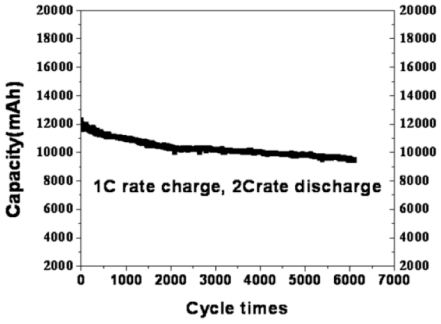

Fig.3. Cycle performance of 12AH full cell

At present, the industrialization of the material has been realized. The scale is above a thousand tons of productivity yearly and the material shows the better consistency.

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Fax: +86-431-85099511

Title:	**LFP – Battery material for a strong growing market**
Presenting Author:	Ruediger Oesten
Organization / Institution:	BASF SE
Co-Author:	
Type:	Oral **Session:** O-11.01

Abstract Summary:

Speaker: Dr. Kirill Bramnik, Director, Cathode Materials Application Technologies, BASF Battery Materials

LFP – Battery material for a strong growing market

The demand for battery materials is significantly increasing globally. In 2013 over 200,000 fully electrified and range extended vehicles were sold globally (all have Lithium-ion batteries). Overall, the battery materials market for the e-mobility segment, which includes also e-bikes and commercial vehicles such as busses, roughly doubled from 2012 to 2013. The consumer market gained a tremendous momentum especially from huge sales numbers of smartphones and tablets. Not only the number of units sold increased but also the amount of material per device which is a result of the higher performance requirements for the end customers. Stationary applications using Lithium-ion batteries also gained traction leading to major amounts of battery materials sold into that market segment.

Among major cathode materials used today, LFP is an established cathode material for all different market segments. LFP's performance and safety profile make it a preferred choice for many applications. An important milestone for the market penetration of LFP was the licensing strategy of the LiFePO4+C Licensing AG as it formed a joint label for reliable and authorized sources of LFP.

While many applications in all segments – e-mobility, stationary, consumer and power tools – use LFP as a battery material due to a variety of unique properties, there are still challenges to overcome. A key challenge is the reduction of LFP processing cost into a cell and battery. BASF developed a new LFP manufacturing process which serves as a platform for materials tailor-made so that our customers can design their coating process in the most efficient way.

OREBA 1.0 (Montreal, 26th – 28th May 2014) – ABSTRACT BASF

Speaker: Dr. Kirill Bramnik, Director, Cathode Materials Application Technologies, BASF Battery Materials

LFP – Battery material for a strong growing market

The demand for battery materials is significantly increasing globally. In 2013 over 200,000 fully electrified and range extended vehicles were sold globally (all have Lithium-ion batteries). Overall, the battery materials market for the e-mobility segment, which includes also e-bikes and commercial vehicles such as busses, roughly doubled from 2012 to 2013. The consumer market gained a tremendous momentum especially from huge sales numbers of smartphones and tablets. Not only the number of units sold increased but also the amount of material per device which is a result of the higher performance requirements for the end customers. Stationary applications using Lithium-ion batteries also gained traction leading to major amounts of battery materials sold into that market segment.

Among major cathode materials used today, LFP is an established cathode material for all different market segments. LFP's performance and safety profile make it a preferred choice for many applications. An important milestone for the market penetration of LFP was the licensing strategy of the LiFePO4+C Licensing AG as it formed a joint label for reliable and authorized sources of LFP.

While many applications in all segments – e-mobility, stationary, consumer and power tools – use LFP as a battery material due to a variety of unique properties, there are still challenges to overcome. A key challenge is the reduction of LFP processing cost into a cell and battery. BASF developed a new LFP manufacturing process which serves as a platform for materials tailor-made so that our customers can design their coating process in the most efficient way.

Title: **TOWARDS A LOW-COST MOLTEN SYNTHESIS PATHWAY FOR C LiFePO4 PRODUCTION**

Presenting Author: Gregory Patience

Organization / Institution: Chemical Engineering department, École Polytechnique de Montréal, Montreal QC, Canada

Co-Author:

Type: Oral **Session:** O-11.02

Abstract Summary:

TOWARDS A LOW-COST MOLTEN SYNTHESIS PATHWAY FOR C LiFePO4 PRODUCTION

Gregory S. Patience1, Michel Gauthier1,2,5, MickaëlDollé2, Patrice Chartrand1, Wojciech Kasprzak4, Delin Li4, Xueliang (Andy) Sun3, Guoxian Liang5

1) Chemical Engineering department, École Polytechnique de Montréal, Montreal QC, Canada
2) Chemistry department, Université de Montréal, Montreal QC, Canada
3) Mechanical and Materials Engineering department, Western University, London ON, Canada
4) CanmetMATERIALS, Hamilton ON, Canada
5) Clariant-Canada Inc, Candiac QC, Canada

Over the last five years, C LiFePO4 (C LFP) has been adopted for various power and large format battery applications supported by progress in manufacturing processes which enabled improved performance while preserving its inherent safety and thermal stability features. Despite such improvements, at the current cost of high quality products, C LFP as most other cathode materials, struggles to make it into large-scale accumulators such as those required in PHEV, EV and grid storage applications [1-2]. Although made up of more abundant elements, namely Fe and P, the present LFP synthesis pathways, due to either requirement of costly reactants or important processing quality assurance step, still yield high production costs for commercial LFP-grades with excellent cycle and calendar life.

Since its invention in 2003 [3], and more recently [4], the molten synthesis pathway was shown to benefit from the thermodynamic stability of C LFP near and above its melting point under reducing or inert conditions. This stability enables the use of a wider range of reactants including: simpler species, commodity chemicals, ores or battery recycling and their mixtures. From 2003 to 2012, UdeM and Clariant-Canada (formerly Phostech-Lithium) scientists verified this top-down approach at the lab-scale and showed that a wide variety of reactants could be used to achieve above 95% purity and that following a particle-size reduction from ingots down to nano-scale, the melt-synthesized LFP could exhibit high specific energy content [5].

In 2013, a research consortium made up of EPM, UdeM, UWO, with the technical support of CanmetMATERIALS and sponsorship of Clariant-Canada, received 7.5M CAD in funding and contributions from the governments and research partners under the Automotive Partnership Canada program to pursue the scale-up of the melt-synthesis of LFP. The aim of the research is to derive key operating parameters from each processing steps, specify raw materials, identify bottlenecks and optimize the melt-synthesis process enabling the synthesis of C LFP at an unrivalled cost potential while capable of electrochemical performance comparable to a good quality product.

In this presentation, we will give an overview of the research program and the ongoing work with special attention to reactant selection, general process flow and preliminary processing cost estimates. This will be complemented with recent experimental results focusing on reactant purity, stoichiometry and thermodynamics, pilot melting trials, grinding experiments, and structural and electrochemical characterizations.

References

[1] Y.Liu, 2013, "Domestic Lithium Battery Market Analysis", presented at the 5th World Cobalt & Lithium Forum, Chengdu, China, 17-20 April 2013.

[2] C. Pillot, 2013, "The worldwide xEV market 2012-2025 Battery is the Key", presented at the Battery Show, Novi, MI, 17-19 September 2013.

[3] L. Gauthier et al., 2003, "Process for Preparing Electroactive Insertion Compounds and Electrode Materials Obtained Therefrom", US pat 7,534,408.

[4] M. Gauthier et al., 2012, "Process for Preparing Crystalline Electrode Materials and Materials Obtained Therefrom ", WO 2013/177671 A1

[5] D. MacNeil et al., 2010, "Melt Casting LiFePO4 - II. Particle Size Reduction and Electrochemical Evaluation", J. Electrochem. Soc., 157(4) A463-A468.

Title: **Safety and high energy density lithium battery with blended cathode material of LiNi1-x-yCoxMnyO2-LiMnzFe1-zPO4**

Presenting Author: Yazhou Xiao

Organization / Institution: China Aviation Lithium Battery

Co-Author:

Type: Oral **Session:** O-11.03

Abstract Summary:

See PDF below

Safety and high energy density lithium battery with blended cathode material of $LiNi_{1-x-y}Co_xMn_yO_2$-$LiMn_zFe_{1-z}PO_4$

Abstract: The blended cathode material of $LiNi_{1-x-y}Co_xMn_yO_2$ and $LiMn_zFe_{1-z}PO_4$ was first studied and applied in full cell. The structure, morphology and stability of the blended cathode material were studied through XRD, SEM and DSC respectively while the electrochemical performance and safety was tested through 20Ah full cell. It was concluded that the blended cathode material has the integrative advantage of $LiNi_{1-x-y}Co_xMn_yO_2$ and $LiMn_zFe_{1-z}PO_4$, and the lithium ion battery for electric vehicle with high energy density, high safety and good cyclic performance could be made in basis of the blended cathode material.

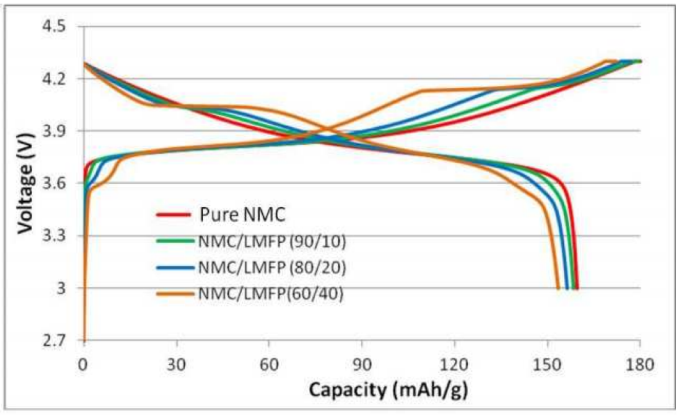

Figure 1 half-cell charge-discharge curve of blended cathod material of NMC and LMFP

It was found from Figure 1 that the capacity of blended material of $LiNi_{1-x-y}Co_xMn_yO_2$ and $LiMn_zFe_{1-z}PO_4$ was 160mAh/g, 158 mAh/g, 156 mAh/g and 152mAh/g with the addition ratio of $LiMn_zFe_{1-z}PO_4$ was 0, 10%, 20% and 40% respectively. There exists one obvious discharge plateau at 4.0 V while the addition ratio of $LiMn_zFe_{1-z}PO_4$ was 40% corresponding to the discharge plateau of $LiMn_zFe_{1-z}PO_4$.

Title:	**Status of LFP industry and market in China & its readiness to support the transport electrification**
Presenting Author:	Xiaoyu Zhang
Organization / Institution:	SynPLi Consulting, CIAPS
Co-Author:	
Type:	Oral **Session:** O-11.04

Abstract Summary:

Status of LFP industry and market in China & its readiness to support the transport electrification

Xiaoyu ZHANG
zhangxiaoyu2001@hotmail.com

Actually, environmental issues like air pollution can no longer be overlooked in China, where developing new-energy vehicles xEV becomes a solution and the foremost priority over the next six years to 2020. The government aims to achieve a new-energy vehicle sales of 500,000 units annually by 2015, and the investment in this industry would be at least 10 billion RMB per year. However, the ultimate goal is not only for government demonstration, but to push xEV in everyday life as well. In addition, lithium-ion batteries (LIB) are considered as the key components for xEV. Taking this background, the market update on China LIB industry in 2013 will be fully presented in this report.

1 Upstream: market review on LFP material
2 Midstream: review on LIB players who use LFP as cathode chemistry
3 Downstream: E-mobility in China
-xEV market : government attitude vs. customer interest
-Strategy trend of main OEMs
The presentation will end with a forecast on key factors to succeed in the battery business in China based on the previous discussion.

Title: **The Fine Structure and Electrochemical Performance Study of Lithium Iron Phosphate and Lithium Vanadium Phosphate Composite Material**

Presenting Author: Jigang Zhou

Organization / Institution: Harbin Institute of Technology, school of chemical engineering and technology

Co-Author: Changsong Dai, Harbin Institute of Technology, school of chemical engineering and technology
Zhenyu Chen, Harbin Institute of Technology, school of chemical engineering and technology
Wenhui Wang, Yongfeng Hu, Canadian Light Source Inc
Lucia Zuin, Canadian Light Source Inc

Type: Oral **Session:** O-11.05

Abstract Summary:

In the previous investigation of cathode materials for lithium-ion batteries (LIBs), lithium metal phosphate (LiyMx(PO4)z) has been considered to be the most promising cathode candidates for power LIBs, due to its excellent safety nature and good insertion/exaction properties of lithium[1]. Among which, LiFePO4 has been studyed most extensively. However, it suffers from low discharge voltage, poor large current charge/discharge performance and difficulty to charge/discharge at low temperature,etal[2]. Instead, Li3V2(PO4)3 possess excellent large current and low temperature charge/discharge performance[3].

First of all, this work introduces the synthesize process, structural and electrochemical property of Li3V2(PO4)3, Mg2+ doped Li3V2(PO4)3 and Zn2+ doped Li3V2(PO4)3. The results shows that Mg2+ doping would great enhance the large current discharge performance and low temperature discharge performance of Li3V2(PO4)3[4] , while, Zn2+ doping would enhance the cyclical ability greatly[5].
Above all, the synthesize process, structural and electrochemical properties of LiFePO4·Li3V2(PO4)3 composite has also been studied in this work. And the influence law of material structure on the electrochemical properties were also analyzed. XANES studies have shown that the Fe site of LFP in the LiFePO4·Li3V2(PO4)3 composite was in fact partially replaced by V3+, and the replaced amount decreases from material surface layer to the surface deep layer.and the V site of LVP in the LiFePO4·Li3V2(PO4)3 composite was partially replaced by Fe2+, as expected. These findings further clarify the mechanism to improve the electrochemical performance of the composite material [5].

Fig.16 Magnitudes of Fourier transforms of the k2-weighted EXAFS spectra at (a) Fe K-edge of LiFePO4 , (b) V K-edge of Li3V2 (PO4)3, (c) Fe K-edge of 7LiFePO4-Li3V2(PO4)3 and (d) V K-edge of 7LiFePO4-Li3V2(PO4)3 (see attached document)

Acknowledgement
This work was supported by the Natural Science Foundation of China (No. 51274075) and China's State Environmental Protection Public Welfare (201009028) and the Ministry of Education of Guangdong Province University-industry Cooperation Project (2012 B091100315). XANES and EXAFS were done at CLS which is supported by supported by NSERC, NRC, CIHR and the University of Saskatchewan.

References

[1] Goodenough J B, Kim Y. Chemistry of Materials. 2010, 22: 587-603.
[2] Zhang W J. Journal of Power Sources. 2011, 196: 2962-2970.
[3] Huang H, Yin S H, Kerr T, et al. Advance Materials. 2002, 14: 1525-1528.
[4] Dai CS, Chen ZY, Jin HZ, Hu XG. Journal of Power Sources. 2010, 195: 5775-5779.
[5] Wang WH, Zhang JL, Jia Z, Dai CS, Hu YF,b Jigang Zhou JG and Qunfeng Xiao QF. Phys. Chem. Chem. Phys. 2014, DOI:10.1039/C3CP55495C

The Fine Structure and Electrochemical Performance Study of Lithium Iron Phosphate and Lithium Vanadium Phosphate Composite Material

Changsong Dai[1]*, Jigang Zhou[1,2], Zhenyu Chen[1], Wenhui Wang[1] Yongfeng Hu[2], Lucia Zuin[2]

(1 Harbin Institute of Technology, school of chemical engineering and technology，Harbin 150001 E-mail: changsd@hit.edu.cn; 2 Canadian Light Source Inc, Saskatoon, Canada.)

In the previous investigation of cathode materials for lithium-ion batteries (LIBs), lithium metal phosphate ($Li_yM_x(PO_4)_z$) has been considered to be the most promising cathode candidates for power LIBs, due to its excellent safety nature and good insertion/exaction properties of lithium[1]. Among which, $LiFePO_4$ has been studyed most extensively. However, it suffers from low discharge voltage, poor large current charge/discharge performance and difficulty to charge/discharge at low temperature,etal[2]. Instead, $Li_3V_2(PO_4)_3$ possess excellent large current and low temperature charge/discharge performance[3].

First of all, this work introduces the synthesize process, structural and electrochemical property of $Li_3V_2(PO_4)_3$, Mg^{2+} doped $Li_3V_2(PO_4)_3$ and Zn^{2+} doped $Li_3V_2(PO_4)_3$. The results shows that Mg^{2+} doping would great enhance the large current discharge performance and low temperature discharge performance of $Li_3V_2(PO_4)_3$[4] , while, Zn^{2+} doping would enhance the cyclical ability greatly[5].

Above all, the synthesize process, structural and electrochemical properties of $LiFePO_4 \cdot Li_3V_2(PO_4)_3$ composite has also been studied in this work. And the influence law of material structure on the electrochemical properties were also analyzed. XANES studies have shown that the Fe site of LFP in the $LiFePO_4 \cdot Li_3V_2(PO_4)_3$ composite was in fact partially replaced by V^{3+}, and the replaced amount decreases from material surface layer to the surface deep layer.and the V site of LVP in the $LiFePO_4 \cdot Li_3V_2(PO_4)_3$ composite was partially replaced by Fe^{2+}, as expected. These findings further clarify the mechanism to improve the electrochemical performance of the composite material [5].

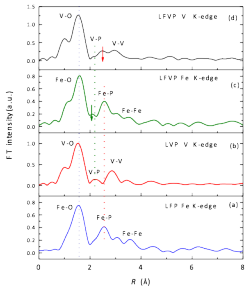

Fig.16 Magnitudes of Fourier transforms of the k2-weighted EXAFS spectra at (a) Fe K-edge of $LiFePO_4$, (b) V K-edge of **$Li_3V_2(PO_4)_3$,** (c) Fe K-edge of **$7LiFePO_4$-$Li_3V_2(PO_4)_3$ and (d)** V K-edge of **$7LiFePO_4$-$Li_3V_2(PO_4)_3$**

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References

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[4] Dai CS, Chen ZY, Jin HZ, Hu XG. *Journal of Power Sources*. 2010, 195: 5775-5779.

[5] Wang WH, Zhang JL, Jia Z, Dai CS, Hu YF,*b* Jigang Zhou JG and Qunfeng Xiao QF. *Phys. Chem. Chem. Phys.* 2014, DOI:10.1039/C3CP55495C

Title: PERFORMANCE AND APPLICATION OF LITHIUM ION BATTERIES WITH LiFePO4 CATHOD FOR XEV & ESS

Presenting Author: Na Zhang

Organization / Institution: Tianjin Lishen Battery Joint-stock Co.， LTD

Co-Author: Yufeng Zou, Tianjin Lishen Battery Joint-stock Co.， LTD

Type: Oral **Session:** O-11.06

Abstract Summary:

Olivine type LiFePO4 has been actively investigated in recent years as cathode material for rechargeable lithium-ion batteries after the pioneering work by Goodenough [1]. Due to its favorable electrochemical properties, relatively low cost， low toxicity, excellent chemical stability, LiFePO4 has been selected as positive material to develop safe high capacity & high power Li ion batteries for power applications [2].

Lishen have been jointly involved in second phase of Chinese 863 National Electrical Vehicle Project for developing Lithium ion batteries with LiFePO4 positive material for EV & HEV applications, since 2008. Based on performance & cost of 863 project target, Lishen focuses on developing high performance cells, modules and mass production technology with high quality assurance.

Since then, series Li ion battery products were developed, as shown in Table1. (see attached document)

Fig 1 shows the cycle performance of the typical LFP products.
Fig 1 LFP cell cycle curves (see attached document)

More tests are carried out. It is preliminarily shown from those test evaluation that such cells and modules can mostly reach the target of relative 863 EV, such as more than 120Wh/kg for energy cells and no burning & explosion for all cells during abuse tests, etc. Such batteries with 320Ah and 538V have been assembled in Swapping E-Bus for demonstration running in Tianjin and Qingdao with overall running mileage has reached 6 million km.

More detailed performance/cost evaluation of such modified batteries for commercial EV & HEV applications will be given in the presentation, based on more data & analysis.

Reference：
[1] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, J. Electrochem. Soc. 144 (1997) 1188.
[2] B. F. Wang, Y. Qiu, L. Yang, Electrochemistry Communications. 8 (2006) 1801–1805

PERFORMANCE AND APPLICATION OF LITHIUM ION BATTERIES WITH LiFePO4 CATHOD FOR XEV & ESS

Zhang Na, Zou Yufeng

Tianjin Lishen Battery Joint-Stock Co., LTD Tianjin 300384, China,

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Since then, series Li ion battery products were developed, as shown in Table1.

