Characterization of New Cathode Materials using Synchrotron-based X-ray Techniques

PI: Xiao-Qing Yang and Won-Sub Yoon
Presenter: Xiao-Qing Yang

Brookhaven National Laboratory
Upton, NY 11973

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Outlines

- Response to Previous Review Comments
- Objectives and Approaches
- Introduction of Synchrotron based Diagnostic Techniques
- Results and Accomplishments
- Collaborative Research
- Publications
- Plans for Next Fiscal Year
- Summary

Response to Previous Review Comments

Comments/Recommendations	BNL FY 2007 Action
1. More SEI work	1. BNL team is working on developing diagnostic methods for SEI studies through collaborations
1. Consider high voltage electrolyte research to complement high voltage cathode work	2. Design and synthesis of new high voltage electrolytes is proposed for FY2008
2. Consider research into additives, alternative solvents, salts etc	3. The research on new additives and new salts design and synthesis is proposed for FY2008

Objectives and Approaches

▣ Objectives

To co-relate the performance with structural changes of the layered, Li-rich transition metal oxides containing Mn, Ni, and Co, like $Li_{1+x}(Mn_{0.5}Ni_{0.5})_{1-x}O_2$ and $Li_{1+x}(Mn_{1/3}Ni_{1/3}Co_{1/3})_{1-x}O_2$

To study the effects of doping and surface coating on the structural changes relating to the performance of $LiFe_{1-x}M_xPO_4$ type of olivine structured cathode materials.

To develop new diagnostic tools for solid electrolyte interface (SEI) and other interfacial studies

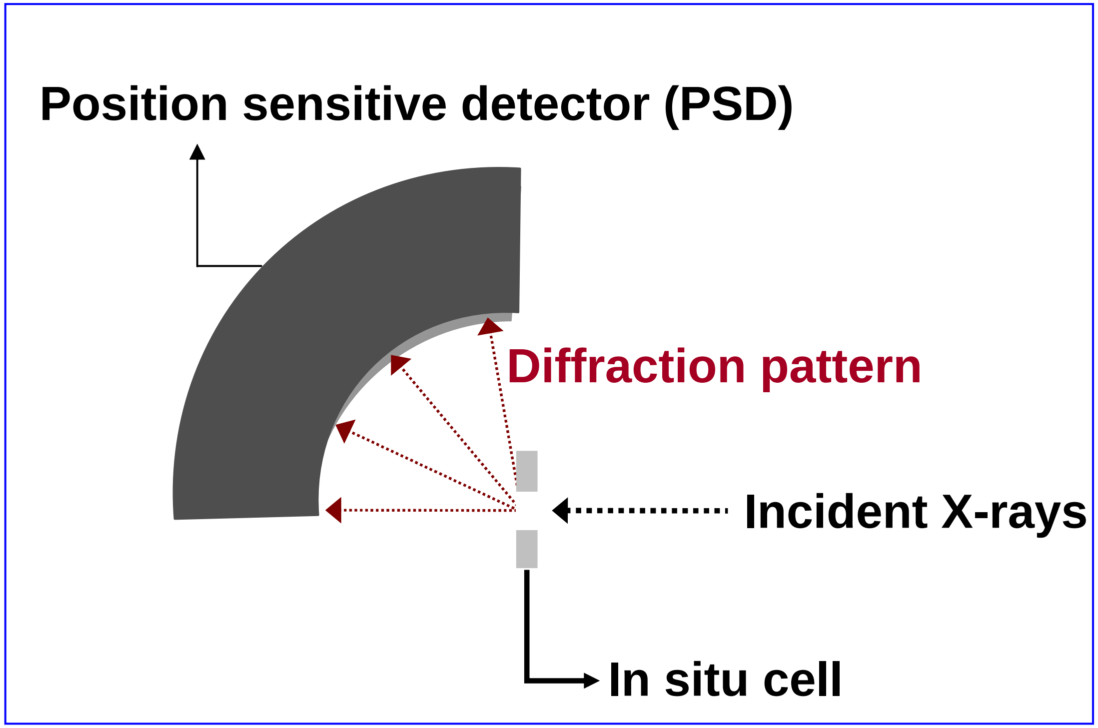
To develop new additives, salts, and solvents for high voltage electrolytes

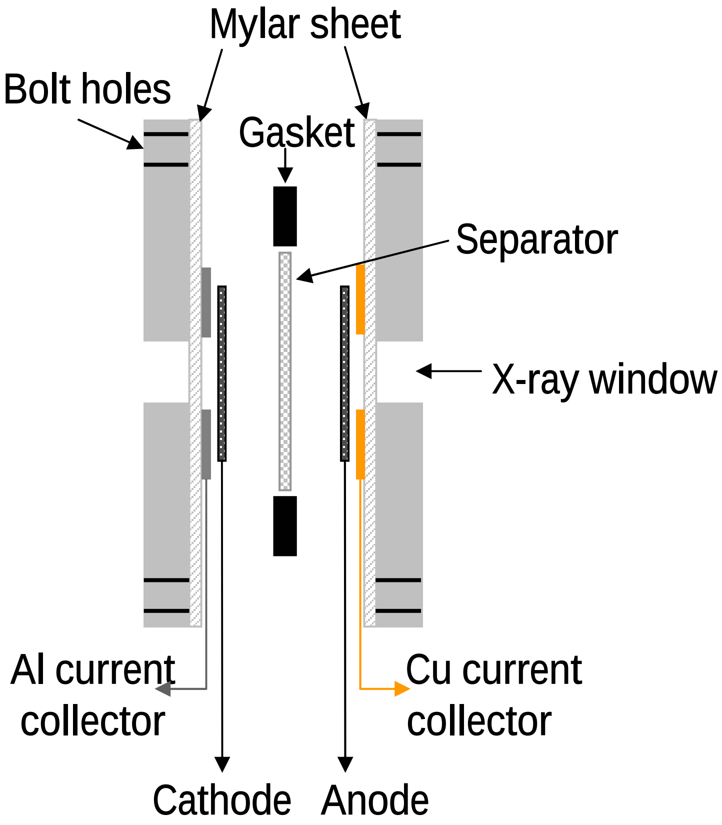
▣ Approach

- ▶ A combination of in situ x-ray absorption (XAS) and in situ x-ray diffraction (XRD) to study bulk processes in electrodes
- ▶ Hard and soft x-ray XAS studies of cathode materials during electrochemical cycling to elucidate the charge compensation mechanisms
- ▶ Transmission electron microscopy (TEM) and electron diffraction for SEI and interfacial studies
- ▶ New electrolyte system development through molecular design and organic synthesis, and extended collaboration with other institutions and industrial partners

Time-resolved X-ray Diffraction (TRXRD), an in situ technique

Experimental setup: Position Sensitive Detector + In situ cell

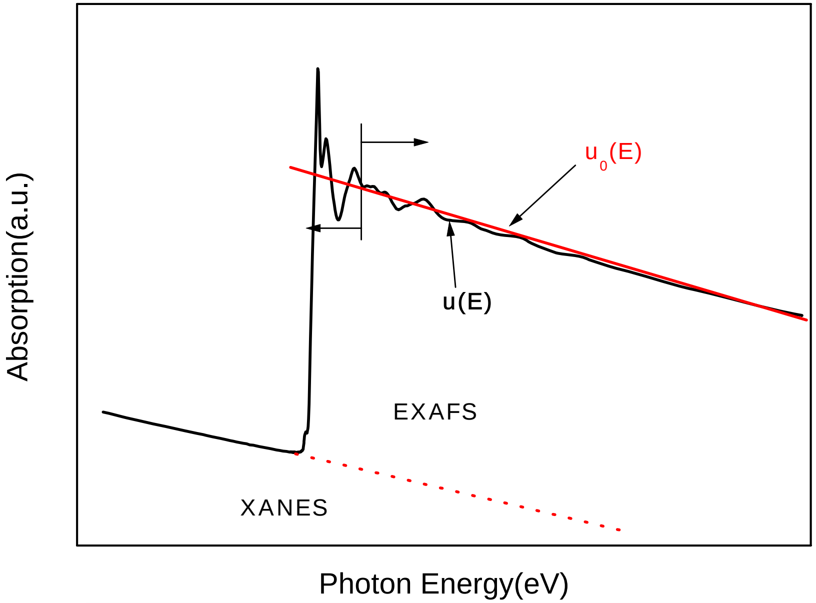


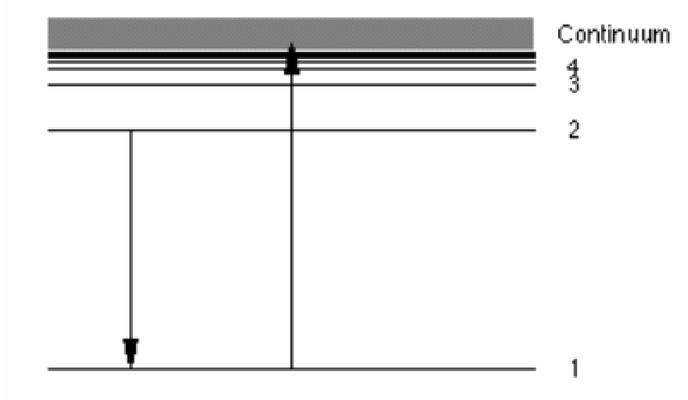


X-ray wavelength: 0.9999 A
Beam size: 0.4 X 0.4 mm
Average scan time: ~ a few minutes

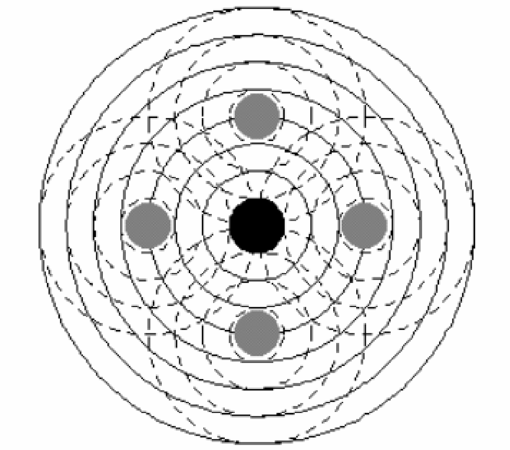
Combination of PSD detector and high intensity synchrotron X-ray enables us to investigate the structural changes during very fast cycling.

