Characterization of New Cathode Materials using Synchrotron-based X-ray Techniques and the Studies of Li-Air Batteries

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May 20, 2009

2009 DOE Hydrogen Program and Vehicle Technologies
Annual Merit Review and Peer Evaluation Meeting
Washington, DC, May 18-22

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BROOKHAVEN
NATIONAL LABORATORY

Overview

Timeline

- ▣ Start: 10/01/2007
- ▣ Finish: 09/30/2010
- ▣ 60% complete

Budget

- ▣ Funding received in FY08

  DOE: $550k
- ▣ Funding received in FY09

  DOE: $550k

Barriers addressed

- Li-ion and Li-metal batteries with superior performance
- Li-ion and Li-metal batteries with long calendar and cycle life
- Li-ion and Li-metal batteries with superior abuse tolerance

Collaborators

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

Milestones

Month/Year	Milestones
Oct/08	Complete *In situ* XRD studies on the structural changes of the layered, lithium-rich transition metal oxides containing manganese, nickel, and cobalt like $Li_{1+x}(Mn_{0.5}Ni_{0.5})_{1-x}O_2$ and $Li_{1+x}(Mn_{1/3}Ni_{1/3}Co_{1/3})_{1-x}O_2$. ↪ *Completed.*
Apr/09	Complete *in situ* X-ray absorption spectroscopy (XAS) studies of $LiFe_{0.25}Mn_{0.25}Co_{0.25}Ni_{0.25}PO_4$ cathode materials during cycling. ↪ *Completed.*
Apr/09	Complete the synthesis and selections of boron based anion receptors (BBAR) with the capability to dissolve Li_2O and Li_2O_2 in non-aqueous solvents for Li-Air battery electrolytes. ↪ *Completed.*
Set/09	Complete *in situ* XRD studies during cycling of $LiFe_{0.25}Mn_{0.25}Co_{0.25}Ni_{0.25}PO_4$ cathode materials in comparison with $LiFe_{1-x}Mn_xPO_4$ materials. ↪ *On schedule.*
Sep/09	Complete the solubility, conductivity and Li^+ transference number studies using BBAR-Li_2O/Li_2O_2 electrolytes in non-aqueous solvents for Li-Air battery electrolytes. Complete the preliminary studies of air-cathode electrode loaded with oxygen reduction catalyst for Li-air batteries. ↪ *On schedule.*

Approaches

- A combination of *in situ* X-ray absorption (XAS) and *in situ* X-ray diffraction (XRD) during heating to study the thermal stability of the electrode materials.

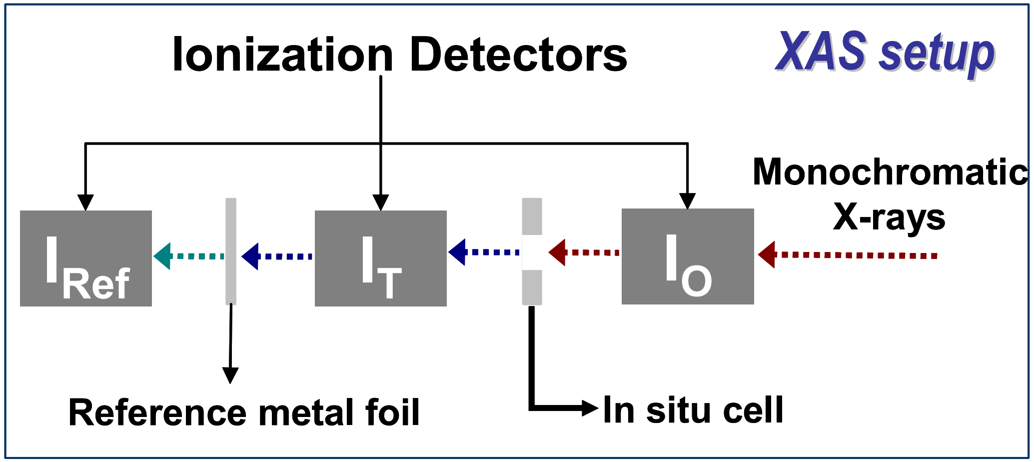
- Hard and soft X-ray XAS studies of new electrode materials during electrochemical cycling to perform the diagnostic studies to extend the calendar and cycling life of Li-ion batteries.

- Transmission electron microscopy (TEM) and electron diffraction for solid electrolyte interface (SEI) and interfacial studies.

- New electrolyte system development through molecular design and organic synthesis for lithium-air batteries. Construct and test lithium-air batteries using organic electrolytes. 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)

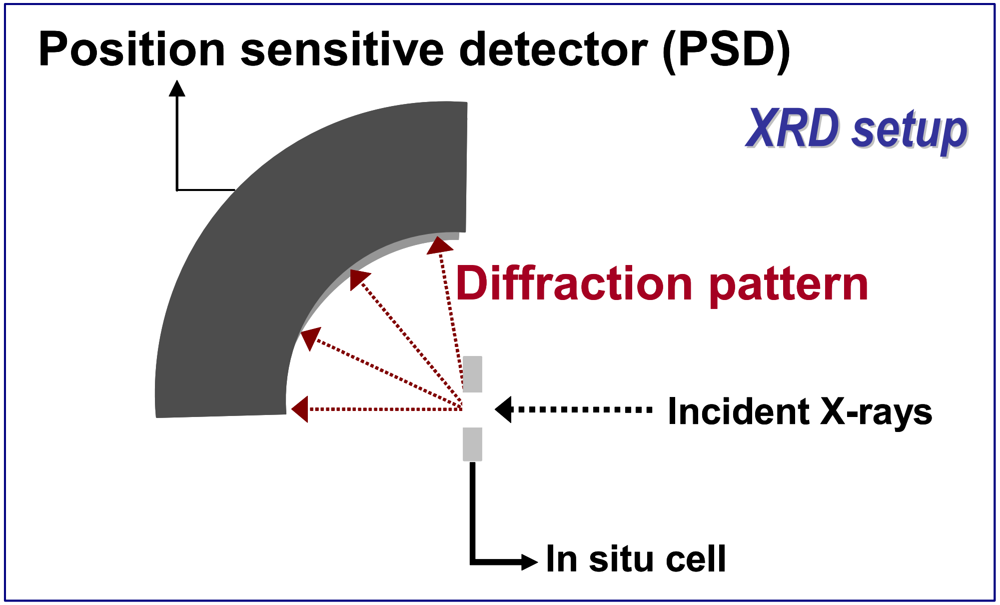

XAS setup

Ionization Detectors

Monochromatic X-rays

Reference metal foil

In situ cell


XRD setup

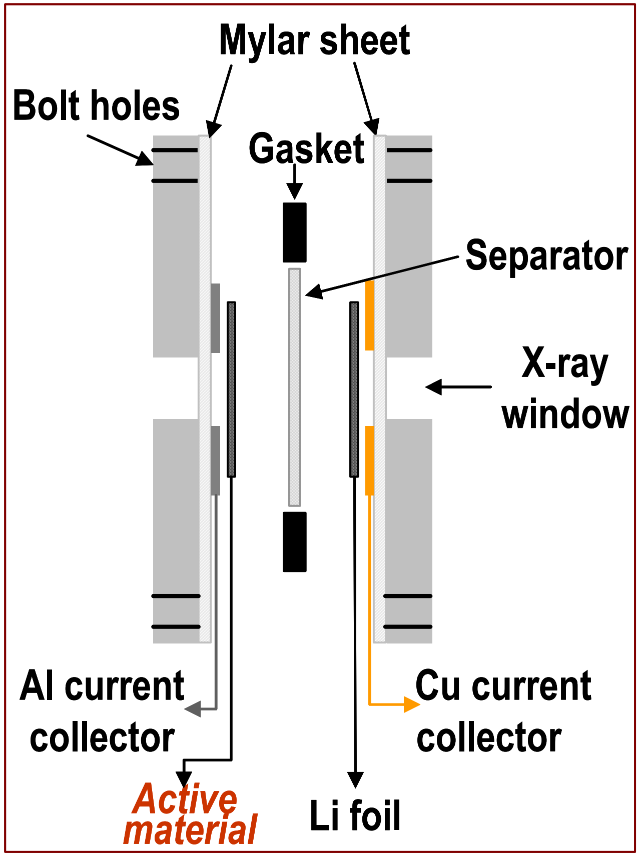
Position sensitive detector (PSD)

Diffraction pattern

Incident X-rays

In situ cell

In situ cell


Mylar sheet

Bolt holes

Gasket

Separator

X-ray window

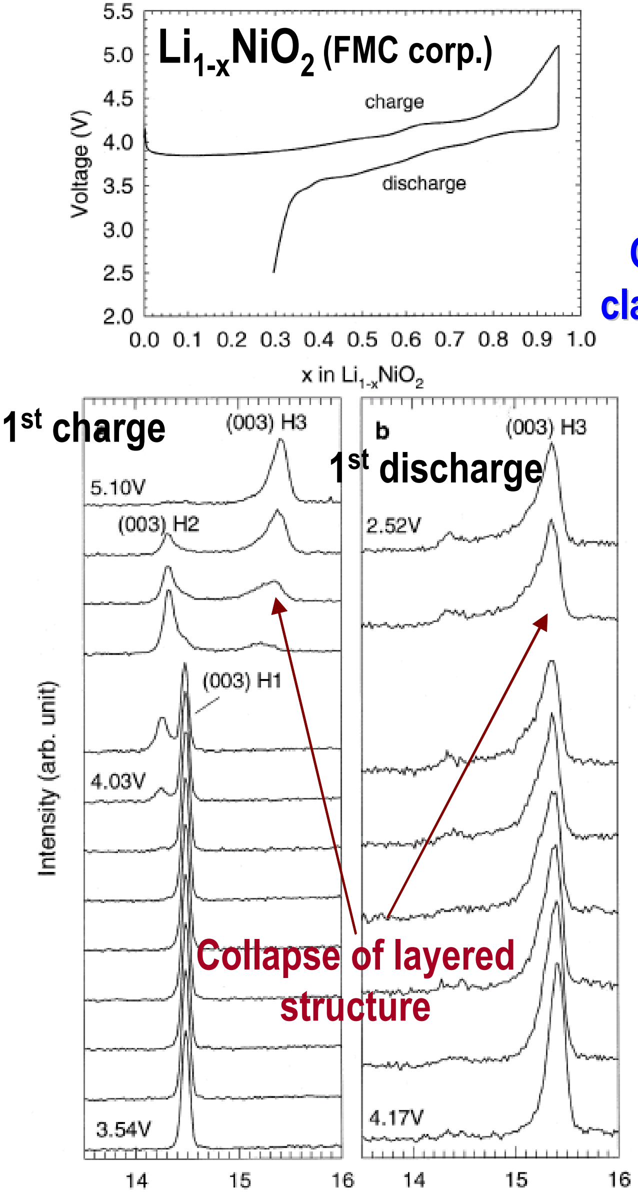
Al current collector

Cu current collector

Active material

Li foil

Examples of using *in situ* XRD to study the relationship between the structural changes and electrochemical performance



