In situ Characterizations of New Battery Materials and the Studies of High Energy Density Li-Air Batteries

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Brookhaven National Lab. (BNL)

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Washington, DC, June 7-11

ES059

BROOKHAVEN NATIONAL LABORATORY

Overview

Timeline

- Start: 10/01/2008
- Finish: 09/30/2011
- 60% complete

Barriers addressed

- Li-ion and Li-metal batteries with long calendar and cycle life
- Li-ion and Li-metal batteries with superior abuse tolerance
- To reduce the production cost of a PHEV batteries

Budget

- Funding received in FY08

  DOE: $650k

- Funding received in FY09

  DOE: $650k

Collaborators

- University of Massachusetts at Boston
- Oakridge National Lab. (ORNL)
- University of Tennessee
- Argonne National Lab. (ANL)
- SUNY Binghamton
- SUNY Stony Brook
- Korean Institute of Science and Technology (KIST)
- Beijing Institute of Physics
- Hydro-Québec (IREQ)

Objectives of This Project

- To determine the contributions of electrode materials changes, interfacial phenomena, and electrolyte decomposition to the cell capacity and power decline.
- To develop and apply synchrotron based *in situ* x-ray techniques to study materials in an environment that is close to the real operating conditions.
- To screen and study the potentially low cost materials such as $LiFe_{1-x}Mn_xPO_4$.
- To carry out fundamental studies of high energy density Li-Air batteries.
- To design, synthesize and characterize high voltage cathode and high voltage electrolytes for high energy density lithium batteries for plug-in hybrid electric vehicles (PHEV).
- To design, synthesize and characterize new electrolyte and electrolyte additives for Lithium-air batteries with capability to dissolve Li_2O and Li_2O_2 oxides.
- To develop new diagnostic tools for battery studies.
- To identify and investigate the new battery materials with low cost potential to meet DOE goals.

Milestones

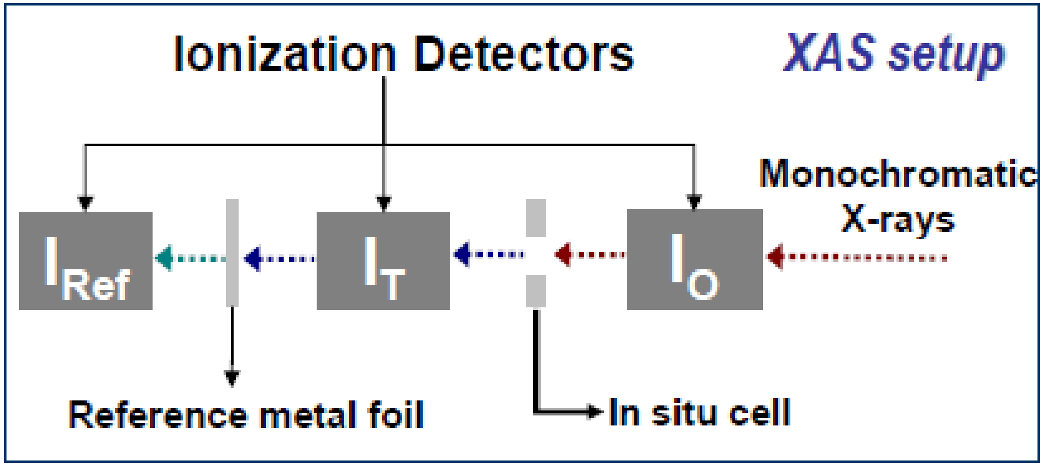
Month/Year	Milestones
Apr/10	Complete *in situ* x-ray diffraction (XRD) studies of $LiFe_{1-x}Mn_xPO_4$ (x=0 to 1) cathode materials during electrochemical cycling. ➥ *Completed.*
Apr/10	Complete the preliminary studies of carbon structure effects on the electrocatalysis performance of air cathode in Li/air cells. ➥ *Completed.*
Apr/10	Complete the studies of the surface modification of carbon gas diffuse electrode (GDE) to improve the electrocatalysis performance in Li/air cells. ➥ *Completed.*
Sep/10	Complete *in situ* X-ray absorption spectroscopy (XAS) studies of $LiFe_{1-x}Mn_xPO_4$ (x=0 to 1) cathode materials during electrochemical cycling. ➥ *On schedule.*
Sep/10	Complete *soft and hard* X-ray absorption spectroscopy (XAS) studies of high voltage cathode materials (e.g., $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ and $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$). ➥ *On schedule.*
Sep/10	Complete the design and construction of Li/air testing cell for rechargeable Li-Air batteries. ➥ *On schedule.*

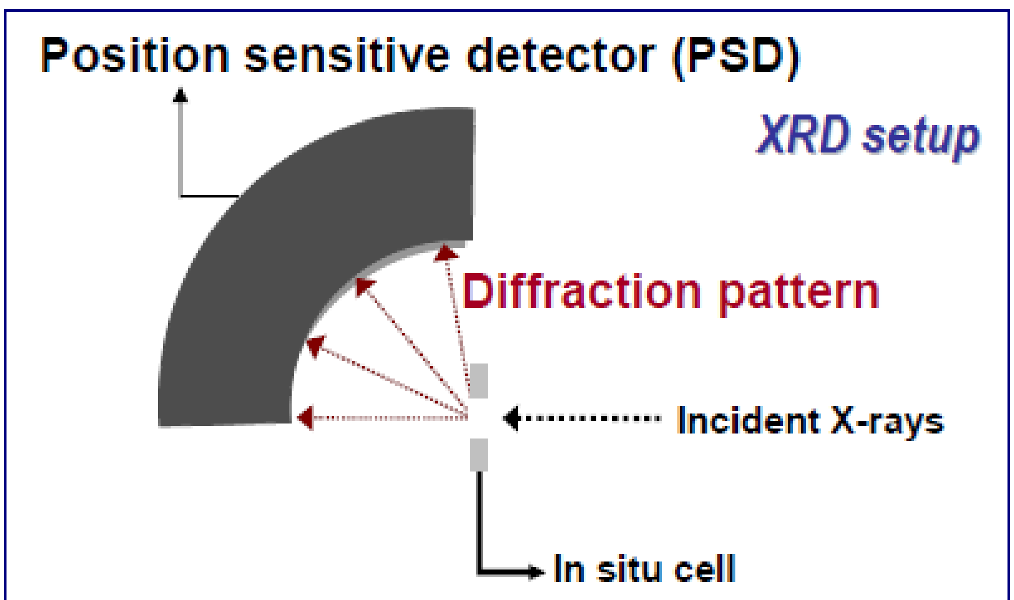
Approaches

- *In situ* X-ray absorption spectroscopy and XRD studies of new electrode materials such as $LiFe_{1-x}M_xPO_4$ (M=Mn, Co, Ni) and $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ during electrochemical cycling to carry out the diagnostic studies to improve the energy density.
- Soft X-ray absorption spectroscopy studies of new electrode materials to distinguish the difference between the surface and the bulk.
- *In situ* and *ex situ* transmission electron microscopy (TEM) and selected area electron diffraction (SAED) to study the structural changes of electrode materials with high location specification and spatial resolution.
- Conduct electrochemical studies of gas diffusion electrode (GDE) for Li-Air batteries. Construct and test lithium-air batteries using organic electrolytes.
- Design and synthesis of new electrolyte system with capability to dissolve Li_2O and Li_2O_2 for lithium-air batteries.
- Develop new solvents, salts, additives, and electrolyte systems through molecular design and organic synthesis, study their effects on the formation and stability of the solid electrolyte interphase (SEI) layer.
- Collaborations with other institutions and industrial partners.

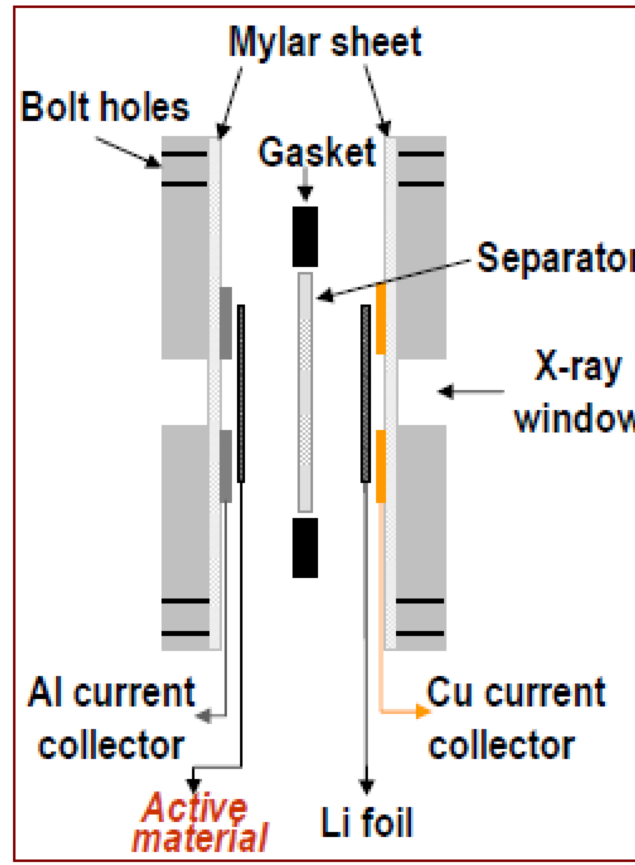
Combining *in situ* synchrotron XAS and XRD techniques to do diagnostic studies of battery materials and components at or near operating conditions

X19A & X18B (XAS) and X14A & X18A (XRD) at National Synchrotron Light Source (NSLS)



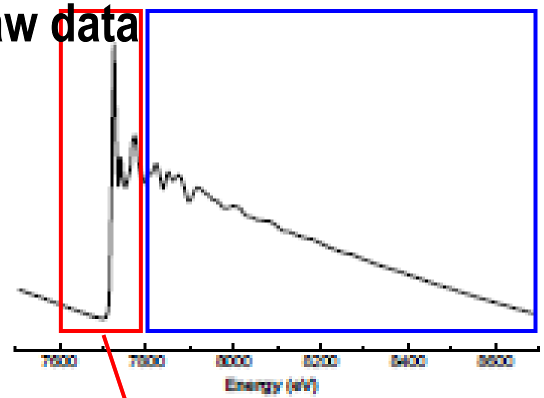


In situ cell



X-ray absorption spectroscopy : *XANES* and *EXAFS*

raw data

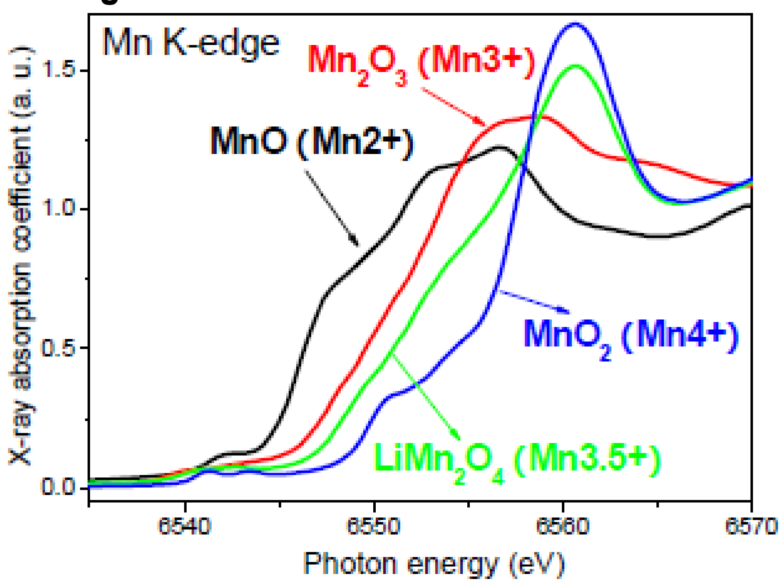


Extended X-ray Absorption Fine Structure (EXAFS)