X-ray Absorption Spectroscopy





- ◈ **XANES**
  - **Oxidation state**
  - **Site symmetry**
  - **Covalent bond strength**
- ◈ **EXAFS**
  - **Interatomic distance**
  - **Coordination number**
  - **Debye-Waller factor**

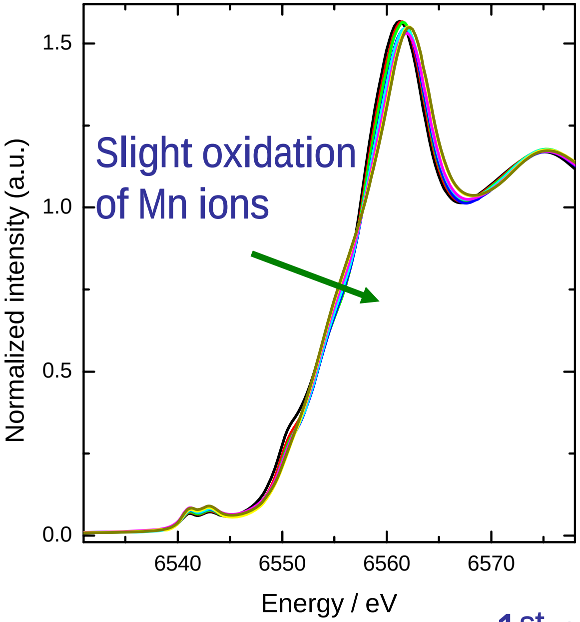


$$\chi(k) = \frac{\mu(E) - \mu_0(E)}{\mu_0(E)}$$

$$= \sum_j N_j S_i(k) F_j(k) e^{-2\sigma_j^2 k^2} e^{-2r_j/\lambda_j(k)} \frac{\sin(2kr_j) + \phi_{ij}(k)}{kr_j^2}$$

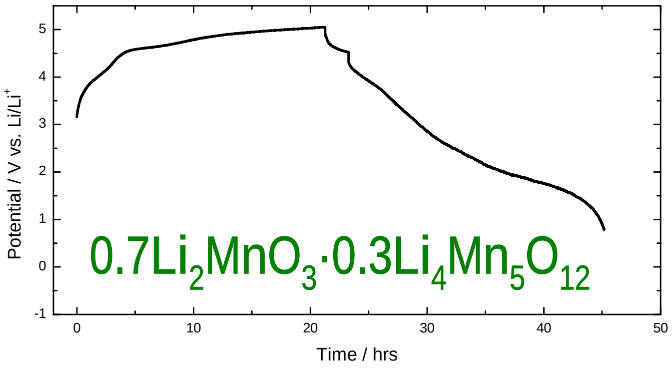
In situ Mn K-edge XAS of $xLi_2MnO_3 \cdot (1-x)Li_{1+y}Mn_{2-y}O_4$
First charge and discharge: In collaboration with Dr. Thackeray (ANL)

Mn K-edge XANES of 1^{st} charge



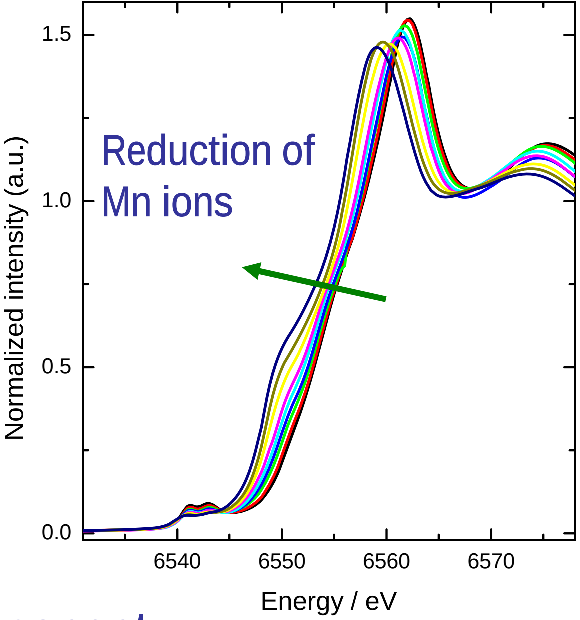
Slight oxidation of Mn ions

“Utilizing Li_2MnO_3 component”



$0.7Li_2MnO_3 \cdot 0.3Li_4Mn_5O_{12}$

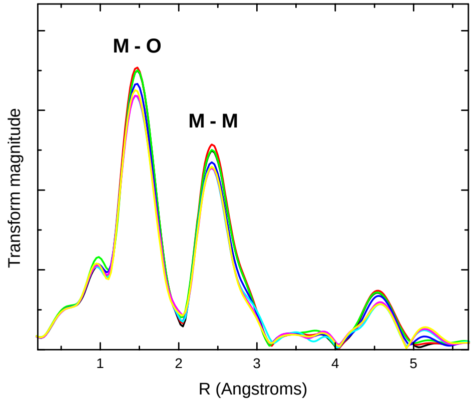
Mn K-edge XANES of 1^{st} discharge



Reduction of Mn ions

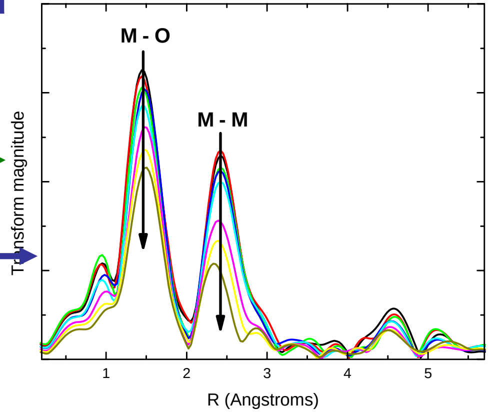
1^{st} charge: activation of Li_2MnO_3 component

1^{st} discharge: layered component derived from Li_2MnO_3



← FT magnitudes of 1^{st} charge and discharge →

Increased local disorder during Li deintercalation →



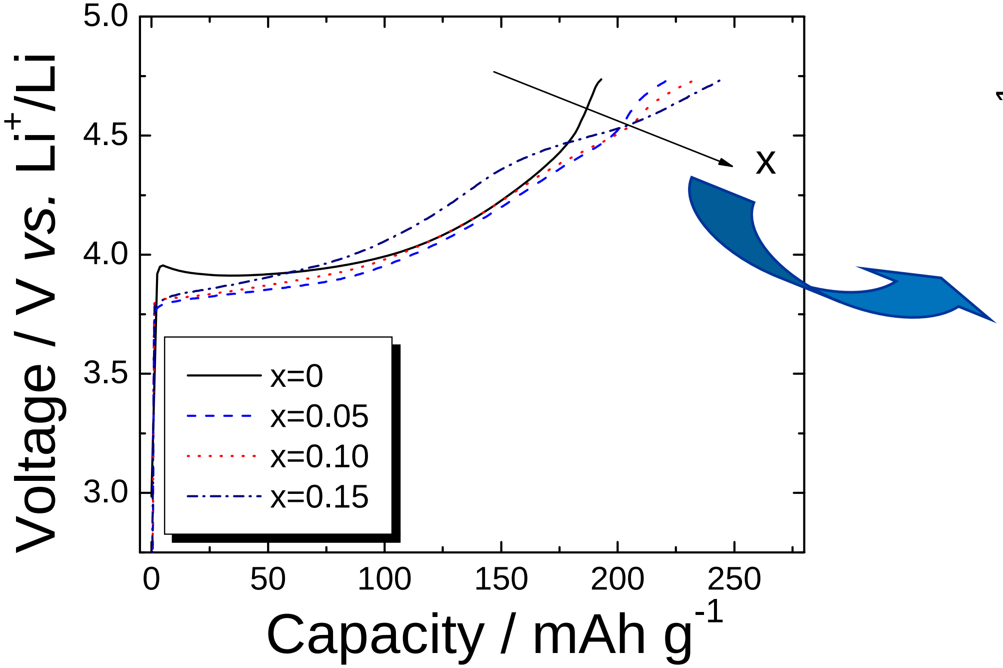
High voltage performance

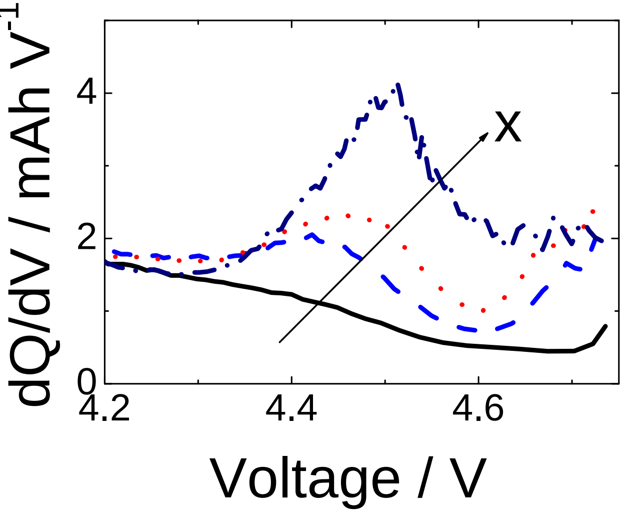
First charge behavior of $Li_{1+x}(Mn_{0.5}Ni_{0.5})_{1-x}O_2$

First charge curve to 4.8 V

In collaboration with Dr. Kang (ANL)