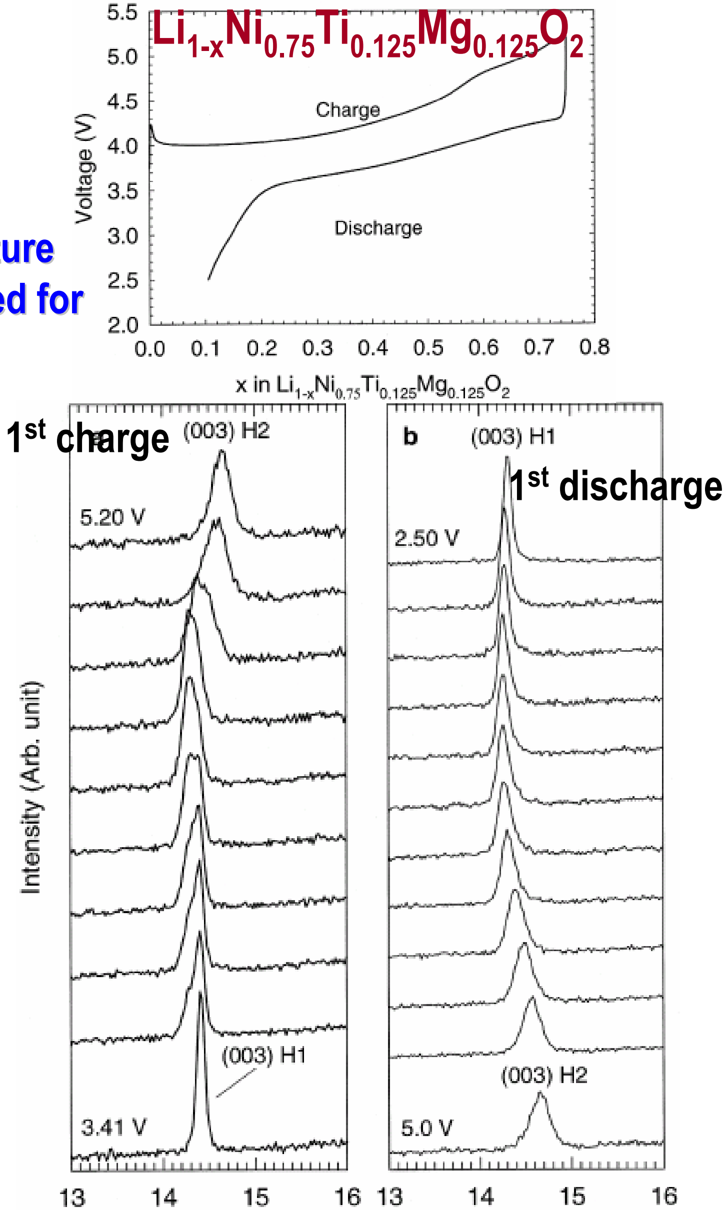
$Li_{1-x}NiO_2$ (FMC corp.)

1st charge

1st discharge

Collapse of layered structure

Overcharge to 5.0V the structure clasped for $LiNiO_2$ but preserved for $LiNi_{0.75}Ti_{0.125}Mg_{0.125}O_2$!

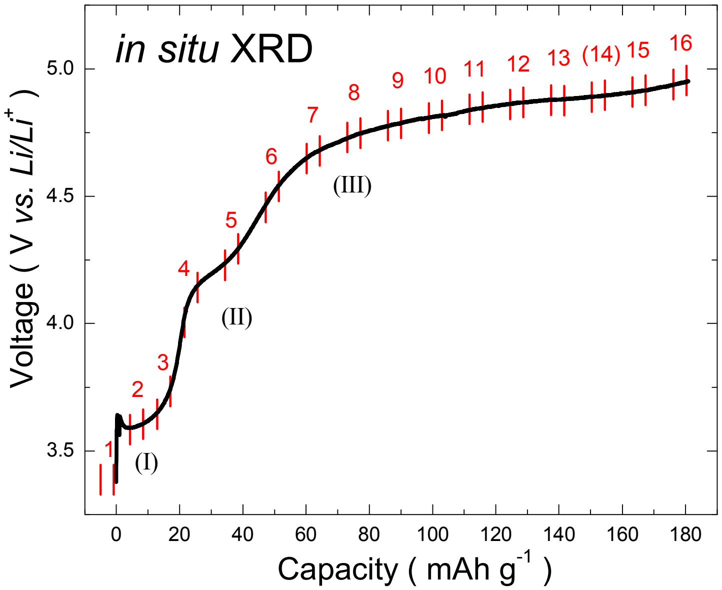


$Li_{1-x}Ni_{0.75}Ti_{0.125}Mg_{0.125}O_2$

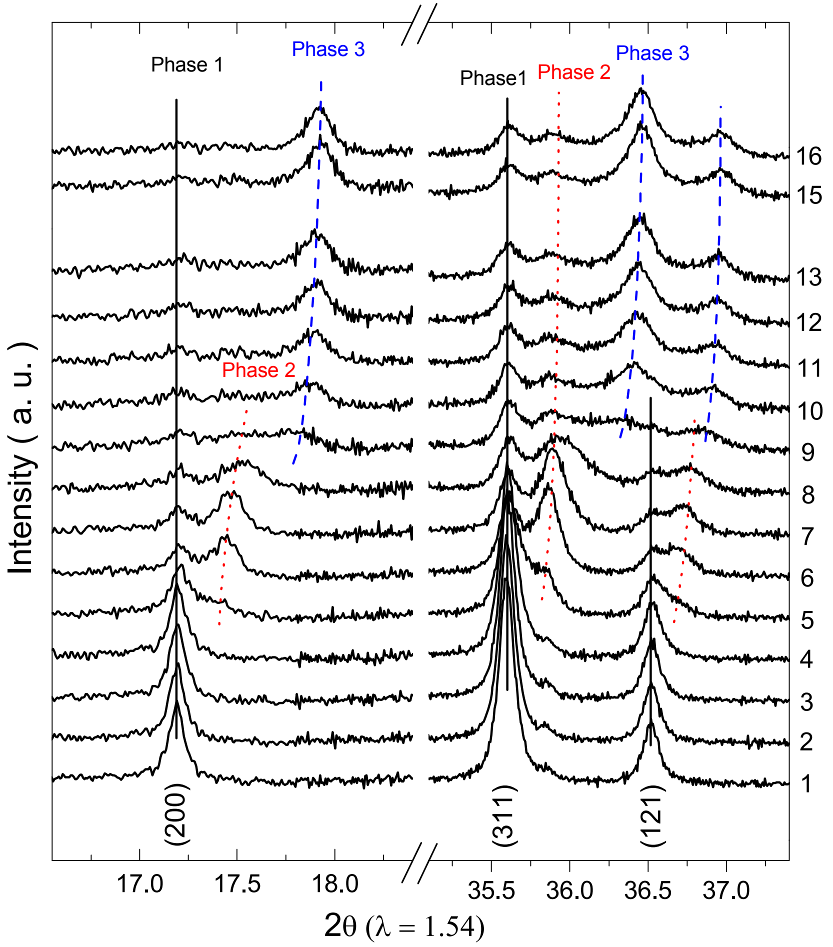
1st charge

1st discharge

In situ XRD of *$C\text{-}LiFe_{1/4}Mn_{1/4}Co_{1/4}Ni_{1/4}PO_4$* during first charge



Cut-off voltage: ~ 5.0 V, C/7 rate



Developing high voltage (high energy density) cathode by Mn Co Ni substitution

- ↪ **Appearance of intermediate phase (phase 2) and solid-solution regions!**
- ↪ **From scan 2 to 4 (1st plateau region), small changes in the XRD patterns (slow crystal structural change).**
- ↪ **Fast electronic structural changes (from *in situ* XAS) and slow bulk crystal structural changes in this system!**