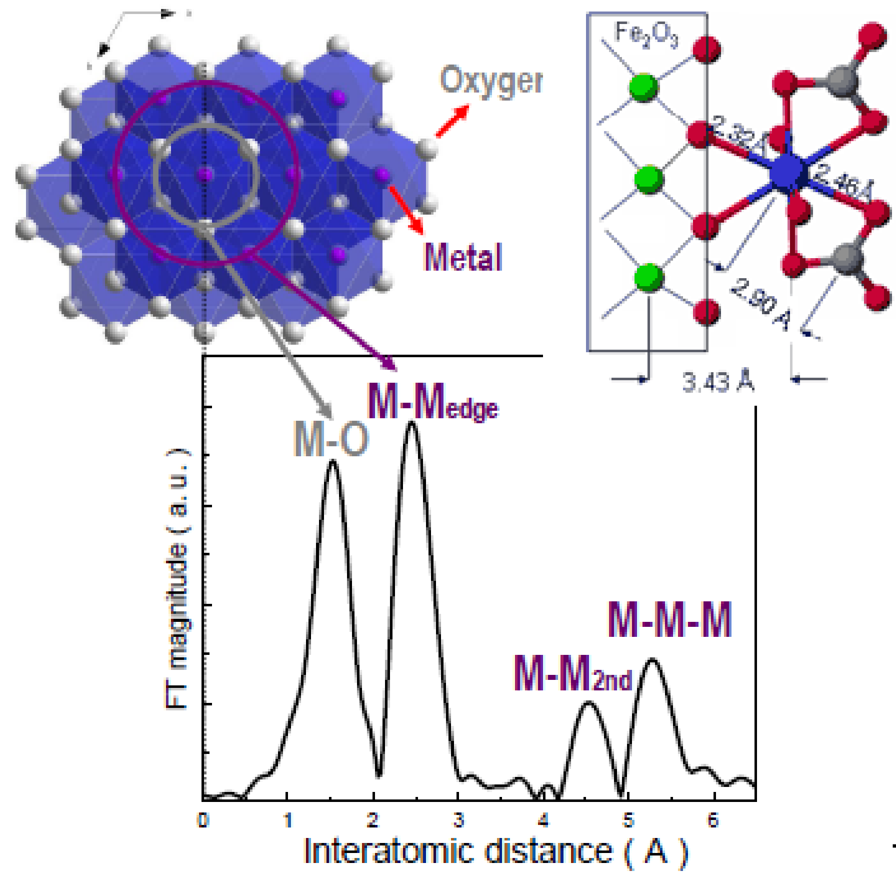
; Local structural information like **bond distance, coordination number, degree of disorder**

X-ray Absorption Near Edge Structure (XANES)

; **Oxidation state**, site symmetry, covalent bond strength



Layered $LiMO_2$ structure



Technical Accomplishments

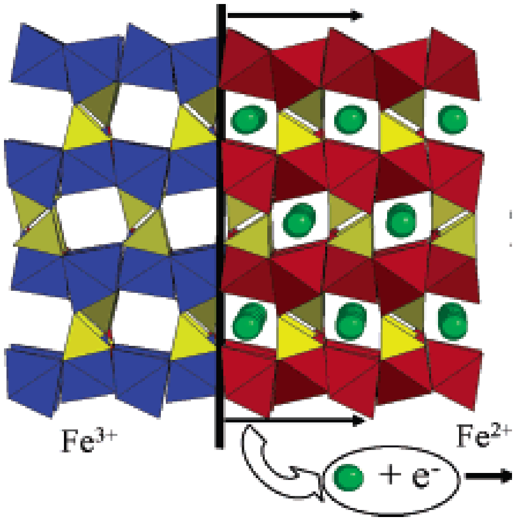
- Completed *in situ* X-ray absorption spectroscopy (XAS) and *in situ* XRD studies on $LiFe_{1-x}Mn_xPO_4$ cathode materials during charge-discharge cycling.
- Completed *in situ* hard X-ray absorption spectroscopy studies on high energy $Li_{1.2}Mn_{0.6}NI_{0.2}O_2$ cathode material during charge-discharge cycling.
- Identified the effects of carbon structure for gas diffuse electrode (GDE) of Lithium-Air-battery and synthesized new carbon materials with larger pore size, which significantly improved the discharge capacity of the Lithium-Air cell.
- Developed novel surface modification of the carbon materials for GDE and obtained dramatic increase in the capacity of the Lithium-Air cell using the surface modified carbon for GDE.
- Developed a family of new boron based additives with good SEI formation capability and anion receptor functionality for lithium battery electrolyte (US patent was filed in 2009).
- Synthesized and tested new additives with capability to dissolve Li_2O_2 and Li_2O_2.

Phase transition behaviors of olivine $LiMPO_4$ cathode materials

- Ongoing debates about the **phase transition behaviors** of olivine structured $LiMPO_4$ materials during lithium extraction/insertion.

Two phase reaction

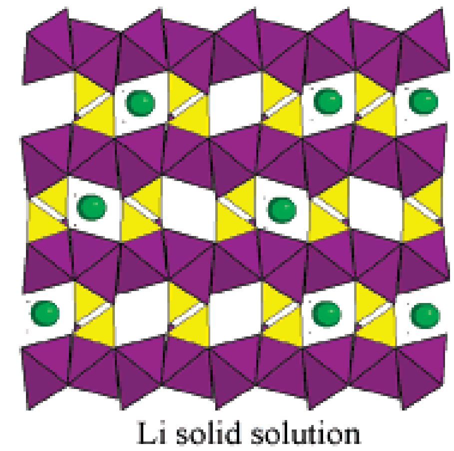
$FePO_4$ $LiFePO_4$



vs.

Single phase reaction
(i.e. solid solution reaction)

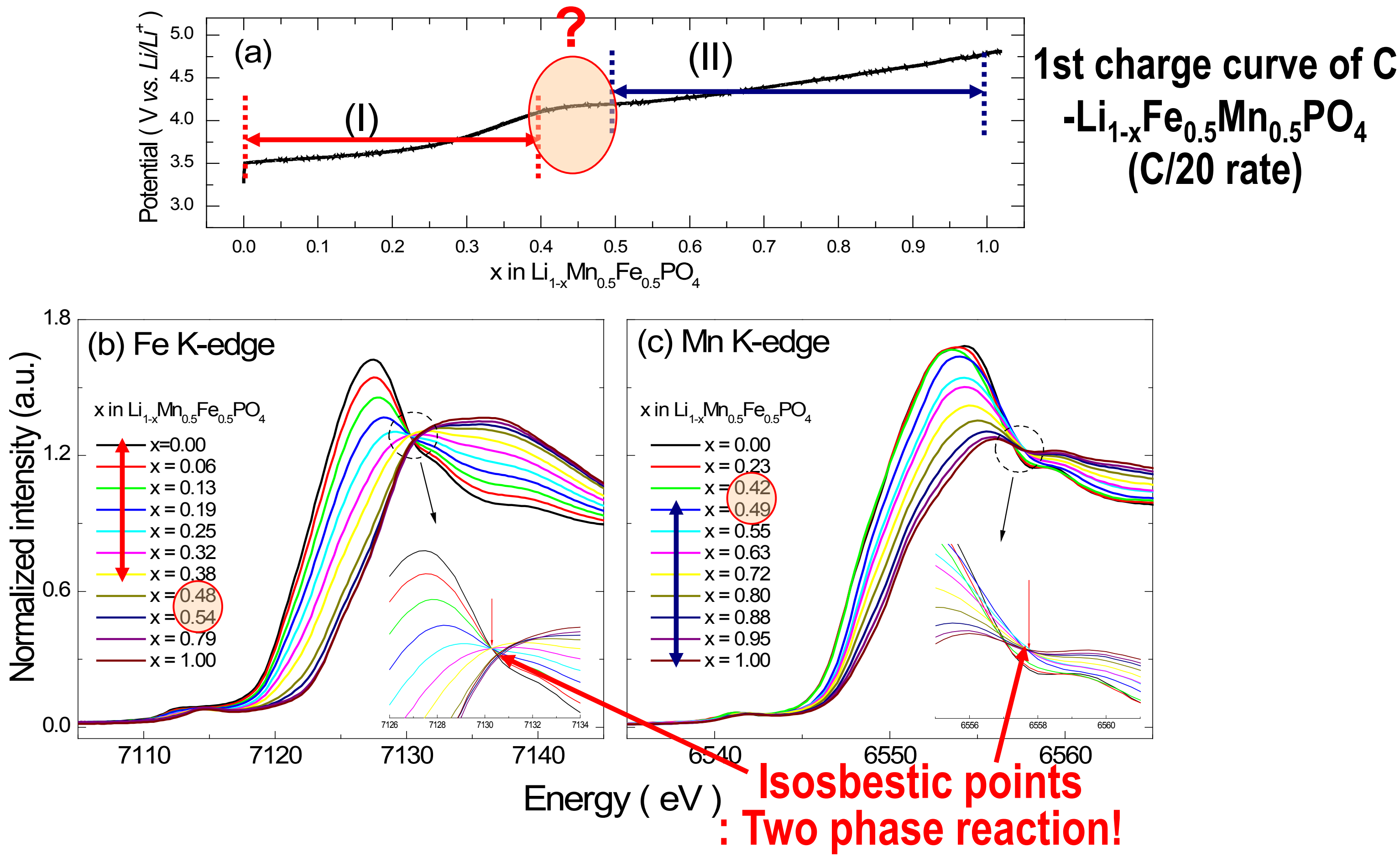
Li_xFePO_4



Images From B. Ellis et al., JACS, Vol. 128 (2006) 11416 p.

➥ Applied *in situ* XAS and XRD to study the relationship between phase transition behaviors and introduction of 3d transition metals (Mn, Co, Ni) in $LiFePO_4$.