Differential capacity

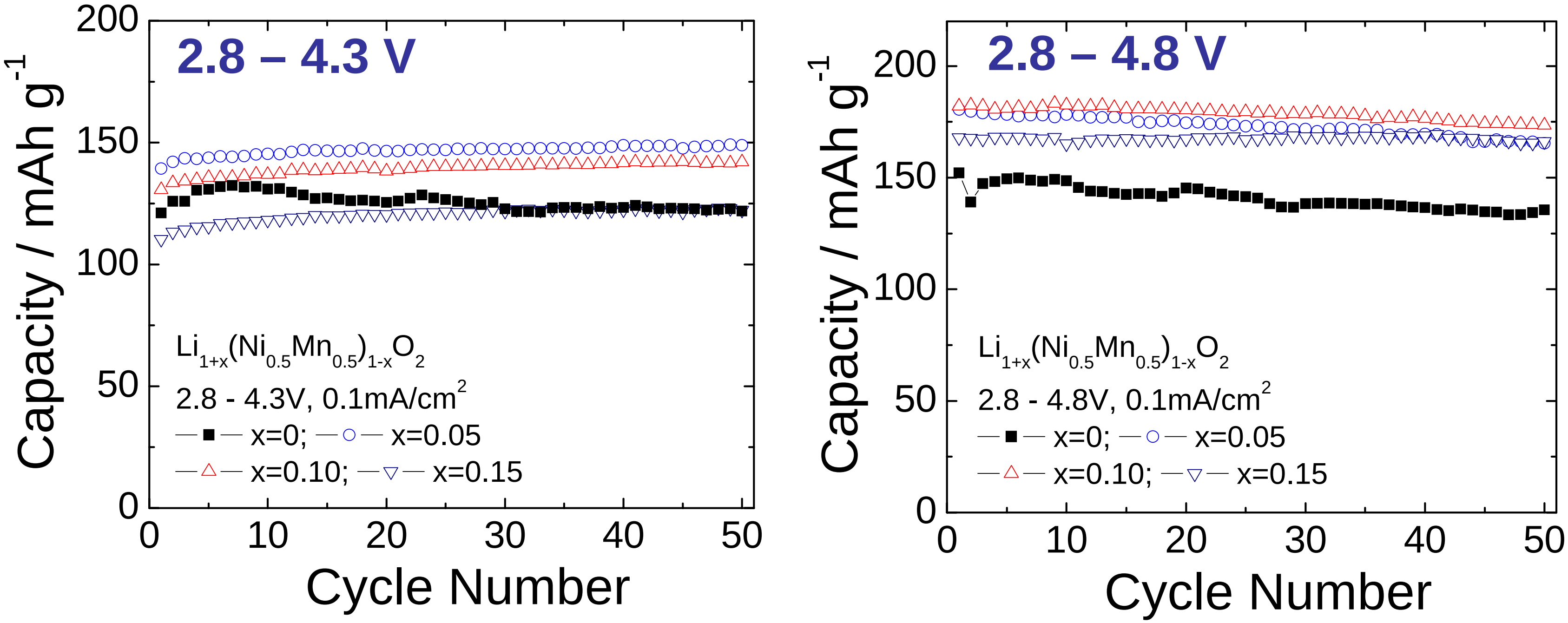




- During the first charge to 4.8 V, the electrodes with excess lithium showed additional dQ/dV peak at ~4.5 V, whose intensity increased with lithium content.
- The additional dQ/dV peak at ~4.5 is attributed to activation of Li_2MnO_3 component in the composite structure ($Li_2MnO_3 \rightarrow 2Li^+ + 2e^- + MnO_2 + 1/2O_2$) as has been commonly observed from $zLi_2MnO_3 \bullet (1-z)Li(Ni_{0.5}Mn_{0.5})O_2$, which is believed to be responsible for the capacity close to or higher than theoretical values.

High voltage performance

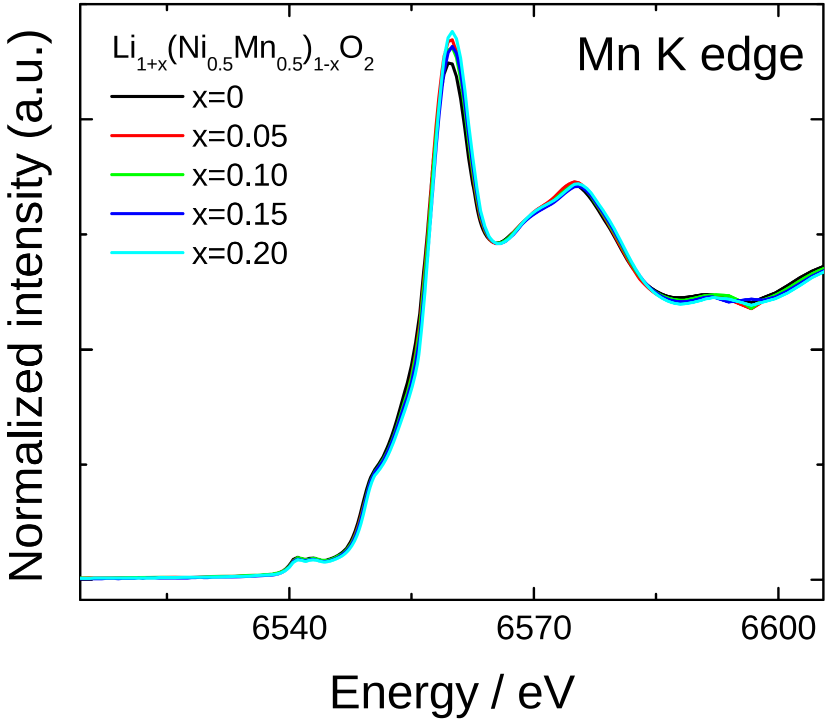
Cycle behavior of $Li_{1+x}(Mn_{0.5}Ni_{0.5})_{1-x}O_2$

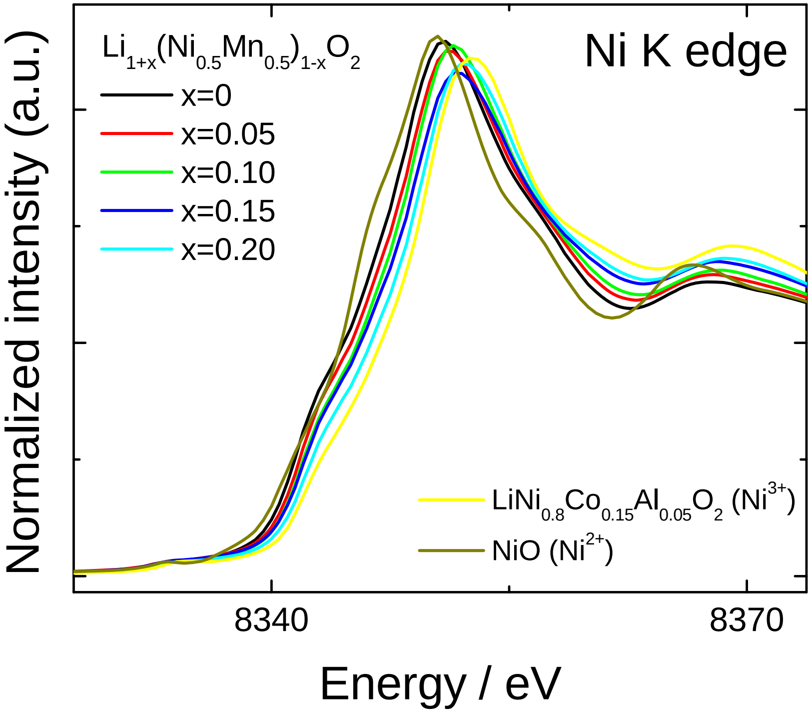


- Li/1M $LiPF_6$ EC:DEC (1:1)/$Li_{1+x}(Ni_{0.5}Mn_{0.5})_{1-x}O_2$, 2.8 – 4.3 V and 2.8 – 4.8 V vs. Li^+/Li
- As the lithium content increased, the discharge capacity increased and the cycling performance was improved.
- The electrodes with excess lithium exhibited discharge capacities close to or larger than theoretical values based on the oxidation state of Ni ions when cycled between 2.8 and 4.8 V.

Mn and Ni K-edge XANES

Pristine $Li_{1+x}(Mn_{0.5}Ni_{0.5})_{1-x}O_2$ powders

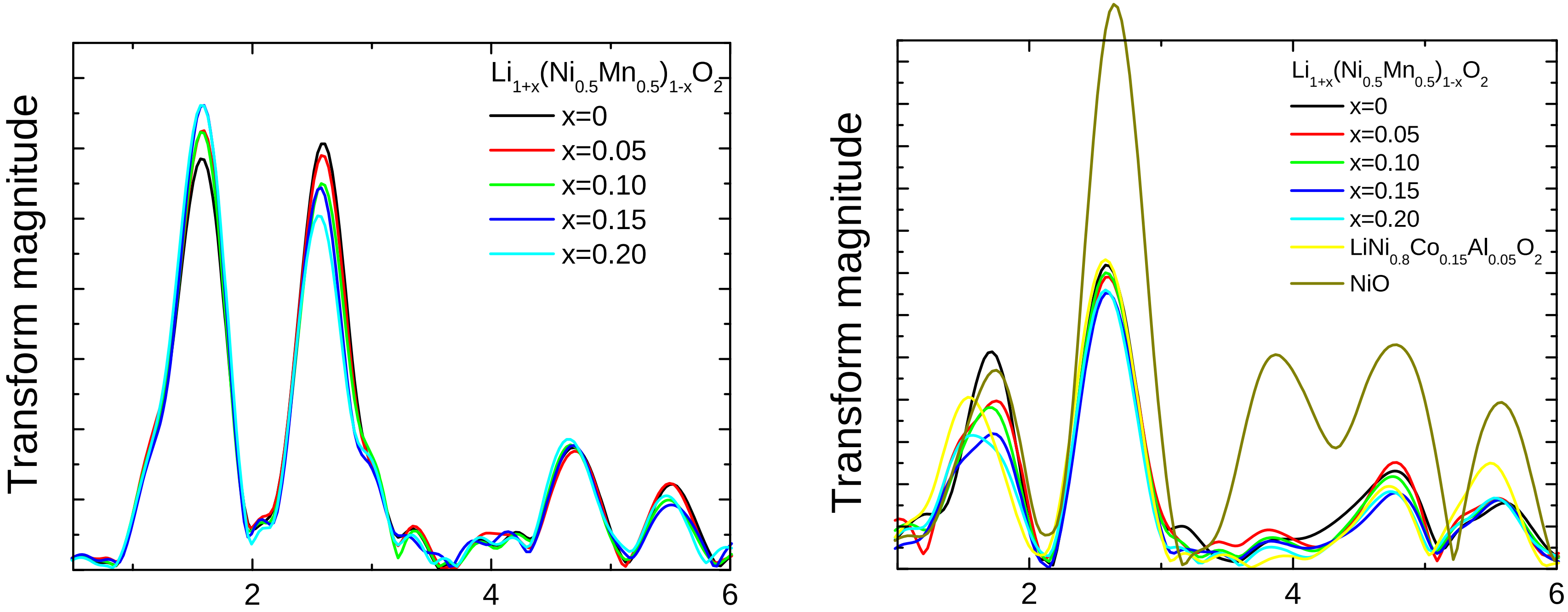




- ➢ The oxidation state of Mn does not change with lithium content.
- ➢ On the other hand, Ni ions are oxidized by incorporating lithium ions in the transition metal layers. The oxidation state of Ni is close to that of NiO (Ni^{2+}) and $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (Ni^{3+}) for x=0 and 0.20, respectively.
- ➢ $2xLi_2Mn^{4+}O_3 \bullet (1-3x)Li(Ni^{2+}{}_{1-y}Ni^{3+}{}_{2y-1}Mn^{4+}{}_{1-y})O_2$ (y=(1-x)/[2(1-3x)]).