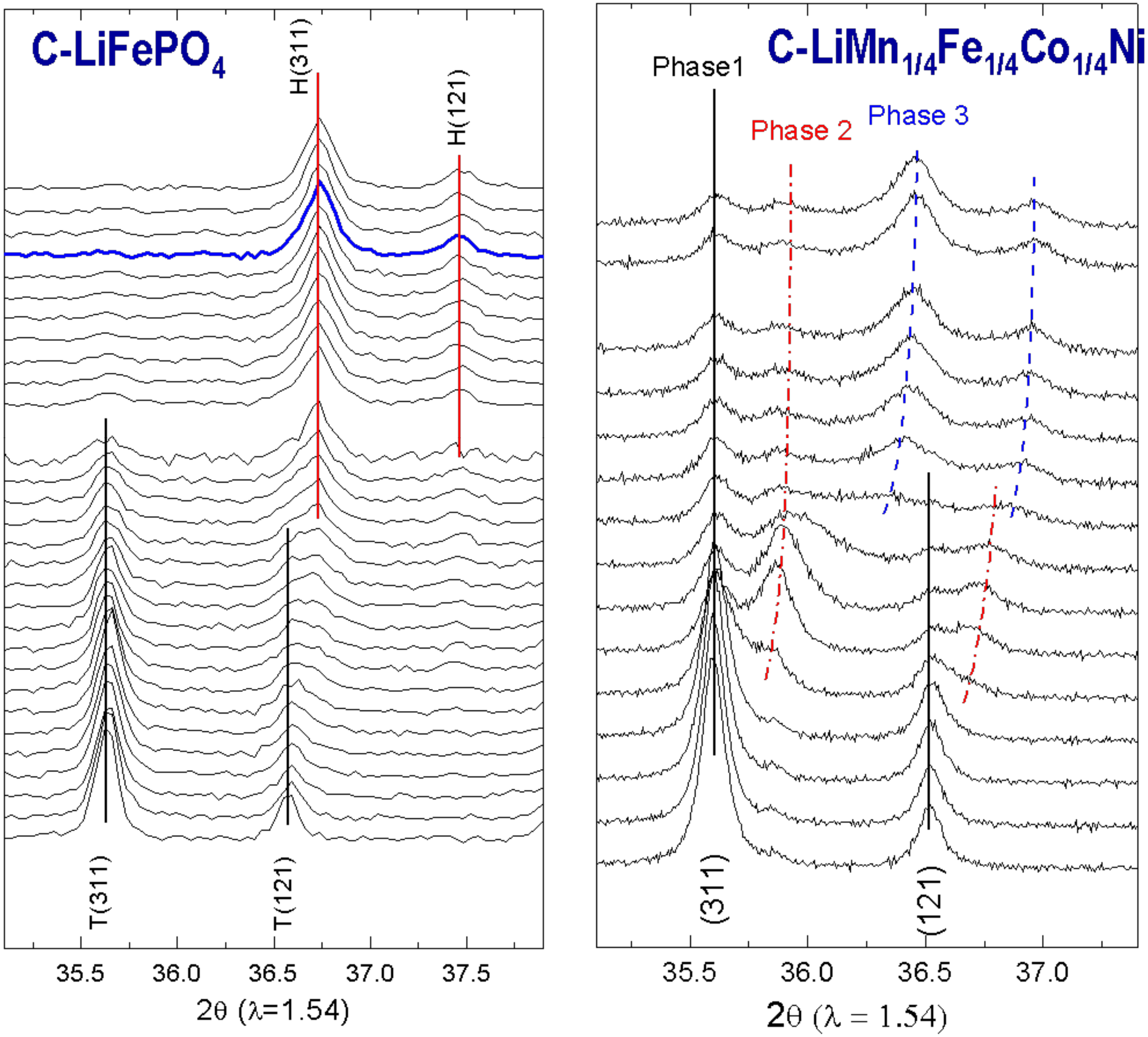
K. W. Nam, X. Q. Yang et al, Electrochemistry Communication, in press (2009).

In situ XRD of $C\text{-}LiFe_{1/4}Mn_{1/4}Co_{1/4}Ni_{1/4}PO_4$ during first charge

Comparison with pure $C\text{-}LiFePO_4$

Two phase reaction

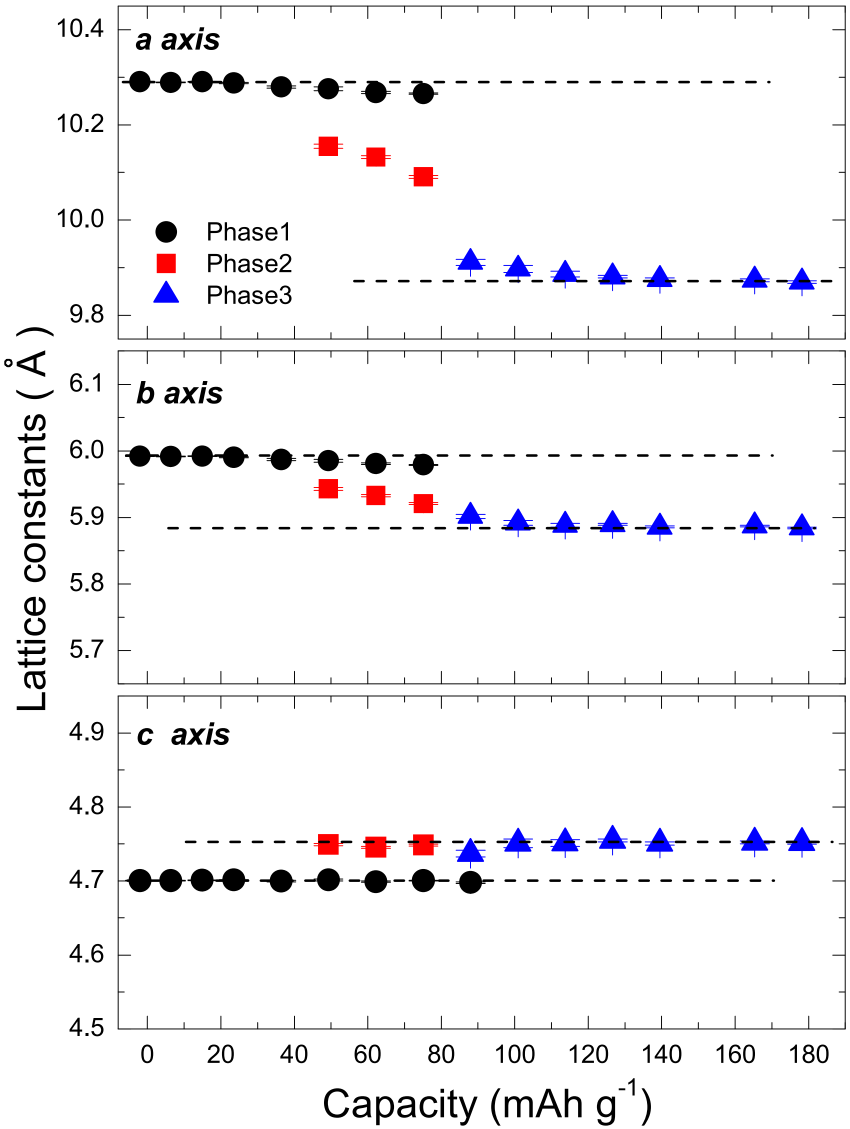
No significant solid solution region

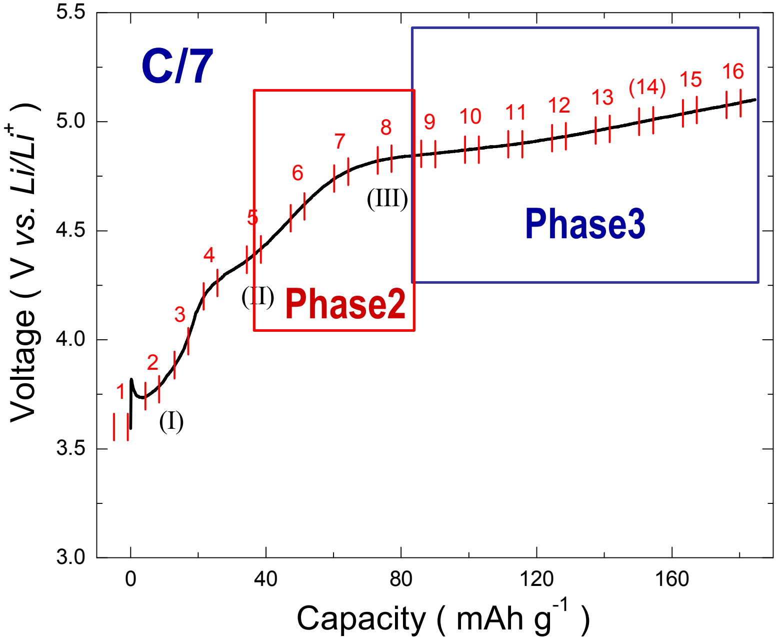


Existence of solid solution regions

Appearance of Intermediate phase

Lattice parameter changes of $C\text{-}LiFe_{1/4}Mn_{1/4}Co_{1/4}Ni_{1/4}PO_4$ during first charge

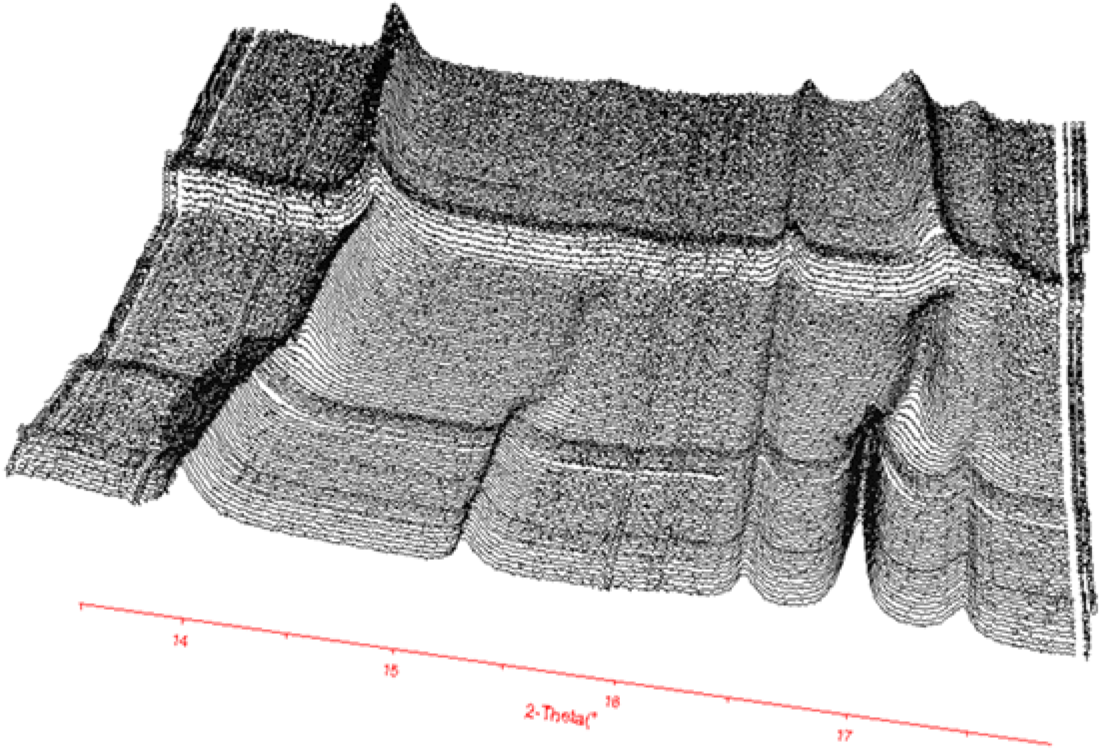


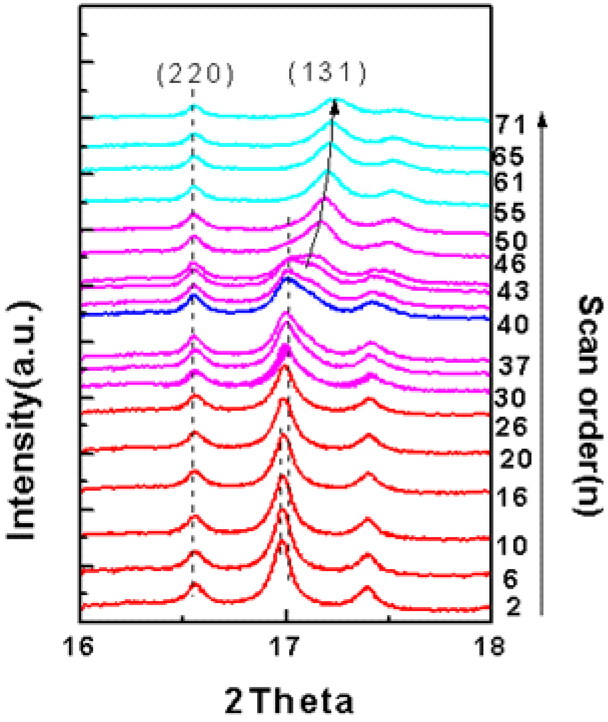


- **Appearance of intermediate phase 2.**
- **Clear solid solution regions in Phase 2 & 3**
- **~4.8% of volume shrinkage from phase 1 to 3.**
- **Intermediate phase and solid solution mechanism ; could be closely related to lattice defects, disorders and cation mixing induced by the substituting metal cations.**