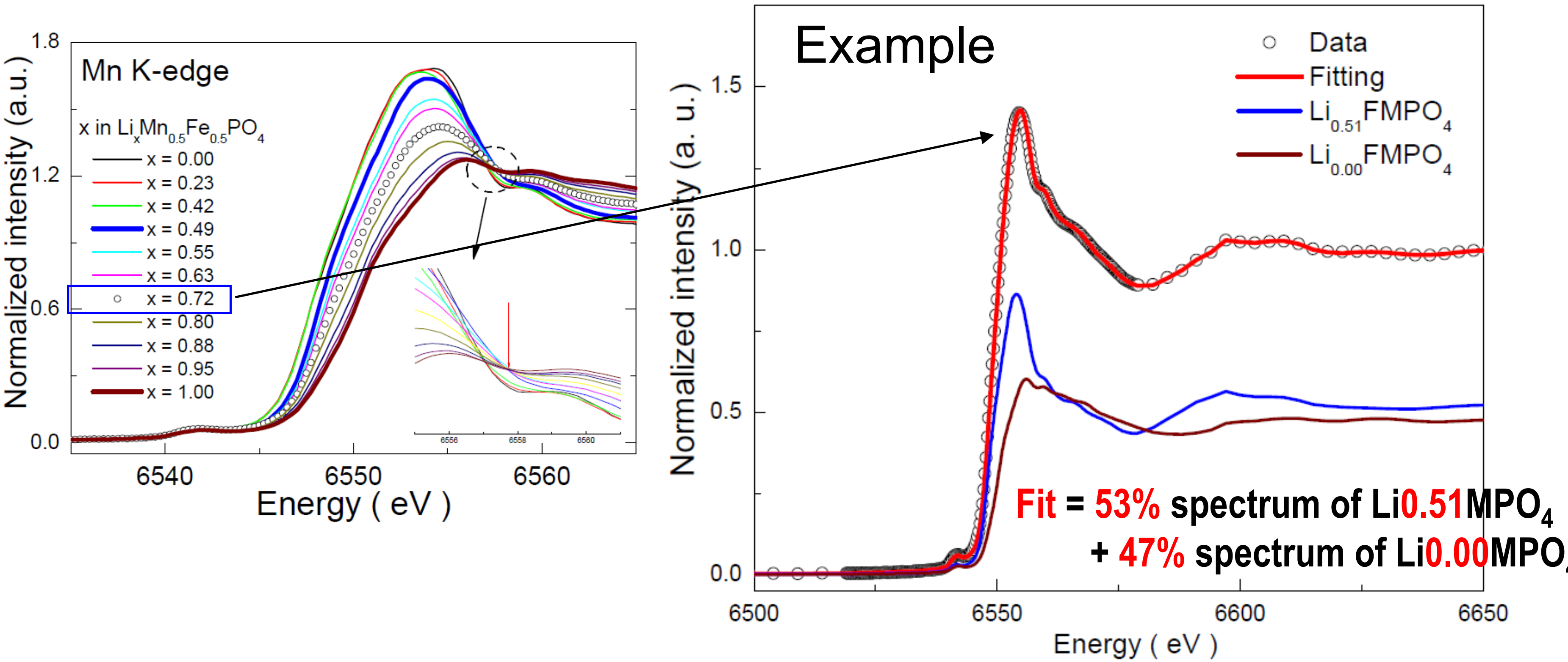
In situ Fe & Mn K-edge XANES spectra of C-Li$Fe_{0.5}Mn_{0.5}PO_4$ (in collaboration with Hydro-Québec)



- ↪ Two voltage plateaus of 3.6 (Fe^{2+}/Fe^{3+}) and 4.2 V (Mn^{2+}/Mn^{3+}) : two phase reactions.
- ↪ Narrow intermediate region ($0.4 \leq x \leq 0.5$ in $Li_{1-x}Fe_{0.5}Mn_{0.5}PO_4$) : single phase reaction? & simultaneous Fe^{2+}/Fe^{3+} and Mn^{2+}/Mn^{3+} redox reactions.

Electrochemistry Communication, 11 (2009) 2023 p.

Linear combination analysis of *in situ* XANES spectra of C-$LiFe_{0.5}Mn_{0.5}PO_4$



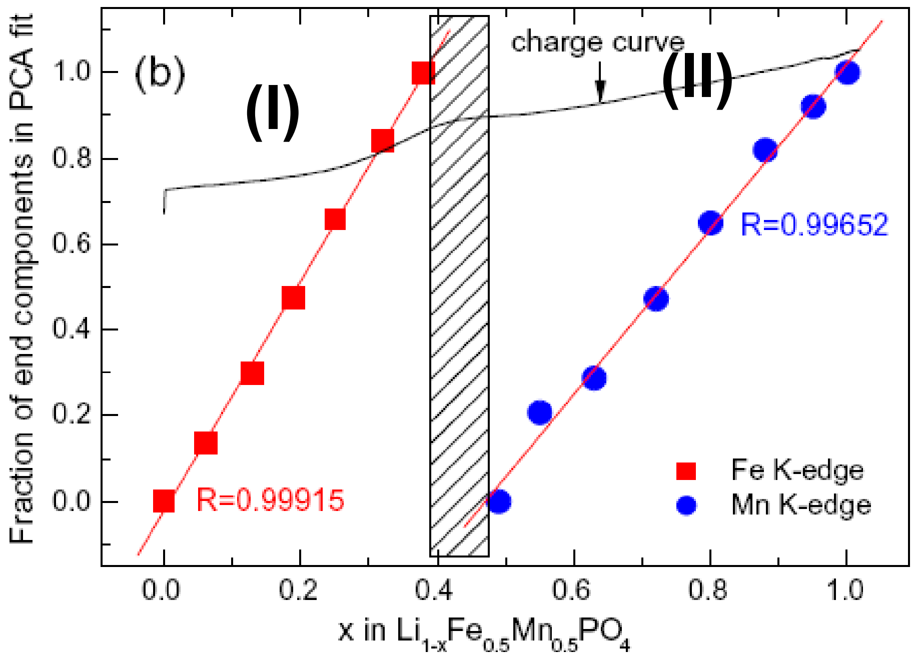
➥ **Excellent fitting result using linear combination analysis indicating the following two phase reaction.**

Two phase reaction

$$Li_{0.51}Mn_{0.5}Fe_{0.5}PO_4 \leftrightarrows 0.53\ Li_{0.51}Mn_{0.5}Fe_{0.5}PO_4 + 0.47\ Li_{0.00}Mn_{0.5}Fe_{0.5}PO_4 + 0.47\ Li^+ + 0.47e^-$$

Electrochemistry Communication, 11 (2009) 2023 p.

Linear combination analysis of *in situ* XANES spectra of C-Li$Fe_{0.5}Mn_{0.5}PO_4$



➥ **Excellent linear combination fitting results confirm the following two phase reactions at voltage plateaus (I) and (II).**

Plateau (I) : 0.0 ≤ x ≤ ~0.4 in C-$Li_{1-x}Mn_{0.5}Fe_{0.5}PO_4$ (*Fe^{2+}/Fe^{3+}* redox reaction);

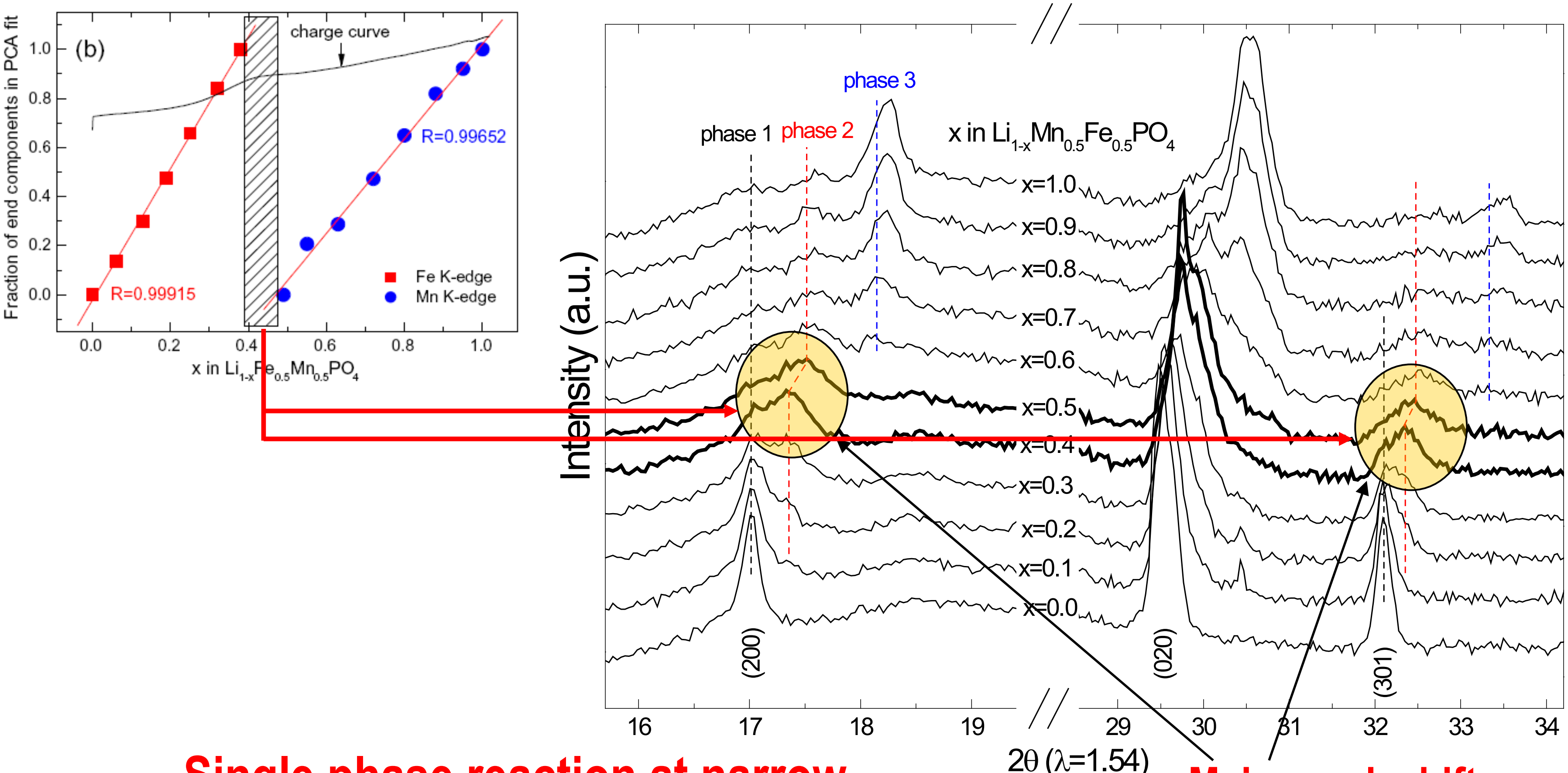
➥ $Li_{1.00}Mn_{0.5}Fe_{0.5}PO_4$ ⇆ (1-z)$Li_{1.00}Mn_{0.5}Fe_{0.5}PO_4$ + z$Li_{0.62}Mn_{0.5}Fe_{0.5}PO_4$ + zLi^+ + ze- (0≤z≤1)

Plateau (II) : ~0.5 ≤ x ≤ 1.0 in C-$Li_{1-x}Mn_{0.5}Fe_{0.5}PO_4$ (*Mn^{2+}/Mn^{3+}* redox reaction);

➥ $Li_{0.51}Mn_{0.5}Fe_{0.5}PO_4$ ⇆ (1-y)$Li_{0.51}Mn_{0.5}Fe_{0.5}PO_4$ + y$Li_{0.00}Mn_{0.5}Fe_{0.5}PO_4$ + yLi^+ + ye- (0≤y≤1)

Electrochemistry Communication, 11 (2009) 2023 p.