Table1. Typical Lithium ion cell products with $LiFePO_4$ positive electrode for xEV & ESS

	Voltage/V	*Capacity/Ah*	*Dimension/mm* T×W×H	***Specific Energy*** */(Wh/Kg)*	***Specific Power*** */(W/Kg)*	***Maximum discharge current*** /A	Applications
LP2770112	*3.2*	*7.5*	*27×70×112*	*55*	1800	*30C,40C(30s)*	*HEV*
LP2770120	*3.2*	16.5	*27×70×120*	*115*	500	*4C,6C(30S)*	*EV/ESS*
LP2770134	*3.2*	20	*27×70×134*	*120*	500	*4C,6C(30S)*	*EV/ESS*
LP2714897	*3.2*	*20*	*27×148×97*	*95*	1200	*8C,10C(30S)*	*EV/PHEV*
LP44147132	*3.2*	*50*	*44×147×132*	*100*	700	*2C,4C(30S)*	*EV/ESS*
LP44147172	*3.2*	*78*	*44×147×172*	*110*	600	*2C,4C(30S)*	*EV/ESS*
LP44147272	*3.2*	*130*	*44×147×272*	*120*	500	*2C,4C(30S)*	*EV/ESS*

Fig 1 shows the cycle performance of the typical LFP products.

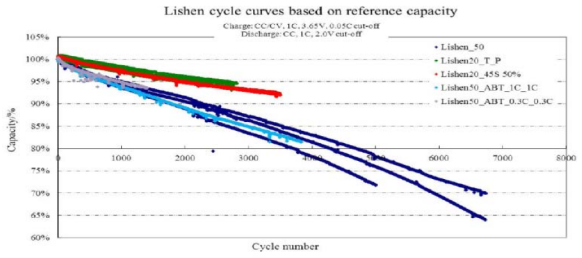

Fig 1 LFP cell cycle curves

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OREBA 1.0

Title: **Improved electrochemical performance of Li3V2(PO4)3 for lithium-ion batteries**

Presenting Author: Yunhui Huang

Organization / Institution: Huazhong University of Science and Technology

Co-Author:

Type: Oral **Session:** O-11.07

Abstract Summary:

Improved electrochemical performance of $Li_3V_2(PO_4)_3$ for lithium-ion batteries

Lulu Zhang [a], Gan Liang [b], Yunhui Huang [a]

[a] Key Laboratory for Advanced Battery Materials and System (MOE), School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China

[b] Department of Physics, Sam Houston State University, Huntsville, Texas 77341, USA

As polyanion cathode material for lithium-ion batteries, $Li_3V_2(PO_4)_3$ (LVP) has attracted much attention due to its stable structure, excellent electrochemical performance and high safety. However, poor intrinsic electronic conductivity of LVP due to separation of VO_6 octahedra by PO_4 tetrahedra in the structure, limits its practical application. Our work presents a systematic investigation on performance improvement in LVP by modification of doping and coating.

Synthesis method has a great effect on the performance of LVP. Carbon coating is necessary to enhance the conductivity. Several routes such as solid-state reaction, sol-gel and spray-drying method have been successfully used to prepare LVP/C composites. For example, via solid-state reaction, the LVP/C composite with 15 wt% glucose as carbon source sintered at 700 °C exhibits the best electrochemical performance and shows a stable monoclinic structure after cycling. For sol-gel process, glucose is important as a second carbon source for the performance of LVP with $LiOHH_2O$, $NH_4H_2PO_4$, V_2O_5 and oxalic acid as starting materials. By spray-drying route, caboxy methyl cellulose can be used as carbon source to control simultaneously the morphology of LVP. Spherical LVP/C composite is attained and shows excellent rate capability.

The effects of Fe, Na, Nb doping and silicon coating on the performance and mechanism in LVP have been systematically investigated. X-ray absorption spectroscopy and X-ray photoelectron spectroscopy are used to monitor the valence change of V ions upon doping and cycling. Experimental results show that, for Fe-doped LVP, $Li_{3+x}V_{2-y}Fe^{2+}_{y}(PO_4)_3$, $LiFePO_4$ and $FePO_4$ co-exist. Compared with pristine LVP/C, significant improvement in capacity, cycling stability and rate capability in LVP/C-Fe are achieved. For Na-doped LVP, Na shows a notable effect on electrochemical behavior of LVP. For Nb-doped LVP, -$NbOPO_4$ exists on the surface of LVP particles. $Li_3V_{1-x}Nb_x(PO_4)_3$/C (x = 0.03) shows improved capacity, rate capability and cyclability. SiO_2 modification in LVP can remarkably improve rate capability and cyclability, which can be ascribed to suppression of vanadium dissolution in the electrolyte, improved structural stability and reduced charge-transfer resistance.

Our work indicates that with optimization of synthesis, doping and coating, satisfactory electrochemical performance can be attained in LVP. The optimized LVP/C composite cathode material is potential for practical application in lithium rechargeable batteries.

Title: **EELS and XANES simulations for Li2MnSiO4 and Li2FeSiO4 cathodes for Li-ion batteries**

Presenting Author: Mohammad Attarian Shandiz

Organization / Institution: McGill University

Co-Author: Francesc Salvat, Universitat de Barcelona
Raynald Gauvin, McGill University

Type: Poster **Session:** P-1

Abstract Summary:

Cathode materials for Li-ion batteries with orthosilicate structure (Li2XSiO4, X=Mn, Fe, ...) are in a great interest for researchers because of providing high capacity and safety with low price. [1]. Hence, development and investigation of proper experimental and computational methods for the characterization of these cathodes are essential. Electron energy loss spectroscopy (EELS) as a method with high spatial and energy resolution for the characterization of materials is a good candidate for this purpose. Also, X-ray absorption near edge structure (XANES) can provide useful information about the chemical composition of materials. In this study, we use Monte Carlo (MC) and density functional theory (DFT) calculations for EELS and XANES simulations of Li2MnSiO4 and Li2FeSiO4 as two types of cathodes for Li-ion batteries.

Optical data models were used successfully for MC simulation of EELS [2]. For optical data models, the optical oscillator strength (OOS) is the main input [3]. OOSs were built by combination of energy loss function (ELF) data from DFT calculations and X-ray photoelectric data [4]. DFT calculations were performed by full potential linear augmented plane wave (FLAPW) method using WIEN2k code [5]. Optical properties were calculated by random phase approximation [6]. Figure. 1 shows the ELF for Li2MnSiO4 and Li2FeSiO4 with different plasmon energies.

The LEEPS code [2] was adapted to perform MC simulation of EELS spectra. Figure. 2a shows the simulated EELS by MC simulation for Li2MnSiO4 at different thicknesses. Figure. 2b compares the EELS at the same condition for Li2MnSiO4 and Li2FeSiO4 .The simulated spectra contain both signals from plasmon excitations and core-loss excitation. Hence, effect of thickness and other parameter of experiment can be studies for both types of excitations at the same time. The beam energy (E0) and collection semi-angle (β) for the simulations were 200keV and 10 mrad respectively.

X-ray photoelectric data does not contain the fine structure of core loss excitations. However, DFT calculations can provide the shape of energy-loss near-edge structure (ELNES). Figure. 3 presents the simulated core loss excitations for Li K, Si L23, Mn L23 and Fe L23 edges for Li2MnSiO4 and Li2FeSiO4 by DFT calculations using Wien2k with no core-hole effect [5]. As it can be seen, the Li K and Si L2-3 edges for Li2MnSiO4 and Li2FeSiO4 have different shapes. Hence, their ELNES can be used for the practical characterization of these electrodes.

Figure 4 shows the simulated XANES for Li K edge in Li2MnSiO4 and Li2FeSiO4 by DFT calculations. As it can be observed the shape of XANES is different because of the different atomic composition and structure.

EELS and XANES simulations for Li_2MnSiO_4 and Li_2FeSiO_4 cathodes for Li-ion batteries

M. Attarian Shandiz[1], F. Salvat[2] and R. Gauvin[1]

[1] Department of Materials Engineering, McGill University, Montreal, Canada.
[2] Facultat de Fisica (ECM), Universitat de Barcelona, Barcelona, Spain.

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Optical data models were used successfully for MC simulation of EELS [2]. For optical data models, the optical oscillator strength (OOS) is the main input [3]. OOSs were built by combination of energy loss function (ELF) data from DFT calculations and X-ray photoelectric data [4]. DFT calculations were performed by full potential linear augmented plane wave (FLAPW) method using WIEN2k code [5]. Optical properties were calculated by random phase approximation [6]. Figure. 1 shows the ELF for Li_2MnSiO_4 and Li_2FeSiO_4 with different plasmon energies.

The LEEPS code [2] was adapted to perform MC simulation of EELS spectra. Figure. 2a shows the simulated EELS by MC simulation for Li_2MnSiO_4 at different thicknesses. Figure. 2b compares the EELS at the same condition for Li_2MnSiO_4 and Li_2FeSiO_4 .The simulated spectra contain both signals from plasmon excitations and core-loss excitation. Hence, effect of thickness and other parameter of experiment can be studies for both types of excitations at the same time. The beam energy (E_0) and collection semi-angle (β) for the simulations were 200keV and 10 mrad respectively.

X-ray photoelectric data does not contain the fine structure of core loss excitations. However, DFT calculations can provide the shape of energy-loss near-edge structure (ELNES). Figure. 3 presents the simulated core loss excitations for Li K, Si L_{23}, Mn L_{23} and Fe L_{23} edges for Li_2MnSiO_4 and Li_2FeSiO_4 by DFT calculations using Wien2k with no core-hole effect [5]. As it can be seen, the Li K and Si $L_{2\text{-}3}$ edges for Li_2MnSiO_4 and Li_2FeSiO_4 have different shapes. Hence, their ELNES can be used for the practical characterization of these electrodes.

Figure 4 shows the simulated XANES for Li K edge in Li_2MnSiO_4 and Li_2FeSiO_4 by DFT calculations. As it can be observed the shape of XANES is different because of the different atomic composition and structure.

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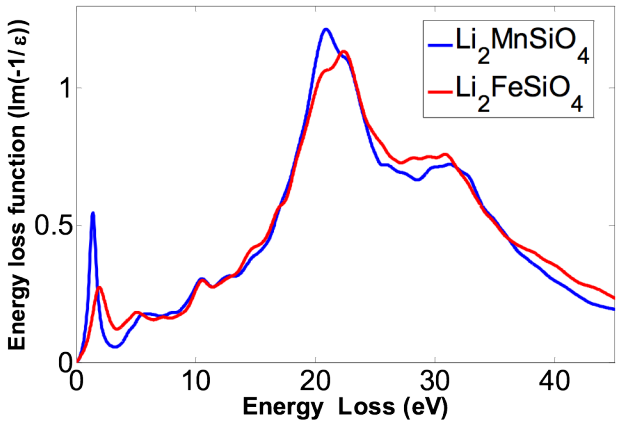

Figure 1. DFT calculations of energy loss function (ELF) for Li_2MnSiO_4 and Li_2FeSiO_4.

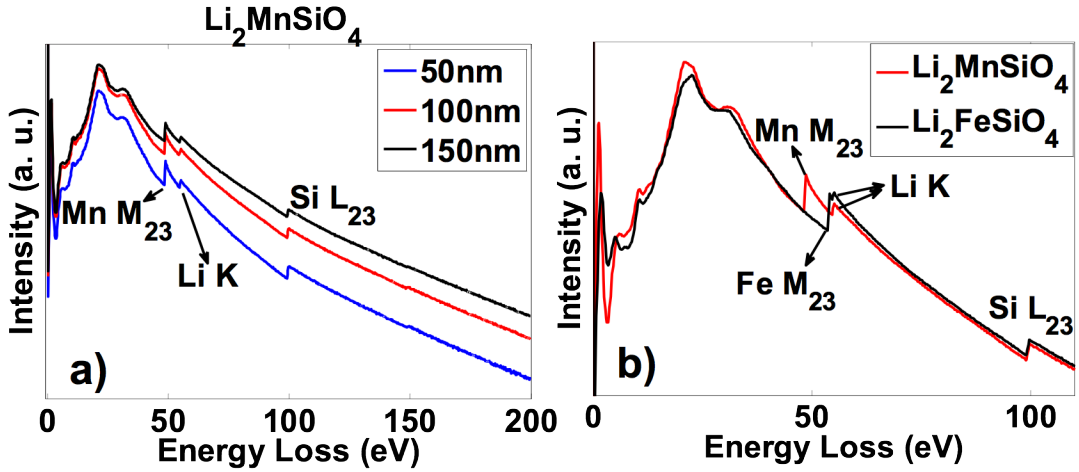

Figure 2. a) Monte Carlo simulations of electron energy loss (EEL) spectra at different thicknesses for Li_2MnSiO_4. b) Comparison between EEL spectra of Li_2MnSiO_4 and Li_2FeSiO_4 at 100nm thickness. For the all EELS simulations, the probe illumination and collection angles were 5 and 10 mrad respectively.

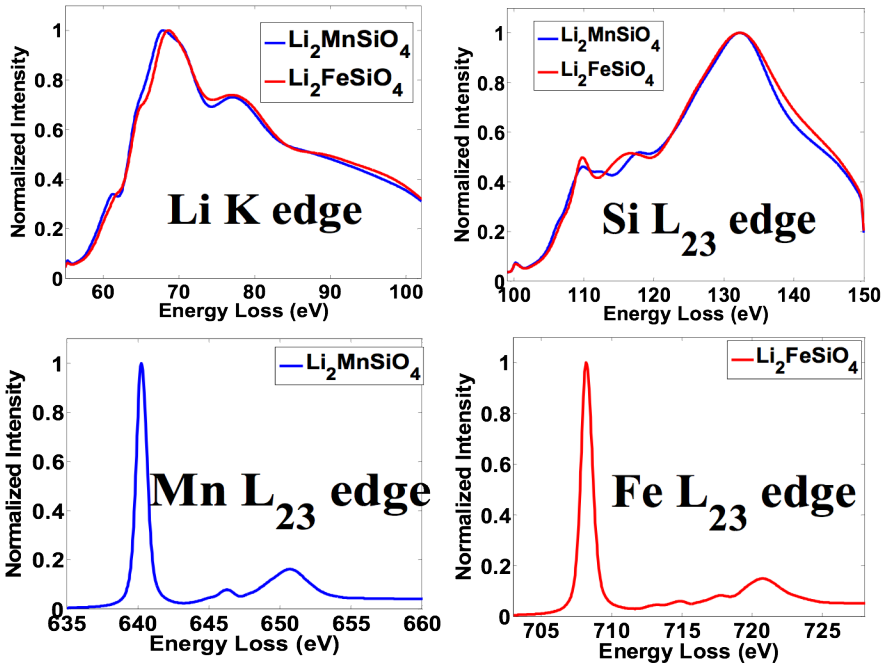

Figure 3. DFT calculations of electron energy-loss near-edge structure (ELNES) of Li K, Si L_{23}, Mn L_{23} and Fe L_{23} edges for Li_2MnSiO_4 and Li_2FeSiO_4.

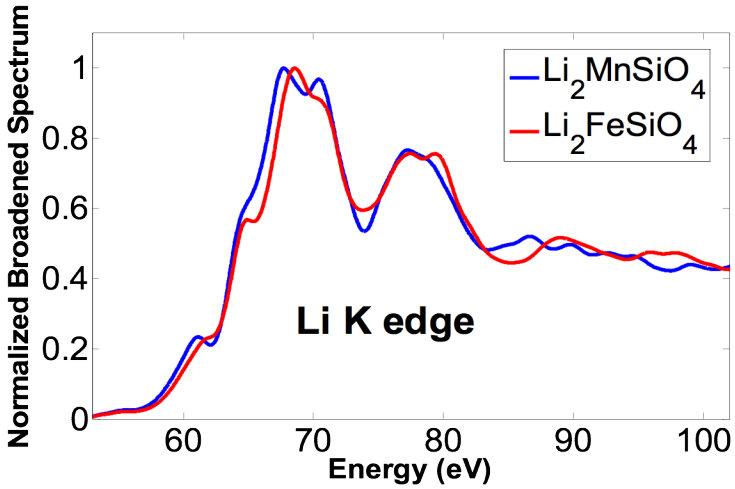

Figure 4. DFT calculations of Li K edge X-ray absorption near edge structure (XANES) for Li_2MnSiO_4 and Li_2FeSiO_4.

Title: **Investigation of Detectability Limits in LiFePO4 by Monte Carlo Simulations of Electron Energy Loss spectra**

Presenting Author: Mohammad Attarian Shandiz

Organization / Institution: McGill University

Co-Author: Francesc Salvat, Universitat de Barcelona
Raynald Gauvin, McGill University

Type: Poster **Session:** P-2

Abstract Summary:

Lithium iron phosphate (LiFePO4) is one of the main candidates as a cathode for rechargeable lithium batteries. LiFePO4 provides high energy density and thermal stability with low cost [1]. Hence, the investigation of proper characterization methods is important for the practical application of these materials. Electron energy loss spectroscopy (EELS) is a capable method for the qualitative and quantitative characterization of materials. Hence, better understanding of the effective parameters of EELS on the detectability of elements in LiFePO4 is important to study. In this research, based on the Monte Carlo (MC) simulation of electron energy loss (EEL) spectra the detectability limit of different elements for LiFePO4 is investigated.

The LEEPS code [2] was adapted to perform MC simulations of EELS spectra. Optical oscillator strength (OOS) was built by combination of low-loss and high-loss regions. For the low-loss region, the energy loss function (ELF) was calculated using Wien2k code [3] based on the density functional theory (DFT) calculations. For the high-loss region, the X-ray photoelectric data [4] was used to build the OOS for the ionization edges.

Figure 1 shows the calculated inverse mean free path (IMFP) and stopping power (SP) for LiFePO4 based on the optical data model calculations. IMFP and SP are essential for the calculations of all the scattering related phenomena in MC simulations. Figure 2 presents the simulated EEL spectra at 200 keV of beam energy with different thicknesses. As it can be seen, by increasing the thickness the jump ratio at different ionization edges decreases. Hence, MC simulation can provide a useful tool to study effect of different parameters of experimental EELS such as thickness on the detection limit of elements.

Figure 3 shows the results of the calculations for the signal-to-noise ratio (SNR) for Li K, O K, P L3 and Fe L2-3 edges at different beam energies (E0) and different thicknesses. The SNR was defined as SNR=(Imax-Imin)/(2Imin)1/2, where Imax and Imin are the intensities above and below the edge. Based on the obtained results at the same conditions of the spectrum acquisition time and the probe current, Li K edge provides the highest amount of SNR. This result demonstrates the potential of EELS for the detection of light elements including Li. After Li K edge, P L3, O K and finally Fe L2-3 edge have the highest SNR. Hence, MC simulations of EELS offers the estimation of detection limits of different elements in LiFePO4. In addition, the results in Figure 3 suggests an optimum thickness for the highest amount of SNR which its value increases by increasing the beam energy.

Investigation of Detectability Limits in $LiFePO_4$ by Monte Carlo Simulations of Electron Energy Loss spectra

M. Attarian Shandiz[1], F. Salvat [2], R. Gauvin[1]

[1] Department of Materials Engineering, McGill University, Quebec Canada.
[2] Facultat de Fisica (ECM), Universitat de Barcelona, Barcelona, Spain

Lithium iron phosphate ($LiFePO_4$) is one of the main candidates as a cathode for rechargeable lithium batteries. $LiFePO_4$ provides high energy density and thermal stability with low cost [1]. Hence, the investigation of proper characterization methods is important for the practical application of these materials. Electron energy loss spectroscopy (EELS) is a capable method for the qualitative and quantitative characterization of materials. Hence, better understanding of the effective parameters of EELS on the detectability of elements in $LiFePO_4$ is important to study. In this research, based on the Monte Carlo (MC) simulation of electron energy loss (EEL) spectra the detectability limit of different elements for $LiFePO_4$ is investigated.

The LEEPS code [2] was adapted to perform MC simulations of EELS spectra. Optical oscillator strength (OOS) was built by combination of low-loss and high-loss regions. For the low-loss region, the energy loss function (ELF) was calculated using Wien2k code [3] based on the density functional theory (DFT) calculations. For the high-loss region, the X-ray photoelectric data [4] was used to build the OOS for the ionization edges.