K. W. Nam, X. Q. Yang et al, Electrochemistry Communication, in press (2009).

In situ XRD of *C-LiFe$_{0.6}$Mn$_{0.4}$PO$_4$* during first charge-discharge



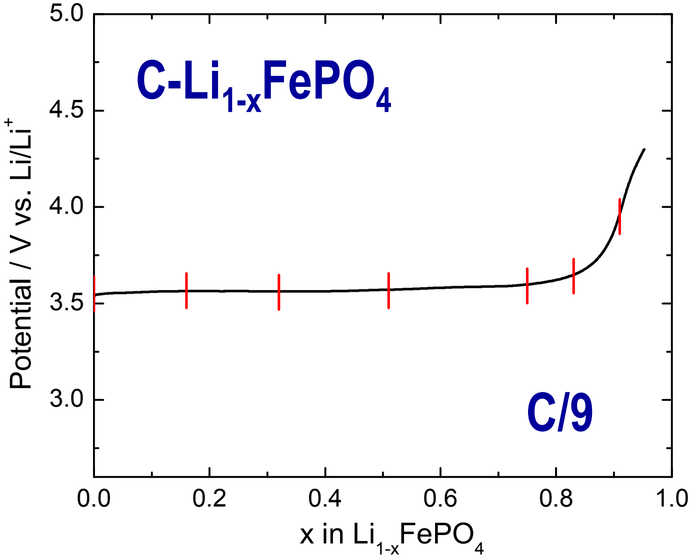


➥ No intermediate phase was observed

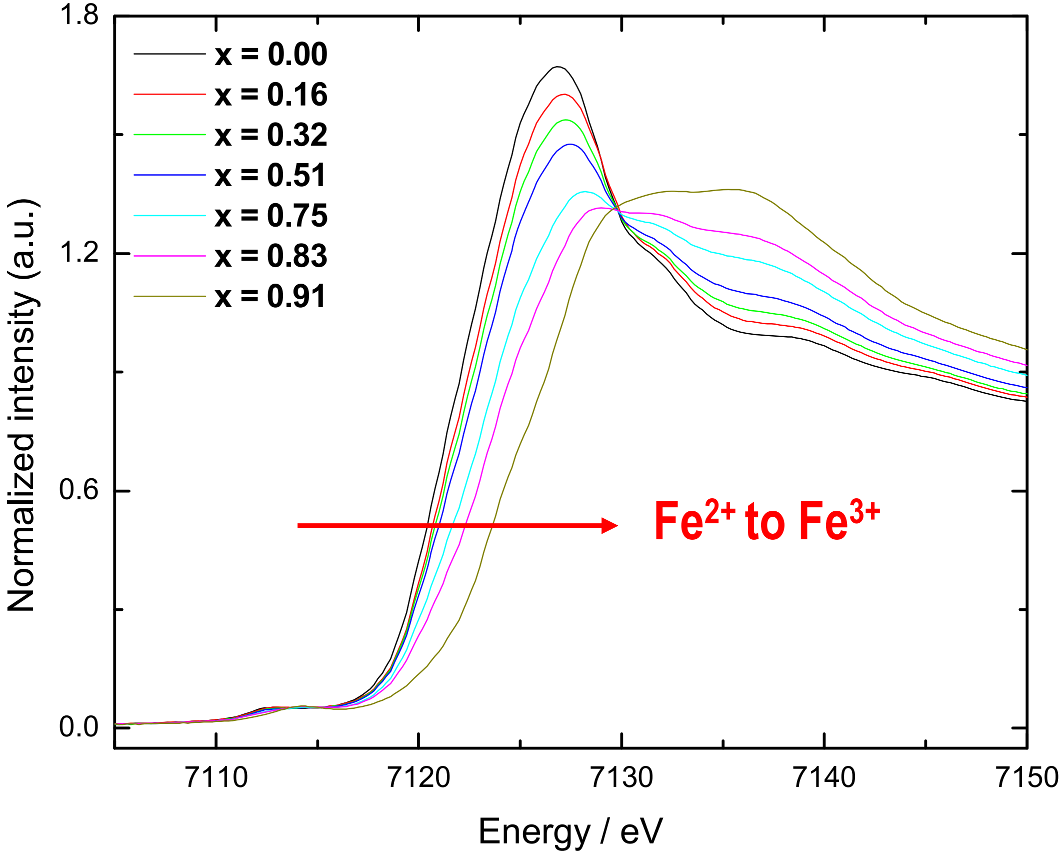
➥ Small changes in the XRD patterns during the Fe^{2+} to Fe^{3+} oxidation and solid solution region for final phase

➥ Pseudo one-phase reaction during first discharge

In situ Fe K-edge XAS of *C-$LiFePO_4$* during first charge



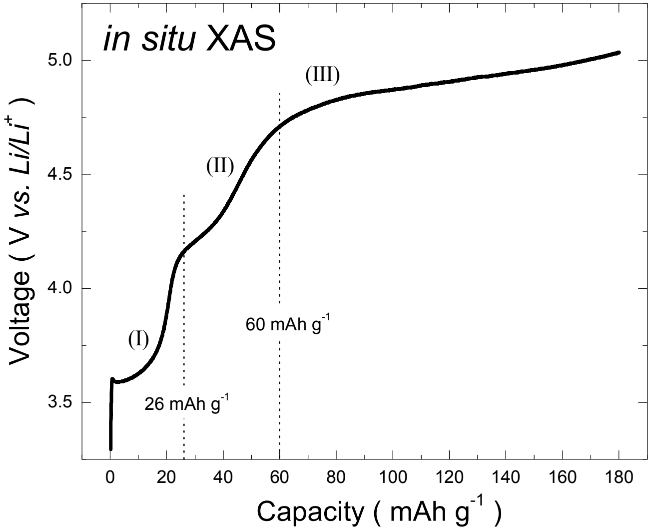
XANES (X-ray Absorption Near Edge Structure)
: Shift of K-edge position toward higher energy
⇨ ***Increase in oxidation state***



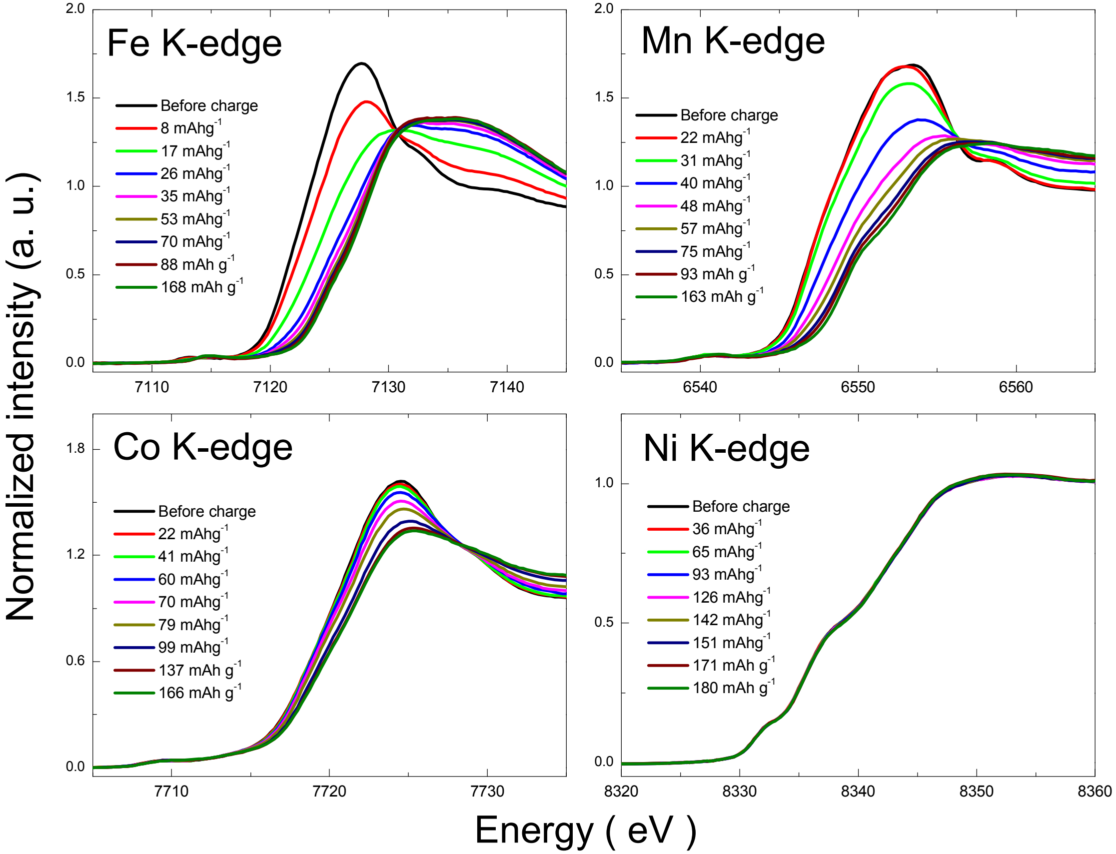
➥ **Major charge compensation during charge ⇨ Oxidation of Fe^{2+} to Fe^{3+}.**