In situ XRD of C-Li$Fe_{0.5}Mn_{0.5}PO_4$



Single phase reaction at narrow intermediate region

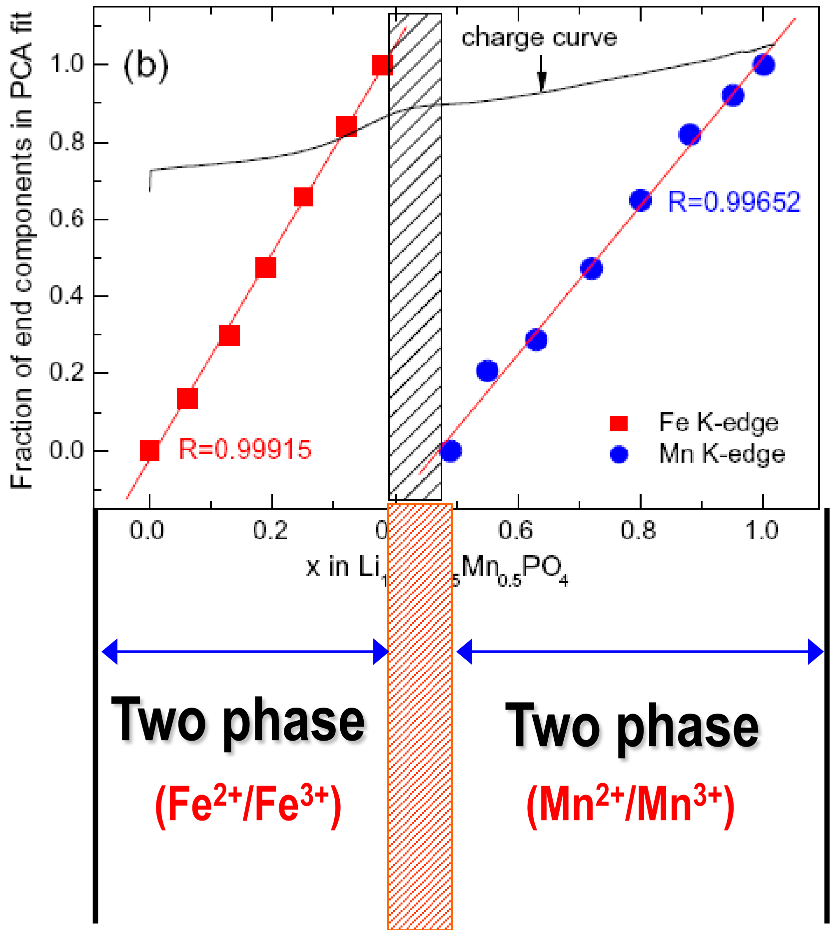
Major peak shift : Single phase reaction!

Intermediate region: 0.40≤x≤~0.50 in C-$Li_{1-x}Mn_{0.5}Fe_{0.5}PO_4$ **(Fe^{2+}/Fe^{3+} & Mn^{2+}/Mn^{3+} redox reactions);**

↪ $Li_{0.60}Mn_{0.5}Fe_{0.5}PO_4$ ⇆ $Li_{0.60-a}Mn_{0.5}Fe_{0.5}PO_4$ + aLi + ae$^-$ (0.0≤ a≤ 0.1)

Electrochemistry Communication, 11 (2009) 2023 p.

Phase transition behavior of C-Li$Fe_{0.5}Mn_{0.5}PO_4$



Single phase (Fe^{2+}/Fe^{3+} & Mn^{2+}/Mn^{3+})

First-principles calculation By Prof. Ceder at MIT

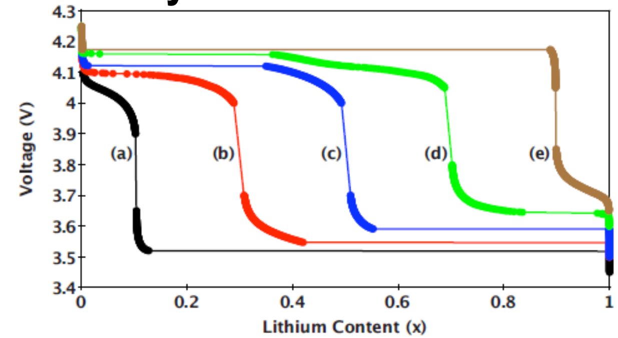
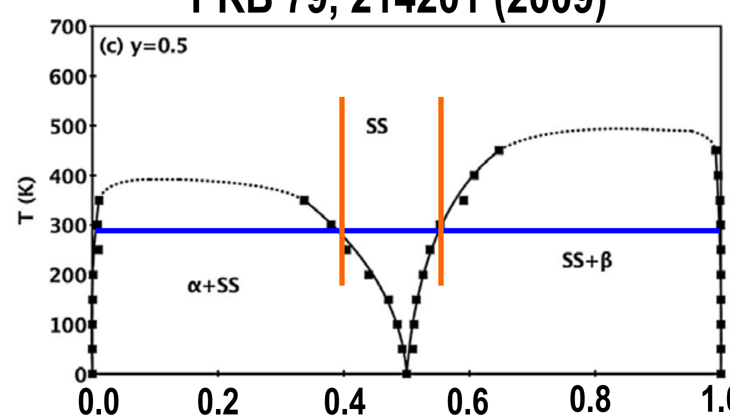


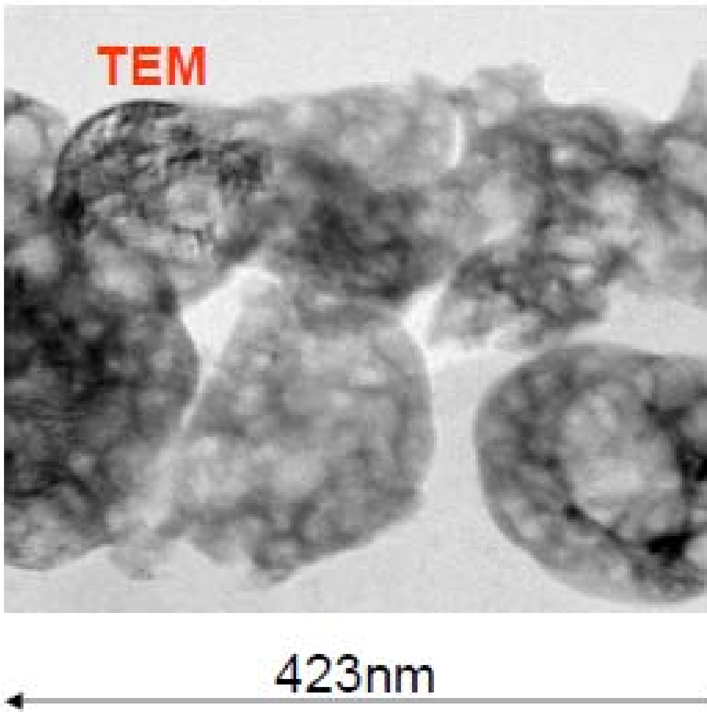
FIG. 2. (Color online) Equilibrium voltage curves of $Li_x(Fe_{1-y}Mn_y)PO_4$ at 300 K for (a) $y=0.1$, (b) $y=0.3$, (c) $y=0.5$, (d) $y=0.7$, and (e) $y=0.9$ as determined by Monte Carlo free-energy integration.

PRB 79, 214201 (2009)

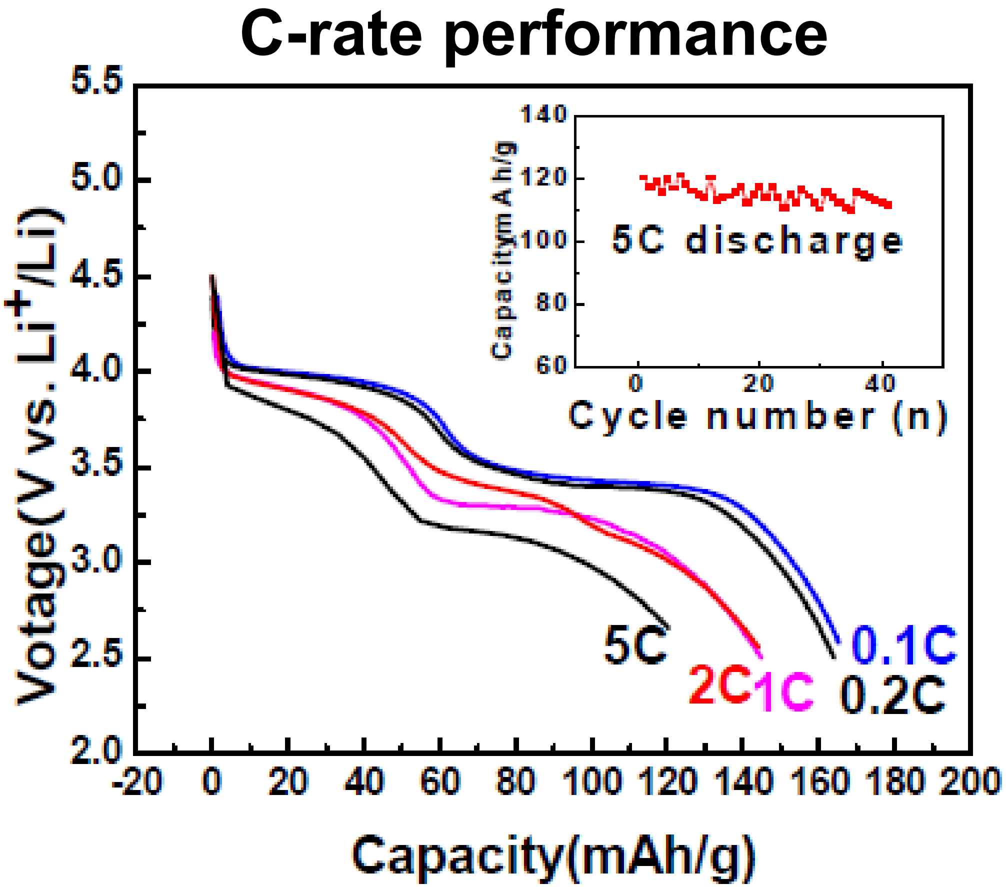


➥ **Observed phase transition behavior of $LiFe_{0.5}Mn_{0.5}PO_4$ using *in situ* XAS and XRD during lithium extraction agrees quite well with the mode proposed using the first-principles calculations (by Prof. Ceder at MIT, *Phys. Rev. B, 79 (2009) 214201*).**

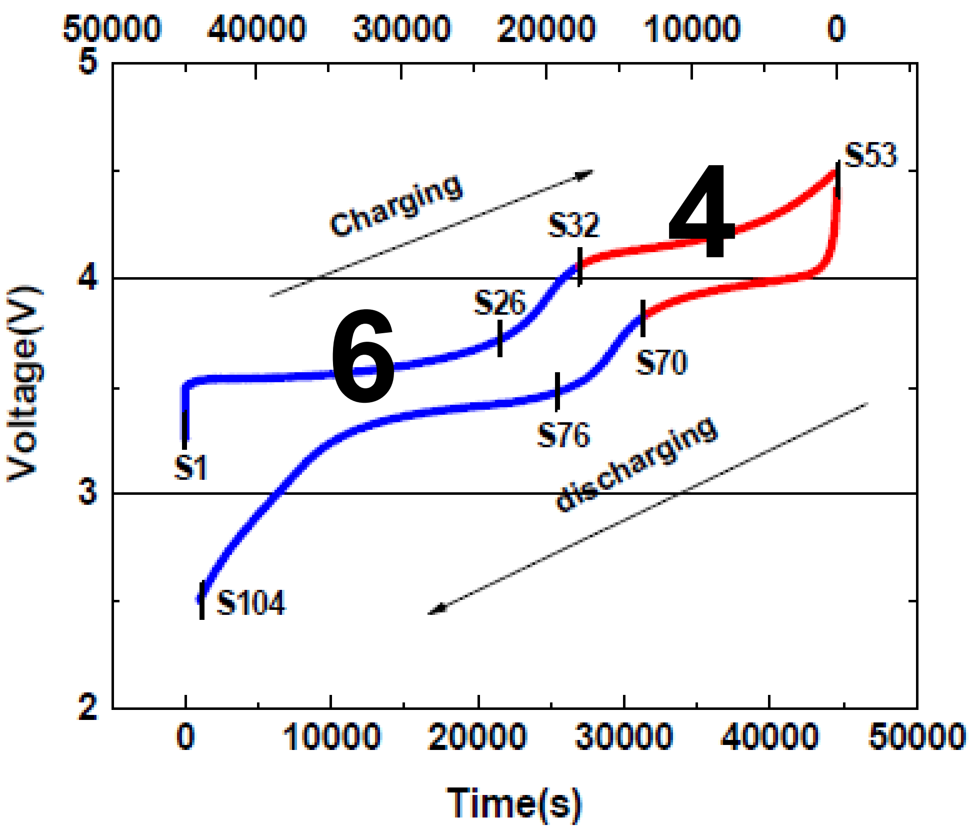
New olivine type $LiFe_{1-x}Mn_xPO_4$ cathode materials with nano-pore structure are being studied using synchrotron based *in situ* x-ray techniques In collaboration with synthesized at Beijing Institute of Physics .