Mn and Ni K-edge EXAFS

Pristine $Li_{1+x}(Mn_{0.5}Ni_{0.5})_{1-x}O_2$ powders

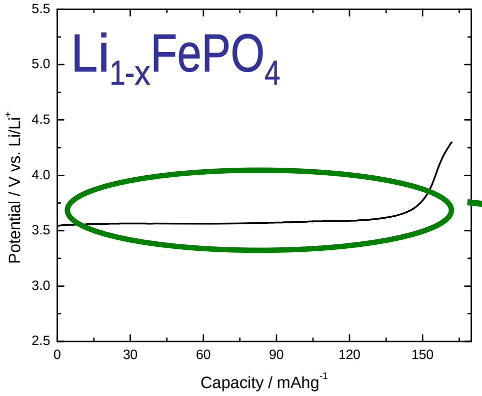


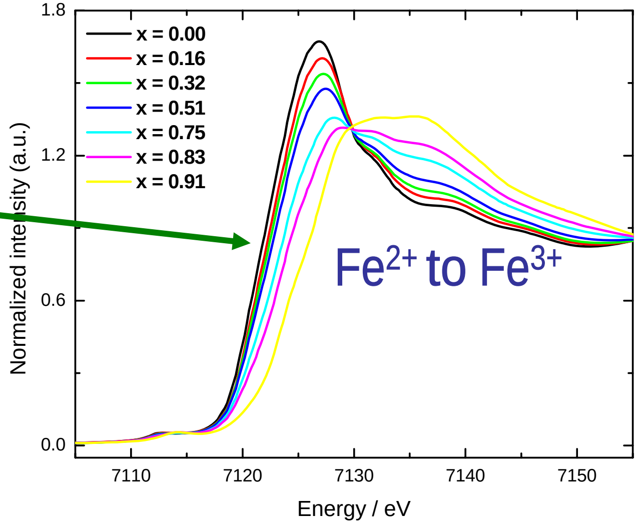
- ➢ The EXAFS data confirms the results of the XANES and the XRD.
  - No change in Mn-O bond length
  - Decrease of Ni-O bond length with x due to increased oxidation state of Ni
  - It is observed, qualitatively, that the coordination number of Mn ions decreases with lithium content due to the formation of Li_2MnO_3-like domains.

In-situ Mn and Fe K-edge XAS

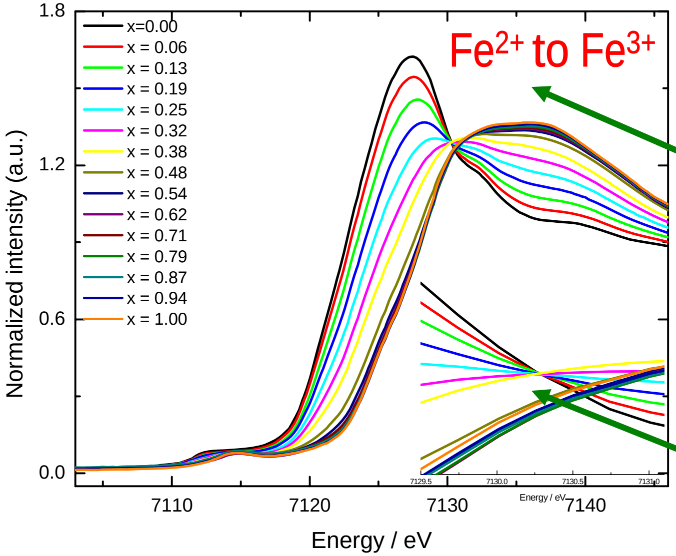
$Li_{1-x}FePO_4$ and $Li_{1-x}Fe_{0.5}Mn_{0.5}PO_4$, electrodes during charge

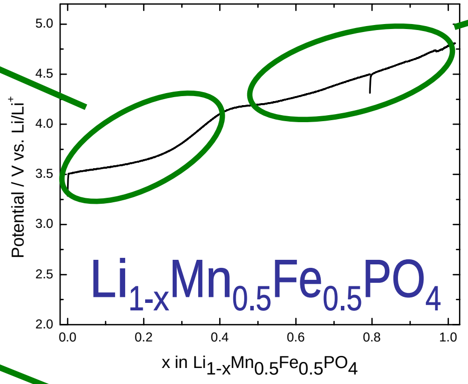
In collaboration with Dr. Zaghib (Hydro Quebec)

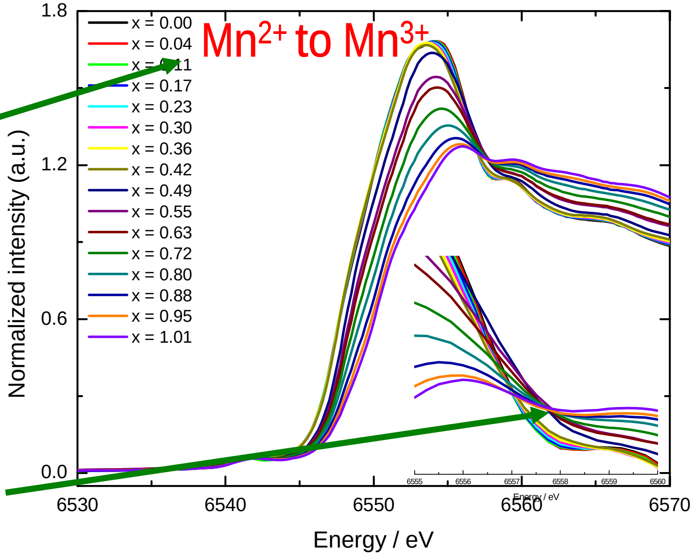




The major charge compensation at the metal site during charge is achieved by the oxidation of Fe^{2+} ions at lower potential (~3.6 V) and the oxidation of Mn^{2+} ions at higher potential (~4.1 V)







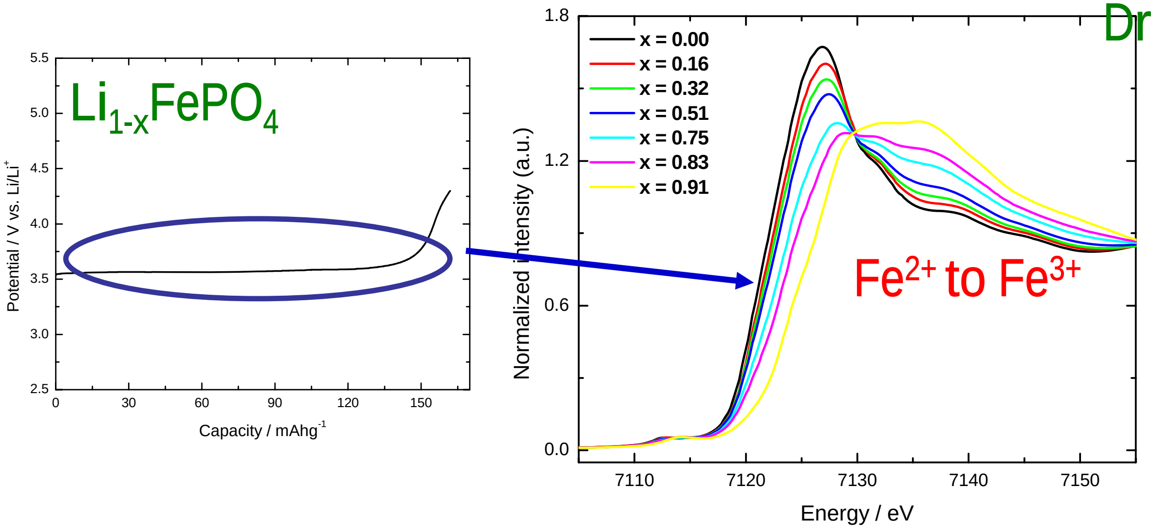
Isosbestic points

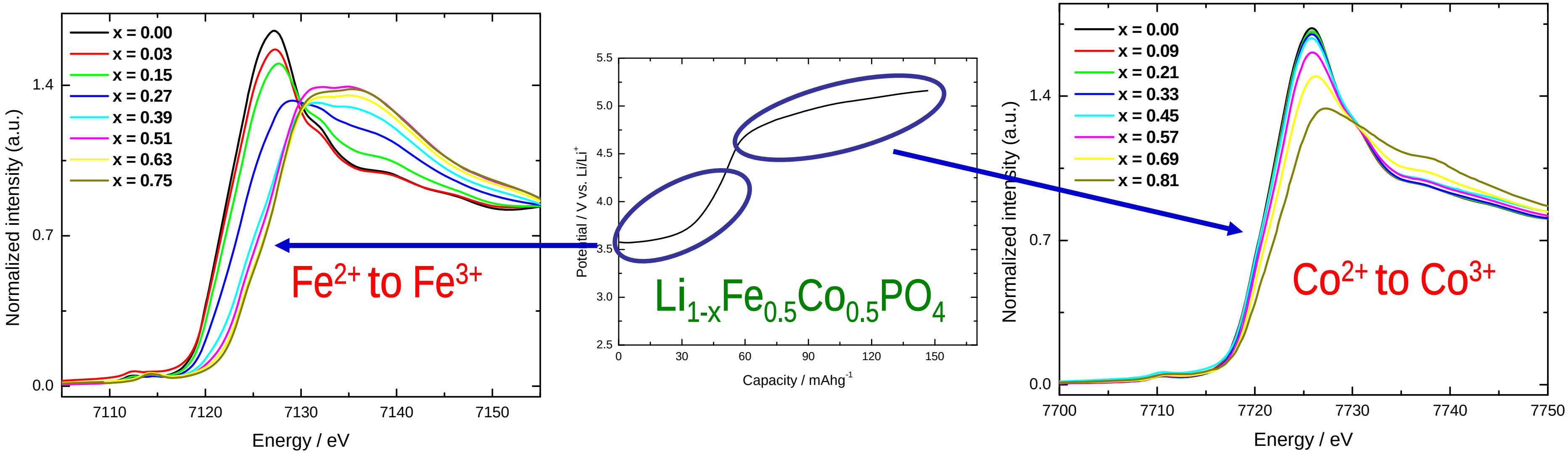
In-situ Fe K-edge XAS

$Li_{1-x}FePO_4$ and $Li_{1-x}Fe_{0.5}Co_{0.5}PO_4$, electrodes during charge

In collaboration with Dr. Huang, Dr.Li Dr. Chen (CAS, Beijing, China)