In situ XAS of $C\text{-}LiFe_{1/4}Mn_{1/4}Co_{1/4}Ni_{1/4}PO_4$ during first charge

Edge shift toward higher energy position
⇨ increase in oxidation state



Cut-off voltage: ~ 5.0 V, C/7 rate



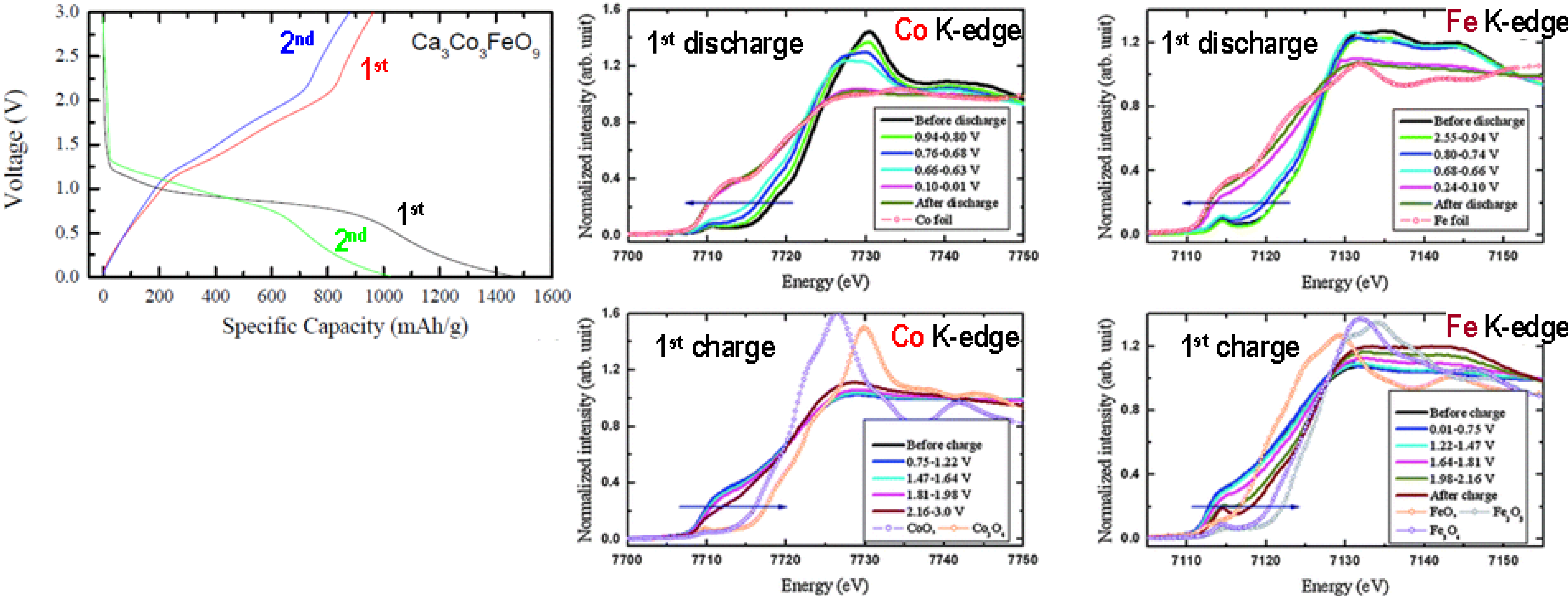
➥ **Three voltage plateaus at ~ 3.6, 4.2 and 4.7 V ⇨ Redox reactions of Fe^{2+}/Fe^{3+}, Mn^{2+}/Mn^{3+} and Co^{2+}/Co^{3+}.**

➥ **Voltage plateau over ~ 4.9V ⇨ Mostly electrolyte decomposition.**

➥ **Electronic structural changes following the lithium extraction quite well to balance the electrical neutrality.**

K. W. Nam, X. Q. Yang et al, Electrochemistry Communication, in press (2009).

In situ XAS of *new anode material* during first charge-discharge; *Iron-substituted calcium cobaltite* ($Ca_3Co_3FeO_9$)



↪ In collaboration with KIST (Korea), charge storage mechanism of new anode material, $Ca_3Co_3FeO_9$, was studied by *in situ* XAS during charge-discharge.

↪ Proposed charge storage mechanism;

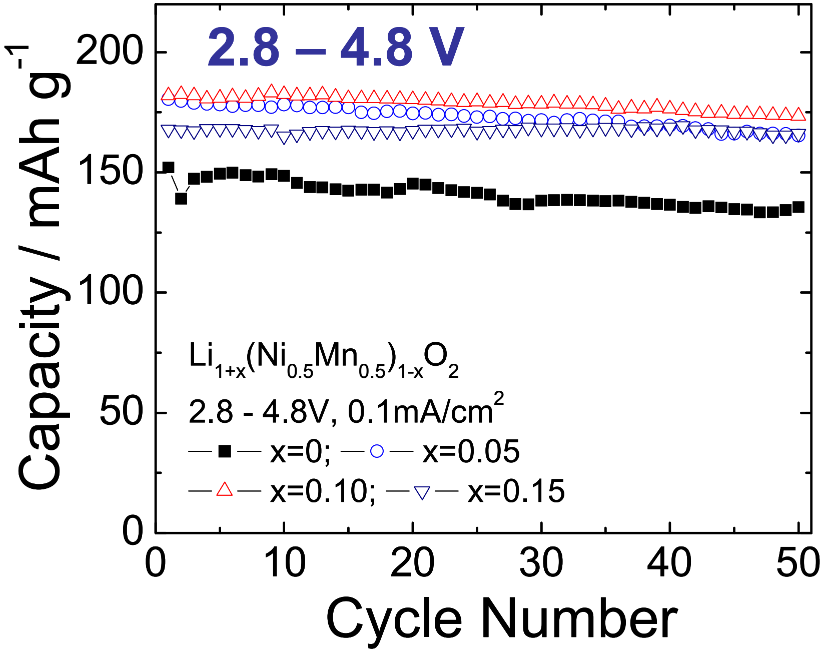
1st discharge: $Ca_3Co_3FeO_9 + 12Li \Rightarrow 3Co + Fe + 6Li_2O + 3CaO$

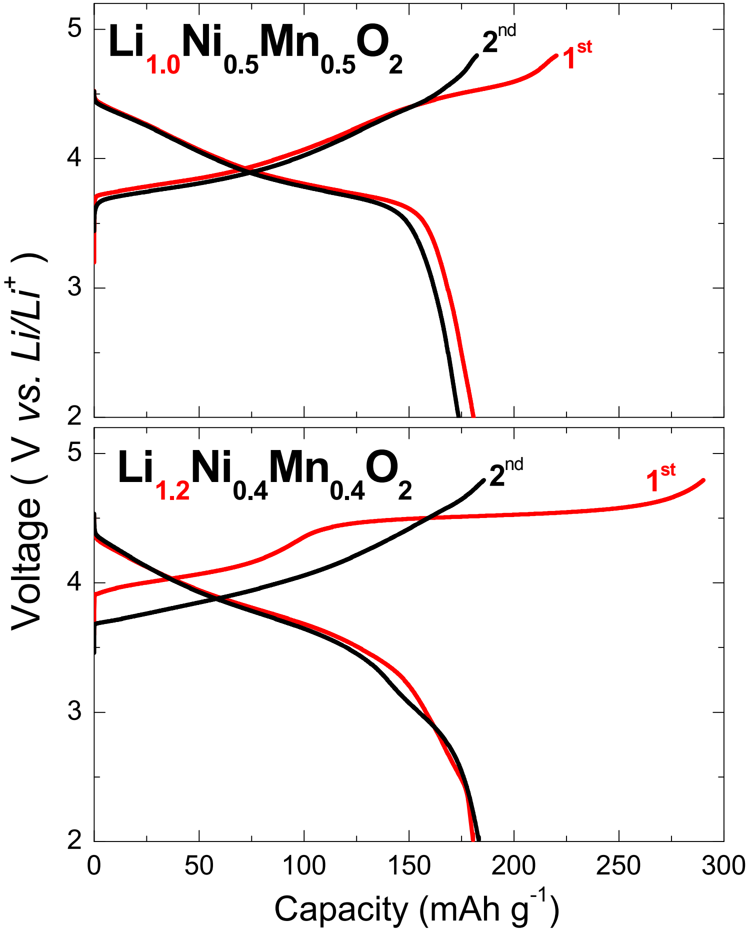
1st charge: $3Co + Fe + 6Li_2O + 3CaO \Rightarrow 3(CoO + 2Li) + 1/3(Fe_3O_4 + 8Li) + 5/3Li_2O + 3CaO$

Y. D. Ko, et al, J. Mater. Chem. (will be appeared as Cover Article), in press (2009).

High voltage layered structure cathode materials with high capacity; $Li_{1+x}(Ni_{0.5}Mn_{0.5})_{1-x}O_2$

Collaboration with Argonne National Lab. (ANL)