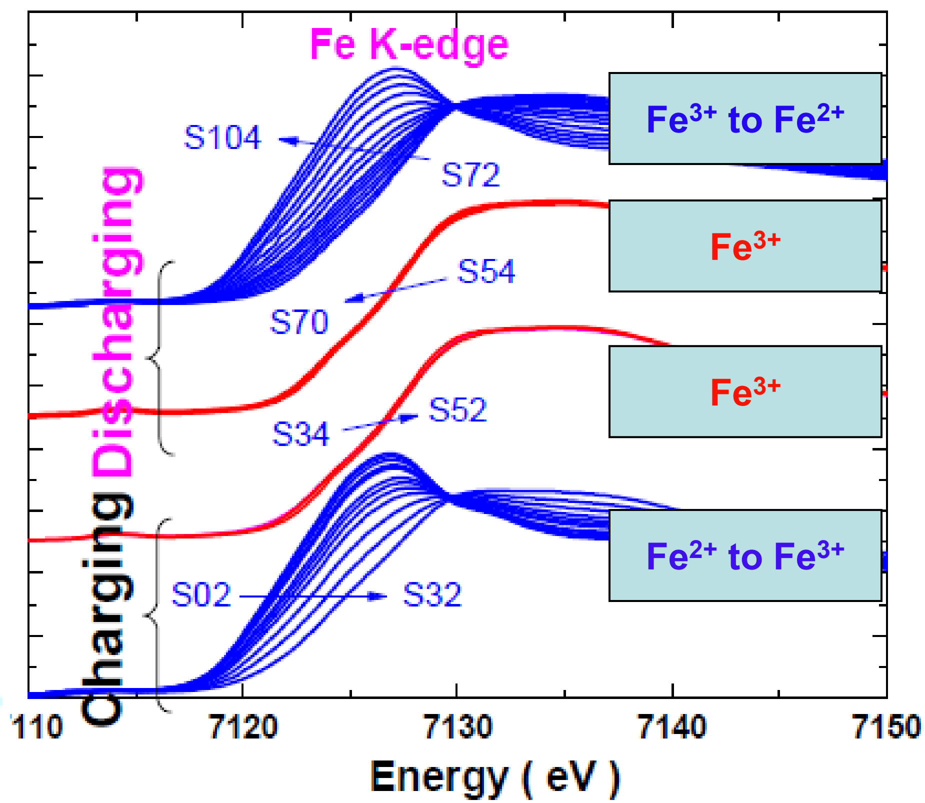
Carbon content: 18 wt%
Surface area: 32 m²/g



Fe K-edge changes of $Li_{1-x}Fe_{0.6}Mn_{0.4}PO_4$ by *in situ* XANES study during cycling



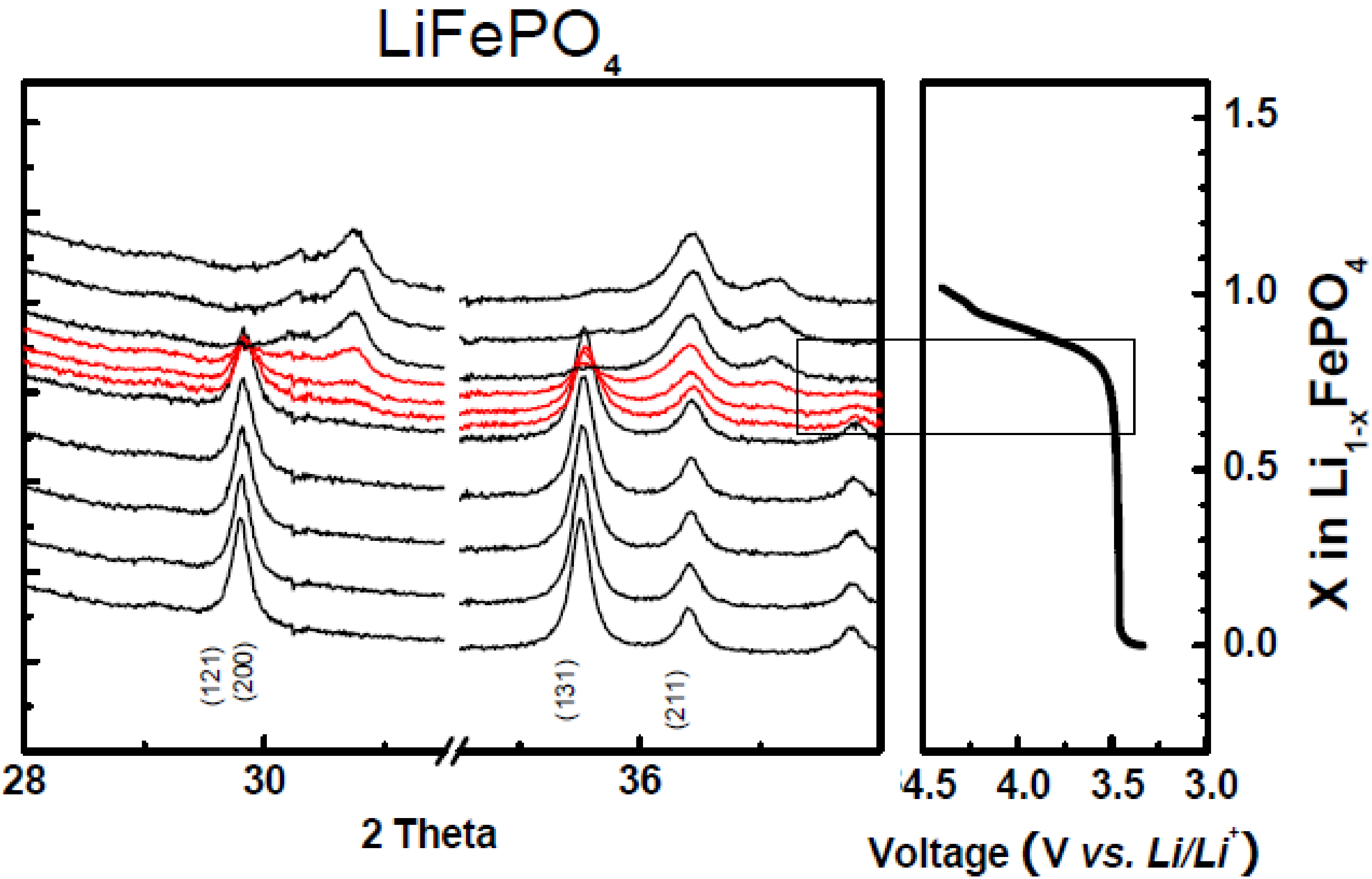
Charge and discharge curves during *in situ* XANES test(C/12)



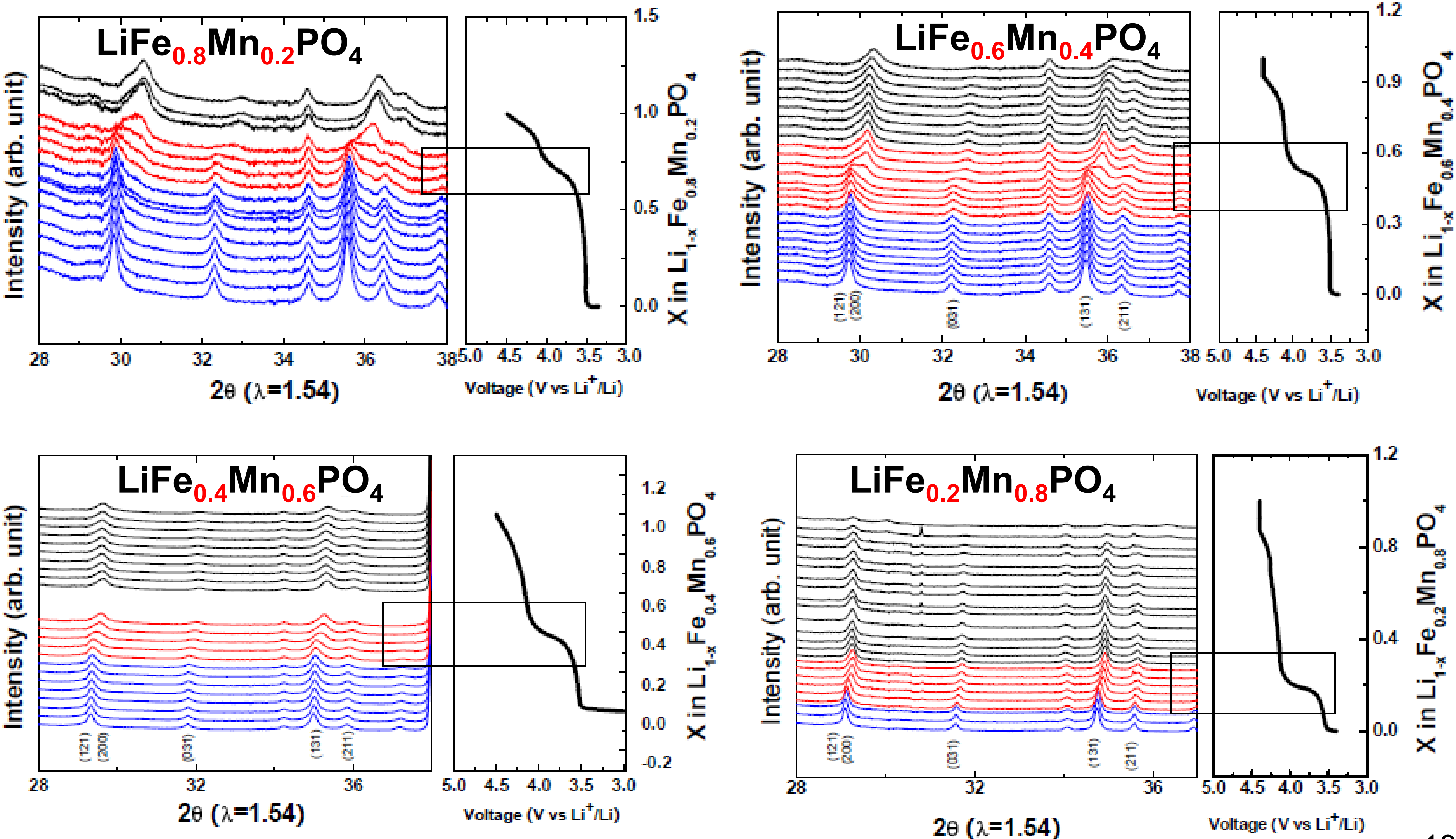
Changes of Fe K-edge

S1 means the scan order of absorption spectrum.