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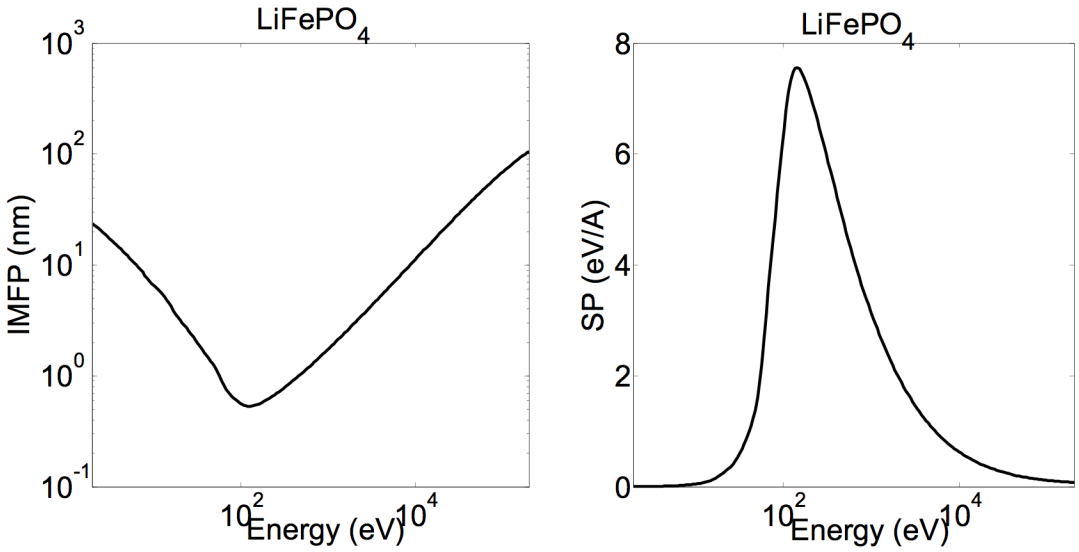

Figure 1. Calculated inverse mean free path (IMFP) and stopping power (SP) for $LiFePO_4$.

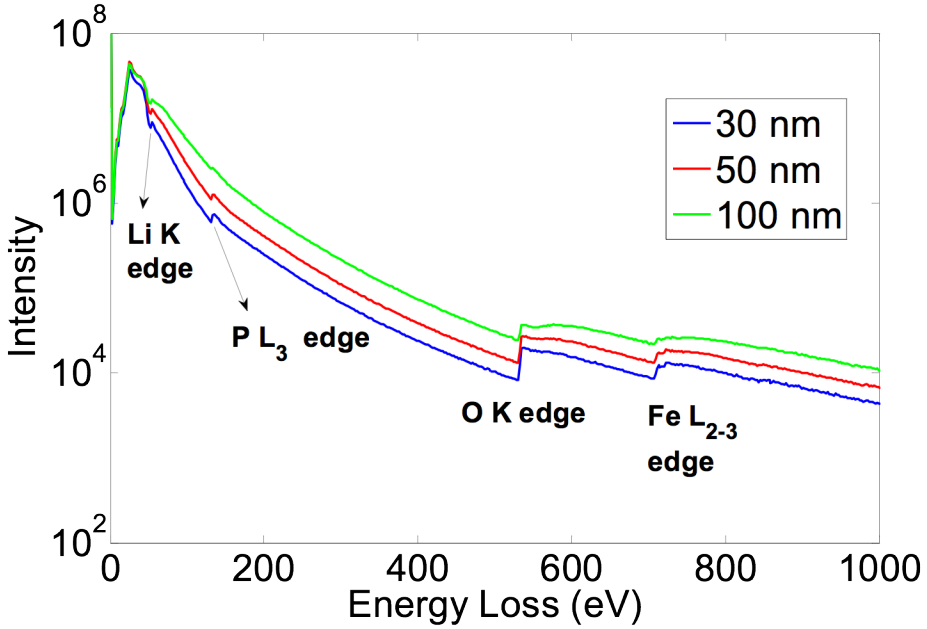

Figure 2. Electron energy loss spectra of $LiFePO_4$ at the beam energy of 200 keV and the thicknesses of 30, 50 and 100 nm. The probe illumination and collection angles were 5 and 10 mrad in the simulations, respectively. Also, the spectrum acquisition time and the probe current were considered 1 s and 1 nA, respectively.

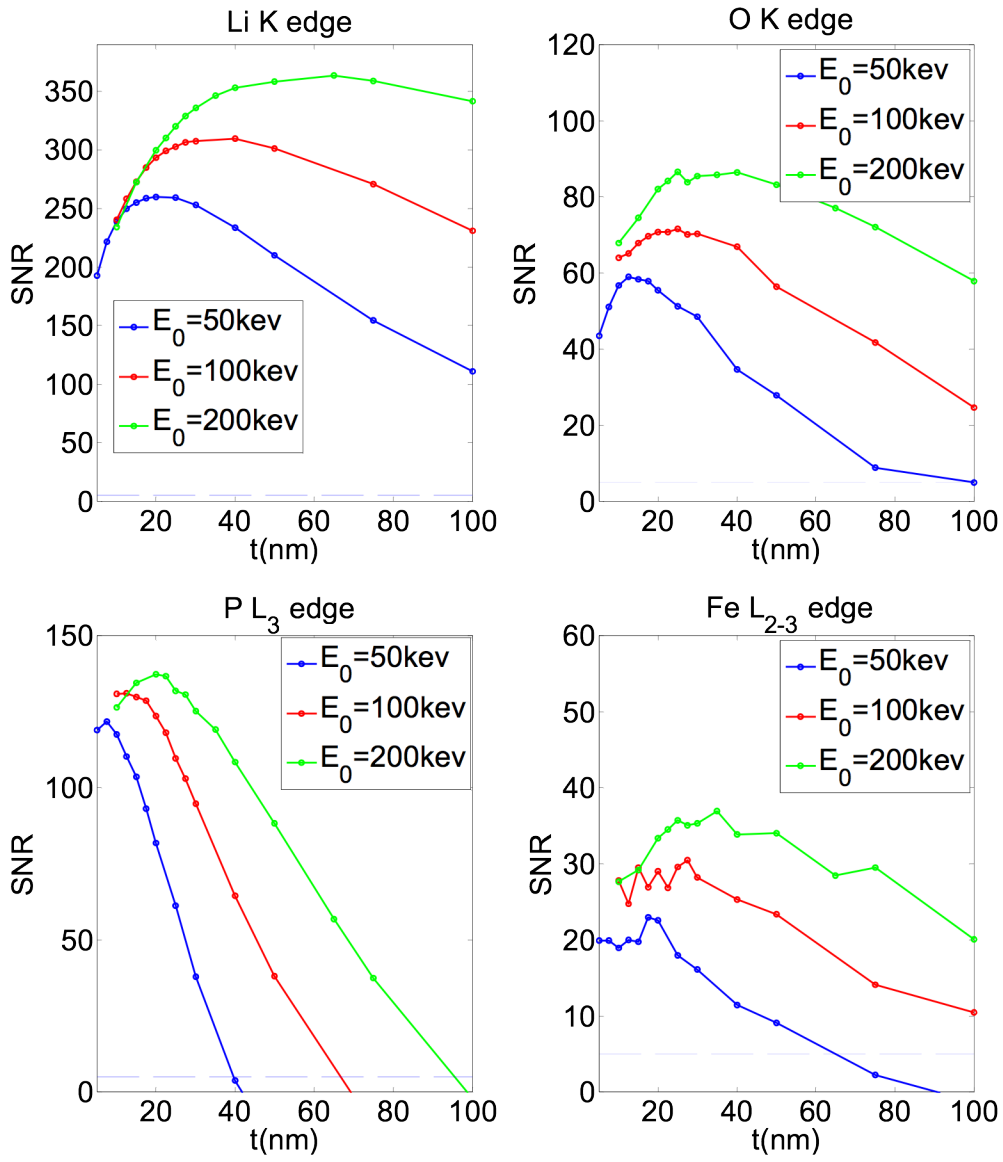

Figure 3. Signal to noise ratio of Li K, O K, P L_3 and Fe L_{2-3} edge at the beam energy (E_0) of 50, 100 and 200 keV with different thicknesses. For the all EELS simulations, the probe illumination and collection angles were 5 and 10 mrad in the simulations, respectively. Also, the spectrum acquisition time and the probe current were set to 1 s and 1 nA, respectively.

Title: MODELISATION OF THE PERFORMANCES OF LiFePO4 COATED WITH CONDUCTING POLYMER

Presenting Author: Danny Chhin

Organization / Institution: UQAM

Co-Author:

Type: Poster **Session:** P-3

Abstract Summary:

Lithium ion batteries has cornered the market for portable electronic device and is currently used in hybrid or electric vehicle. Moreover, the low cost, low toxicity and stability of olivine LiFePO4 makes it a prime candidate as a cathode material for lithium ion batteries. To overcome its poor electronic conductivity, LiFePO4 is often coated with carbon at elevated temperatures (500-700°C). This process leads to the formation of volatile organic compound, CO and CO2.

As an alternative to carbon, the use of conducting polymer as a coating material has been previously explored with positive result. Conducting polymer are both excellent electronic and ionic conductor which makes them as performing as carbon. Also the coating with conducting polymer can be made in much softer condition, i.e. at low temperature in alcoholic solution.

With the growing interest in conducting polymer as a coating for olivine cathode material, an effective model will provide the power vs. energy density trade-off crucial to designing electrodes optimized for a given application. Further, the physical parameters of the model, will yield new insight into the role of the conducting polymer, and why high performance can be obtained from composite electrodes without adding the carbon normally required to ensure good electronic connectivity between the particles. The model that we present is based on Newman's set of equations governing charge transfer and transport which are solved numerically.

Title: **Mesoporous Li4Ti5O12 nanosheets as a negative electrode candidate for LiFePO4 power batteries**

Presenting Author: Hsien-chieh Chiu

Organization / Institution: McGill University

Co-Author: George Demopoulos, McGill University
Karim Zaghib, Institut de recherche d'Hydro-Québec

Type: Poster **Session:** P-4

Abstract Summary:

The growing market of electric and hybrid electric vehicles (EVs/HEVs) stimulates the demand for lithium ion batteries (LIBs) characterized by good specific energy, rate capabilily, safety and overall reliability. A promising battery system in this context is the LiFePO4-Li4Ti5O12 (LFP-LTO) couple that shows superior performance as was demonstrated for example by Guerfi et al. [1], who presented extended cycle life data for about 20,000 cycles; and by Zaghib et al. [2], who reported a remarkable thermal stability. In the present research, mesoporous LTO nanosheets prepared via a purely aqueous process [3] are evaluated from the standpoint of a high power LFP battery by performing extensive structural and electrochemical characterization, including TEM, Raman, FTIR, synchrotron XRD and XANES.

The newly-synthesized mesoporous LTO nanosheets have pores in 12±5.7 nm range, which are generated during grain growth upon annealing of the precursor phase at 500 oC. Meanwhile, annealing helps stabilize the structure of the synthesized LTO nanosheets via strain relief and Li ion redistribution. As a result of their particular physical characteristics the mesoporous LTO nanosheets attain 225 mAh/g discharge capacity during the first cycle, which is in line with the description of nano-LTO [4]; and exhibit excellent stability during cycling (>90% retention after 150 1C rate cycles). In conclusion, the mesoporous LTO nanosheet material looks very promising as anode in LFP-LTO power batteries.

Mesoporous $Li_4Ti_5O_{12}$ nanosheets as a negative electrode candidate for $LiFePO_4$ power batteries

Hsien-chieh Chiu[1], Jigang Zhou[2], Joel Reid[2], Samir Elouatik[3], Nicolas Brodusch[1], Xia Lu[1], Raynald Gauvin[1], AbdelbastGuerfi[4], Karim Zaghib[4] and George P. Demopoulos[1,*]

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The growing market of electric and hybrid electric vehicles (EVs/HEVs) stimulates the demand for lithium ion batteries (LIBs) characterized by good specific energy, rate capabilily, safety and overall reliability. A promising battery system in this context is the $LiFePO_4$-$Li_4Ti_5O_{12}$ (LFP-LTO) couple that shows superior performance as was demonstrated for example by Guerfi et al. [1], who presented extended cycle life data for about 20,000 cycles; and by Zaghib et al. [2], who reported a remarkable thermal stability. In the present research, mesoporous LTO nanosheets prepared via a purely aqueous process [3] are evaluated from the standpoint of a high power LFP battery by performing extensive structural and electrochemical characterization, including TEM, Raman, FTIR, synchrotron XRD and XANES.

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Title: **Chemical grafted carbon-coated LiFePO4 using diazonium chemistry**

Presenting Author: Nicolas Delaporte

Organization / Institution: UQAM

Co-Author:

Type: Poster **Session:** P-5

Abstract Summary:

Chemical grafted carbon-coated LiFePO4 using diazonium chemistry

Nicolas Delaporte1, Alexis Perea1, Ruhul Amin1, Karim Zaghib2# and Daniel Bélanger1*

1. Département de Chimie, Université du Québec à Montréal, Case Postale 8888, succursale Centre-Ville, Montréal (Québec) Canada H3C 3P8.
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Lithium iron phosphate LiFePO4 with olivine structure has become of great interest as a potential storage cathode for the next generation lithium-ion batteries, particularly for hybrid electric vehicle applications, because of its high energy density, low cost, safety and environmental compatibility [1]. The Li+ ion can be extracted/inserted from/into LiFePO4 at the electrode potential of 3.5 V versus Li/Li+, and the theoretical discharge capacity is 170 mA.h.g-1. The stability of LiFePO4 is ensured with strong P-O covalency of the polyanion (PO4)3- [2]. On the other hand, the major drawback of LiFePO4 is the decrease of capacity with increasing charge/discharge current density, associated with its fundamentally low electronic and ionic conductivity. Since the first work of Padhi et al.[1], many studies have attempted to overcome this obstacle with particle-size reduction, surface coating, doping and conducting agents [3] [4] [5] [6] [7].

In order to improve the electrochemical properties of LiFePO4/C powder, a new grafting method for carbon coated cathode material was adopted in this study inspired from the previous studies of carbon modification [8]. The reduction of diazonium cations has been widely investigated during the past decades in order to functionalize surfaces [8-9]. Toupin and Bélanger [10] have undertaken detailed studies of the spontaneous reaction between Vulcan carbon black and aryldiazonium salts in aqueous solution. This method allows the attachment of various substituted aryl groups with a strongly C-C bond in order to change the surface properties. The reduction of in situ generated diazonium cations in organic media leads to the functionalization of the carbon coating of LiFePO4/C.

This presentation will focus on the study of LiFePO4/C cathodes for Li-ion batteries. More specifically, the aim of this work is to functionalize the carbon coating of LiFePO4/C particles using diazonium chemistry. Up to now, the work focused on grafting aromatic amine molecules in order to increase the electrode capacity and to enhance the surface reactivity between electrolyte and active material. Several organic groups were successfully grafted on carbon coating by reduction of in situ generated diazonium ions. An increase of specific capacity has been observed during cycling in coin-cell and more specifically at high rate.

The grafting reaction onto the carbon coating leads to a partial oxidation of LiFePO4/C related to the amount of precursors used for the reaction. X-ray diffraction patterns show the presence of LiFePO4/C and FePO4 phases.. ICP analyses were performed in order to determine accurately the lithium content of the grafted samples. The ratios of LiFePO4 and FePO4 deduced from ICP analyses are consistent with those obtained with XRD measurements. Using EDX, the presence of grafted molecules on the carbon coating of LiFePO4/C was confirmed.

Galvanostatic measurements at various current rates were carried out to further compare the electrochemical performances of LiFePO4/C blank and grafted samples. At current rates of 0.1 and 5C, the grafted LiFePO4/C electrode displays an improvement of 7 and 28 % of the discharge capacity, respectively, compared to the blank LiFePO4/C sample. The specific capacity of the grafted LiFePO4/C sample is enhanced even at high current rates and the discharged capacity reach up to 109 mAh.g−1 at 5 C retaining almost 64 % of the theoretical capacity. From these results, the rate capability enhancement of the grafted samples can be explained by the presence of specific grafted groups onto the surface of the LiFePO4/C particles that can “improve” the interfacial properties at the electrode particles/electrolyte interface. Future work will focus on the characterization of the surface of the grafted LiFePO4/C.

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Title: **Redox Centers Evolution in Phospho-Olivine Type (LiFe0.5Mn0.5 PO4) Nanoplatelets with Uniform Cation Distribution**

Presenting Author: Enrico Dilena

Organization / Institution: Italian institute of technology

Co-Author: Andrea Paolella, McGill
George Chandramohan, Italian institute of technology

Type: Poster **Session:** P-6

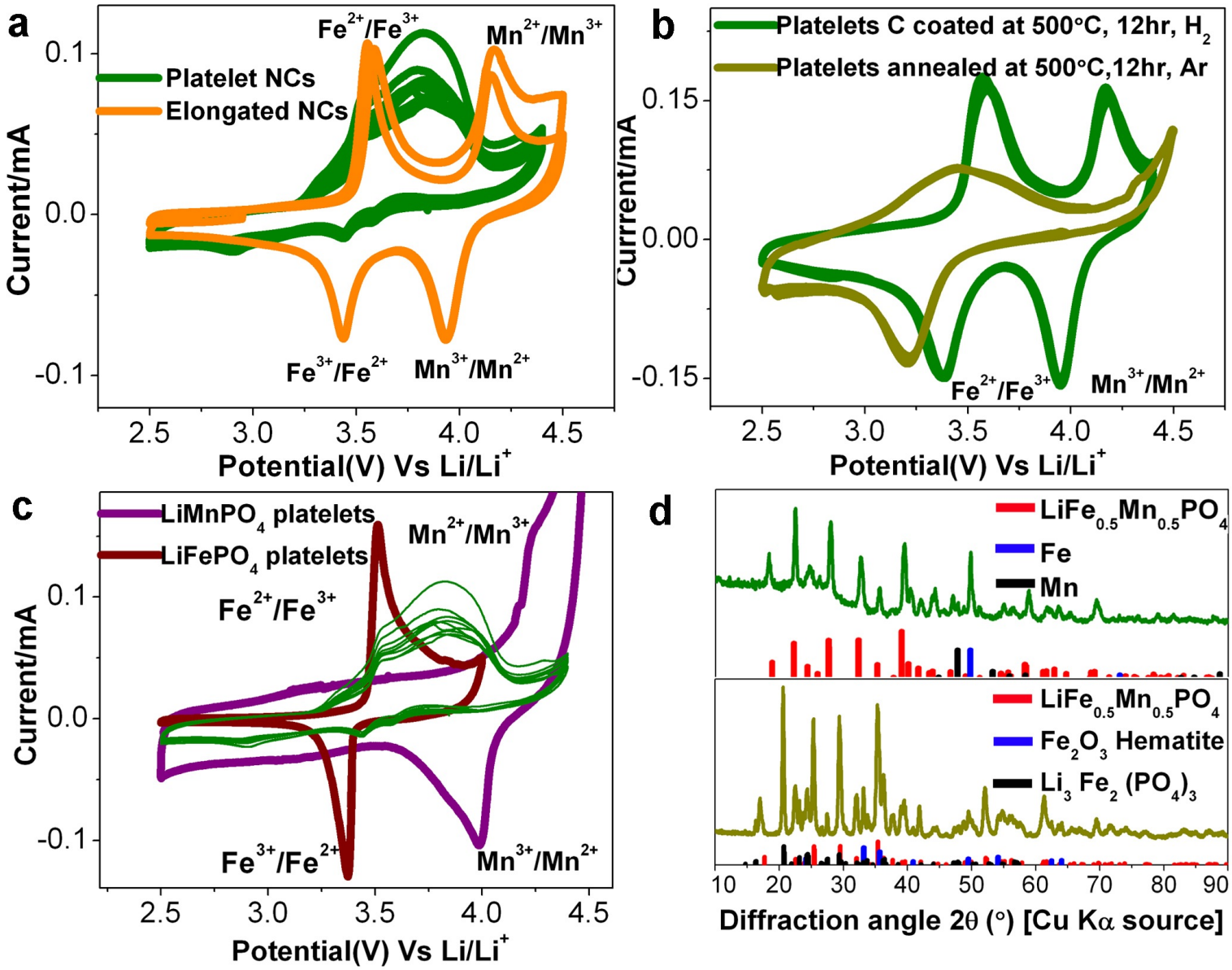
Abstract Summary:

Abstract Summary: We report colloidal LiFe0.5Mn 0.5PO4 nanocrystals that exhibit a more homogenous distribution of cations in the lattice, leading to a synergetic effect on the redox potentials in contrast to the samples obtained via hydrothermal route.

Introduction: Over the last decades of intensive research, phospho-olivine type electrode materials have been identified as serious contenders for high power electrode series, pioneered by Padhi and Goodenough. LiFePO4 with a redox potential of 3.4 V vs. Li/Li+ is extremely interesting due to its reversible topotactic Li extraction, cyclability, exceptional stability, and flat-voltage characteristics. The influence of Mn on the reversible Li ions extraction process on LiFe0.4Mn0.6PO4 was further detailed by Yamada and co workers9,10 by analyzing their phase diagram. LiFe0.5Mn0.5PO4 platelet shaped nanocystals (NCs) obtained via colloidal synthesis, exhibit different redox behavior when compared structurally with submicron crystals prepared via hydrothermal route.