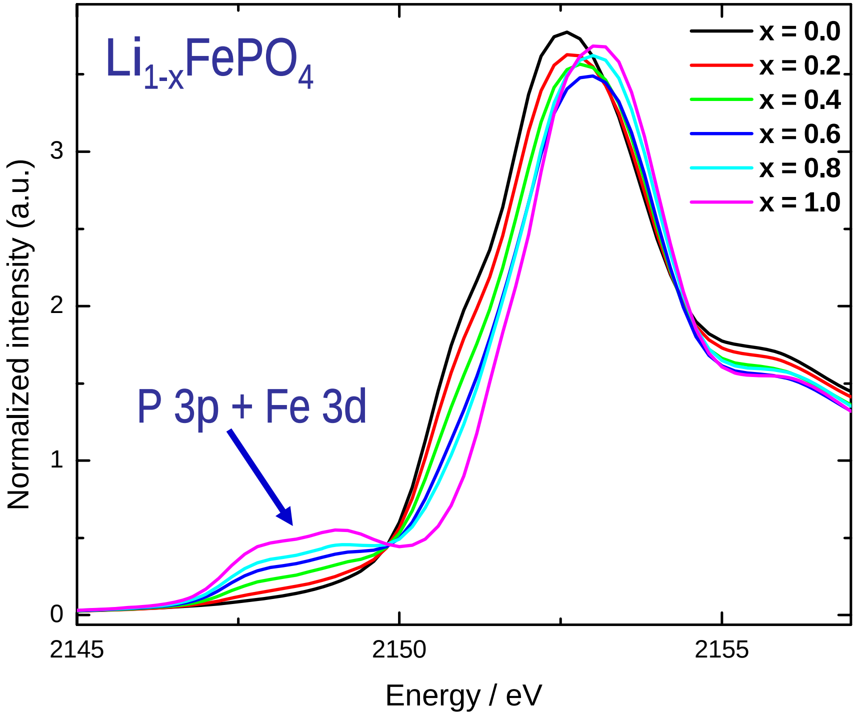
The major charge compensation at the metal site during charge is achieved by the oxidation of Fe^{2+} ions at lower potential (~3.6 V) and the oxidation of Co^{2+} ions at higher potential (~5.0 V)

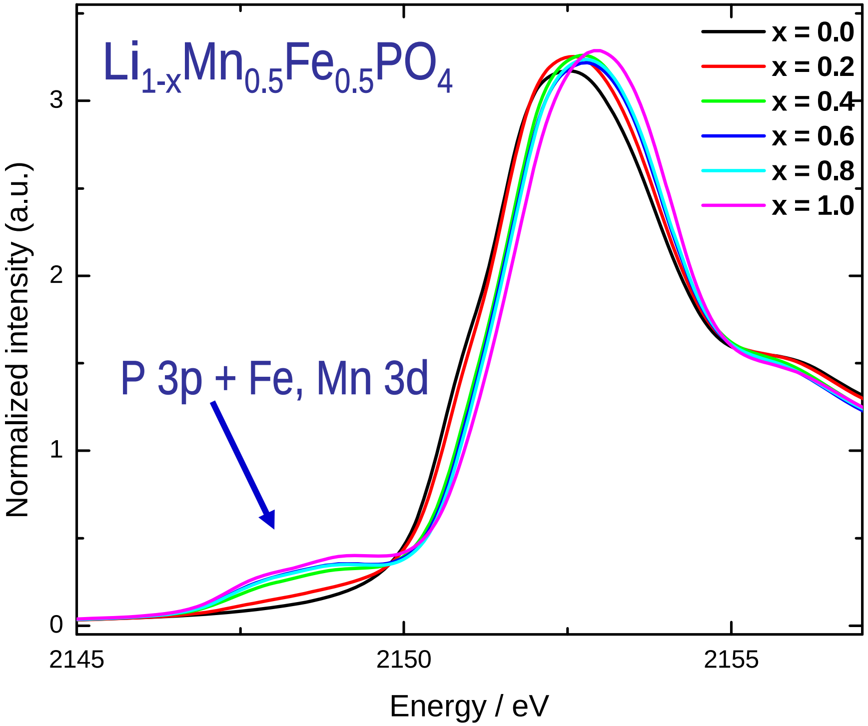




Ex situ P K-edge XAS

$Li_{1-x}FePO_4$ and $Li_{1-x}Fe_{0.5}Mn_{0.5}PO_4$ electrode system during charge





- The chemical changes beyond the first coordination sphere around the phosphorus atoms have a systematic influence on the P K-edge XANES spectrum.

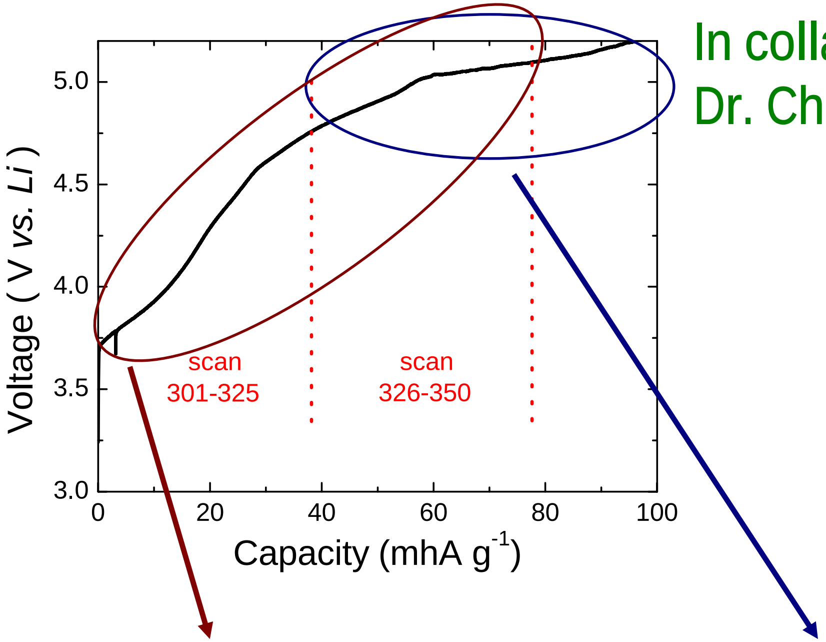
- Pre-edge peak was not observed in P K-edge XAS spectrum for the pristine $LiFePO_4$. Upon delithiation, however, pre-edge peaks start to appear in the lower energy region of main edge.

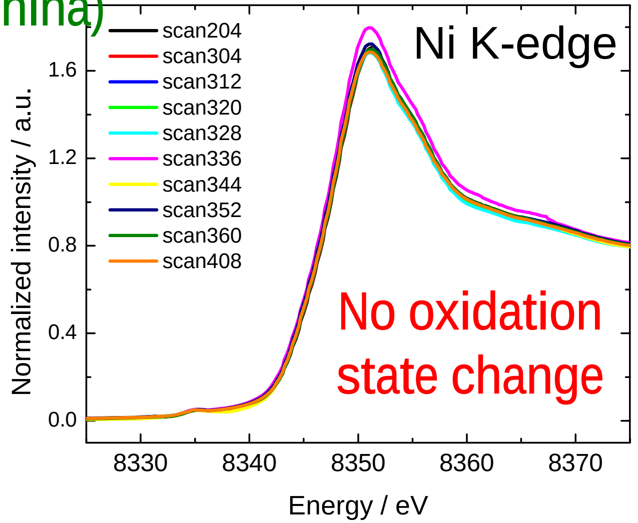
- P and O K XAS shows that the bond characters change during delithiation: as Fe-O bond become less ionic, P-O bond become less covalent via inductive effect.

In-situ Mn, Fe, Co and Ni K-edge XAS

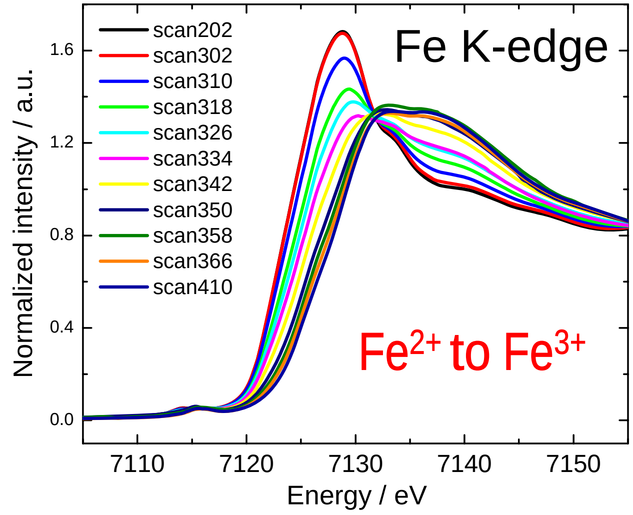
$Li_{1-x}Mn_{1/4}Fe_{1/4}Co_{1/4}Ni_{1/4}PO_4$ electrodes during charge

In collaboration with Dr. Huang, Dr.Li
Dr. Chen (CAS, Beijing, China)

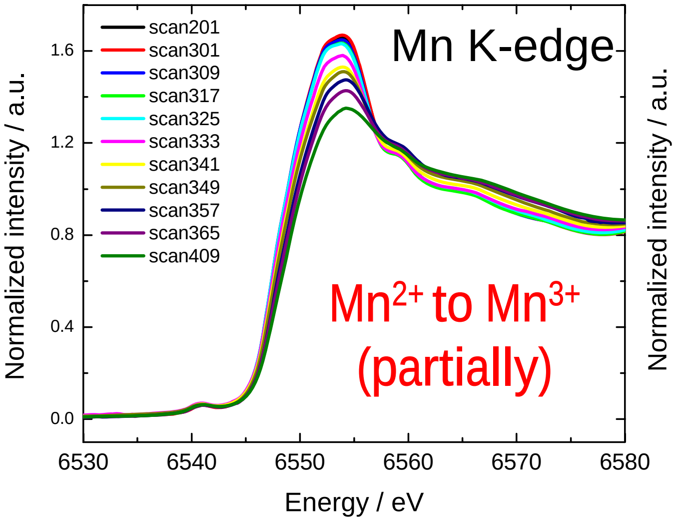




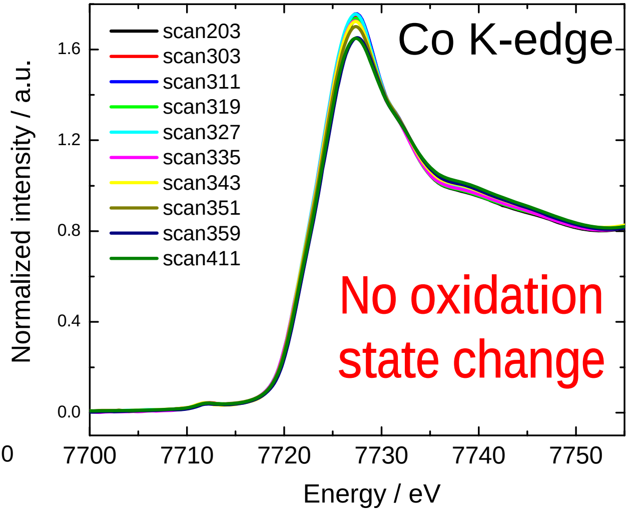
No oxidation state change



Fe^{2+} to Fe^{3+}



Mn^{2+} to Mn^{3+} (partially)