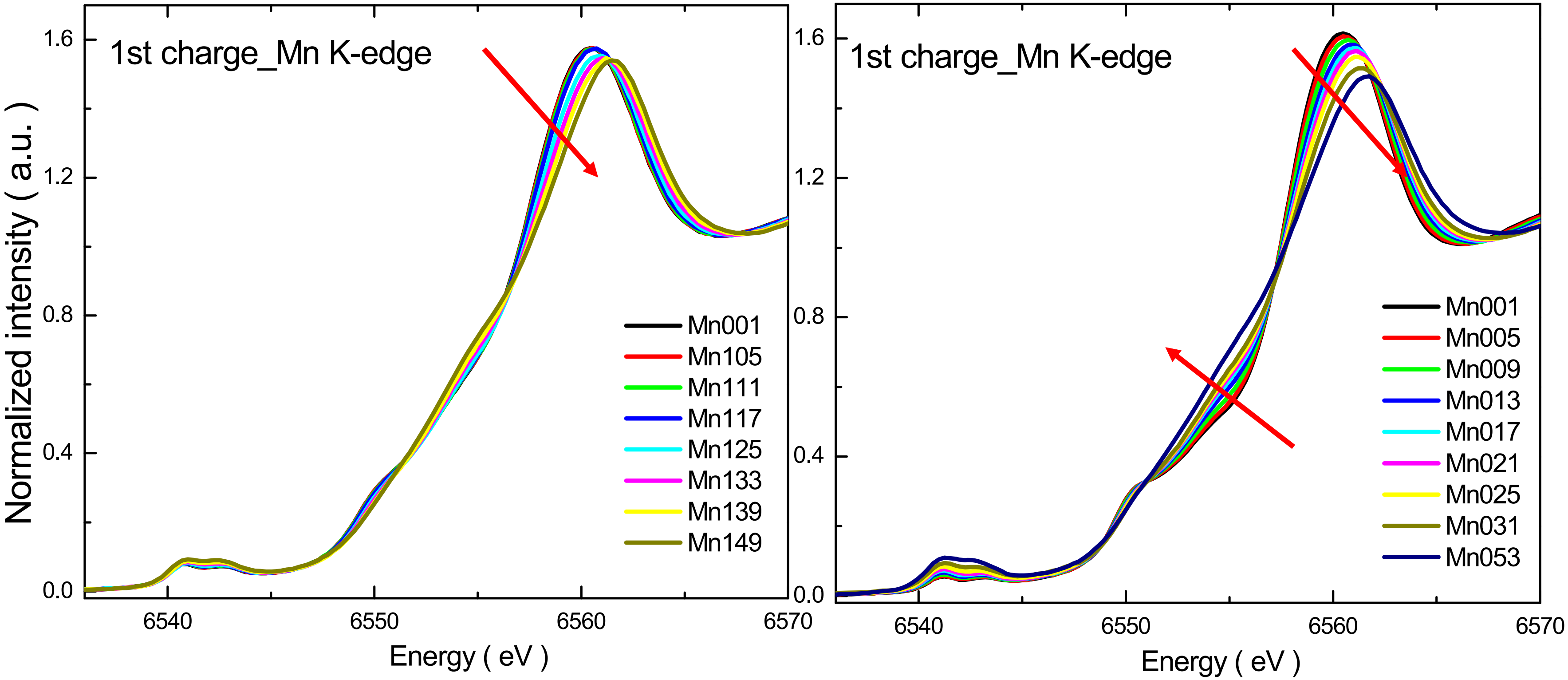




- In collaboration with Dr. Kang and Dr. Thackeray in ANL, the local electronic and structural changes of $Li_{1+x}(Ni_{0.5}Mn_{0.5})_{1-x}O_2$ electrode during charge-discharge at high voltages were studied by *in situ* XAS.
- The lithium rich $Li_{1+x}(Ni_{0.5}Mn_{0.5})_{1-x}O_2$ show higher capacity and better capacity retention if activated during first charge above 4.6V.

Mn K-edge XANES during *1st charge*

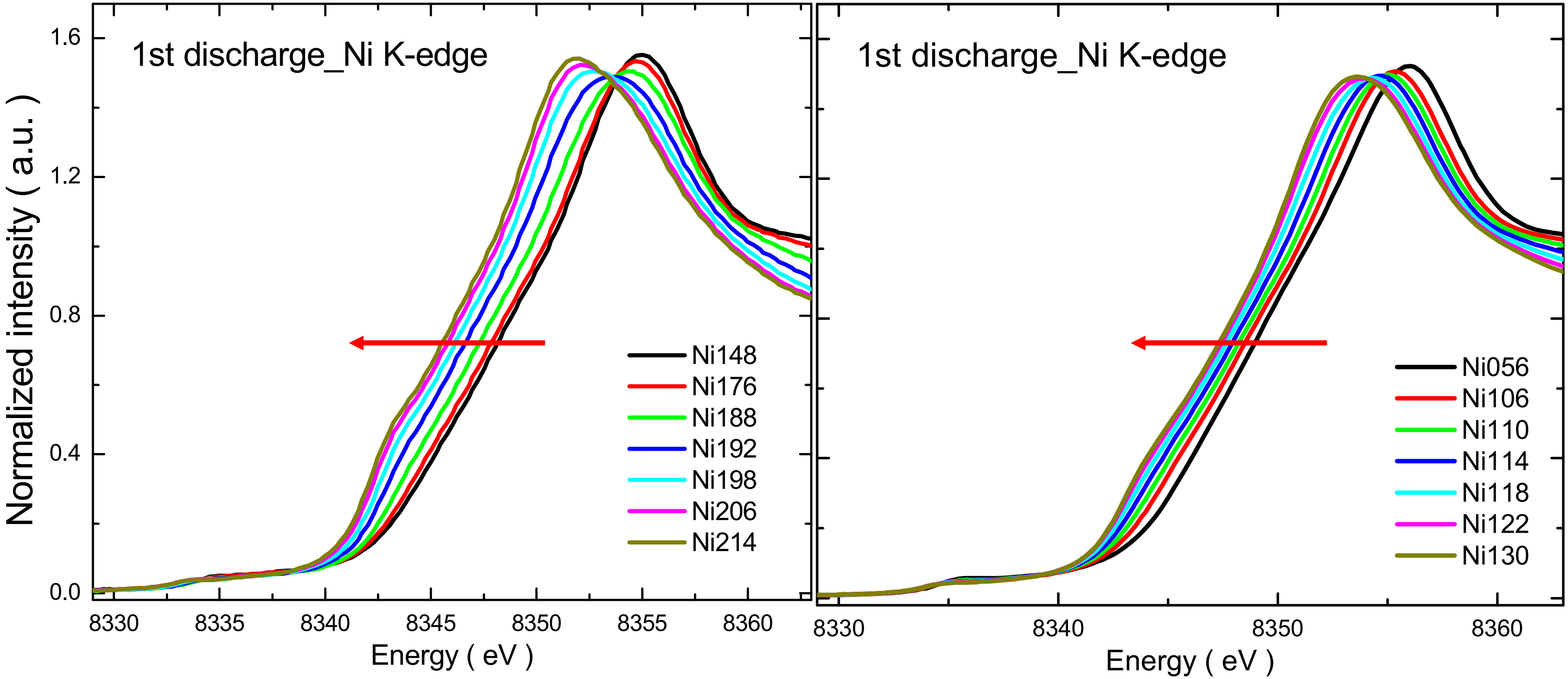
$Li_{1.0}Mn_{0.5}Ni_{0.5}O_2$ $Li_{1.2}Mn_{0.4}Ni_{0.4}O_2$



➥ **The near edge spectra changes much more significantly in $Li_{1.2}Mn_{0.4}Ni_{0.4}O_2$ than in $LiMn_{0.5}Ni_{0.5}O_2$ supporting to the proposed model of activating Li_2MnO_3 alike phase during first high V charge.**

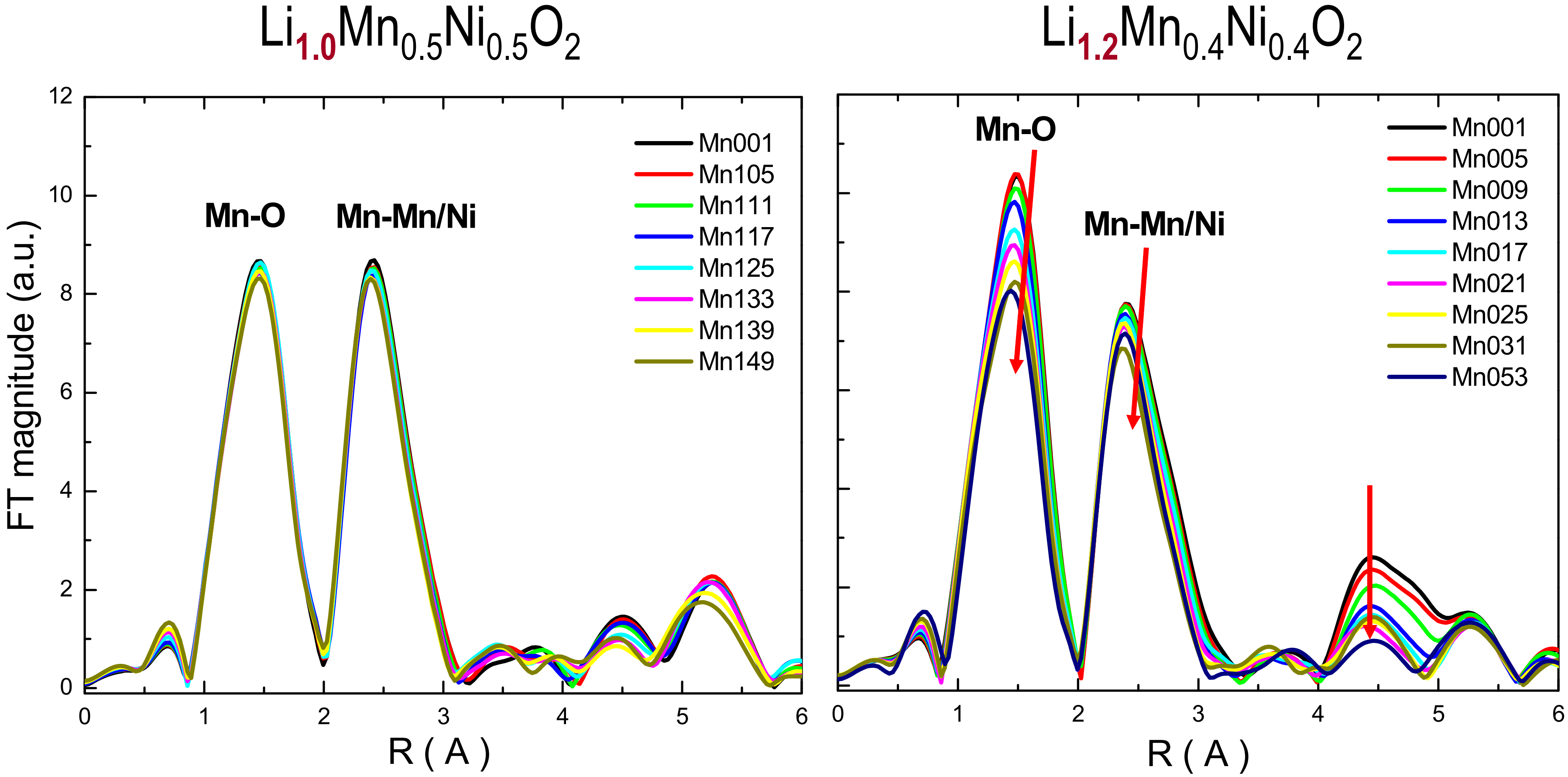
Ni K-edge XANES during *1st discharge*

$Li_{1.0}Mn_{0.5}Ni_{0.5}O_2$ $Li_{1.2}Mn_{0.4}Ni_{0.4}O_2$



➥ **The narrower energy shift range of Ni K-edge during discharge for $Li_{1.2}Mn_{0.4}Ni_{0.4}O_2$ comparing with $LiMn_{0.5}Ni_{0.5}O_2$ showing that the extra capacity for $Li_{1.2}Mn_{0.4}Ni_{0.4}O_2$ is not contributed by Ni.**