A direct comparison between the colloidal NCs and hydrothermal samples reveals that Fe and Mn were well mixed in the colloidal NCs. The CV data as reported in the Figure (the orange curve) clearly evidenced both the redox centers by two distinct redox peak positions at 3.5 V and 4.1V, corresponding to Fe2+/Fe3+ and Mn2+/Mn3+ respectively in the case of hydrothermal LiFe0.5Mn0.5PO4. On the other hand, the colloidal NCs differ strikingly from the hydrothermal sub-micron crystals in their redox peaks (Figure 4a green curve), and their corresponding charge/discharge curves that exhibited only a sloping plateau from 3.9 to 2.5V, instead of the two standard plateaus. We gave a carbon coating around the NCs at 500□C for 12hr under H2. For instance, after 1 hr of carbon coating at 500°C under H2, the samples showed clear peaks related to mainly Mn redox (Mn2+/Mn3+ at 4.1V) in CV, while almost no activity for Fe was observed. This was reflected in the STEM images acquired after the first 1 hr annealing, revealing that Fe cations diffused out of the NCs, forming Fe metallic grains. The presence of the metallic domains (Fe or Mn) was not observed in CV measurements since they are much active in potentials below 2.5V. In the samples (that were in carbon coating for 6hr at 500°C under H2/Ar), both the redox peaks were slightly evolved with a decrease in Mn activity, indicating a continuous cations re-arrangement in the carbon coating process. On the other hand, we also annealed the samples only under Ar at 500□C for 12hr. The CV response of those samples was not in exact match as that of LiFe0.5Mn0.5PO4 but evidenced a redox activity much lower than standard olivine structures. XRD patterns of those samples showed that the extracted Fe cations form hematite (Fe2O3) crystals, which could indeed distort heavily the metal phosphates crystals by removing their oxygen (since there was no hydrogen to reduce the metals). We then again analyzed via HRTEM the samples that gave well defined two redox peaks. Now, a pronounced separation between Mn and Fe rich regions was clearly visible in the colloidal NCs after annealing in the carbon coating, showing pronounced contrast differences in the Mn and Fe maps observed from EFTEM, similar to what was observed in the hydrothermal sample. The two peaks in the CV are related to Fe or Mn preferential channels present in the Fe or Mn rich regions on the samples. This separation cannot be observed in the original colloidal platelets due to the higher mixing of Mn and Fe atoms in the crystals.

In conclusion, we reported colloidal LiFe0.5Mn0.5PO4 platelet NCs with the Fe and Mn cations well intermixed. During the typical carbon coating process under H2, the NCs underwent annealing at 500°C. EFTEM data revealed a rearrangement of the Fe and Mn cations into domains with preferential Fe or Mn occupation at the M2 sites (i.e. closer to either triphylite or lithiophilite, respectively). CV and charge/ discharge profiles of the LiFeMnPO4 NCs have been followed as a function of annealing (during carbon coating) time, in order to study their electrochemical properties. Our electrochemical data in conjunction with EFTEM/HRTEM analysis clearly point out that the cations (Fe and Mn) mixing with respect to the Li ion position in the olivine lattices may be responsible for the distinct activity for both (Mn 2+/Mn 3+ at 4.1V) and (Fe 2+/Fe 3+ at 3.5 V) redox centers in the olivine type LiFe0.5Mn0.5PO4 structures. Our findings open new ways into the structural engineering of olivine structures, for instance, nanostructures with target cation arrangements in olivine lattices, or nanostructures with a complete phase-segregated dumbbells/dimers or core/shells type structures for better optimizing their electrochemical properties.


a
Platelet NCs
Elongated NCs
Fe2+/Fe3+
Mn2+/Mn3+
Fe3+/Fe2+
Mn3+/Mn2+
Current/mA
Potential(V) Vs Li/Li+
b
Platelets C coated at 500°C, 12hr, H2
Platelets annealed at 500°C,12hr, Ar
Fe2+/Fe3+
Mn3+/Mn2+
Currrent/mA
Potential(V) Vs Li/Li+
c
LiMnPO4 platelets
LiFePO4 platelets
Mn2+/Mn3+
Fe2+/Fe3+
Fe3+/Fe2+
Mn3+/Mn2+
Current/mA
Potential(V) Vs Li/Li+
d
LiFe0.5Mn0.5PO4
Fe
Mn
LiFe0.5Mn0.5PO4
Fe2O3 Hematite
Li3 Fe2 (PO4)3
Diffraction angle 2θ (°) [Cu Kα source]

Title: **Surface Reactivity of Nano-LiFePO4 in Water Ambient: Electrochemical Performance vs. Aging**

Presenting Author: Martin Dontigny

Organization / Institution: IREQ

Co-Author: Christian M. Julien, Sorbonne Universités, UPMC Univ. Paris 6
Alain Mauger, Université Pierre et Marie Curie
Julie Trottier, IREQ
Abdelfast Guerfi, IREQ
Pierre Hovington, IREQ

Type: Poster **Session:** P-7

Abstract Summary:

See PDF below

Surface Reactivity of Nano-$LiFePO_4$ in Water Ambient: Electrochemical Performance vs. Aging

M. Dontigny[1], J. Trottier[1], P. Hovington[1], A. Guerfi[1], A. Mauger[2], C.M. Julien[3], K. Zaghib[1]

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$LiFePO_4$ is the active element of cathode in a new generation of Li-ion batteries. For high-power applications, like electric or hybrid vehicles, however, the size of the particles needs to be reduced to few nanometers, in which case the physical as well as chemical properties are mainly surface effects. Recently, the investigation of iron properties at the surface has shown the existence of a surface layer, a few Å thick, which is disordered. In this layer, the iron ions are in the Fe^{3+} low-spin or high-spin configuration, depending on the carbon coating and thermal treatment. Results show the evidence that the surface is sensitive to its environment. First investigations also show that the surface reacts with H_2O [1-3].

We present in this work the study of the reaction of the particles with this molecule, through the change in the properties when the C-$LiFePO_4$ particles are dropped into water, or are simply exposed to humid (ambient) atmosphere. The reactivity has been studied for particles prepared by two synthesis routes (solid-state and hydrothermal). In both cases, we find that the carbon coat is permeable to water, and does not protect the particles against dissolution of the surface layer when the powder is dropped in water.

The analysis of the water composition, however, shows that only the more or less disordered surface layer, about 4 nm-thick, is dissolved. The reaction, however, stops after this dissolution of the first layer has been achieved, presumably because of the formation of a $FePO_4$ layer that is hydrophobic, and not permeable to water. The result is about the same as that of the phosphatation industrial process forming an iron phosphate layer at the surface of iron, to protect it against oxidation and exposure to water. In addition, we find that part of the carbon coat detaches from the particles upon immersion in water. However, the amount of carbon that is detached, easily detected by the fact that it floats in water, is small, so that the percolation of the particles through the carbon layer is still insured. This important result explains that the electrochemical properties measured after drying of the particles have not been degraded significantly by the immersion in water.

When exposed to ambient (humid) atmosphere, the reaction is much more limited, because the iron and phosphate that could dissolve in water cannot evaporate. As a consequence, the only sizeable effect of the air exposure is the loss of lithium in the surface layer, again leading to the formation of an iron phosphate layer that protects the particles from further degradation, at least at the scale of few months. The reactivity of the first layer with H_2O is then essentially the reactivity of Li, and it implies hydrophilic behavior of the $LiFePO_4$ particles that has been measured as a function of time exposure to humid ambient. However, the water that has been captured by the material can easily be removed by simply heating it in dry atmosphere, and the electrochemical performance after drying has not been degraded. Like in the case of the immersion of water, the exposure to humidity does not degrade the electrochemical performance either.

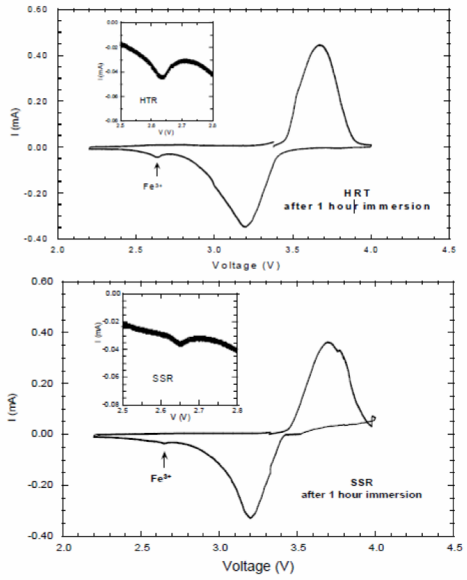

Fig. 1. Voltammetry for the SSR- and HTR-LFP samples, after immersion in water for 1 h. Arrows point to the Fe^{3+} peak. In these measurements, an initial 3.2 V working potential was applied. Then, the voltage was varied at the rate 1.25 mV/min.

As a conclusion, we find that the reactivity to humidity is effective, but limited to the first disordered layer of the $LiFePO_4$ particles. After drying, the electrochemical performance is recovered, since the $FePO_4$ layer that has been formed can be lithiated again, so that on overall the initial configuration of the product is recovered.

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OREBA 1.0

Title: **LiFePO4 Nanoparticles Synthesized by the Molten Ingot Route**

Presenting Author: Amélie Forand

Organization / Institution: Hyro-Quebec

Co-Author:

Type: Poster **Session:** P-8

Abstract Summary:

See PDF below

$LiFePO_4$ Nanoparticles Synthesized by the Molten Ingot Route

A. Forand[1], M. Dontigny[1], J. Trottier[1], P. Hovington[1], A. Guerfi[1], A. Mauger[2], C. Julien[2], K. Zaghib[1]

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Prior woks have shown that lithium iron phosphates (LFP) crystallized with olivine structure could be used as positive electrode materials for high power density lithium ion batteries applied for HEV and EV. However, for such applications, three drastic conditions are required in formatting $LiFePO_4$ particles: (i) their size must be in the range 20-50 nm to reduce the pathway of Li^+-ion, (ii) a conductive film must be deposited at their surface, e.g. carbon coating, to enhance the electronic conduction, and (iii) particles must be free of any impurities, e.g. Fe^{3+}-containing phase [1-3].

Implementation of such mandatory terms requires combination of efficient and cheap synthetic procedure and studies of bulk and surface properties of prepared LFP particles [4].

This was the aim of this work. LFP particles have been obtained by grinding ingot synthesized in the molten state. Fig. 1 shows the flowchart for the preparation of $LiFePO_4$ powders (*d* is the mean size of the primary particles investigated in this work). Particles were obtained at the different steps of the process and measured from the analysis of SEM images.

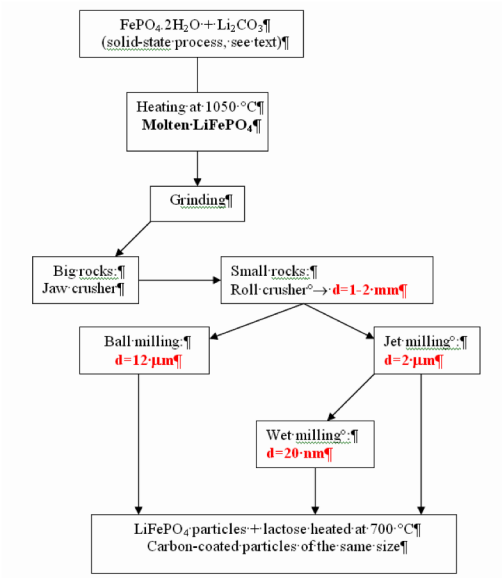

FIG. 1. Flowchart for the preparation of $LiFePO_4$ powders from the synthesis in the molten state.

This process, followed by jet milling, and then wet milling, provides a simple way to obtain powders with monitored size of the particles in the whole range from macroscopic to 20 nm, although at this stage, we find that these particles tend to segregate to form secondary particles of size ~100 nm.

The electrochemical properties of LFP particles have also been investigated at the different steps of preparation: ball milling, jet milling, wet milling and after carbon coating. As shown in Fig. 2, results display (A) the charge-discharge profiles of the cell prepared with the wet-milled powder after carbon coating with heat treatment under Ar (a) and N_2 (b) atmosphere and (B) the Peukert plot for wet-milled C-$LiFePO_4$//Li cell using 1*M* $LiPF_6$+EC:DEC (1:1) as electrolyte.

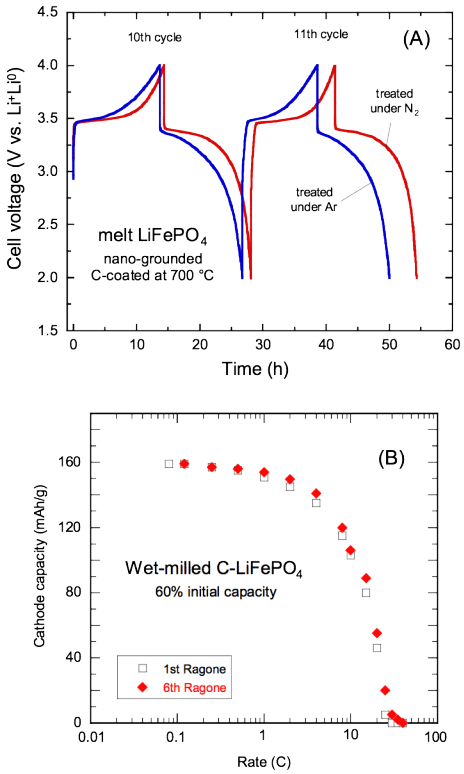

FIG. 2. (A) Charge-discharge profiles of Li//LFP cells prepared with the wet-milled LFP powder after carbon coating with heat treatment under Ar (a) and N_2 (b) ambient. (B) Peukert plot for wet-milled Li//LFP cell.

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[1] C.M. Julien, A. Mauger, A. Ait-Salah, M. Massot, F. Gendron, K. Zaghib; *Ionics* **13** (2007) 395.
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OREBA 1.0

Title: **Fast Charge of LTO-LFP Li-ion Batteries**

Presenting Author: Catherine Gagnon

Organization / Institution: Hydro-Québec

Co-Author:

Type: Poster **Session:** P-9

Abstract Summary:

See PDF below

Fast Charge of LTO-LFP Li-ion Batteries

C. Gagnon[1], F. Barray[1], P. Hovington[1], J. Trottier[1], A. Guerfi[1], K. Zaghib[1], A. Mauger[2], C.M. Julien[3]

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The standard anode of the Li-batteries is carbon based. However, carbon requires formation of a solid/electrolyte-interface (SEI) to prevent the formation plating of Li on the carbon anode during a fast charge of the battery, and the SEI layer is responsible of an irreversible capacity loss. Instead, we used $Li_4Ti_5O_{12}$ (LTO). This spinel structure has been proposed as a promising candidate as a negative electrode with different positive electrodes, including $LiFePO_4$. The electro-activity occurs at a voltage higher than 1.0 V. Therefore, the electrode does not experience the passivation of the anode materials and their inevitable electrolyte reaction. Also the lack of strain in this material improves the shelf life, and is another improvement with respect to the carbon that suffers dilatation/contraction upon insertion/extraction of lithium resulting in aging.

We report a 18650-type Li-ion battery that can be charged within few minutes, passes the safety tests, and has a very long shelf life. The active materials are nanoparticles of LFP and LTO for the positive and negative electrodes, respectively. LFP particles are covered with 2 wt.% carbon to optimize the electrical conductivity, but not the LTO particles. The electrolyte is the usual carbonate solvent. The binder is a water-soluble elastomer.

LFP was synthesized by the molten-ingot route in a rock of 10 cm size that was later reduces using roll-crusher and jet-mill process in isopropyl alcohol down to 100 nm. The carbon coating (5 wt.%) was performed using the lactose technique. LTO was prepared by solid-state reaction of precursor materials TiO_2, Li_2CO_3 and carbon heated at 850 °C for 18 h. After milling, LTO nanoparticles were obtained with 150 nm size. The electrochemical performance of the LFP and LTO materials has been tested separately in half cell with respect to Li metal anode, using the same electrolyte 1mol L^{-1} $LiPF_6$ in EC-DEC. It is shown that LFP//Li and LTO//Li 18650-type cells exhibit good coulombic efficiency (CE)

Galvanostatic charge-discharge curves at different cycles, i.e. 1st, 10,000th, 20,000th and 30,000th, for both 10C charge rate and 15C charge rate are shown in Figs. 1. To complement the electrochemical performance of the LFP//LTO 18650-batteries, the cycling life is illustrated for charge rate at 10C (6 min) and discharge rate 5C (12 min). Even after 20,000 cycles, the cell did not loose its initial capacity. The voltage-capacity curves for the LTO//LFP cell during the test are showing very little difference, even at the end of the test.

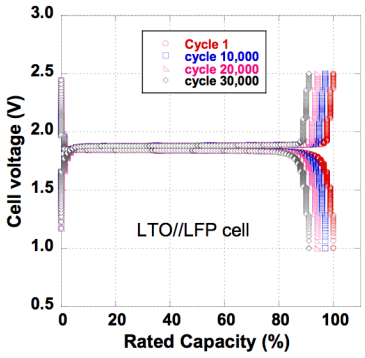

FIG. 1.

Demonstrator (Fig. 2). Car equipped with the battery C-LFP/LTO studied. Charging time is reduced to 5 min with three levels charger in parallel (500 V, 125 A).

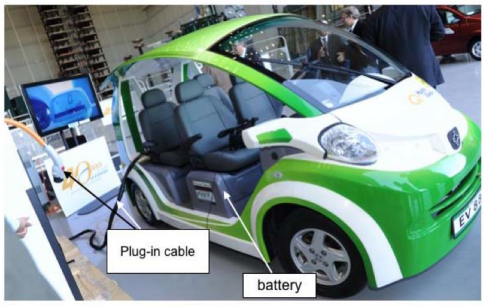

FIG. 2.

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Title: **Synthesis of Nanosized LiFePO4 Powders by Hydrothermal Method via Solution Stirring**

Presenting Author: Vincent Gariépy

Organization / Institution: IREQ

Co-Author: Christian M. Julien, F. Barray, C. Gagnon, Pierre Hovington, Alain Mauger

Type: Poster **Session:** P-10

Abstract Summary:

See PDF below

Synthesis of Nanosized $LiFePO_4$ Powders by Hydrothermal Method via Solution Stirring

V. Gariépy[1], J. Trottier[1], C. Gagnon[1], F. Barray[1], P. Hovington[1], A. Guerfi[1], A. Mauger[2], C.M. Julien[3], K. Zaghib[1]

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Among the various methods developed for the preparation of $LiFePO_4$ (LFP) cathode materials, the hydrothermal synthesis offers a simple solution to the practical and scale-up problems [1-2]. The hydrothermal/solvothermal approach is particularly successful to control the chemical composition and crystallite size. The conventional hydrothermal process involves a reaction time 5-12 h to synthesize LFP with the advantage of synthesis temperature as low as 180°C. It is thus a low energy consuming synthesis process.

In this work, LFP cathode materials were prepared by hydrothermal method assisted by steering that maintained the agitation of the solution during the sample synthesis. Structural identification, surface morphology and electrochemical cycling are reported for two samples, one synthesized by conventional hydrothermal process, the other one assisted by stirring at 600 rpm, for comparison. In both cases the same types and ratios of precursors were used, namely: $LiOH{\bullet}H_2O$, $FeSO_4{\bullet}7H_2O$, H_3PO_4 (85 wt.%) and ascorbic acid as carbon source in stoichiometric molar ratios of Li, Fe, P and C (3:1:1:0.2). Annealing was done at 700°C under nitrogen atmosphere as previously described in [2].

The net result of the hydrothermal synthesis of $LiFePO_4$ via solution steering is twofold (i) formation of nano-particles (<50 nm) and (ii) narrow grain size distribution. Fig. 1 shows the SEM images of LFP particles prepared by (a) the conventional and (b) the rotating-assisted hydro-thermal methods.

The electrochemical properties were analyzed in the cut-off voltage range 2-4.0 V *vs*. Li at room temperature and at 55 °C (Fig. 2). The LFP material synthesized via the rotating method retains more than 98% of the coulombic efficiency even after 20 cycles at C/20 rate. The hydrothermal synthesis of nano-$LiFePO_4$ via solution steering is very effective in producing smaller cathode particles at high yield with very good capacity retention characteristics for use in rechargeable Li-ion batteries.