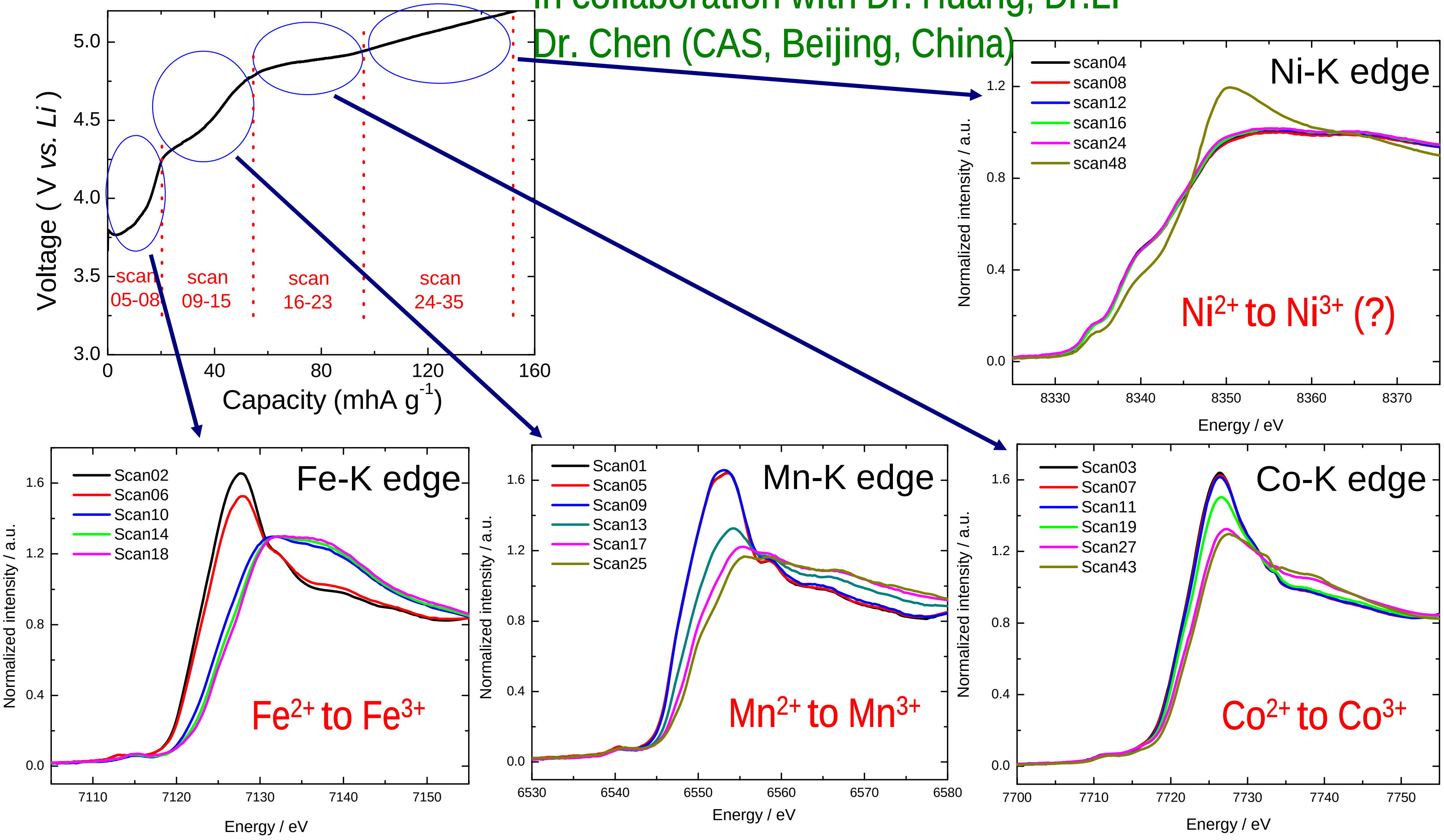


No oxidation state change

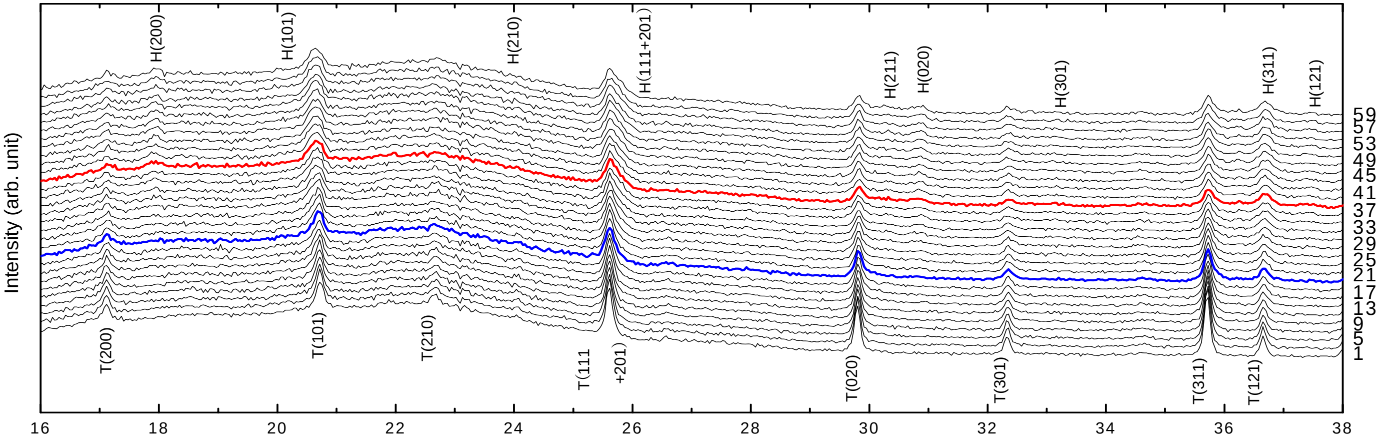
In-situ Mn, Fe, Co and Ni K-edge XAS

Carbon coated $Li_{1-x}Mn_{1/4}Fe_{1/4}Co_{1/4}Ni_{1/4}PO_4$ electrodes during charge

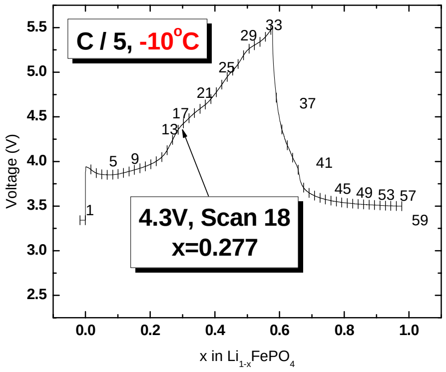
In collaboration with Dr. Huang, Dr.Li
Dr. Chen (CAS, Beijing, China)

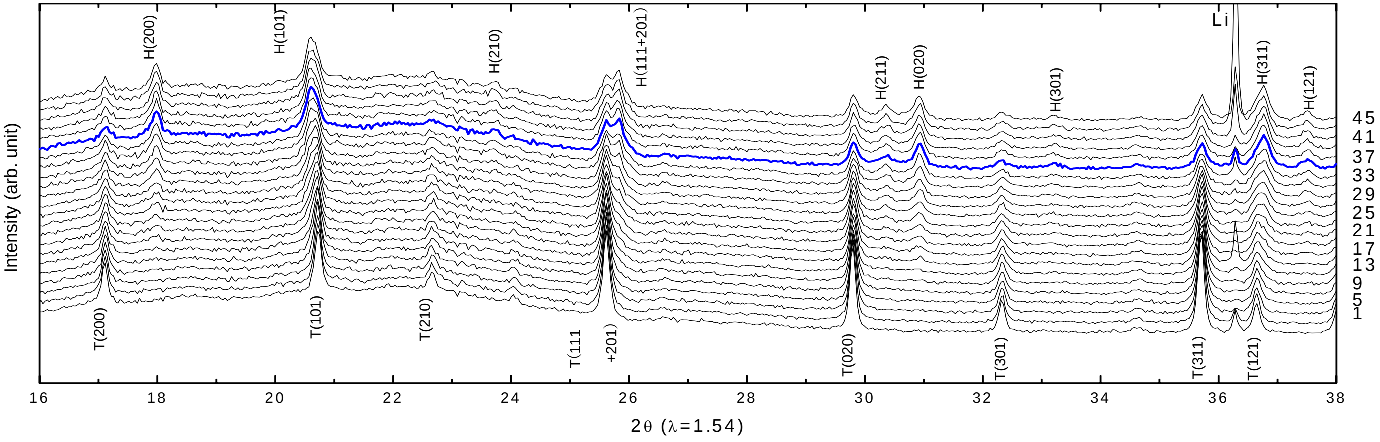


Comparison of *In Situ* X-ray Diffraction Patterns of uncoated & C-coated $LiFePO_4$ at -10°C, C/5 Rate in collaboration with Dr. Cho and Dr. Chung, KIST, South Korea