Mn K-edge EXAFS during *1st charge*



- **The decreasing coordination number for Mn-O shell during first charge for $Li_{1.2}Mn_{0.4}Ni_{0.4}O_2$ indicating that the some oxygen atoms surrounding Mn were lost during high V first charge.**

Solubility and Li^+ transference number of Li_2O-TPFPB and Li_2O_2-TPFPB based electrolytes

Solubility

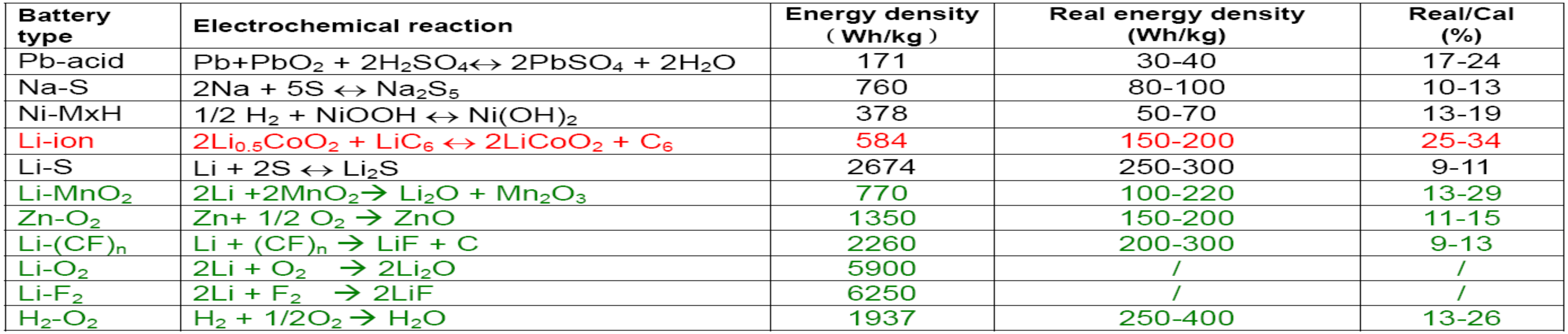
Nominal molar concentration	Solubility (mol/L)
0.2 M Li_2O	0.0104 ± 0.002
0.2 M Li_2O_2	0.0198 ± 0.0017
0.2 M Li_2O/ 0.4 M TPFPB	0.1919 ± 0.002
0.4 M Li_2O/ 0.8 M TPFPB	0.2398 ± 0.002
0.2 M Li_2O_2/ 0.4 M TPFPB	0.1896 ± 0.0017

Transfer numbers

No.	Electrolyte	t_{Li+}	t_{x-}
a	0.4 M TPFPB-0.2 M Li_2O-PC:DMC (1:1)	0.78	0.22
e	0.4M TPFPB-0.2 M Li_2O_2-PC:DMC (1:1)	0.74	0.26
f	0.4 M TPFPB-0.2 M Li_2O-EC:DMC (1:1)	0.89	0.11

➥ Significant improvement of solubility and Li^+ transfer numbers for Li_2O and Li_2O_2 based electrolytes by adding TPPFPB.

What Chemistry beyond Li-ion?



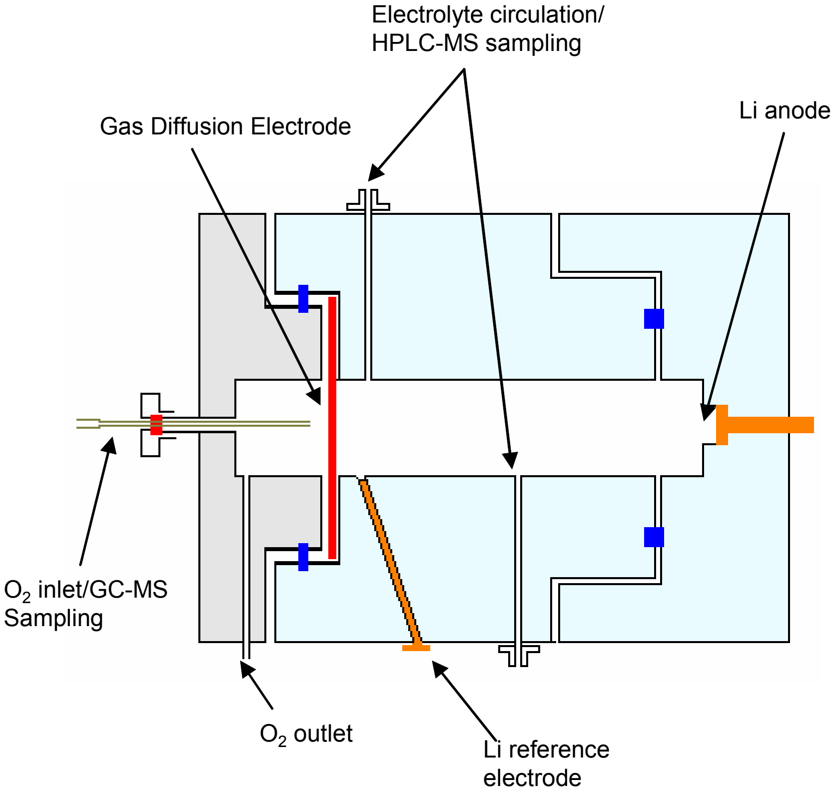
Battery type	Electrochemical reaction	Energy density (Wh/kg)	Real energy density (Wh/kg)	Real/Cal (%)
Pb-acid	$Pb+PbO_2 + 2H_2SO_4 \leftrightarrow 2PbSO_4 + 2H_2O$	171	30-40	17-24
Na-S	$2Na + 5S \leftrightarrow Na_2S_5$	760	80-100	10-13
Ni-MxH	$1/2\ H_2 + NiOOH \leftrightarrow Ni(OH)_2$	378	50-70	13-19
Li-ion	$2Li_{0.5}CoO_2 + LiC_6 \leftrightarrow 2LiCoO_2 + C_6$	584	150-200	25-34
Li-S	$Li + 2S \leftrightarrow Li_2S$	2674	250-300	9-11
$Li-MnO_2$	$2Li + 2MnO_2 \rightarrow Li_2O + Mn_2O_3$	770	100-220	13-29
$Zn-O_2$	$Zn + 1/2\ O_2 \rightarrow ZnO$	1350	150-200	11-15
$Li-(CF)_n$	$Li + (CF)_n \rightarrow LiF + C$	2260	200-300	9-13
$Li-O_2$	$2Li + O_2 \rightarrow 2Li_2O$	5900	/	/
$Li-F_2$	$2Li + F_2 \rightarrow 2LiF$	6250	/	/
H_2-O_2	$H_2 + 1/2O_2 \rightarrow H_2O$	1937	250-400	13-26

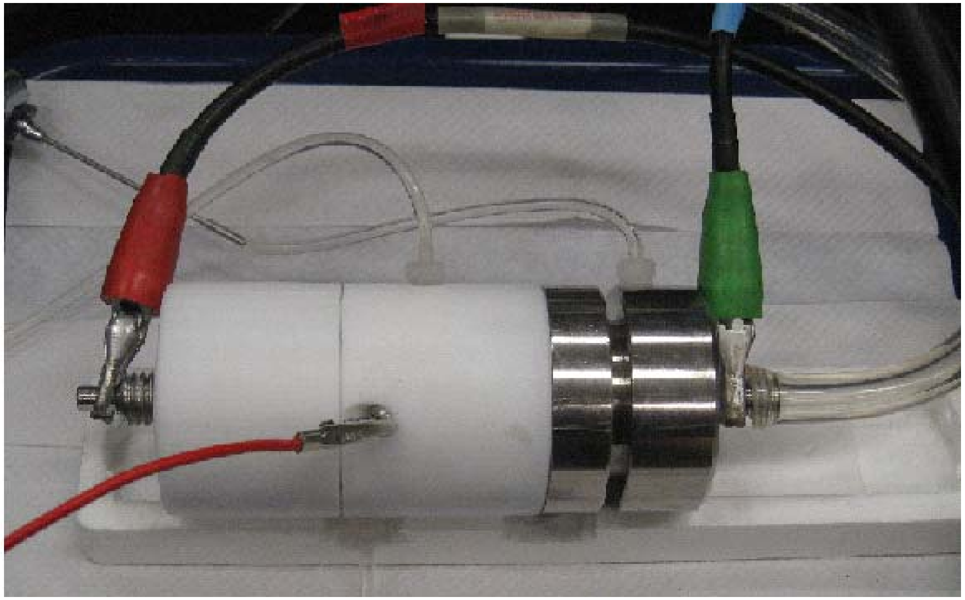
Among the 24 on-going NEDO projects, one is Li-air and another one is Zn-air