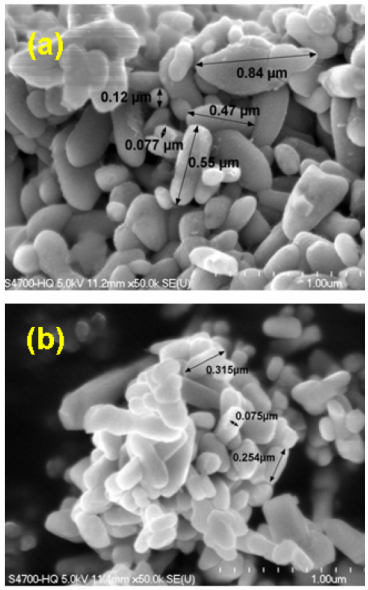

FIG. 1 SEM images of LFP particles prepared by (a) the conventional and (b) the rotating-assisted hydrothermal methods.

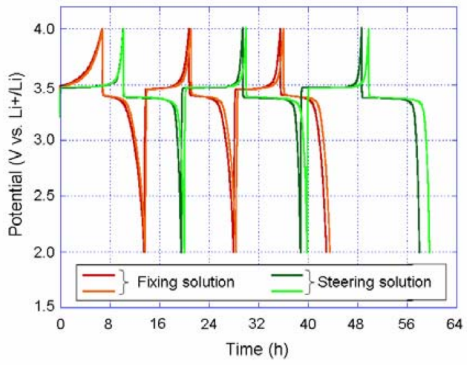

FIG.2. Charge-discharge profiles of Li//LFP cells with cathode materials synthesized by conventional and rotating hydrothermal routes. The electrolyte was 1.0 $mol.L^{-1}$ $LiPF_6$ in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1, v/v).

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[2] F. Brochu, A. Guerfi, J. Trottier, M. Kopec, A. Mauger, H. Groult, C.M. Julien, K. Zaghib, J Power Sources 214 (2012) 1.

Title: **Electrochemistry of Mn-substituted LiFePO4 electrode materials for Li-ion batteries**

Presenting Author: Abdelbast Guerfi

Organization / Institution: Hydro-Québec

Co-Author: Pierre Hovington, Hydro-Québec
Julie Trottier, Hydro-Québec

Type: Poster **Session:** P-11

Abstract Summary:

See PDF below

Electrochemistry of Mn-substituted $LiFePO_4$ electrode materials for Li-ion batteries

A. Guerfi[1], P. Hovington[1], J. Trottier[1], V. Gariépy[1], M. Trudeau[1], A. Mauger[2], C.M. Julien[3], K. Zaghib[1]

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Among the lithium transition-metal phosphates $LiMPO_4$ (M=Fe, Mn, Co, Ni) with an ordered olivine structure, $LiMn_yFe_{1-y}PO_4$ is of particular interest because the high structural stability due to strong covalent bonds between P^{5+} and O^{2-} to form the PO_4^{3-} tetrahedral polyanion. The P_{tet}-O-M_{oct} linkage in the structure induced the superexchange interaction that tunes the M^{2+}/M^{3+} redox potential to useful levels (3.45 and 4.15 V *vs.* Li^0/Li^+ for Fe^{2+}/Fe^{3+} and Mn^{2+}/Mn^{3+}, respectively), which is called the "inductive effect". Thus, the position of the redox couple Mn^{2+}/Mn^{3+} at 4.1 V *vs.* Li^+/Li^0 is compatible with the cathode used in commercial lithium-ion batteries. The solid solution $LiFe_{1-y}Mn_yPO_4$ looks promising because it operates at 3.4-4.1 V that is not so high as to decompose the organic electrolyte but not so low as sacrifice energy density [1-3].

We report the structural and electrochemical properties of the series $LiMn_yFe_{1-y}PO_4$ ($0.5<y<0.8$) electrode materials synthesized by hydrothermal route. The synthesis, morphology and cathode performance are also presented in details.

The optimized LMFP powders were prepared by the hydrothermal route with control of the pH at 5.5. SEM and TEM pictures (Fig. 1) show that the morphology of $LiFe_{0.5}Mn_{0.5}PO_4$ powders is appropriate as cathode materials for Li-ion batteries. The characteristics of the carbon coating were analyzed by Raman spectroscopy, while the structural properties upon Li extraction-insertion reaction were investigated by FTIR spectroscopy.

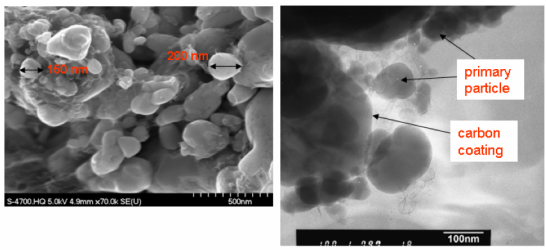

FIG. 1. SEM and TEM image of $LiFe_{0.5}Mn_{0.5}PO_4$ powders.

Fig. 2 shows the typical charge-discharge profiles of the Li//$LiMn_yFe_{1-y}PO_4$ (y=0.5) cells carried out at the 1C rate (170 mA/g) and the rate capability for y=0.8. The charging curve displays two distinct plateaus with small different width which indicate that the Li extraction occurs at the Fe^{2+}/Fe^{3+} and Mn^{2+}/Mn^{3+}, respectively. Electro-chemical features show that the coexistence of Mn with Fe at 4*c* site does not influence the redox behavior of Fe^{2+}/Fe^{3+} but improves the redox kinetics.

The polarization potential increases slightly for the Mn-rich compounds due to the formation of the intrinsic defect-type with the lowest energy in the cation antisite defect, in which Li and Fe/Mn ions exchange positions. The LMFP solid solution looks promising because it operates at 3.4–4.1 V that is not so high as to decompose the organic electrolyte but not so low as to sacrifice energy density.

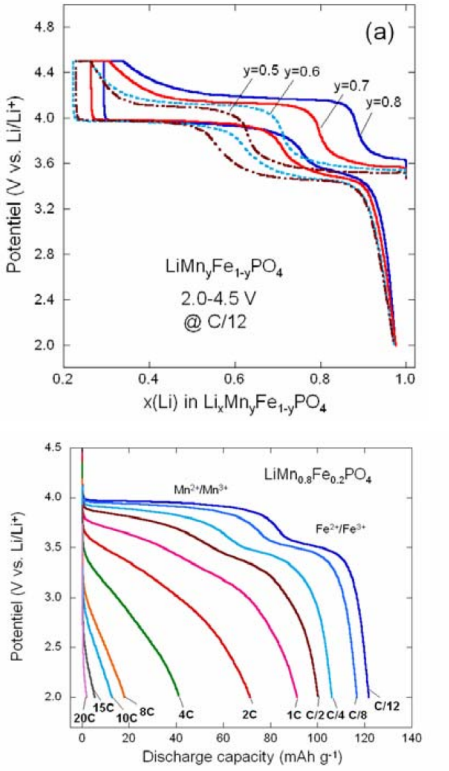

FIG. 2. The typical charge-discharge curves for the optimized LMFP for y=0.5 and rate capability for y=0.8.

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3. K. Zaghib, M. Trudeau, A. Guerfi, J. Trottier, A. Mauger, R. Veillette, C.M. Julien, *J. Power Sources* 204 (2012) 177.

Title: **High Stability of Solid State Li/LiFePO4 Polymer Electrolyte rechargeable battery**

Presenting Author: Julie Hamel

Organization / Institution: Hydro-Quebec

Co-Author:

Type: Poster **Session:** P-12

Abstract Summary:

See PDF below

High Stability of Solid State Li/LiFePO4 Polymer Electrolyte rechargeable battery

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Introduction

Dry-polymer electrolyte lithium secondary batteries have been extensively studied for three decades, with the intention that this technology will overcome the safety problem, the energy density, and the cost of conventional liquid electrolyte systems [1,2]. However, by using a polymer electrolyte, there is a voltage limitation in the positive electrode side. Conventional cathodes such as $LiCoO_2$ and $LiMn_2O_4$, which operate at > 4.0V, are difficult to use stably the PEO-based electrolyte [3,4]. In the other side, reversible electrode material, $LiFePO_4$ is known to be safe at elevated temperatures and shows a reversible electrode potential of around 3.5V vs. Li° which is consistent with the polymer performance. Furthermore, $LiFePO_4$ comprises abundant elemental iron, which is environmentally favorable. Among the cathodes, $LiFePO_4$ is considered as a one of the best candidate for the positive electrode for dry polymer lithium-ion battery. Hydro-Quebec is developing new advanced technology beyond Li-ion that can provide autonomy between 250-300 km per discharge. In the present study, we evaluated $LiFePO_4$ cathode material in polymer matrix with well optimized porosity.

Experimental

A carbon-coated $LiFePO_4$ (C-$LiFePO_4$) was used as cathode active material, and vapor grown carbon fiber (VGCF, Showa Denko) as a conductive agent and Denka black (DB, Denki Kagaku Kogyo). The weight ratio of LFP:VGCF:DB:SPE was 65:2.5:2.5:30 with < 1% of UV initiator (Irgacure 651). The polymer salt ratio (O/Li) was fixed to 30:1. A mixture of the components in AN was cast on aluminum foil with Doctor blade applicator. The film was cross-linked by UV lamp irradiation at in a nitrogen atmosphere. After vacuum drying at 90 °C for 12 h, the $LiFePO_4$-C/SPE/Li cell was constructed by over coating of thin layer of the same PEO-based polymer, and then pressing the lithium metal at the top of the cell.

Results

Fig. 1 reports the formation cycles at C/24 and 80°C of Li/Polymer LiTFSI /$LiFePO_4$ cell. In the first charge, the cell delivered 176 mAh g^{-1} (based on the active material mass) and then discharging a capacity of 169mAh g^{-1}. The reversible capacity in the second cycle was 166mAh g^{-1} corresponding to 95% of the theoretic capacity.

The cycleability at 100% DoD of the cell was measured between 3.7 and 2V at C/3 and T=80°C. The capacity decreased gradually at rate of 2.4% par cycle to reach 20% of capacity fade after 1380 cycles. With well stabilized interfaces and porosity control of the cathode is allowing having such stability.

The results show clearly the good performance in terms of capacity and reversibility for the polymer electrolyte (solvent-free) battery as high energy technology for the next generation of batteries.

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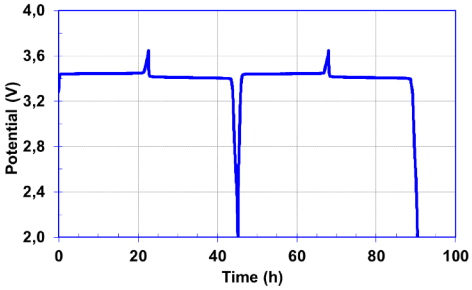

Fig. 1: Formation cycles of $LiFeO_4$ /EC-Polymer-LiTFSI/Li cells at 80°C.

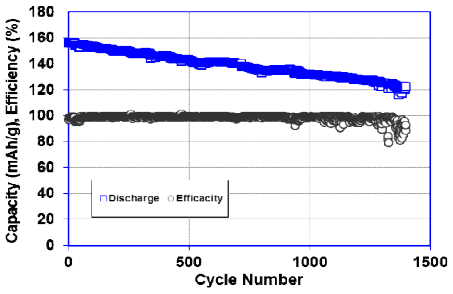

Fig. 2 : Cycleability of the of $LiFeO_4$ / Polymer-LiTFSI/Li cells at 80°C and C/3.

Title: **Post-Mortem Analysis of “18650” LFP-LTO Battery after 15,000 Cycles**

Presenting Author: Pierre Hovington

Organization / Institution: Hydro-Québec

Co-Author:

Type: Poster **Session:** P-13

Abstract Summary:

See PDF below

Post-Mortem Analysis of "18650" LFP-LTO Battery after 15,000 Cycles

P. Hovington[1], M. Dontigny[1], P. Perret[1], A. Guerfi[1], A. Mauger[2], C.M. Julien[3], K. Zaghib[1]

[1] Institut de Recherches d'Hydro-Québec (IREQ), 1800 Bd Lionel-Boulet, Varennes, QC, Canada J3X 1S1
[2] Université Pierre et Marie Curie-Paris-6, IMPMC, 4 place Jussieu, 752525 Paris, France
[3] Université Pierre et Marie Curie-Paris-6, PHENIX, UMR 8234, 4 place Jussieu, 75005 Paris, France

$LiFePO_4$ (LFP) combined with $Li_4Ti_5O_{12}$ (LTO) is a very promising cell configuration for high current and high cycle life application. IREQ has cycled '18650'-type LFP-LTO battery up to 30,000 cycles using 15C charge and 5C discharge rate that retained more than 90% of the discharge rate [JPS 196 (2011) 3949]. This presentation will focus on the post-mortem analysis of LFP/LTO cells after 15,000 cycles that suffer some catastrophic failure and some capacity lost.

Fig. 1 shows the cycling behaviour of those cells (LFP/1M $LiPF_6$ in EC-DEC/LTO). A beneficial effect of adding floating current of 5mins is shown at the end of the discharge. Note a catastrophic failure for all cells. After investigation, it was found that the sealant of the '18650' cells we used shows some leaks and electrolyte was evaporating during the increase of temperature during the 5 minutes floating period. It is shown that, if electrolyte is injected back into the 18650 cell we recovered all of the capacity after the failure. In addition, after opening the cells for *post-mortem* analysis, a color change is observed at the most outer part of the Celgard® separator (greyer) which when analysed in the Scanning Electron microscope (SEM) shows a region with salt precipitation has a result of electrolyte evaporation.

Fig. 2 presents micrographs (plan view) of LTO particles near the current collector and near the separator. An important amount of cracks particles is shown only near the separator. In addition, at higher magnification, there is an additional layer at the particle surface (SEI layer). This layer was not visible in the particle closer to the current collector. Those results confirmed that, most probably because of the higher rate used (+15C/-5C), the voltage was not in equilibrium and particles near the separator suffer more stress.

Fig. 3 shows micrographs of LFP near the separator. Those particles did not suffer any cracking upon cycling or an increase in the SEI. However, we notice a much wider range in particle size than the LTO, which could results in a more heterogeneous voltage across the electrode during charge. Hence, floating should be also important to LFP than LTO at high rate.

This *post-mortem* analysis of an LFP/LTO '18650' cell zshows that (i) the catastrophic failure was due to the lost of electrolyte, (ii) the anode (LTO) degradation was due to particle cracking (contact lost), (iii) the SEI build up only on the LTO close to the Celgard® separator which could explained the importance for floating to obtained voltage uniformity throughout both the electrode and good capacity retention.

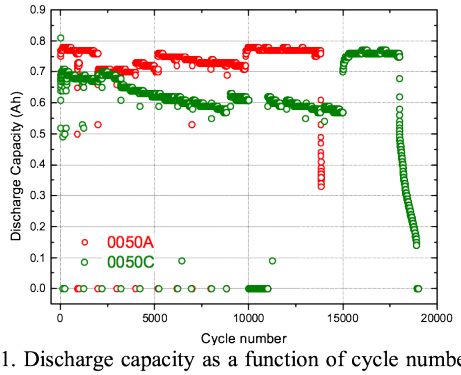

Fig.1. Discharge capacity as a function of cycle number at 30°C for LFP/1M $LiPF_6$ in EC-DEC/LTO '18650' cells (+15C/-5C). Cell 0050A was cycled with a small float (30 sec). Cell 0050C was cycled without float from 0-15k cycles. After 15k cycles, a 5 min floating time was used.

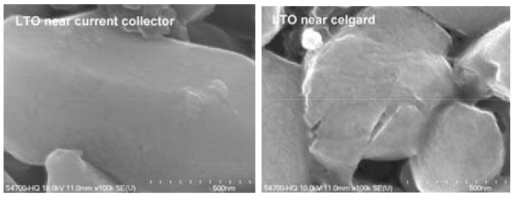

Fig. 2.Electron micrograph showing the difference in LTO structure from particle near the separator and near the current collector.

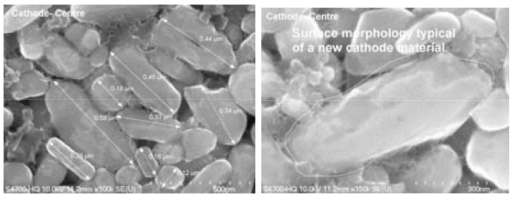

Fig. 3.Electron micrograph showing no cracking and no SEI layer increase for the LFP at the near the separator surface.

OREBA 1.0

Title: **Qualitative and Quantitative Studies of the Local Conductivity of C-LiFePO4**

Presenting Author: Pierre Hovington

Organization / Institution: Hydro-Québec

Co-Author:

Type: Poster **Session:** P-14

Abstract Summary:

See PDF below

Qualitative and Quantitative Studies of the Local Conductivity of C-LiFePO$_4$

P. Hovington[1], D. Clément[1], C. Gagnon[1], C.M. Julien[2], A. Mauger[3], A. Guerfi[1], K. Zaghib[1]

[1] Institut de Recherches d'Hydro-Québec, 1800 Bd Lionel-Boulet, Varennes, QC, Canada J3X 1S1
[2] Sorbonne Universités, UPMC Univ. Paris 6, PHENIX, UMR 8234, 75005 Paris, France
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Electrochemical performance of $LiFePO_4$ (LFP) is strongly dependant on the microstructure of the particle (size, shape, electronic conductivity) and the electrode (dispersion, porosity, tortuosity). Hence, it is of great economical importance to establish a direct relationship between microstructure and electrochemical features. In order to achieve this goal, several characterization techniques have been developed over the years at Hydro-Quebec Research Center. This work addresses the studies of the local conductivity of carbon deposited onto LFP particles (C-LFP).

The good electrical contact (high conductivity, σ_e) of LFP particles is the key issue to obtained high capacity at relatively high charge/discharge rate. This is currently achieved using a uniform and very thin carbon coating (US Pat. 6,855,273 B2). σ_e is measured on LFP powder using the 4-points probe method on pressed pellet as a function of pressure, P_{pellet} (Loresta GP Model MCP-T610, Mitsubishi Chemical). Fig. 1 shows σ_e of several syntheses from two suppliers. We notice (i) that all samples show the expected increase of σ_e with P_{pellet} because increase of number of contact points; (ii) that the solid-state synthesis (A) has a higher σ_e than the hydro-thermal synthesis (B). This could be explained by the amount of excess carbon that is found around the A particles compare to the B. Fig. 2 presents the microstructure of the A and B samples. We clearly see much more 'excess' carbon for A than for B since, for the same amount (±2 wt.%), the carbon nanopaint (CNP) is much thinner for a smaller size due to the high surface area.

However, the most important properties of CNP is uniformity. The local electronic conductivity was evaluated using an Hitachi Field emission gun Scanning Electron microscope (FE-SEM) equipped with an 'in-lens' secondary electron detector (or upper SE detector) which is sensible to charging of the sample. Hence, by using a relatively controlled high-beam current we clearly notice grains or parts of a grain that are less conductive that shows charging effect on the SE images. For negative charging those regions are brighter and do not show any microstructural features. Fig. 3 presents some grains having charging problem for supplier B. This SEM method evaluating the local electronic conductivity is very fast and easy to perform and was demonstrated to be very useful for the interpretation of cycling results. In conclusion, we have developed and tested a simple method to measure the local conductivity of C-LFP using the electron beam of an SEM apparatus. A good correlation was established between the conductivity and the electrochemistry performance (Fig. 4). This method must be optimized and validate depending on the SEM manufacturer and, most importantly, the secondary detector used.

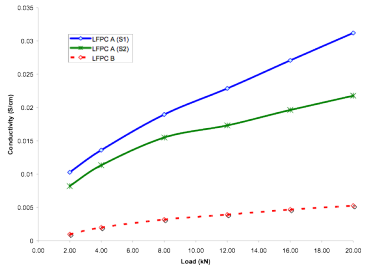

Fig. 1. σ_e of C-LFP pellets vs. applied pressure.

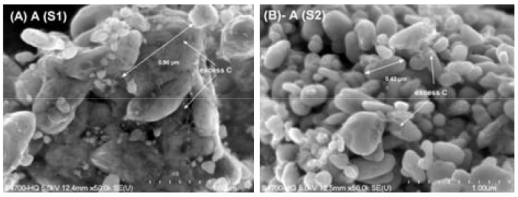

Fig. 2. Electron micrograph showing the difference in size and in excess C from samples A and B.

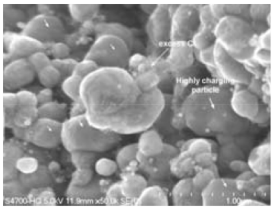

Fig. 3. Electron micrograph showing highly charging particle or area of a particle for supplier B.