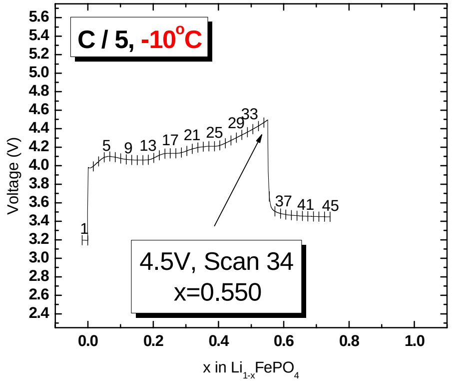


Uncoated





C-coated

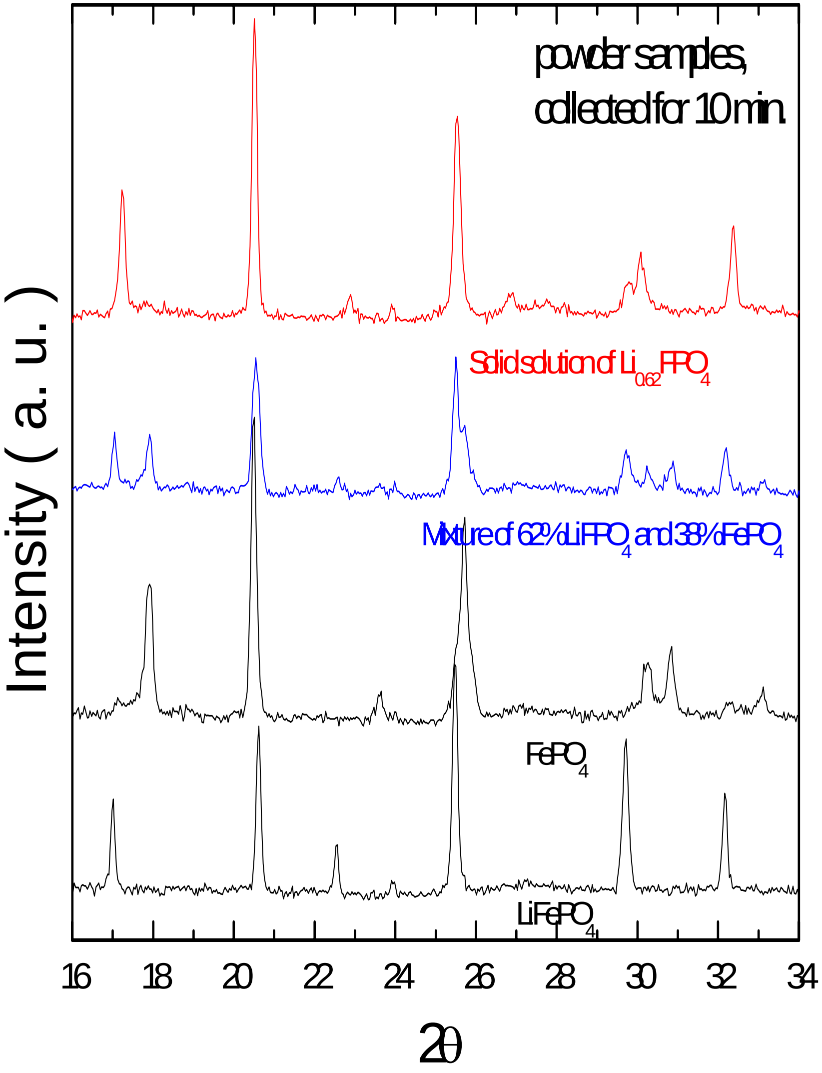


The C-coated $LiFePO_4$ shows much better performance than the uncoated ones at low temperature. The in situ XRD shows the structural changes during low temperature cycling

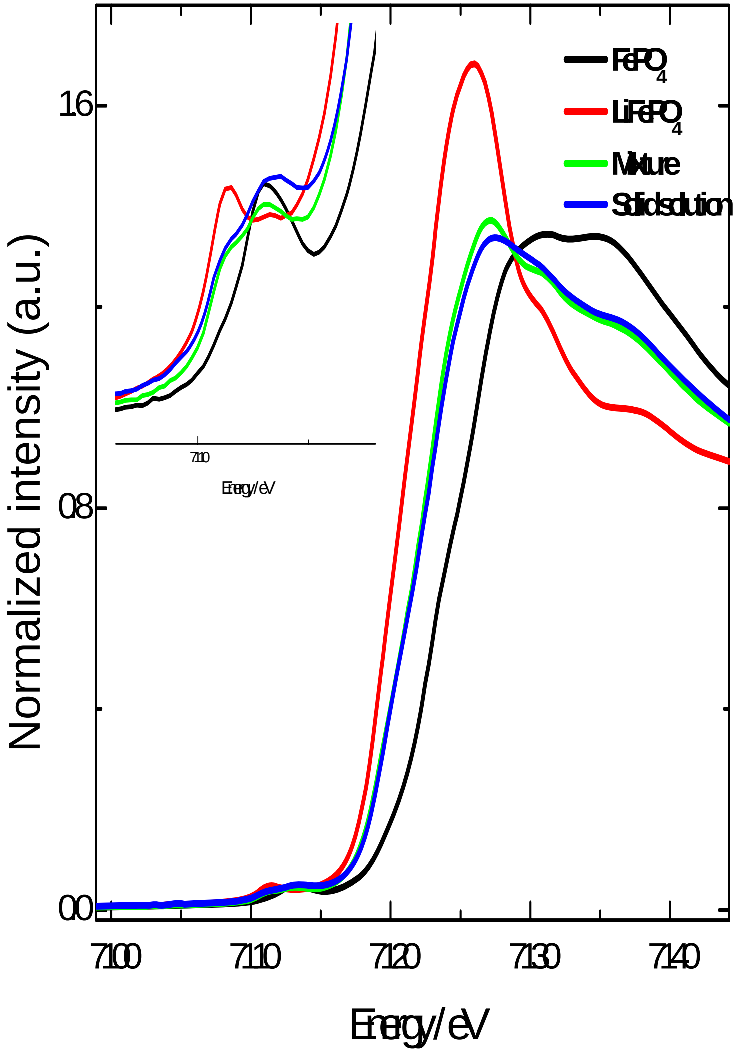
Solid solution of $Li_{1-x}FePO_4$

In collaboration with Dr. Richardson (LBNL)