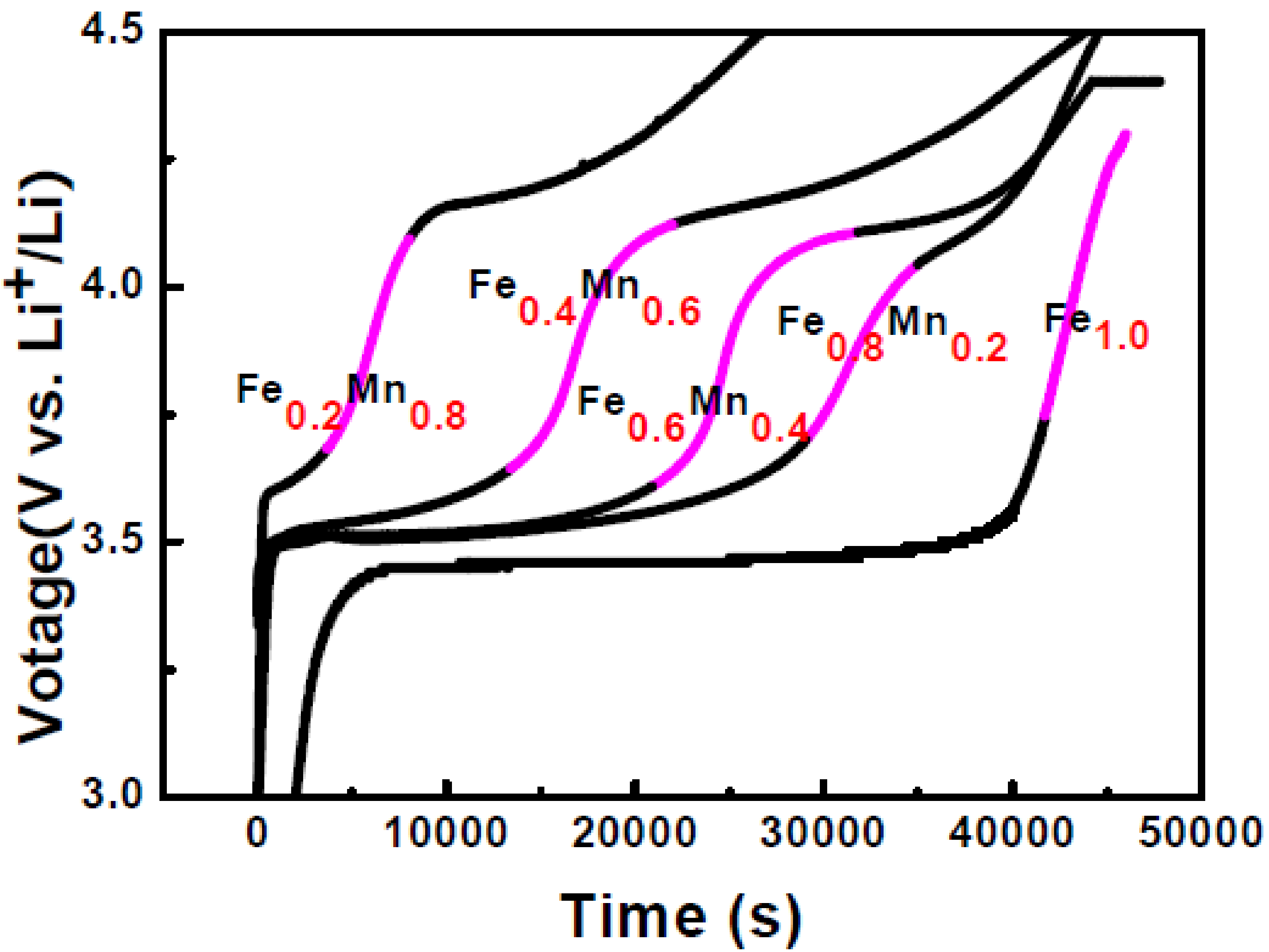
For LiFePO$_4$ at C/10, the end phase FePO$_4$ start appearing at late charge stage when the voltage rising rapidly, rather than at early stage of charge stage, as observed for conventional LiFePO$_4$



For $LiFe_xMn_{1-x}PO_4$, with x=0.2, 0.4, 0.6, 0.8, two plateaus are observed and the length of second plateau increases with increasing x. Every intermediate phase starts appearing at the end of the first plateau, when the voltage is rising rapidly

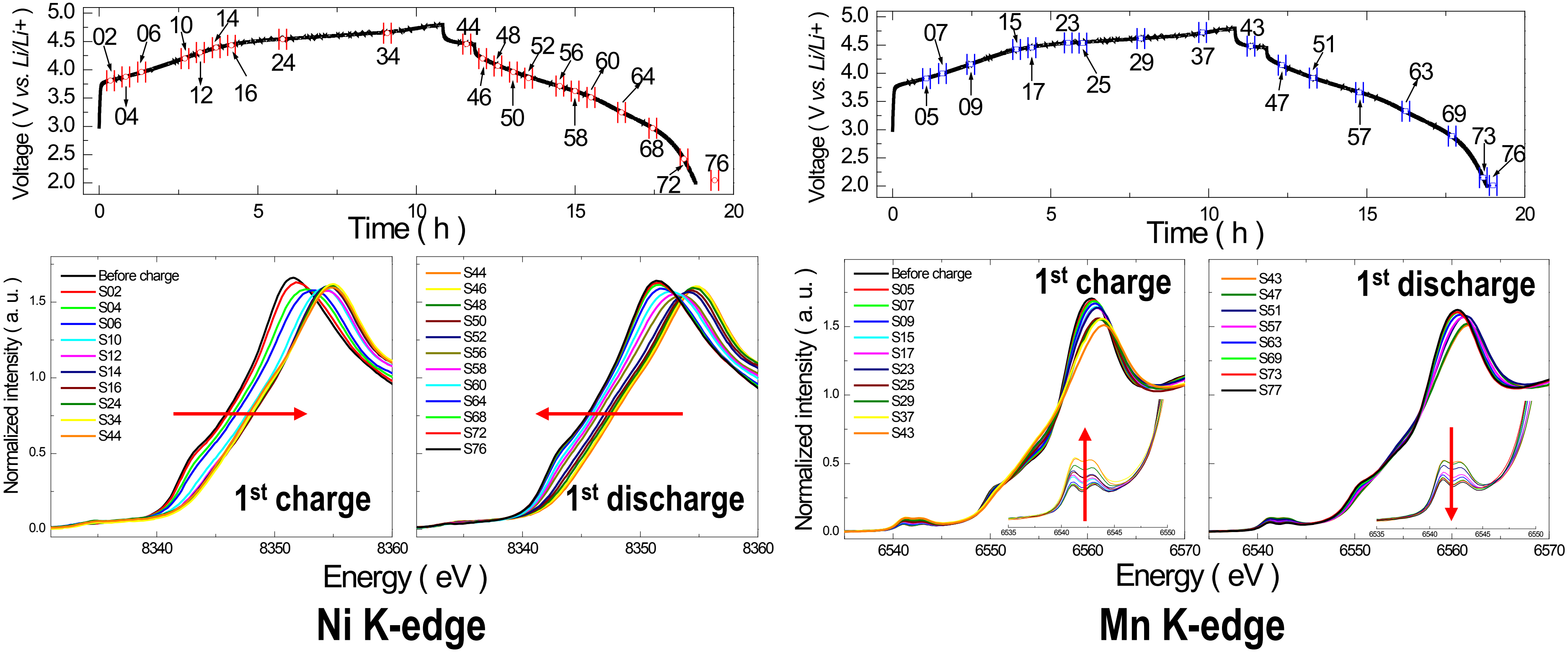


The systematic studies of the nano-pore structured $LiFe_{1-x}Mn_xPO_4$ materials showed the interesting co-relation of two phase co-existence region with the redox couples transition region and the composition, indicating the influence of over-potential on the formation of new phases for a non-equilibrium system



In situ XAS study of high energy $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ cathode during cycling in collaboration with Argonne Nat'l Lab.

collaboration with Dr. Kang at Argonne Nat'l Lab.

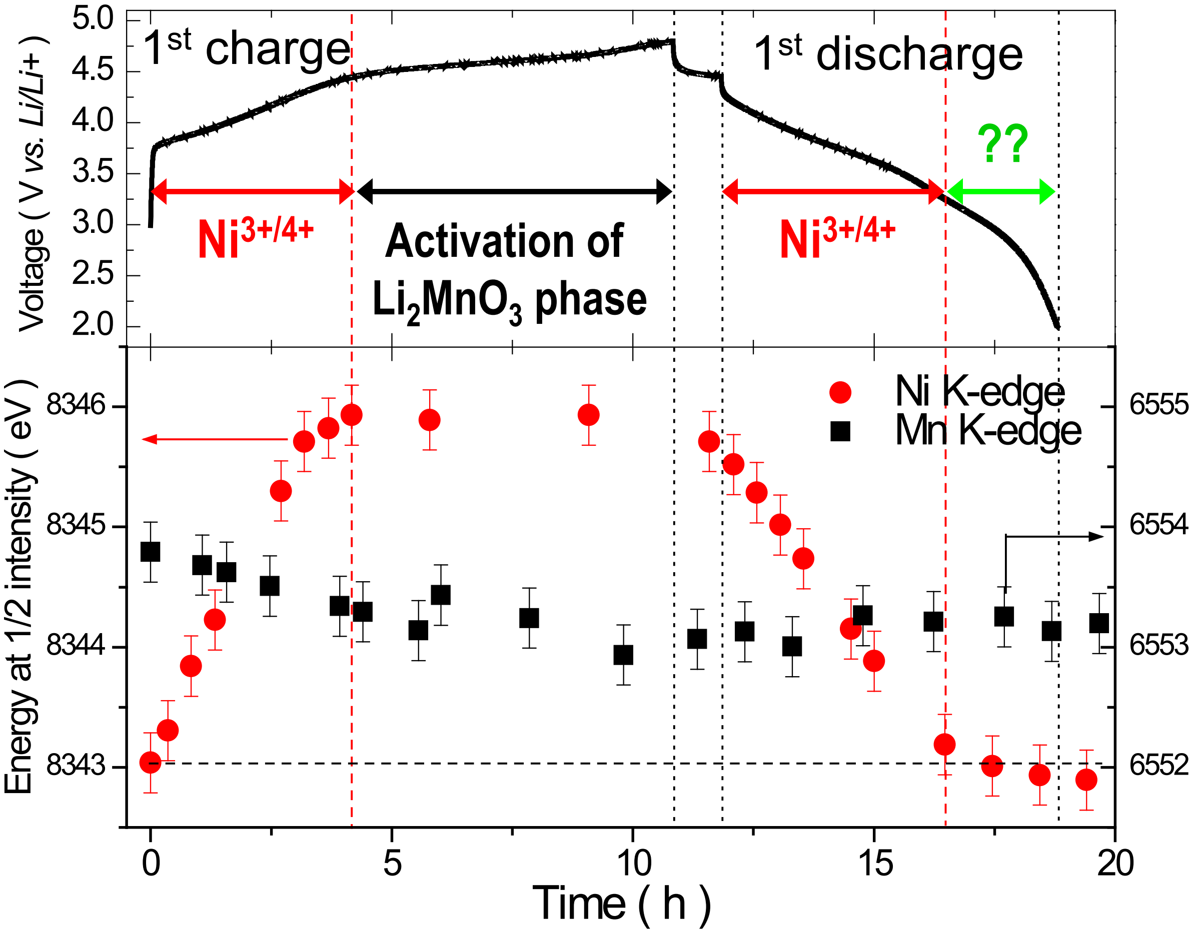


Ni & Mn K-edge *in situ* XANES spectra during 1st charge-discharge

- ***In situ*** **XAS of high energy $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ cathode during cycling has been done.**
- **Ni K-edge *in situ* XANES spectra show clear edge shift in a reversible manner while Mn K-edge spectra do not show entire edge shift during 1st charge-discharge cycle.**

In situ XAS study of high energy $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ cathode during cycling in collaboration with Argonne Nat'l Lab.