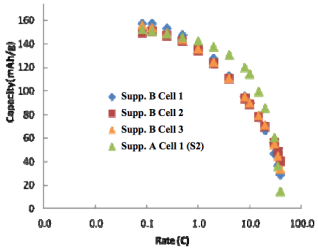

Fig. 4. Ragone plots at 25°C for supplier B and A (S2 synthesis). Li-ion with 200 µm Li anode and 1M $LiPF_6$ EC-DEC+2%VC electrolyte (1.2-2.5 V)

Title: **Investigating the intrinsic rate limiting mechanisms of LiFePO4 with chemical reactions**

Presenting Author: Christian Kuss

Organization / Institution: Université du Québec à Montréal

Co-Author: Guoxian Liang, Clariant (Canada), Inc.
Steen B. Schougaard, Université du Québec à Montréal
David Lepage, Ngoc Duc Trinh, Murielle Carmant-Dérival

Type: Poster **Session:** P-15

Abstract Summary:

Investigating the intrinsic rate limiting mechanisms of LiFePO4 with chemical reactions
Christian Kuss, David Lepage, Murielle Carmant-Dérival, Ngoc Duc Trinh, Guoxian Liang, Steen B. Schougaard

Only in recent years has LiFePO4 become known as a high power material. This is because in the common battery environment, ionic and electronic transport by other battery constituents limit the charge/discharge rates. As such, only studies that carefully remove such limitations have been able to report ultrafast performance.
One approach to avoid the battery environment's influence on kinetics is to use chemical reduction and oxidation of LiFePO4, since these reactions mimic the charge/discharge reactions of LiFePO4. The distinct advantage of chemical reactions is that ionic transport paths can be kept short, and electronic transport need not to be considered at all. As such, these chemical reactions are highly suited to study the intrinsic limiting mechanisms of lithium dynamics in battery materials.
This presentation will report on different chemical reactions that are suited for fundamental studies of LiFePO4 redox kinetics. To this end, the reactions need to (de-)lithiate LiFePO4 in the same manner as electrochemical techniques. A spectrum of materials characterization techniques have hence been employed to show that the reaction products of the electrochemical and chemical redox reaction are identical both physically and chemically.
Further, in situ studies of the chemical oxidation and reduction of LiFePO4 are reported. Measurements of the reaction rate were performed by in situ photometry and ex situ elemental analysis, and are analyzed on the basis of classical solid state reaction models. Furthermore, in situ X-ray diffraction is presented, providing insight into the structural mechanism of ultrafast lithiation and delithiation.
We hope that the produced insights will be helpful in designing new, better performing materials. At the very least, they stimulate optimism for the future of lithium batteries, since the intrinsic olivine chemistry allows for complete charge in one minute and discharging in five minutes.

OREBA 1.0

Title: **Core-Shell Technology for Olivine-olivine and Oxide- Olivine Composites**

Presenting Author: Dongqiang Liu

Organization / Institution: Hydro-Quebec

Co-Author:

Type: Poster **Session:** P-16

Abstract Summary:

See PDF below

Core-Shell Technology for Olivine-olivine and Oxide-Olivine Composites

D. Liu[1], C. Kim[1], J. Trottier[1], C. Gagnon[1], A. Guerfi[1], A. Mauger[2], C.M. Julien[3], and K. Zaghib[1]

[1] Institut de Recherches d'Hydro-Québec, 1800 Bd Lionel-Boulet, Varennes, QC, Canada J3X 1S1
[2] Université Pierre et Marie Curie-Paris-6, IMPMC, 4 place Jussieu, 752525 Paris, France
[3] Sorbonne Universités, UPMC Univ. Paris 6, PHENIX, UMR 8234, 4 place Jussieu, 75005 Paris, France

In recent years, materials with core-shell nanostructures, which were initially a common concept in semiconductors, have been introduced to the field of Li-ion batteries in order to overcome the disadvantages of nano-materials, and increase their general performances in Li-ion batteries. Many efforts have been devoted to exploit the core-shell Li-ion battery materials, in which lithium transition metal phosphates with carbon shells, especially the carbon-coated $LiFePO_4$ (C-LFP), exhibits excellent high-rate performance as well as long cycling life. Whereas much work have been devoted to study the LFP as a promising cathode material for Li-ion batteries, only little investigations focused on the LFP itself as a functional shell except for $LiCoO_2$, $Li[Ni_{0.5}Co_{0.2}Mn_{0.3}]O_2$ and $LiMn_{0.85}Fe_{0.15}PO_4$. In this work, we introduce the LFP-based core-shell technology used for Li-ion battery tests at IREQ.

Two core-materials have been chosen in this study, namely 4-V cathode olivine $LiMnPO_4$ (LMP) and 5-V cathode spinel $LiMn_{1.5}Ni_{0.5}O_4$ (LMN). As described in our previous work, a traditional hydrothermal method was used to make the C-coated LMP-LFP core-shell composite, while a new mechano fusion dry process was successfully employed to prepare the LMN-LFP composite [1-2]. These composites were characterized by XRD, SEM, TEM and EDX analysis.

Peukert plots are displayed in Figs. 1-2. Bare LMP delivers very low capacity at high rate due to the fact that coating the Mn-type olivine with conductive carbon is difficult. In comparison, C-LFP-LMN composite shows much higher capacity at the same rate (Fig. 1). Similar improvement can be observed for the 5-V spinel LMN cathode in Fig. 2, especially at high rate (≥10 C). We assume that the C-LFP shells can suppress the detrimental side reactions between core materials and electrolyte, therefore slow down surface elemental dissolution and electrolyte decomposition. Meanwhile, nano-sized C-LFP layer increases the conductivity of the cathode and reduces the charge transfer resistance. These should be responsible for the improved rate property in both cases.

This work demonstrates that LFP shell serves as both active and protective material, which leads to better performance at high rate. These studies suggest that the C-LFP shell should offer important benefits to increase the rate property as well as cycling performance for lithium-ion batteries, which is further evidenced by our lithium-sulfur battery research [3].

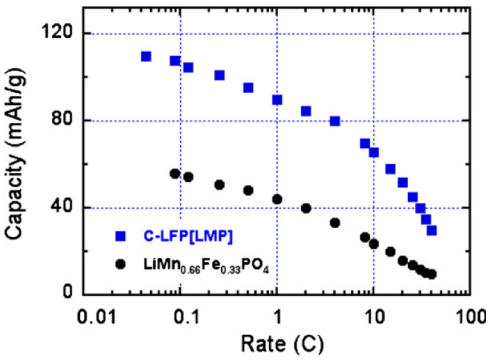

Fig. 1. Peukert plot of the 0.33LFP-0.66LMP composite. The behavior of the $LiMn_{0.66}Fe_{0.33}PO_4$ compound is also shown for comparison.

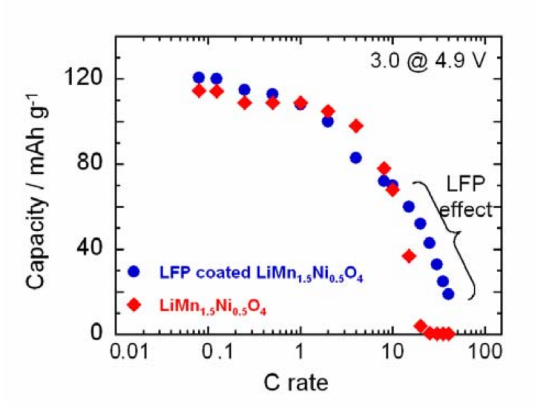

Fig. 2. Peukert plot of the LFP coated LNM sample. The behavior of the $LiMn_{1.5}Ni_{0.5}O_4$ compound is also shown for comparison.

References

[1] K. Zaghib, T. Trudeau, A. Guerfi, J. Trottier, A. Mauger, R. Veillette, C. M. Julien, J. Power Sources 195 (2010) 8280.
[2] D. Liu, J. Trotier, P. Charest, J. Fréchette, A. Guerfi, A. Mauger, C. M. Julien, K. Zaghib, J. Power Sources 204 (2012) 127.
[3] C.-S. Kim, A. Guerfi, P. Hovington, J. Trotier, C. Gagnon, F. Barray, A. Vijh, M. Armand, K. Zaghib, Electrochem. Commun. 32 (2013) 35.

Title: **Li-Staging Related Phenomena in Delithiated LiFePO4 Olivine Cathode**

Presenting Author: Xia Lu

Organization / Institution: Department of Materials Engineering, McGill University

Co-Author: Hong Li, Institute of Physics, Chinese Academy of Sciences
George Demopoulos, Department of Materials Engineering, McGill University

Type: Poster **Session:** P-17

Abstract Summary:

Li-Staging Related Phenomena in Delithiated LiFePO4 Olivine Cathode

Xia Lu1,2,*, Yang Sun1, Lin Gu1, Hong Li,1 Xuejie Huang1, Karim Zaghib3 and George P. Demopoulos2

1 Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China.
2 Department of Materials Engineering, McGill University, Montréal, Québec H3A 0C5, Canada.
3 Institut de recherche d'Hydro-Québec (IREQ), Varennes, Québec J3X 1S1, Canada.

Corresponding author: xia.lu@mail.mcgill.ca

Employing aberration-corrected annular-bright-field (ABF) scanning transmission electron microscopy (STEM) technique1-3, the atomic occupations of Li, Fe, P and O can be acquired clearly from the LiFePO4 olivine structure (space group: Pnma) at sub-Ångstrom resolution in real-space. Moreover, Li-staging arrangements are found in delithiated LiFePO4 nanowires4 and nanoparticles, which means that lithium-ions and lithium-vacancies align alternatively perpendicular to b axis as an intermediate phase (stage-II). This intermediate phase moves along ac plane and also acts as the phase transition from LiFePO4 to FePO4 upon delithiation5. Furthermore according to first-principles prediction, the stage-II configuration is thermodynamically metastable, i.e. is kinetically controlled. Formation of this type of lithium-staging configuration is mainly attributed to the Fe center mediated inter-layer Li-Li interactions, which involve indirect electrostatic forces6. The indirect interaction originates from the localized nature of Fe-3d electrons, for which the effective oxidation state of Fe redox is determined by the Li-ion arrangement, which in turn has an impact on the mechanism of Li-ion diffusion. Hereby a dual-interface model is proposed to describe the delithiation mechanism of LiFePO4 upon charging.

References
1 Chung, S. Y., Choi, S. Y., Yamamoto, T. & Ikuhara, Y. Atomic-scale visualization of antisite defects in LiFePO(4). Phys Rev Lett 100, doi:Artn 125502, Doi 10.1103/Physrevlett.100.125502 (2008).
2 Chung, S. Y., Choi, S. Y., Yamamoto, T. & Ikuhara, Y. Orientation-Dependent Arrangement of Antisite Defects in Lithium Iron(II) Phosphate Crystals. Angew Chem Int Edit 48, 543-546, doi:DOI 10.1002/anie.200803520 (2009).
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4 Gu, L. et al. Direct Observation of Lithium Staging in Partially Delithiated LiFePO4 at Atomic Resolution. J Am Chem Soc 133, 4661 -4663, doi:Doi 10.1021/Ja109412x (2011).
5 Suo, L. M. et al. Highly ordered staging structural interface between LiFePO4 and FePO4. Phys Chem Chem Phys 14, 5363-5367, doi:Doi 10.1039/C2cp40610a (2012).
6 Sun, Y., Lu, X., Xiao, R. J., Li, H. & Huang, X. J. Kinetically Controlled Lithium-Staging in Delithiated LiFePO4 Driven by the Fe Center Mediated Interlayer Li-Li Interactions. Chem Mater 24, 4693-4703, doi:Doi 10.1021/Cm3028324 (2012).

OREBA 1.0

Title: **Structural studies on NaFePO4 as a cathode material for Na+/Li+ mixed-ion batteries**

Presenting Author: Ayyakkannu Manivannan

Organization / Institution: US DOE, West VIrginia University

Co-Author: Faith Beck, US DOE, Penn State University
Parans Paranthaman, ORNL

Type: Poster **Session:** P-18

Abstract Summary:

Structural studies on $NaFePO_4$ as a cathode material for Na^+/Li^+ mixed-ion batteries

Faith R. Beck ,[1] Zhonghe Bi[2], Craig Bridges,[2] Ashfia Huq,[2]
M. Parans Paranthaman[2], A. Manivannan[1]
[1]National Energy Technology Laboratory, Morgantown, WV 26507
[2]Oak Ridge National Laboratory, Oak Ridge, TN 37831

Lithium-ion batteries constitute the current technology of choice for use in portable electronics and plug-in hybrid electric vehicles since they offer higher energy density compared to other available rechargeable battery systems such as lead-acid, nickel-cadmium, and nickel-metal hydride. Transformational advances in battery science still remain elusive even today, however, despite significant effort. The sodium-ion battery has long been overshadowed by the structurally similar lithium-ion battery due to the lithium-ion battery's higher capacity, energy density, and power density. However, the high cost and limited natural abundance of lithium and the possibility of using much safer aqueous electrolytes in sodium-ion batteries [1] have sparked renewed interest in sodium-ion battery development, particularly for applications with land-based power requirements, such as electrical grid stabilization. In such applications, portability is not an issue, so the benefits of high capacity, or low weight, are not as prevalent here. The success of $LiFePO_4$ as a cathode material for Li-ion batteries inspired the present investigation on the analogous $NaFePO_4$, as a cathode material for Na-ion batteries and Na^+/Li^+ mixed-ion batteries. To date, $NaFePO_4$ is not well characterized or examined for battery applications, and some have claimed that it is not viable as a cathode material [2].

In this research we examined a novel cathode material $NaFePO_4$ which has a structure similar to $LiFePO_4$ for both Lithium-ion and Sodium-ion batteries. We have synthesized $NaFePO_4$ through a Pechini process. We will perform detailed X-ray and neutron powder diffraction studies on $NaFePO_4$ and evaluate the charge discharge measurements as well. Electrochemical cycling to date has shown low capacity but long cycle life for Na^+/Li^+ mixed-ion batteries at both slow and fast cycling rates. Figure 1 (left) shows the XRD and the (right) demonstrates the cell's charge and discharge capacities over time when cycled at 5 mA g^{-1}. The capacity steadily rose over the first 100 cycles from 12 mAh g^{-1} before leveling out at 18 mAh g^{-1} and remaining steady for at least the next 40 cycles. Irreversible capacity in the first cycle is 17.1% but is practically zero for all subsequent cycles.

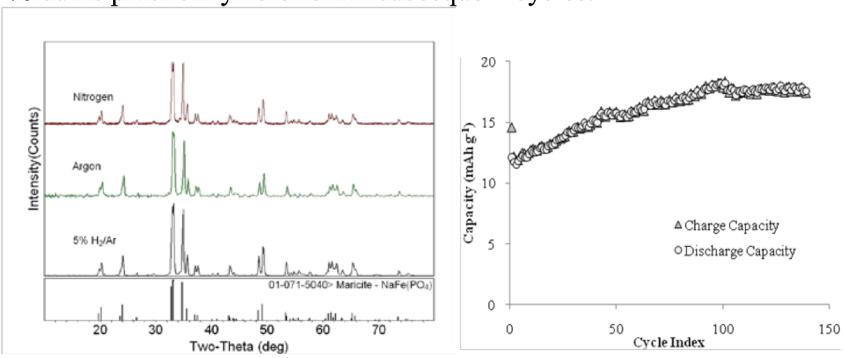

Figure 1. (left) X-ray diffraction patterns of $NaFePO_4$ annealed at 600 °C for 1 h in three different gases. An accepted pattern reported in the literature for $NaFePO_4$ is shown below.

(right) Charge and discharge capacities of Na^+/Li^+ mixed-ion $NaFePO_4$ cell cycled at 5 mA g^{-1} for 138 cycles.

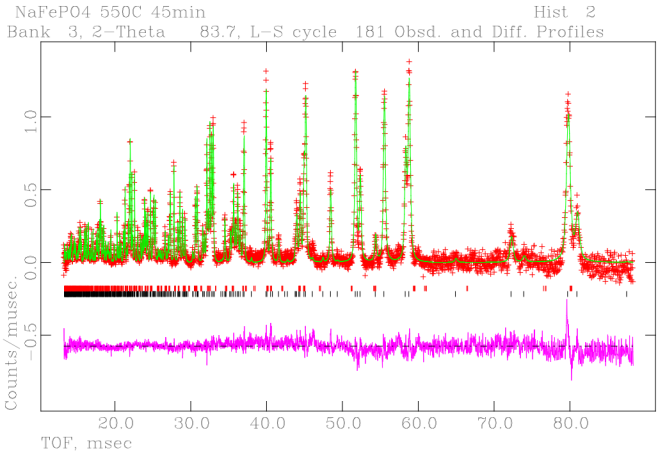

Figure 2. Neutron diffraction pattern of $NaFePO_4$.

Figure 4 Shows the Neutron diffraction pattern for $NaFePO_4$. In-situ frequency response analysis after charging and after discharging was performed every fourth cycle for 30 cycles. The impedance after discharge demonstrates the steady decreasing internal resistance of the cell. The long cycle life of these cells is promising, and even though capacity is low compared to state-of-the-art Li-ion battery cathodes, the comparison is unimportant due to this cell's advantages in other respects. As long as the battery can maintain long cycle life and is more economical to produce than Li-ion batteries of equivalent total capacity, $NaFePO_4$ cathodes will be more feasible for non-portable electrical storage applications.

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[2] B.L. Ellis, W.R.M. Makahnouk, Y. Makimura, K. Toghill, L.F. Nazar. *Nat. Mater.* 6 (2007) 749.

Acknowledgements

Research performed at Oak Ridge National Laboratory was sponsored by U.S. Department of Energy (US DOE), Office of Basic Energy Sciences, Materials Sciences and Engineering Division (MSED). The neutron powder diffraction work conducted at Spallation Neutron Source (SNS) was sponsored by Office of Science User Facilities operated for the US DOE Office of Science by Oak Ridge National Laboratory, which managed by UT-Battelle, LLC.

Title: **Improvement of Lithium Iron Phosphate and next generation cathode material**

Presenting Author: Hironari Miyauchi

Organization / Institution: Mitsui Engineering & Shipbuilding CO., LTD.

Co-Author: Hiroki Tomita, Mitsui Engineering & Shipbuilding CO., LTD.
Takanori Mahara, Mitsui Engineering & Shipbuilding CO., LTD.

Type: Poster **Session:** P-19

Abstract Summary:

These days, rechargeable lithium batteries have been used in many situations. Lithium Iron Phosphate (LFP) which is one of the cathode materials has long cycle life and high input-output characteristic.

Because of these feature, LFP is used for large scale energy storage system and applications which require high input-output characteristic.

Mitsui Engineering & Shipbuilding Co., Ltd. Started research of olivine materials for rechargeable lithium batteries in 2000. Our subsidiary company M&T Olivine Co., Ltd. Started manufacturing of LFP cathode material in 2013.

Our manufacturing process is the solid state reaction, and its advantages are low manufacturing cost, lower impurities and consistent quality of products. By controlling particle configuration, it is easy to achieve various improvements.

Now we are developing high energy type LFP and high power type fine particle size LFP. High energy type LFP shows high tap density over 1.4 g/cm3 and its electrode density of 2.5 g/cm3. Of course, its rate performance is at the same level as standard type LFP.

High power type fine LFP shows good rate performance at thin coating around 40 µm.

For the next generation cathode material, we are also developing Lithium Manganese Iron Phosphate (LMFP). Its performance shows around 150 mAh/g at 1 C rate and 140 mAh/g at 5 C rate.

The details of these materials will be explained in the poster of the day.

OREBA 1.0

Title: **Comparative Study of LiTDI vs. LiPF6 Based Electrolytes in Lithium-ion LiFePO4 Batteries**

Presenting Author: Sabrina Paillet

Organization / Institution: Hydro-Québec

Co-Author:

Type: Poster **Session:** P-20

Abstract Summary:

See PDF below

Comparative Study of LiTDI vs. $LiPF_6$ Based Electrolytes in Lithium-ion $LiFePO_4$ Batteries

S. Paillet[1], J. Fréchette[1], F. Barray[1], D. Clément[1], P Hovington[1], A. Guerfi[1], G. Schmidt[2], I. Cayrefourcq[3], and K. Zaghib[1]

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Lithium-ion batteries supplying energy for electric cars and other devices are mostly based on electrolytes using $LiPF_6$. The popularity of this salt is mostly due to the formation of a passivation layer with aluminum, which makes possible the utilization of this low cost material as current collector. In counter part, the thermal instability of $LiPF_6$ and its reactivity with moisture or protic species release a toxic, highly aggressive and undesirable gaz, HF. These major drawbacks have prompt researchers to replace $LiPF_6$ by alternatives salts with improved thermal, chemical and electrochemical properties. Unfortunately, most attempts, to replace $LiPF_6$ with hydrolytically-stable salts, have been unsuccessful because of Al corrosion [1].