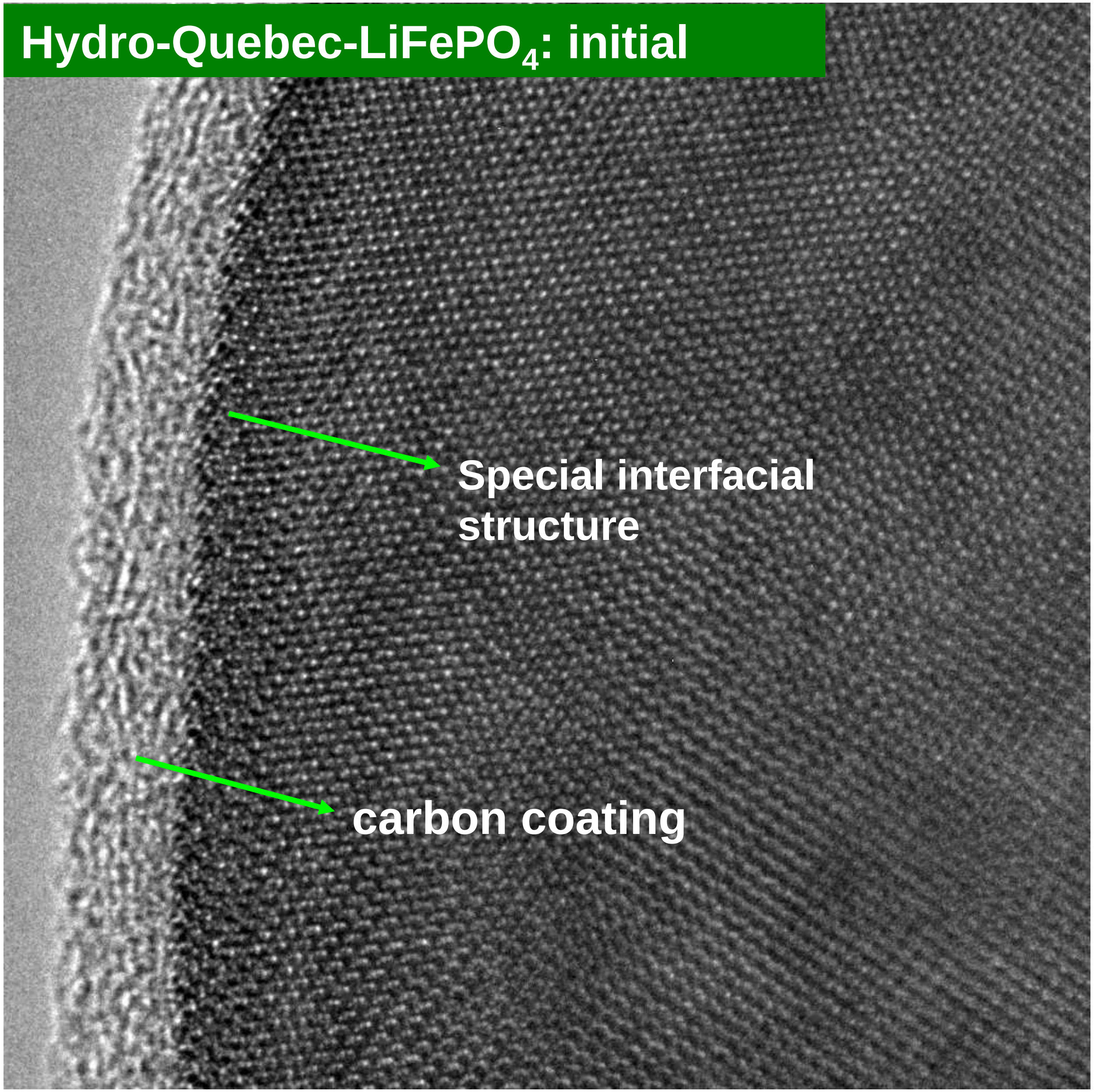
ex situ power XRD patterns

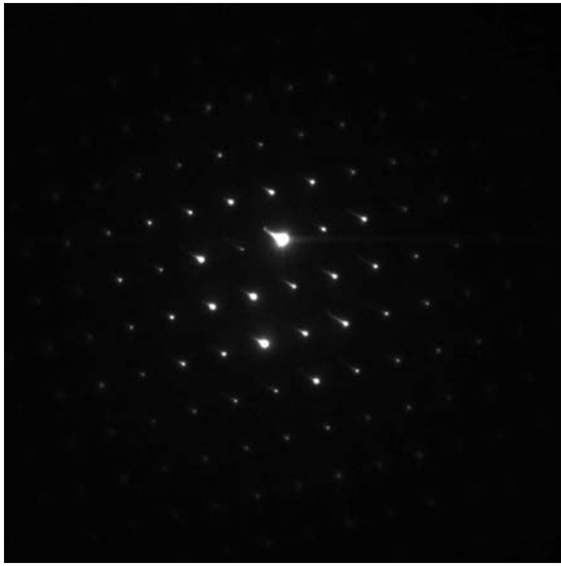


ex situ Fe K-edge XANES spectra

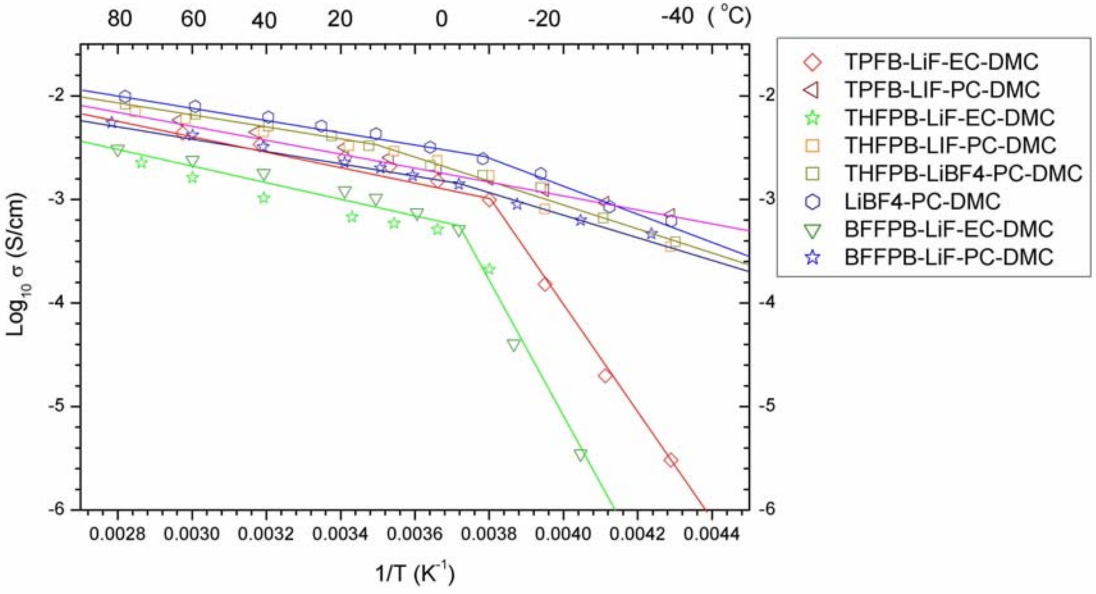


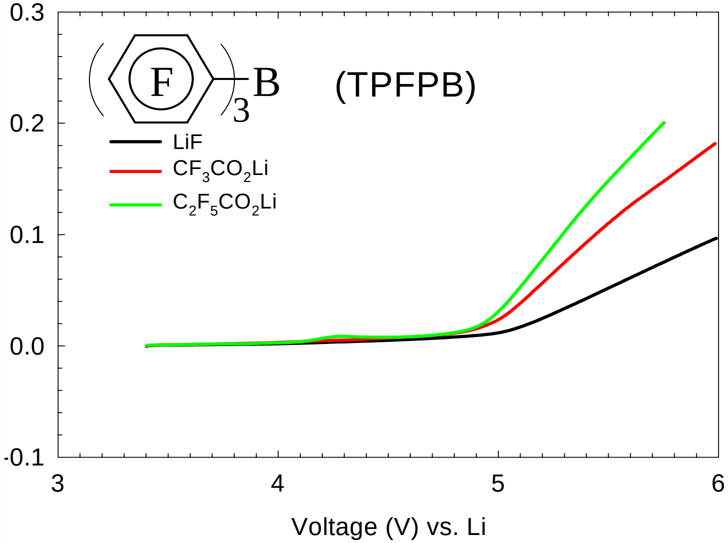
Investigate surface and interfacial structure in details using HRTEM

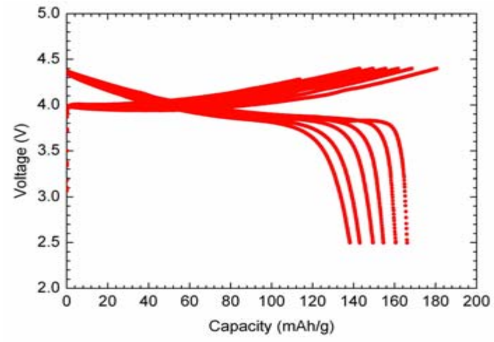




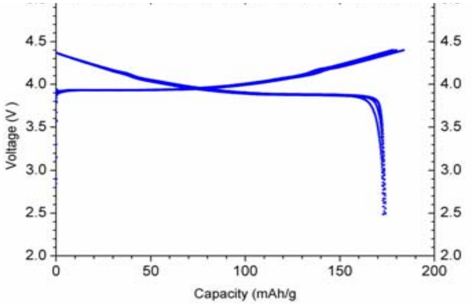
Develop novel electrolyte, which will play important role in improving interfacial stability and electrochemical stability for high energy/power batteries







Electrolyte: 1.0 M $LiBF_4$,
PC:DMC(1:1)



Electrolyte: 1.0 M TPFPB+0.2M $LiBF_4$,
PC:DMC(1:1)

New boron based LiF electrolyte:

Wide electrochemical window, High ionic conductivity, High stability, High Li^+ transfer number

Selected Publications and Invited Presentations

Selected Publications

- Won-Sub Yoon, Kyung Yoon Chung, James McBreen, Deyu Wang, Xuejie Huang, Liquan Chen, and Xiao-Qing Yang “Electronic Structural Changes of the Electrochemically Delithiated LiFe0.5Co0.5PO4 Cathode Material studied by X-ray Absorption Spectroscopy” *Journal of Power Sources*, Vol. 174(2) (2007) 1015.
- Kyung Yoon Chung, Won-Sub Yoon, James McBreen, Xiao-Qing Yang, Si Hyoung Oh, Ho Chul Shin, Won Il Cho, and Byung Won Cho “In Situ X-Ray Diffraction Studies on the Mechanism of Capacity Retention Improvement by Coating at the Surface of LiCoO2” *Journal of Power Sources*, Vol. 174(2) (2007) 619.
- Won-Sub Yoon, Kyung Yoon Chung, James McBreen, Daniel A. Fischer, and Xiao-Qing Yang “Electronic Structural Changes of the Electrochemically Li-ion Deintercalated LiNi0.8Co0.15Al0.05O2 Cathode Material Investigated by X-ray Absorption Spectroscopy” *Journal of Power Sources*, accepted.
- Won-Sub Yoon, Kyung Yoon Chung, Kyung-Wan Nam, and Kwang-Bum Kim “Characterization of LiMn2O4 - Coated LiCoO2 Film Electrode Prepared by Electrostatic Spray Deposition” *Journal of Power Sources*, Vol. 163 (2006) 207.
- Won-Sub Yoon, Kyung Yoon Chung, Mahalingam Balasubramanian, Jonathan Hanson, James McBreen, and Xiao-Qing Yang “Time Resolved XRD Study on the Thermal Decomposition of Nickel-Based Layered Cathode Materials for Li-ion Batteries” *Journal of Power Sources*, Vol. 163 (2006) 219.
- Won-Sub Yoon, Kyung Yoon Chung, James McBreen, Daniel A. Fischer, and Xiao-Qing Yang, “Changes in Electronic Structure of the Electrochemically Li-ion Deintercalated LiNiO2 System Investigated by Soft X-ray Absorption Spectroscopy” *Journal of Power Sources*, Vol. 163 (2006) 234.
- Dongli Zeng, Jordi Cabana, Julien Bréger, Won-Sub Yoon and Clare P. Grey “Cation Ordering in Li[NixMnxCo(1-2x)-]O2 Layered Materials; An NMR, Pair Distribution Function and X-ray Absorption Spectroscopy Study” *Chemistry of Materials*, accepted.

Invited Presentations

- X. Q. Yang, W. S. Yoon, K. W. Nam, H. S. Lee, J. McBreen, H. Li, X. Huang, L. Chen J-M. Chen, K. Y. Chung and B. W. Cho, “Structural Stability and Safety Related Issues of Electrode Materials for Lithium Batteries Studied by Synchrotron Based X-ray”, Invited, presented at The 48th Battery Symposium in Japan, November 13-15, 2007, Fukuoka, Japan.
- X. Q. Yang, H. S. Lee, H. Li, W. S. Yoon, K. W. Nam, J. McBreen, X. Huang, L. Chen, “Boron-Based Lewis Acids as Additives in LiF and LiBO4 Based Electrolytes and Their potential to be Used in High Voltage Lithium-ion Batteries” Invited, presented at the 2007 meeting of International Battery Materials Association (IBA2007), November 20, 2007, Shenzhen, China
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Collaborators

M. Thackeray and S. Kang (ANL, cathode materials)

Stan Whittingham (SUNY Binghampton, new anode and cathode materials)

C. Grey (SUNY Stony Brook, Solid state NMR studies, in situ XAS and XRD studies)

Karim Zaghib (Institut de Recherche d'Hydro-Québec (IREQ), $LiFePO_4$, $LiMn_{0.5}Fe_{0.5}PO_4$, $LiMnPO_4$)

Thomas Richardson (LBNL, Solid-solution $LiFePO_4$)

Arumugam Manthiram (University of Texas at Austin, Multi-doped spinel)

G. Ceder (MIT, Ion-exchanged $LiNi_{0.5}Mn_{0.5}O_2$, $LiFePO_4$)

Yimei Zhu (BNL, Electron diffraction and TEM studies of battery materials.)

K.Y. Chung and Dr. B.W. Cho, (KIST, South Korea, coated $LiFePO_4$)

Y. K. Sun (Hanyang University, South Korea, AlF_3 coating)

L. Chen, X. Huang, and H. Li (Beijing Institute of Physics, New cathode Materials and new electrolytes, SEI layer formation.)

M-H Yang and J-M Chen (Industrial Technology Research Institute, Taiwan, Power-type Li-ion Battery Development for HEV Application.)

Prof. M. Yoshio, Saga University, Japan

Planned work for FY 2008

- In collaboration with ANL, using synchrotron based In situ XRD and XAS techniques to study $Li_{1+x}(Mn_{0.5}Ni_{0.5})_{1-x}$ type and $Li_{1+x}Mn_{1/3}Ni_{1/3}Co_{1/3}O_2$ type cathodes for high energy density lithium-ion batteries.

- In situ XRD and XAS studies in collaboration with Hydro-Quebec and CAS on coated and uncoated $LiFe_{1-x}M_xPO_4$ (M=Mn, Co, and Ni) type of olivine structured cathodes.

- Further development of in situ soft XAS technique for thermal stability studies. Apply this new technique to various electrode materials to probe the structural changes at the surface and in the bulk simultaneously. Co-relate these changes to understand the fundamental aspects of the safety related thermal run away of lithium-ion cells.

- Further development of surface and interface techniques, such as TEM, electron diffraction, and electron energy loss spectroscopy (EELS) for SEI layer formation and functionality studies

- Design, synthesis, and characterization of new salts, new additives, and new electrolyte systems for high voltage lithium-ion cells in collaboration with CAS, MER, and ARL.

Summaries

◆ In situ X-ray absorption studies on the $Li_{1+x}(Mn_{0.5}Ni_{0.5})_{1-x}$ type cathode materials give an in-depth understanding of the charge compensation and energy storage mechanisms of this type of materials.

◆ In situ X-ray diffraction and absorption studies on coated and uncoated $LiFe_{1-x}M_xPO_4$ (M=Mn, Co, and Ni) type of olivine structured cathode materials showed the important effects of doping and surface coating on the structural changes and performance of the lithium-ion cells

◆ The HRTEM and electron spectroscopy based techniques will provide more diagnostic tools for battery materials studies. Combining them with synchrotron x-ray based techniques will be quite beneficial for the SEI studies.

◆ The studies and development of new salts, new additives, and new electrolyte systems will be crucial for the high voltage lithium-ion batteries.

◆ More collaborative work with other members of the hybrid and electric systems program and with international collaborators will be continued

Preliminary studies on surface structure variation of $LiCoO_2$ under high speed charging (15 minutes)