Ni and Mn K-edge position (at ½ height in XANES spectra) shift during 1st charge-discharge



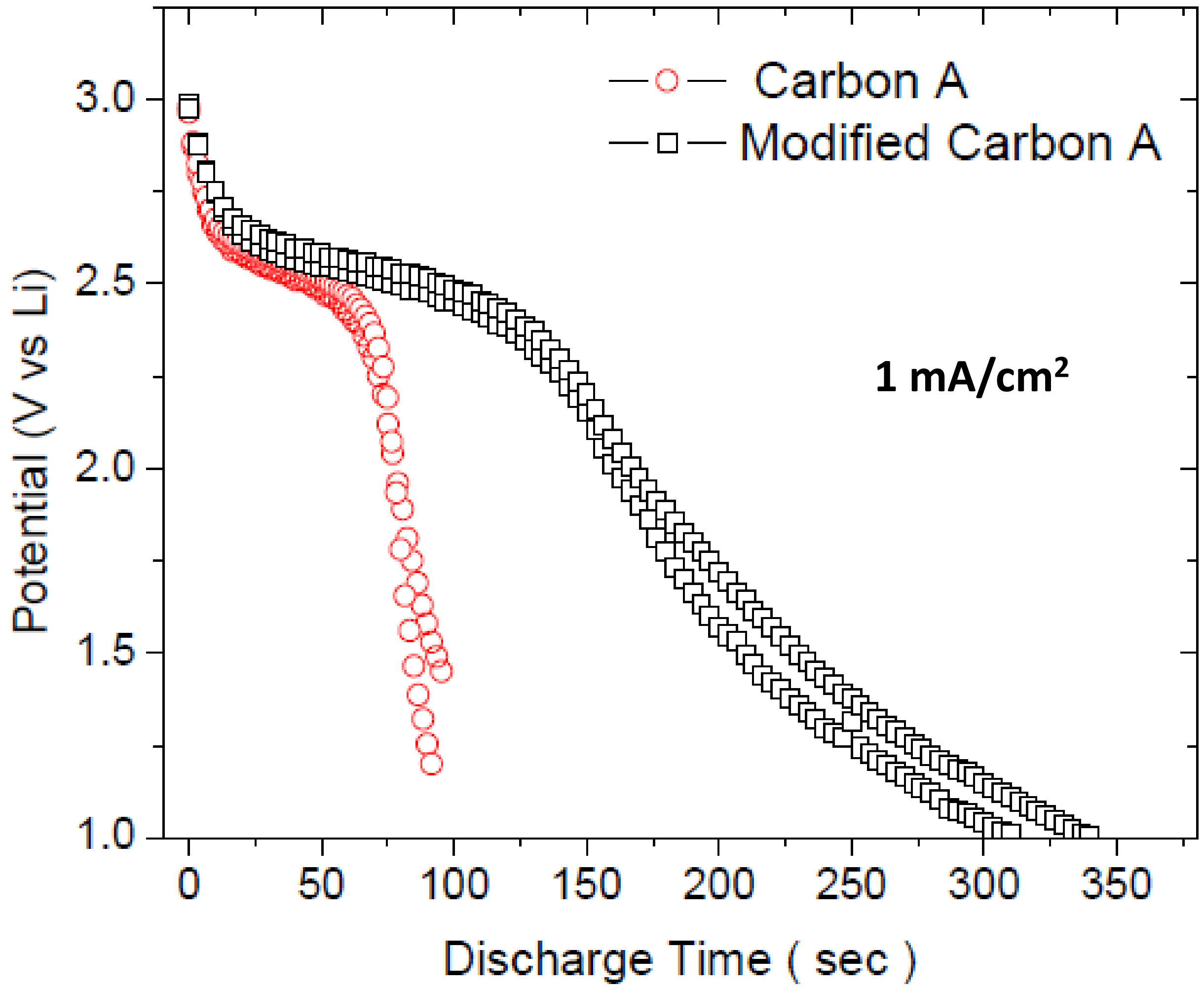
- **Charge compensation reaction of $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ at certain voltages is clearly identified by plotting edge shift at Ni and Mn K-edge XANES spectra during 1st charge-discharge cycle.**
- **However, Mn contribution to the charge compensation reaction after 1st charge remains unclear.**
  - ☞ **Need further study!**

Addressing the Obstacles for Rechargeable Lithium Air Cells in collaboration with Prof. Deyang Qu at UMASS at Boston

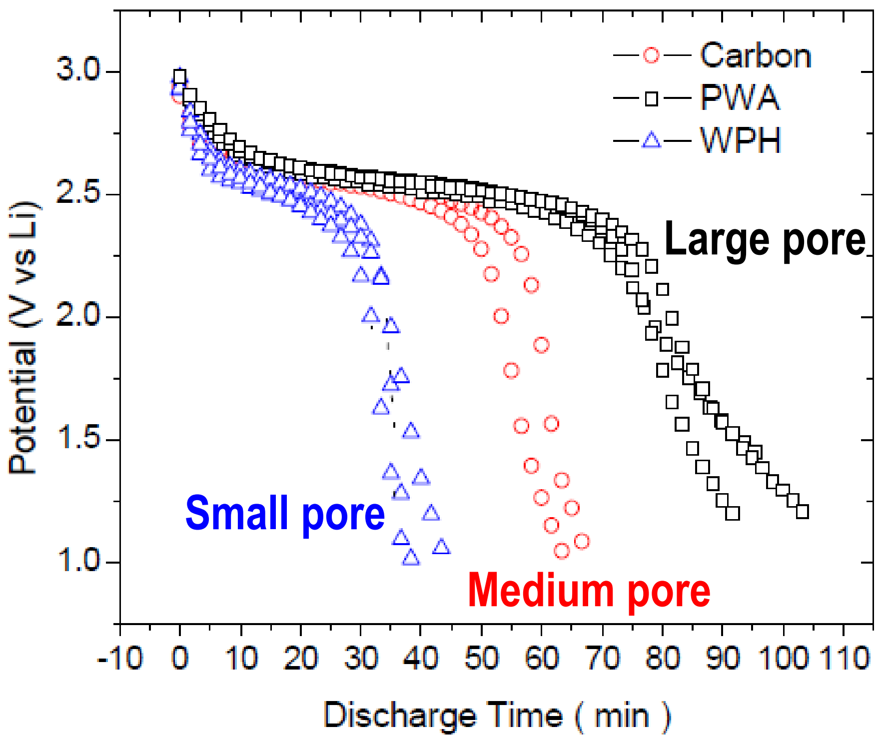
- Feasibility for the air cathode: gas diffusion electrode in non-aqueous electrolyte.
- Li_2O_2 deposition on the carbon electrode and filling up pores causing the premature passivation of the gas-diffusion-electrode.
- Solubility of Li oxides.
- Oxygen solubility in non-aqueous electrolytes
- High efficient catalysts and carbon support
- Li Peroxide (Li_2O_2), safety
- Rechargeability.

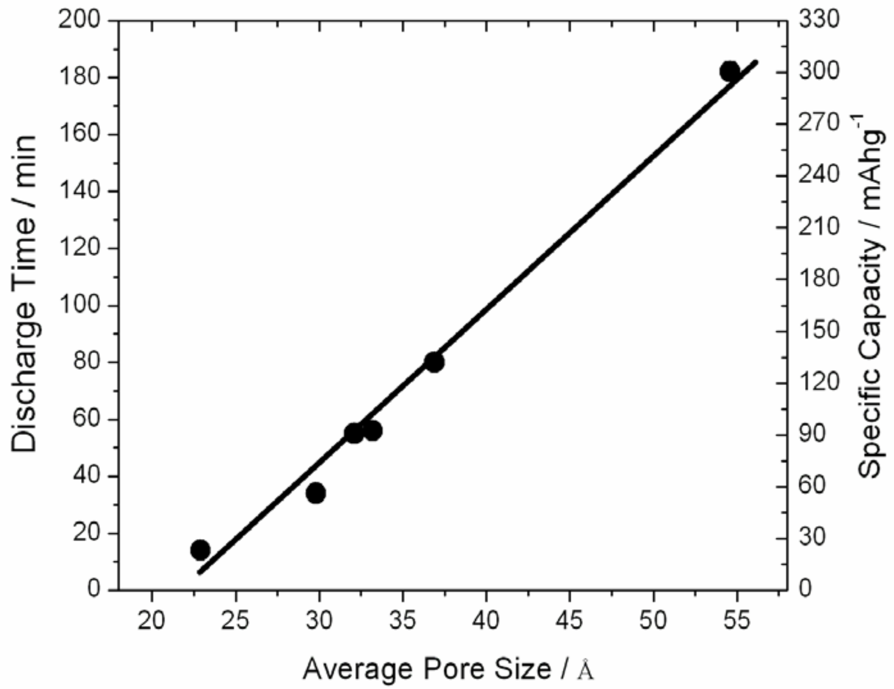
Red : on-going for the first year, Blue: starting year 2

Significant improvement was obtained by the modification of carbon surface to prevent the direct Li oxide deposition