Niedzicki *et al.* [2] showed that *lithium 4,5-dicyano-2-(trifluoromethyl) imidazolide,* commonly known as LiTDI could be an interesting substitute to $LiPF_6$. They showed LiTDI didn't corrode Al, which is consistent with our results, and have a thermal stability up to 250°C. It has a satisfactory conductivity thereby showing good performances with $LiMn_2O_4$ at operational voltage range of 3.0 - 4.3 V.

In the present study, we are interested to compare performances of $LiPF_6$ and LiTDI salts. This research is in collaboration between Arkema [3], which has developed an industrial process to synthesize battery-grade LiTDI, and Hydro-Québec. Electrochemical performances of LiTDI in EC-DEC (3-7 v-v) were evaluated in coin cells with $LiFePO_4$ (*vs.* Li metal anode) in the potential range 2-4 V, and also with two types of anode materials: graphite [0-2.5 V] and $Li_4Ti_5O_{12}$ [1.2-2.5 V].

The results obtained in this study with LiTDI are very promising. For all materials tested, the LiTDI has showed good compatibilities and features are comparable with those of $LiPF_6$.

After the cell formation, we found that:

- for $LiFePO_4$ based electrodes, results with and without FEC gave similar discharged and irreversible capacities compared to $LiPF_6$
- for graphite, results showed that it's necessary to use FEC to form a thin and stable SEI (validated by SEM analysis).
- for $Li_4Ti_5O_{12}$, the use of additive increases the irreversible capacity.

For all materials, the Peukert analysis showed competitive results between LiTDI and $LiPF_6$, as it can be seen in Figs. 1 and 2, for $LiFePO_4$ *vs.* Li and graphite *vs.* Li, respectively. Moreover, thanks to its high chemical stability, LiTDI has showed better performance than $LiPF_6$ in term of safety. Indeed, burning experiments have been realized and clearly showed a decrease of generated dangerous gas.

Finally, Pouch cells batteries with $LiFePO_4$//$Li_4Ti_5O_{12}$ and $LiFePO_4$//graphite will be assembled for long-term cycling at 25, 40 and 60°C.

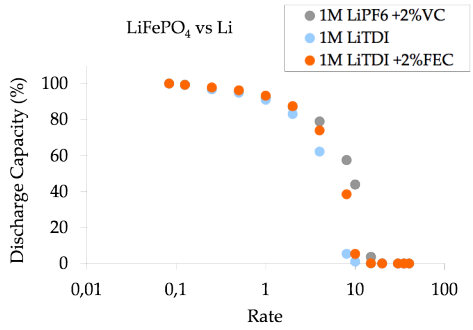

Fig. 1. Peukert plots of $LiFeO_4$/EC-DEC with several salts/Li cells at 25°C.

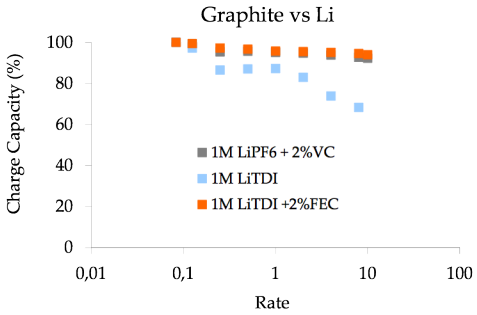

Fig. 2. Peukert plots of graphite/EC-DEC with several salts/Li cells at 25°C.

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1. K. Krause *et al*, *J. Power Sources,* 68 (1997), 320-325.
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3. G. Schmidt *et al.*, French patent FR2982610.

OREBA 1.0

Title: **LiTFSI-Based Electrolyte for Olivine Li-ion Cells**

Presenting Author: Sabrina Paillet

Organization / Institution: Hydro-Québec

Co-Author:

Type: Poster **Session:** P-21

Abstract Summary:

See PDF below

LiTFSI-Based Electrolyte for Olivine Li-ion Cells

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[2] Université Pierre et Marie Curie-Paris-6, IMPMC, 4 place Jussieu, 752525 Paris, France
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The first goal of the present work is to investigate the C-LFP//C-LTO cell in which both the active electrode particles have been carbon coated by the lactose process. Earlier works also motivates the alternative choice of LiTFSI instead of $LiBF_4$ [1-2]. The conductivity of the LiTFSI-based electrolyte is about 8×10^{-3} S cm^{-1} and its molecular weight is only 197 g. LiTFSI is known for its corrosive effect on the collector that is in aluminum However, this corrosive effect of LiTFSI occurs at 4 V and beyond, and the operating voltage with the C-LFP//C-LTO is smaller. That is why we took this opportunity to use this salt here.

With the aim of improving high-power Li-ion battery with increased thermal operating range, carbon-coated $LiFePO_4$ (C-LFP) and C-$Li_4Ti_5O_{12}$ (C-LTO) particles of 90 nm in diameter have been tested as active elements of electrodes of C-$LiFePO_4$//C-$Li_4Ti_5O_{12}$ Li-ion cell batteries in different electrolytes that include the usual one, c.a. 1 mol L^{-1} $LiPF_6$ in ethlene carbonate (EC) and diethylene carbonate (DEC) and two other: 1.5 mol L^{-1} lithium tetrafluoroborate $LiBF_4$ in EC+ γ-butyrolactone (GBL), and 0.5 mol L^{-1} lithium bis(trifluoromethane-sulfonyl)imide ($LiN(CF_3SO_2)_2$ and LiTFSI) + 1 mol L^{-1} $LiBF_4$ in EC+ GBL, aiming to replace the less stable $LiPF_6$ salt.

The cells display a capacity of 130 mAh g^{-1} at low C-rate and retain more than 80 mAh g^{-1} at 40C rate (Fig. 1). The maximum temperature reached by the cell is 34 °C at 40C-rate. The LiTFSI-based electrolyte than can be used owing to the low operating voltage that voltage that avoids the corrosion of the aluminum of the collector shows the best results as the performance is even higher at 60 °C, thus increasing importantly the operating temperature range for the battery. The aim of this work has been verified by the observation of the infrared images of the cells. It is shown that the temperature of the cells never reaches 60 °C during cycling, making the C-LFP//C-LTO battery a high-power system with remarkable thermal stability.

The C-LFP/0.5 mol L^{-1} LiTFSI + 1 mol L^{-1} $LiBF_4$ in EC-GBL/$Li_4Ti_5O_{12}$ realizes a cell that can operate at least up to 60 °C without aging over thousands of cycle, even at very fast C-rates of 60C (Fig. 1b). This performance has been possible because this electrolyte is compatible with both electrodes, allowing the substitution of the $LiPF_6$ salt that ages above 30 °C by the much more stable LiTFSI. This unprecedented performance makes this battery quite promising for different applications including rechargeable hybrid vehicles and regulation of the current to solve intermittence problems on smart grids. Even float charging under severe conditions is possible without thermal runaway since the temperature never exceeded 60 °C, while the use a temperature-compensated battery charger is usually needed for valve-regulated batteries.

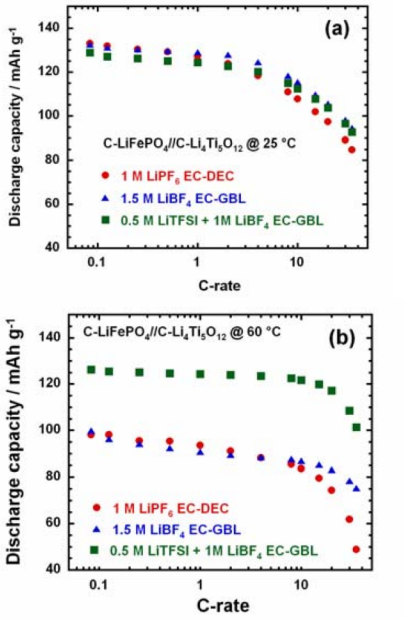

FIG. 1. Peukert plots of the LTO//LFP cells with different electrolytes (a) at room temperature and (b) at 60 °C.

LiTFSI-based electrolyte considered in the present work has shown that it is promising for use in high-power Li-ion batteries.

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[2] K. Zaghib et al., *J. Power Sources* 216 (2012) 192.

Title: **Redox Centers Evolution in Phospho-Olivine Type (LiFe0.5Mn0.5 PO4) Nanoplatelets with Uniform Cation Distribution**

Presenting Author: Andrea Paolella

Organization / Institution: IREQ

Co-Author: Enrico Dilena, Istituto Italiano di Tecnologia
George Chandramohan, Istituto Italiano di Tecnologia

Type: Poster **Session:** P-22

Abstract Summary:

In phospho-olivine type structures with mixed cations (LiM1M2PO4), the octahedral M1 and M2 sites that dictate the degree of inter-sites order/disorder play a key role in determining their electrochemical redox potentials. In the case of LiFexMn1-xPO4 – e.g., in micron sized particles synthesized via hydrothermal route – two separate redox centers corresponding to Fe2+/Fe3+ (3.5V vs. Li/Li+) and Mn2+/Mn3+ (4.1V vs. Li/Li+), due to the collective Mn-O-Fe interactions in the olivinelattice, are commonly observed in the electrochemical measurements. These two redox processes are directly reflected as two distinct peak potentials in cyclic voltammetry (CV) and equivalently as two voltage plateaus in their standard charge/discharge characteristics (in Li ion batteries). On the contrary, we observed a single broad peak in CV from LiFe0.5Mn0.5PO4 platelet-shaped (~10nm thick) nanocrystals (NCs) that we are reporting in this work. Structural and compositional analysis showed that in these nanoplatelets the cations (Fe, Mn) are rather homogeneously distributed in the lattice, which is apparently the reason for a synergetic effect on the redox potentials, in contrast to LiFe0.5Mn0.5PO4 samples obtained via hydrothermal routes. These LiFe0.5Mn0.5PO4 nanoplatelets, after a typical carbon coating process in a reducing atmosphere (Ar/H2), undergo a rearrangement of their cations into Mnrich
and Fe-rich domains. Only after such cation re-arrangement (via segregation) in the nanocrystals, the redox processes evolved at two distinct potentials, corresponding to the standard Fe2+/Fe3+ and Mn2+/Mn3+ redox centers. Our experimental findings provide new insight into mixed-cation olivine structures in which the degree of cations mixing in the olivine lattice directly influences the redox potentials, which in turn determine their charge/discharge characteristics.

Title: **Intrinsic Safety of Olivine Cathode Materials for Li-ion Batteries**

Presenting Author: Philippe Perret

Organization / Institution: Hydro-Québec

Co-Author:

Type: Poster **Session:** P-23

Abstract Summary:

See PDF below

Intrinsic Safety of Olivine Cathode Materials for Li-ion Batteries

P. Perret[1], J. Dubé[1], A. Dallaire[1], K. Galoustov[1], A. Guerfi[1], M. Ramanathan[2], A. Benmayza[2], J. Prakash[2], A. Mauger[3], C.M. Julien[4], K. Zaghib[1]

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[3] Université Pierre et Marie Curie-Paris-6, IMPMC, 4 place Jussieu, 752525 Paris, France
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Safety of lithium-ion rechargeable batteries has been the technical obstacle for high power demand applications [1]. Even though the mechanism of thermal runaway is initiated by the anode in combination with the electrolyte [2], the rapid temperature rise in the cell, which dominates the overall heat generated during this process, is produced by the cathode reacting with the electrolyte [3]. Therefore, it is of utmost importance to find a more structurally stable cathode in order to use lithium batteries at their fullest potential.

$LiFePO_4$ (LFP) material suffers from poor electronic conductivity. This leads to poor rate capability that has limited the use of LFP for high power density HEV and EV applications. Hence, a conductive carbon coating on the surface of LFP (C-LFP) was introduced to enhance the conductivity of the electrode and tailor LFP electrode more suitable to high power density HEV and EV applications. This paper will discuss the improvement in electrochemical and thermal properties of LFP protected with a thin layer of carbon as a cathode material.

The Hybrid Pulse Power Characterization (HPPC) test profile was developed to study the useable power and voltage range of cells at different depths of discharge (DOD) [1]. HPPC results are shown (Fig. 1) for a C-LFP//graphite 18,650-type cell after 70 and 100 cycles of charge/discharge at 0.1C rate.

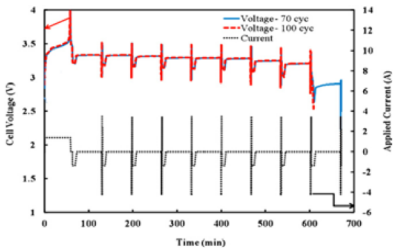

FIG. 1. HPPC results for a C-$LiFePO_4$//graphite 18650-cell after 70 and 100 cycles of charge/discharge at 0.1C rate.

The results after 70 cycles and 100 cycles cannot be distinguished, and the two voltage-time profiles are superposed. This cell was able to deliver 3.2 V down to 80% DOD and the calculated cell resistances ($\Delta V/\Delta I$) at different SOC indicated that cell resistance remained lower than 34.3 mV to 80% DOD for both 18 s discharge pulses and 10 s regenerative charge pulses.

Fig. 2 presents the Self-heat rate (SHR) *vs.* cell temperature of several 18650-type cells subjected to ARC test. Comparison of ARC parameters for the different chemistries (anode in graphite) provides the maximum values of SHR: 532, 878, 6.1 and 158 °C/min for $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$//C, $LiMn_2O_4$//C, $LiFePO_4$//C (4V) and $LiFePO_4$//C (4.2V), respectively.

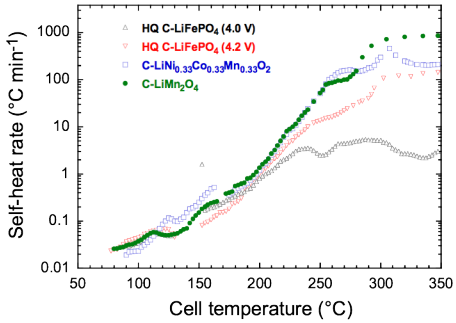

FIG. 2. Self-heat rate (SHR) vs. cell temperature of several 18650-type cells subjected to ARC test.

The C-LFP showed excellent electrochemical performance reaching 152 mAh/g. This electrode also exhibited a reversible capacity corresponding to more than 89% of the theoretical capacity when cycled between 2.5 and 4.0 V. Cylindrical 18,650 cells with C-LFP showed only 1.3% discharge capacity loss for 100 cycles at 0.1C rate and also delivered 90% of capacity retention at higher discharge rates up to 5C rate. The heat generation during charge and discharge at C/2 rate, studied using IMC, indicated that the cell temperature is not raised above 34°C in absence of external cooling. Thermal studies were also investigated by DSC and ARC, which showed that C-LFP is safer, upon thermal and electrochemical abuse, than the commonly used lithium metal oxide cathodes with layered and spinel structures.

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Title: **Synthesis of lithium titanates nanoparticles in an inductive plasma reactor**

Presenting Author: Francois Quesnel

Organization / Institution: Université de Sherbrooke

Co-Author: Gervais Soucy, Université de Sherbrooke
Jocelyn Veilleux, Université de Sherbrooke
Pascal Lamontagne, Pierre Hovington, Institut de recherche d'Hydro-Québec
Wen Zhu, Institut de recherche d'Hydro-Québec

Type: Poster **Session:** P-24

Abstract Summary:

The use of inductive plasma reactors constitute a well-established way to produce spheroidal nanoparticles by the rapid quenching of a vapor phase. Various morphologies and compositions of lithium titanate nanoparticles were produced from common and inexpensive solid reagents (Li2CO3, LiOH, TiO2) through variations in the plasma gas and quenching conditions. A regular distribution of nanoparticles in-between 20 nm and 60 nm was obtained. These particles were composed of a variety of phases, including Li4Ti5O12, Li2TiO3 and Li2Ti3O7, which are all candidates or current components to anode in lithium-ion batteries. While good phase selectivity and high crystallinity was also achieved, the characterization work provides insights into the influence of chemical and thermal conditions into the nucleation and growth mechanisms of the nanoparticles, opening the way for further developments into customized size and possible composites.

Title: **Synthesis of silicon nanowires from a carbothermic reduction of silica fume in radio-frequency thermal plasma reactor**

Presenting Author: Gervais Soucy

Organization / Institution: Université de Sherbrooke

Co-Author: Pascal Lamontagne, Université de Sherbrooke
Jocelyn Veilleux, Université de Sherbrooke
François Quesnel, Université de Sherbrooke
Pierre Hovington, Institut de Recherche d'Hydro-Québec
Wen Zhu, Institut de Recherche d'Hydro-Québec

Type: Poster **Session:** P-25

Abstract Summary:

Silica fume, which is a by-product of metallurgical-grade silicon production, is a low cost material with high SiO2 concentration and small particle size (< 1 µm). These properties make it a good candidate for radio-frequency (RF) thermal plasma processing. In this communication, the use of silica fume as a reactant is promoted for the RF thermal plasma synthesis of high charge capacity, high cyclability anode materials for lithium-ion batteries. The use of characterization instrumentation such as X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersion spectrometry (EDS), transmission electron microscope (TEM) and thermo-gravimetric analysis (TGA) allowed for the demonstration of silicon nanowire synthesis from the carboreduction of silica fumes in an inductive plasma reactor. Furthermore, it was found that the use of metallic catalysts (Fe, Ni, Al) promoted the formation of the nanowires and increased the effective yield of the carboreduction reaction significantly. Thermodynamic equilibrium analysis provided some insight relative to the mechanism of formation and growth of the silicon nanowires, which appears to vary according to the type of catalyst used.

Title: **Novel co-precipitation method of LiFePO4 synthesis in an anhydrous environment**

Presenting Author: Michal Swietoslawski

Organization / Institution: Faculty of Chemistry, Jagiellonian University

Co-Author: Joanna Swider, Faculty of Chemistry, Jagiellonian University
Marcin Molenda, Faculty of Chemistry, Jagiellonian University

Type: Poster **Session:** P-26

Abstract Summary:

Introduction

In the past decades the demand for improvement of electroactive materials for lithium-ion batteries was growing due to disadvantages and limitation of commercially used electrode materials, particularly oxide-based cathode materials [1,2]. The low production costs, low toxicity and environmental friendliness become the most important feature for new cathode materials especially for large-scale energy storage systems. Polyanionic cathode materials which satisfy all of the aforementioned conditions seems to be the best alternative for layered oxides [3]. Lithium iron phosphate LiFePO4 (LFP), with olivine-type structure, thanks to its low price, non-toxicity, high thermal and chemical stability and good theoretical capacity (170 mAh/g) is the most promising one from whole polyanionic materials family [4].

LFP preparation techniques are designed to obtain nanomaterials with highest possible electrochemical properties and to reduce production costs to minimum in the same time. Wide variety of synthetic methods have been proposed in recent years. The most common ones are: high temperature solid state [5,6], ball milling [7], sol-gel [4], carbothermal [8], hydrothermal, microwave, co-precipitation and spray-pyrolysis methods [9]. Despite the multiplicity of LFP synthesis methods the attempts to improve this process is still ongoing.

The aim of this work is a synthesis of nanostructured olivine-type LiFePO4 by a novel anhydrous precipitation method. The use of ethylene glycol as reaction medium allows precipitation of LFP precursor at room temperature and provides the ability of the grain size and shape control. The proposed method requires low-energy costs, inexpensive and commercially available reagents and should be easily scalable.

Experimental

LiFePO4 was synthesized using a two-step process. In the first step, precipitation method was used to synthesized an intermediate compound. This precursors of LiFePO4 was obtained in nonaqueous environment (ethylen glicol) at room temperature. FeSO4, LiCH3COO and (NH4)H2PO4 were used as starting reagents. After reaction precipitate is separated from ethylene glycol by centrifugation and reaction medium can be recovered and reused. Second step requires heat treatment of precursor. Controlled pyrolysis was performed under inert atmosphere at the range of temperatures 550-750 °C for 12 h.

The propose method enables receiving nanometric LiFePO4 with controlled grain size in simple and low-energy way by using technical grade reagent.

Acknowledgment

This work is financial supported by the Foundation for Polish Science under the International PhD-studies programme (MPD) realized at the Faculty of Chemistry JU and the European Institute of Innovation and Technology under the KIC InnoEnergy NewMat project.