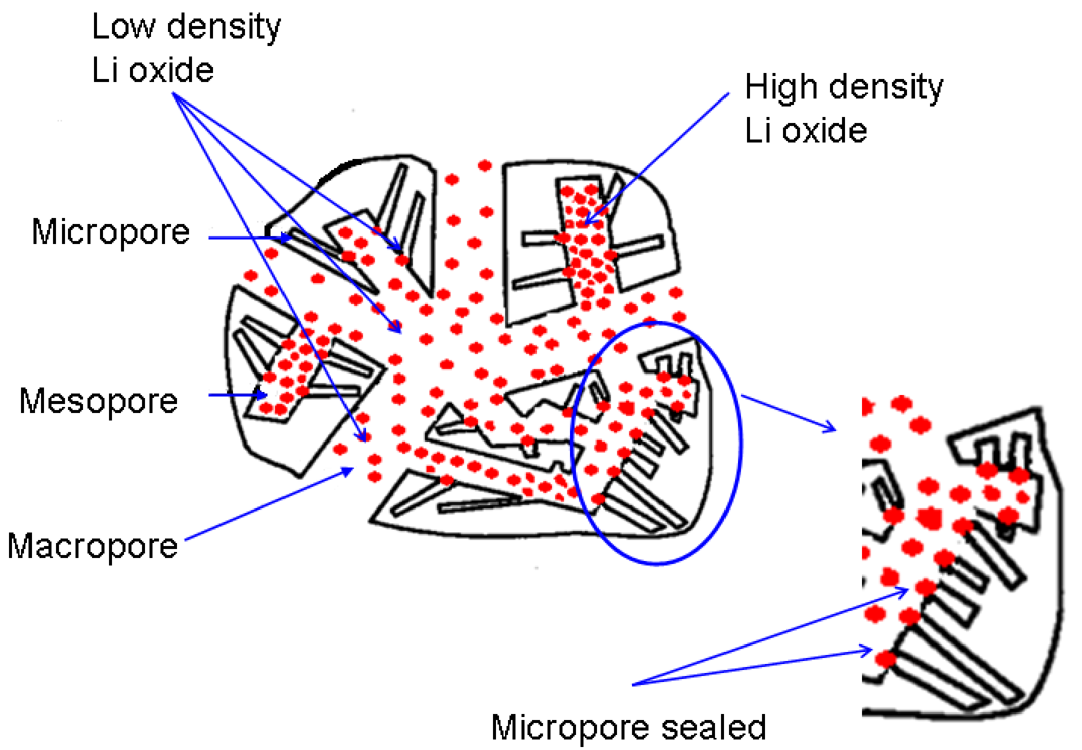


The performance of GDE is related to the average pore size of carbon material





The Li_2O_2 and Li_2O accumulated as reaction products can seal-off the small pores, making the inner surface of these small pores not available for the electrochemical reaction anymore

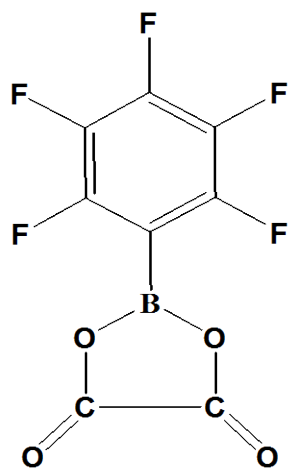


Summaries for the Li-Air cell studies

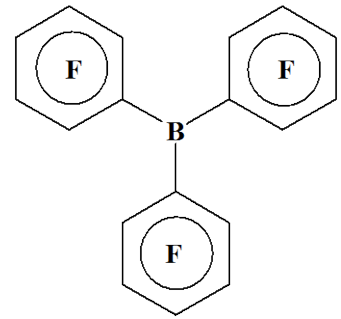
- Positive gas pressure is needed to maintain good 3-phase reaction interface.
- Li_2O_2 deposition on the surface of carbon GDE should be prevented. Surface modification is helpful.
- Carbon with large pore size is preferred, which could facilitate fast Li_2O_2 departure from the pores.

New Boron based additives synthesized and tested at BNL

Example of New Additives

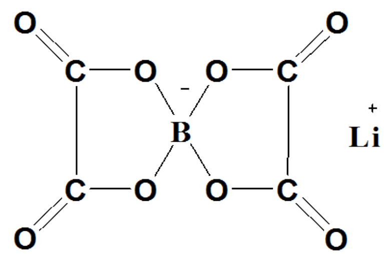


PFPBO combines the structure of both TPFPB and LiBOB, is a good anion receptor and a good SEI formation additive.



tris(pentafluorophenyl) borane (TPFPB)
An anion receptor

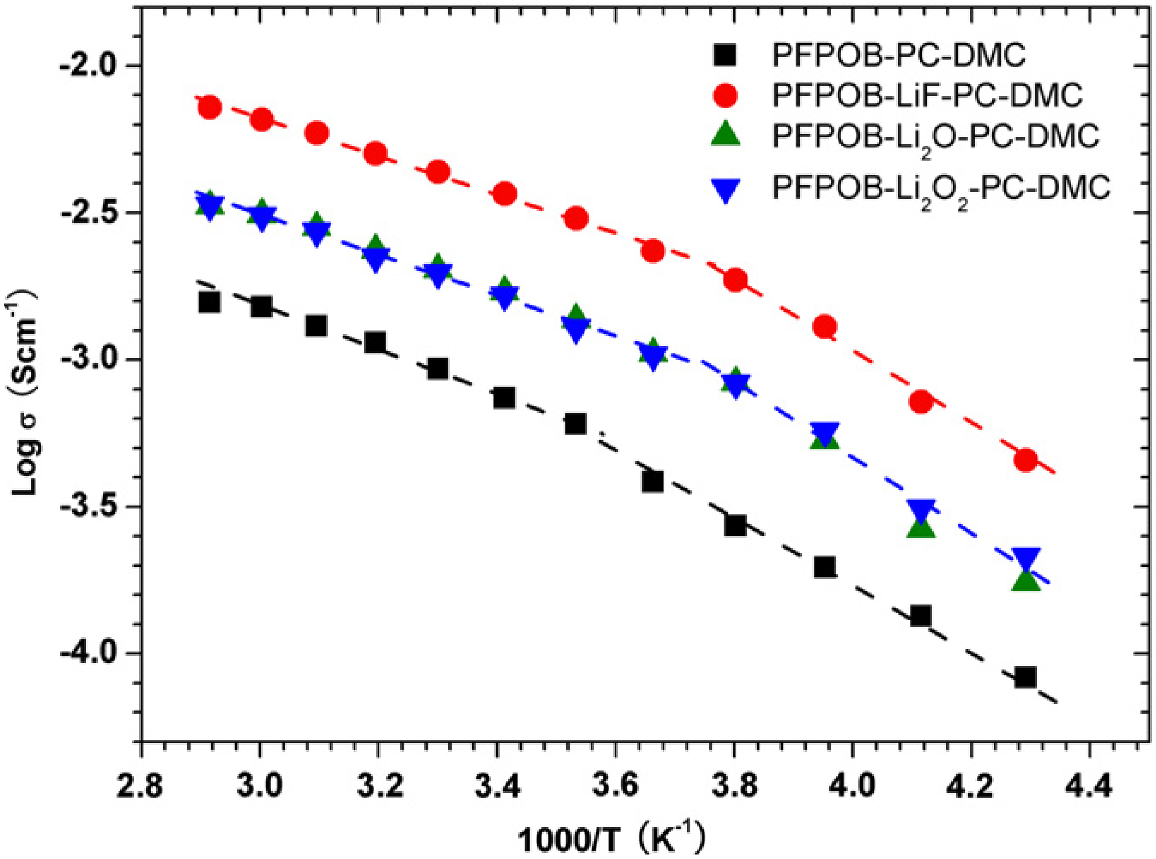
TPFPB is a good anion receptor, but a poor SEI formation additive.



Lithium bisoxalatoborate (LiBOB)
An lithium salt

LiBOB is a good SEI formation additive, but not an anion receptor.

Temperature-dependent conductivities of different electrolytes containing PFPBO additive showing good capability to dissolve LiF, Li_2O_2, and Li_2O



➥ Use of PFPBO additive in the electrolyte for rechargeable Li-Air cell could solve the problems related to the lithium oxide deposition on the surface of carbon GDE.

Collaborations with Other Institutions and Companies

- **University of Massachusetts**
  - ↪ Lithium air battery.
- **Argonne National Lab. (ANL)**
  - ↪ *In situ* XAS study of high energy $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ cathode material.
- **Oakridge National Lab. (ONL) & University of Tennessee**
  - ↪ *In situ* XRD technology development for Li-ion battery material research at NSLS.
- **Beijing Institute of Physics**
  - ↪ New electrolyte additives and olivine structured $LiFe_{1-x}Mn_xPO_4$ cathode materials.
- **Korea Institute of Science and Technology (KIST)**
  - ↪ Surface coated (e.g., ZrO_2, $AlPO_4$, and Al_2O_3) layered cathode materials.
- **Hydro-Québec (IREQ)**
  - ↪ Olivine structured $LiMPO_4$ cathode materials.
- **SUNY at Stony Brook**
  - ↪ NMR study of olivine structured $LiMPO_4$ cathode materials.
- **SUNY at Binghamton**
  - ↪ XAS and XRD study of olivine structured $LiMPO_4$ cathode materials.

Planned work for FY 2010 and FY2011

- Complete XAS studies of $LiFe_{1-x}Mn_xPO_4$ (x=0 to 1) cathode materials during electrochemical cycling.
- Complete soft and *in situ* hard XAS study of high energy $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ cathode material and identify the charge compensation mechanisms (e.g., activation of Li_2MnO_3 like phase at voltages over ~4.5V and oxygen contribution) during prolonged cyclings.
- Further development of surface and interface sensitive techniques, such as soft x-ray absorption, TEM, SAED, and electron energy loss spectroscopy (EELS) for diagnostic studies on surface-bulk differences and phase transition kinetics of electrode materials.
- In collaboration with UMASS at Boston, continue on the efforts to develop gas diffusion electrode for Li-air batteries using organic electrolytes. Start the preliminary studies of the rechargeable Lithium-Air cells.
- Develop new electrolyte systems to increase the solubility of oxygen in the electrolyte in order to overcome the oxygen deficiency in organic electrolytes.
- Design, synthesize and test new organic solvents, salts, additives and electrolyte systems for Li-ion batteries.

Summary

- **In collaboration with Hydro-Québec, *in situ* XRD and XAS studies of $LiFe_{0.5}Mn_{0.5}PO_4$ have been carried out and clearly identified the phase transition behavior during lithium extraction.**

- **In collaboration with Institute of Physics, Chinese Academy of Sciences, the nano-porous structured $LiFe_{1-x}Mn_xPF_4$ (x=0 , 0.2, 0.4, 0.6, 0.8) cathode material system are being studied by *in situ* XRD and XAS. The results of this systematic studies provide important information about the phase transition kinetics of this type of olivine structured cathode materials and will be further investigated.**

- **In collaboration with ANL, $Li_{1.2}Ni_{0.6}Mn_{0.2}O_2$ high energy density cathode materials have been studied using *in situ* XAS. The results of these studies provide useful information for improving the energy density and cycleability of high energy density Li-ion batteries.**

- **The effects of carbon structure for gas diffuse electrode (GDE) for Lithium-Air battery was investigated and new carbon materials with larger pore size have been synthesized, which significantly improved the discharge capacity of the Lithium-Air cell.**

Summary (cont'd)

- **Novel surface modification of the carbon materials for GDE has been developed. The capacity of the Lithium-Air cell using the surface modified carbon for GDE is increased dramatically.**

- **New boron based additives with capability to dissolve Li_2O and Li_2O_2 in organic solvents have been synthesized and studied. These new electrolytes have high potential to be used in high energy density Li-Air and lithium metal batteries.**

- **Collaborations with US industrial partners, as well as with US and international research institutions have been established. The results of these collaborations have been published or presented at invited talks at international conferences.**