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9. Jugović, D. Uskoković, Journal of Power Sources 19-0 (2009) 538-544

Novel co-precipitation method of $LiFePO_4$ synthesis in an anhydrous environment

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Keywords: Li-ion batteries, lithium iron phosphate ($LiFePO_4$), precipitation method

Introduction

In the past decades the demand for improvement of electroactive materials for lithium-ion batteries was growing due to disadvantages and limitation of commercially used electrode materials, particularly oxide-based cathode materials [1,2]. The low production costs, low toxicity and environmental friendliness become the most important feature for new cathode materials especially for large-scale energy storage systems. Polyanionic cathode materials which satisfy all of the aforementioned conditions seems to be the best alternative for layered oxides [3]. Lithium iron phosphate $LiFePO_4$ (LFP), with olivine-type structure, thanks to its low price, non-toxicity, high thermal and chemical stability and good theoretical capacity (170 mAh/g) is the most promising one from whole polyanionic materials family [4].

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Experimental

$LiFePO_4$ was synthesized using a two-step process. In the first step, precipitation method was used to synthesized an intermediate compound. This precursors of $LiFePO_4$ was obtained in nonaqueous environment (ethylen glicol) at room temperature. $FeSO_4$, $LiCH_3COO$ and $(NH_4)H_2PO_4$ were used as starting reagents. After reaction precipitate is separated from ethylene glycol by centrifugation and reaction medium can be recovered and reused. Second step requires heat treatment of precursor. Controlled pyrolysis was performed under inert atmosphere at the range of temperatures 550-750 °C for 12 h.

The propose method enables receiving nanometric $LiFePO_4$ with controlled grain size in simple and low-energy way by using technical grade reagent.

Acknowledgment

This work is financial supported by the Foundation for Polish Science under the International PhD-studies programme (MPD) realized at the Faculty of Chemistry JU and the European Institute of Innovation and Technology under the KIC InnoEnergy NewMat project.

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9. Jugović, D. Uskoković, *Journal of Power Sources* 19-0 (2009) 538-544

Title: **Preparation and characterization of LiFePO4/C doped with palladium using sol-gel method**

Presenting Author: Majid Talebi-Esfandarani

Organization / Institution: Laboratory of New Materials for Electrochemistry and Energy, École Polytechnique de Montréal

Co-Author: Oumarou Savadogo, Laboratory of New Materials for Electrochemistry and Energy, École Polytechnique de Montréal

Type: Poster **Session:** P-27

Abstract Summary:

In the aim of improving the ion diffusion rate of LiFePO4 material via a metal doping approach, LiFe1-xPdxPO4 (x =0, 0.02, 0.04) composite materials were synthesized using a sol-gel method followed by carbon coating with sucrose. The influence of palladium doping on the physical-chemical properties and the electrochemical performance of the LiFePO4/C material were investigated by XRD, XPS, SEM, BET, charge/discharge testing, and cyclic voltammetry. Increase of the palladium content in the LiFe1-xPdxPO4/C material led to a decrease of the electrochemical performances, which can be correlated with an increase of Li3PO4 content. This behaviour will be discussed considering the evolution of the lattice parameter and the morphology of material as a function of the Pd content.

Title: **Free-standing LiFePO4 nanoparticles/PEDOT hybrid film for advanced lithium ion batteries**

Presenting Author: Ngoc Duc Trinh

Organization / Institution: Université du Québec à Montréal

Co-Author: Mathieu Saulnier, Université du Québec à Montréal
Steen Schougaard, Université du Québec à Montréal

Type: Poster **Session:** P-28

Abstract Summary:

The utilization of conductive polymer in the field of lithium ion batteries has steadily increases for the last 20 years. Particularly, poly(3,4-ethylenedioxythiophene) (PEDOT) shows great conductivity, mechanical flexibility and thermal stability [1]. Recently, free-standing conductive polymer film was synthesized by using dynamic three phase interline electropolymerization (D3PIE) [2]. This procedure can be improved by adding LiFePO4 particles in the reactional media [3]. During the polymerization process, the conductive polymer anchored the LiFePO4 particles at the aqueous/organic interphase to generate in situ a functional electrode. The PEDOT-LiFePO4 composite electrode is free of current collector/binder and used without any further modifications in coin cell batteries.

The PEDOT-LiFePO4 composite film offers a high active material capacity of 160 mAh.g-1 which translates into an electrode capacity of 75 mAh g-1 at C/10, and high performance retention up to the C/2 rate. Electrochemical impedance spectroscopy shows high electronic conductivity in the LiFePO4 operating potential range. These results open a new avenue to explore for the development of ionic/electronic conducting support structures for LiFePO4 composite electrodes.

References

[1] D. Lepage, C. Michot, G. Liang, M. Gauthier, S.B. Schougaard, Angew. Chem. Int. Ed., 50 (2011) 6884-6887.
[2] H. Zhu, L. Gao, M. Li, H. Yin, D. Wang, Electro. Comm., 13 (2011) 1479-1483.
[3] N.D. Trinh, M. Saulnier, D. Lepage, S.B. Schougaard, J. Power Sources, 221 (2013) 284-289.

Free-standing $LiFePO_4$ nanoparticles/PEDOT hybrid film for advanced lithium ion batteries

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The utilization of conductive polymer in the field of lithium ion batteries has steadily increases for the last 20 years. Particularly, poly(3,4-ethylenedioxythiophene) (PEDOT) shows great conductivity, mechanical flexibility and thermal stability [1]. Recently, free-standing conductive polymer film was synthesized by using dynamic three phase interline electropolymerization (D3PIE) [2]. This procedure can be improved by adding $LiFePO_4$ particles in the reactional media [3]. During the polymerization process, the conductive polymer anchored the $LiFePO_4$ particles at the aqueous/organic interphase to generate *in situ* a functional electrode. The PEDOT-$LiFePO_4$ composite electrode is free of current collector/binder and used without any further modifications in coin cell batteries.

The PEDOT-$LiFePO_4$ composite film offers a high active material capacity of 160 $mAh.g^{-1}$ which translates into an electrode capacity of 75 mAh g^{-1} at C/10, and high performance retention up to the C/2 rate. Electrochemical impedance spectroscopy shows high electronic conductivity in the $LiFePO_4$ operating potential range. These results open a new avenue to explore for the development of ionic/electronic conducting support structures for $LiFePO_4$ composite electrodes.

References

[1] D. Lepage, C. Michot, G. Liang, M. Gauthier, S.B. Schougaard, Angew. Chem. Int. Ed., 50 (2011) 6884-6887.
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Title: **Olivine vs. Oxide as Cathode Materials for Li-ion Batteries**

Presenting Author: Julie Trottier

Organization / Institution: Hydro-Quebec

Co-Author:

Type: Poster **Session:** P-29

Abstract Summary:

See PDF below

Olivine vs. Oxide as Cathode Materials for Li-ion Batteries

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Since three decades, lithium-ion batteries (LIBs) have been amongst the most promising chemical-electrical energy converter (rechargeable or secondary sources) for power electronic devices such as cellular phones, laptop computers, camera, etc. In 1992, the commercial success of LIBs based on carbon, a non-aqueous electrolyte, and $LiCoO_2$ offered great promise as being the first rechargeable battery technology for personal electronics in the near future. Today, new technologies with spinel $LiMn_2O_4$, layered $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ and olivine $LiFePO_4$ are applied to green transportation systems such as electric vehicles (EVs) or hybrid EVs (HEVs). Layered compounds have been selected for high-energy uses, spinel compounds have been selected in cases of low cost and/or high power, and olivine compounds have been selected for high power and long-life requirements. This paper deals with the advantages and disadvantages of the positive electrodes materials used in Li-ion batteries: layered $LiCoO_2$ (LCO), $LiNi_yMn_yCo_{1-2y}O_2$ (NMC), $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA); spinel $LiMn_2O_4$ (LMO), $LiMn_{1.5}Ni_{0.5}O_4$ (LMN) and olivine $LiFePO_4$ (LFP) materials.

The open-circuit voltage of an Li-intercalation cell is given by $V_{OCV} = \mu_C - \mu_A$, where μ_A and μ_C are the electrode electrochemical potentials. The energy of a given μ_A or μ_C may correspond to the Fermi energy in an itinerant-electron band, as in the case for carbon, or the energy of a redox couple of a transition-metal cation [1]. The position of a redox couple relative to the bottom of a broad conduction band or to the top of an anion p band may determine the intrinsic voltage limit versus Li^+/Li^0 of a given electrode. This problem arises for a μ_C where the active redox couple is "pinned" at the top of the anion *p* bands (Fig. 1).

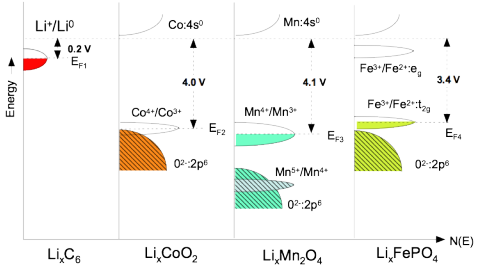

Fig. 1. Range of voltages that are exhibited by host structures into/from which Li^+ ions have been inserted reversibly.

The Li_xCoO_2 cathode is known to cycle well for $x>0.5$ and, therefore, no oxygen loss may occur in electrochemical cells. The observation of the beginning of oxygen loss at a slightly higher Li content $x\approx0.45$ could be due to a rapid and deeper extraction of lithium on the surface although the average lithium content is > 0.5, which may result in overall oxygen content slightly less than 2 for $0.5\leq x\leq0.45$. The energy *vs*. DOS diagram shows the differences in the chemical instability with respect to oxygen loss due to the overlapping of the $Co^{4+/3+}$:t_{2g} band with the O:2*p* orbitals (Fig. 1)

Thermal studies were also investigated by DSC and ARC, which showed that $LiFePO_4$ is safer, upon thermal and electrochemical abuse, than the commonly used lithium metal oxide cathodes with layered and spinel structures. DSC spectra of the over charged spinel $LiMn_2O_4$, layered $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode and C-LFP, all electrodes with traces of electrolyte, measured at a scan rate of 10 C/min from 50 to 400°C (Fig. 2). We can observe that both spinel and olivine cathodes have delayed onset temperature by at least 70°C with respect to the layered cathode. The layered cathode was found to be thermally unsafe, as this cathode undergoes its exothermic reaction with very large enthalpy (941 J/g) and the reaction gets completed at much earlier temperature, lower than the onset temperature of spinel and olivine. Spinel cathode showed roughly half the exothermic reaction enthalpy (439 J/g), whereas carbon-coated olivine showed even lesser exothermic reaction enthalpy (250 J/g).

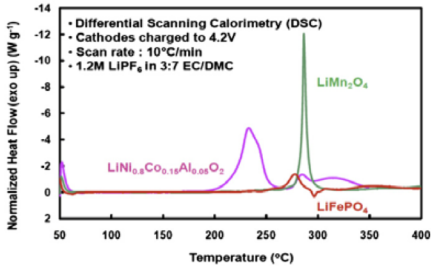

FIG. 2. DSC spectra of over charged layered, spinel and olivine cathodes with traces of 1.2 mol L^{-1} $LiPF_6$ in EC-EMC (3:7) electrolyte at 10°C/min.

The Hydro-Québec group showed the incomparable safety of the $LiFePO_4$//C Li-ion battery which is the only one that passes the crushing and perforation tests without the need of any battery monitoring system. Studies in 2011 showed that $LiFePO_4$//$Li_4Ti_5O_{12}$ batteries can be cycled 30,000 times without capacity loss. As the promising cathode materials of the next generation of large-scale lithium-ion battery for EVs or HEVs, $LiFePO_4$ is almost ready.

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OREBA 1.0

Title: **In-situ TEM studies of LiFePO4 Cathode Materials for Li-ion Batteries**

Presenting Author: Michel Trudeau

Organization / Institution: Hydro-Quebec

Co-Author:

Type: Poster **Session:** P-30

Abstract Summary:

See PDF below

In-situ TEM studies of $LiFePO_4$ Cathode Materials for Li-ion Batteries

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The synthesis and characterization of $LiFePO_4$ (LFP) and other promising cathode materials has received extensive attention. By directly observing the structural changes in materials and/or the synthesis of new compounds under different temperatures and even different ambient, the efficiency of the synthesis processes can be dramatically improved. High-resolution transmission electron microscopy (HRTEM) is one technique to examine the properties and the structure of the carbon layer. In particular, in situ transmission electron microscopy is uniquely well suited to study atomic-level transformations in the microstructure of electrode materials, following events in real time the morphological as well as the crystallographic changes that occur during heat treatment because of its high image resolution in observing crystal lattices.

In this work, we report in situ high-resolution transmission electron microscopy (HRTEM) studies of the structural transformations that occur during the synthesis of carbon-coated $LiFePO_4$ (C–LFP) and heat treatment to elevated temperatures were conducted in two different electron microscopes. Both microscopes have sample holders that are capable of heating up to 1500°C, with one working under high vacuum and the other capable of operating with the sample surrounded by a low gaseous environment. The C–LFP samples were prepared using three different compositions of precursor materials with Fe(0), Fe(II) or Fe(III), a Li-containing salt and a polyethylene-block poly(ethylene glycol)-50% ethylene oxide or lactose. In situ TEM studies suggest that low-cost Fe(0) and a low-cost carbon-containing compound such as lactose are very attractive precursors for mass production of C–LFP, and that 700°C is the optimum synthesis temperature (Fig. 1). At temperatures higher than 800°C, LFP has a tendency to decompose. The same in situ measurements were made on particles without carbon coat.

Another question that is still pending is the exact role played by the carbon coat, besides the role of conducting the electric current for which it has been introduced. In particular, the results reported in the present work shows unambiguously that the interface between carbon and LFP annealed at 700°C for 45 min is sharp, and that the surface layer is very well crystallized, while uncoated particles are known to have a surface layer which is severely disordered [2]. We determine unambiguously whether the recrystallization of the surface layer is due to the annealing at 700°C, or it is due to the interaction of the carbon with the iron. The STEM images of the uncoated LFP sample at room temperature (Fig. 2a) shows the disordered surface layer of thickness ~6 nm and the same sample after heating at 700°C. There is no longer any surface layer (Fig. 2b).

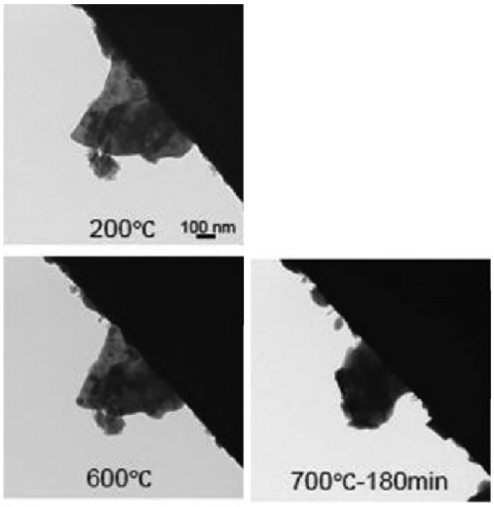
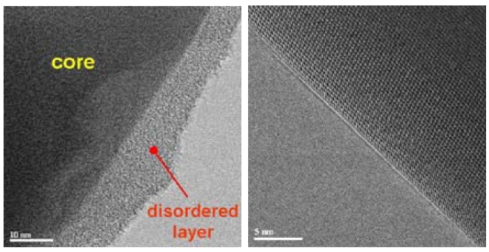


Fig. 1. Sequence of TEM micrographs obtained during heat treatment of a mixture of $FePO_4$, Li_2CO_3 and polymer (method A) under 12 mPa of nitrogen to 700°C.



(a) (b)

Fig. 2. STEM images of the uncoated LFP particle before (a) and after recrystallization (b).

The results show that the homogeneous deposit of the carbon deposit at 700°C is the result of the annealing that cures the disorder of the surface layer of bare LFP. Electrochemical tests supported the conclusion that the C–LFP derived from Fe(0) is the most attractive for mass production.

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1. M.L. Trudeau, D. Laul, R. Veillette, A.M. Serventi, K. Zaghib, A. Mauger and C.M. Julien, *J. Power Sources* **196** (2011) 7383.
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OREBA 1.0

Title: **In-situ X-ray Diffraction Study for Structural Characterizations of LiFePO4**

Presenting Author: Wen Zhu

Organization / Institution: Hydro-Quebec

Co-Author:

Type: Poster **Session:** P-31

Abstract Summary:

See PDF below

In-situ X-ray Diffraction Study for Structural Characterizations of $LiFePO_4$

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In this study, the phase evolution of $LiFePO_4$ during the electrochemical cycling is monitored by in situ X-ray diffraction (XRD) to have a better knowledge of the phase transformation during the dynamic charge/discharge in a regime out-of-equilibrium according the delithiation-insertion process [1]

$$LiFePO_4 \leftrightarrows (1-y)LiFePO_4 + yFePO_4 + yLi^+ + ye^-.$$

$LiFePO_4$ and $FePO_4$ have similar crystal structure described by space group *Pnma*. When the $LiFePO_4$ cathode is in charge and discharge, Li^+ ions are de-intercalated and intercalated along a channel in [010] direction, respectively.

The phase change of Li_xFePO_4 during the galvanostatic cycling at a rate of C/24 is shown Fig. 1. When charge proceeds to x=0.84, small peaks of $FePO_4$ are observed, from then on to the end of the charge, $LiFePO_4$ decreases accompanied by the increase of the $FePO_4$. At the end of charge, x=0.15, and $LiFePO_4$ y=~15%. All residual $LiFePO_4$ transforms to $FePO_4$ at the beginning of discharge, as if the transformation between $LiFePO_4$ and $FePO_4$ proceeds in both forward and backward directions at this initial stage of discharge. $LiFePO_4$ emerge at x=0.27 and it continues to form at the expense of $FePO_4$. At the end of discharge, small amount of $FePO_4$ is left which disappears at the beginning of next charge.

Fig. 2 presents the percentage of triphylite phase and the voltage E versus x(Li) in Li_xFePO_4. The rate of $FePO_4$ formation increases as charge proceeds and reaches the maximum towards the end of charge which is related to the acceleration of Li^+ out diffusion caused by sudden electric potential increase. We notice a deviation of the $LiFePO_4$ content from the electrochemically calculated value (the green dot line in Fig. 2) despite the overall phase transition is reversible. Small 2θ shift, i.e. $\Delta(2\theta) \leq 0.05^o$, of $LiFePO_4$ peaks to the large two theta direction has been detected in XRD spectra. This shift may due to the formation of solid solution which leads to the delayed appearance of $FePO_4$.

The variation of the lattice parameters of $LiFePO_4$ and $FePO_4$ phases are small, especially the "a" and "b" directions. The observed cell parameter changes may due to the stress induced in the phase transition process or the composition variation. These results demonstrate that there is a delayed $FePO_4$ phase formation at the initial stage of charge, which can be understood as the formation of Li_xFePO_4 solid solution before the nucleation of $FePO_4$ and its growth beyond the detecting limit of XRD measurements.

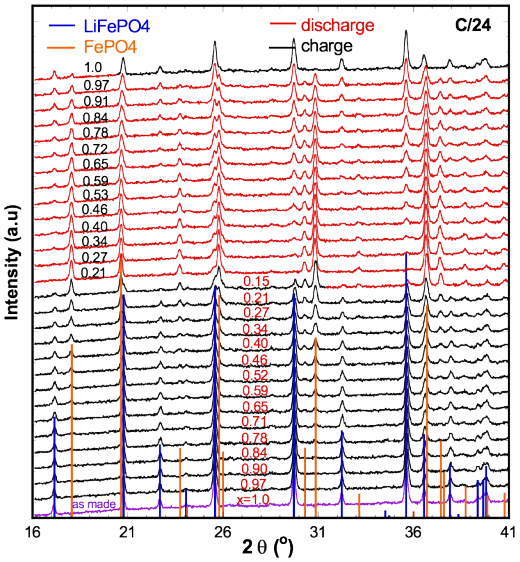

Fig. 1. In situ XRD spectra of $LiFePO_4$ cell cycled at rate C/24.

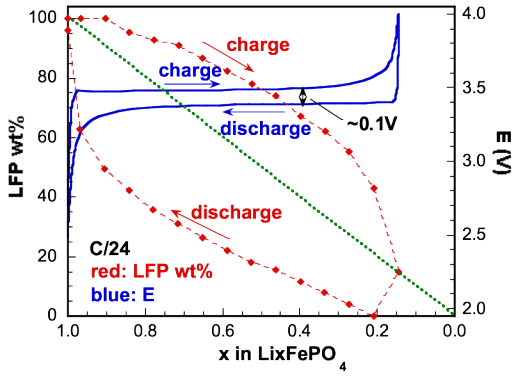

Fig. 2. Variation of $LiFePO_4$ wt% and cell voltage as functions of Li^+ ion concentration (x) during galvanostatic cycling.

References

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