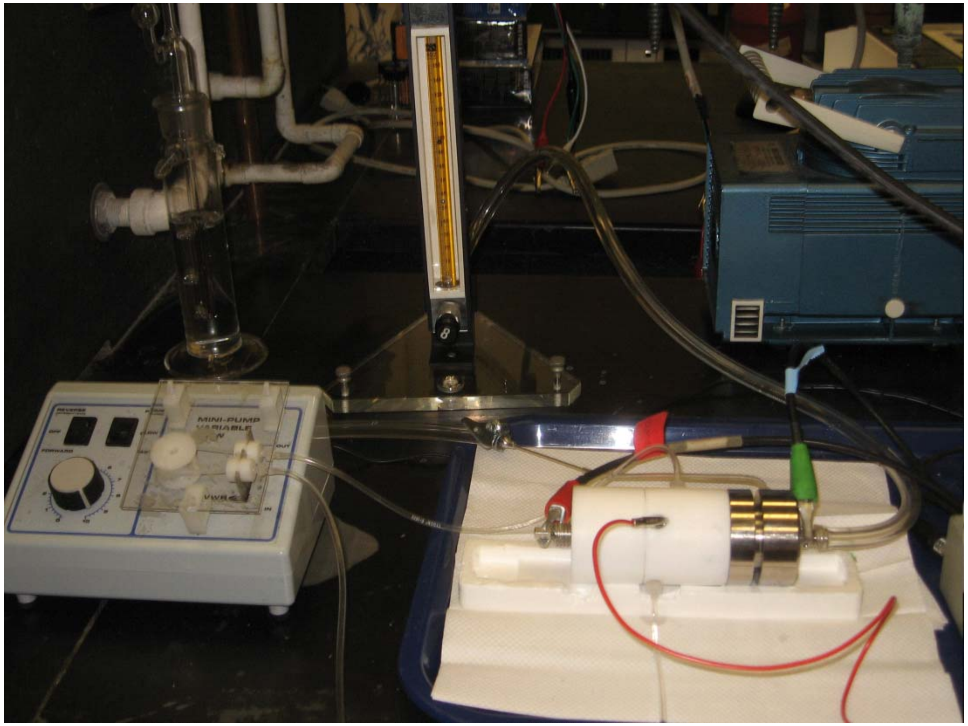
Obstacles for Rechargeable Metal Air Cells

Metal air in non-aqueous electrolyte
Li-air
Feasibility for air cathode: gas diffusion electrode.
Rechargeability (Li oxide)
Electrode structure (prevent the pores from being filled by Li Oxide - solubility).
Solubility of Li oxides.
Oxygen solubility in non-aqueous electrolytes
Li Peroxide (Li_2O_2), safety

New organic electrolytes, new air cathodes and testing Zn-Air and Li-Air cells
Are being developed by the collaboration between UMASS Boston and BNL



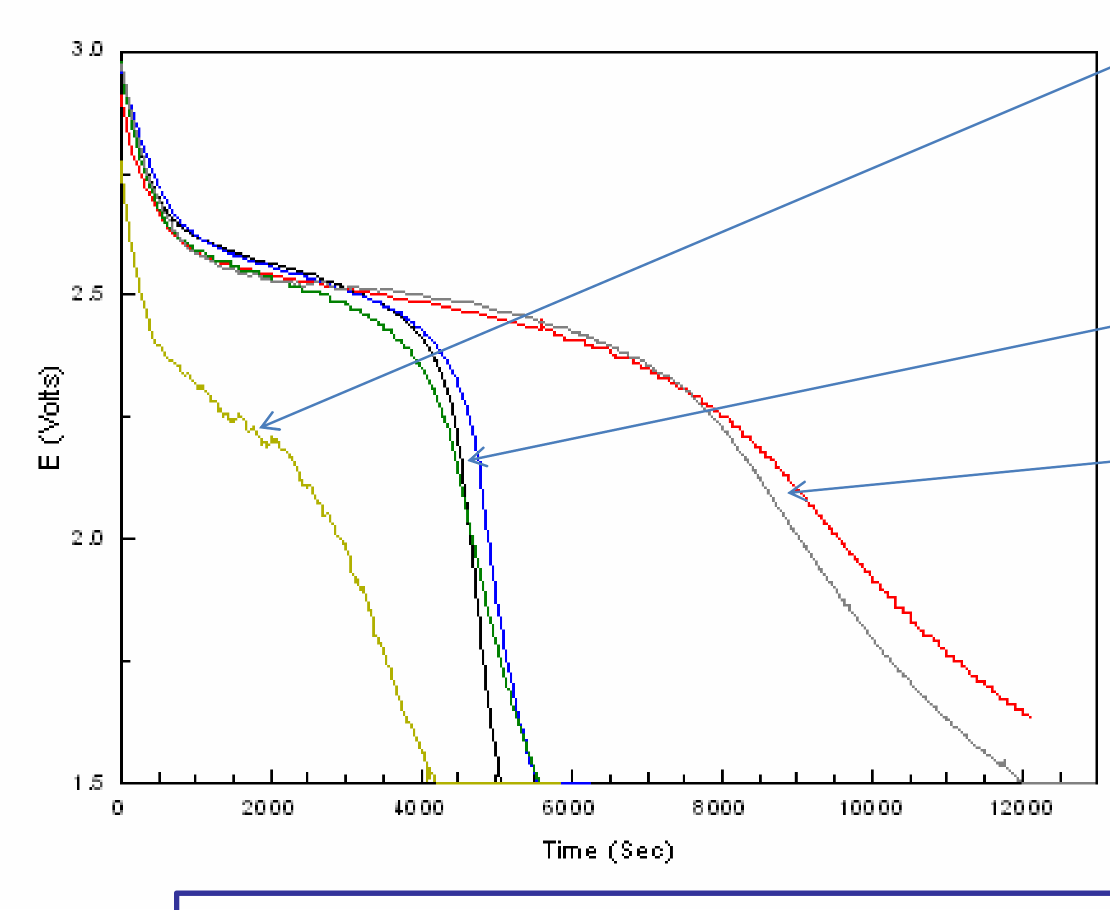




Electrochemical cell designed and constructed at UMASS Boston for Li-air cell

- **discharge and recharge**
- **while the forming gas and electrolyte composition can be monitored real-time by GC-MS and HPLC-MS, respectively.**
- **Electrolyte circulation for Li oxide removal and re-dissolution.**

Establishing 3-phase Interface by adjusting O_2 pressure



No positive pressure. Pores in GDE were filled by electrolyte – double-layer capacitor behavior.

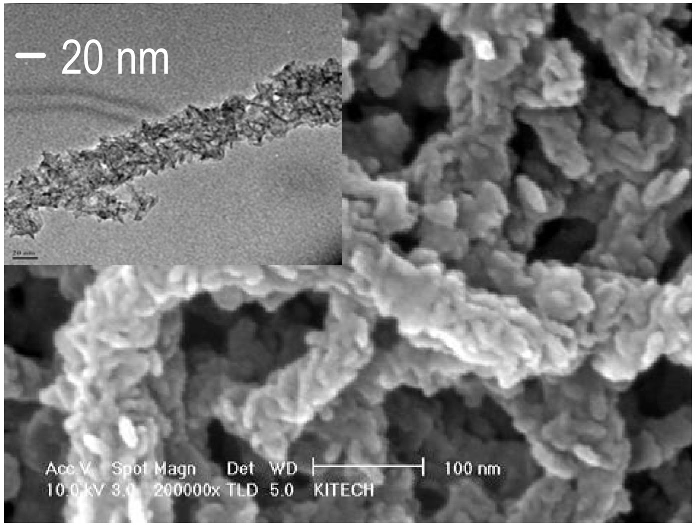
P_{O2} was about 2 psig

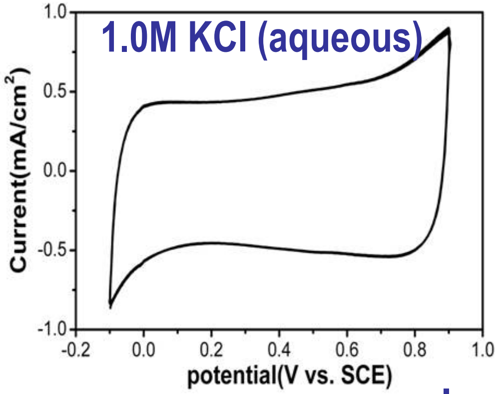
P_{O2} = 6 psig

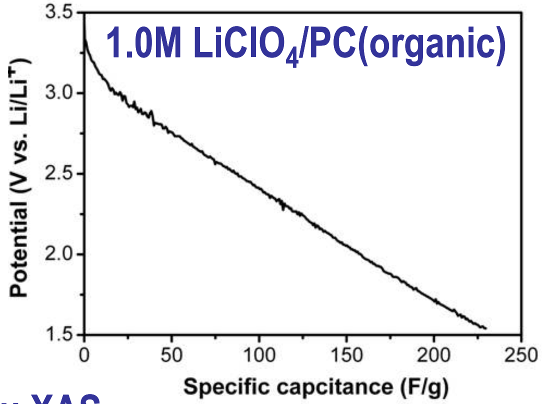
Higher gas pressure creates larger reaction interface for oxygen reduction. Too high pressure will cause cell leakage

MnO_2/CNT nanocomposite materials for supercapacitor applications

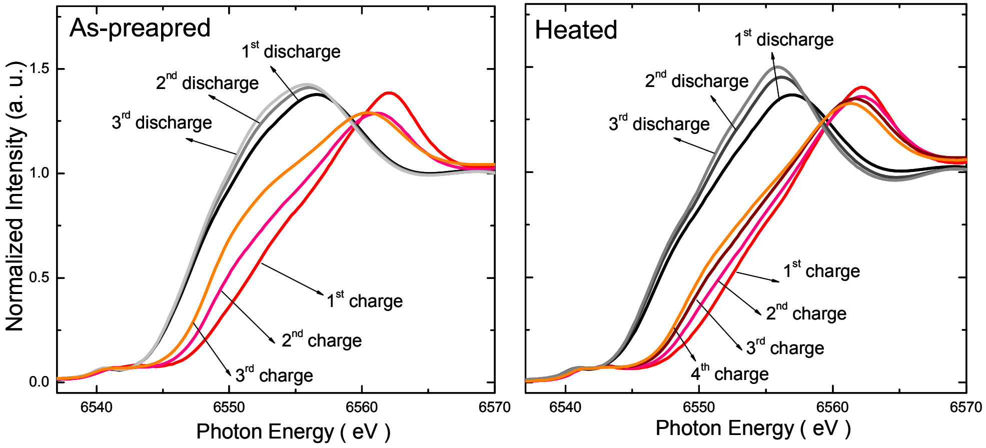
Synthesized by solution based direct redox reaction







In situ XAS



- In collaboration with Yonsei University in Korea, MnO_2/CNT nanocomposite electrode materials for supercapacitor applications were studied by using *in situ* XAS during charge-discharge.
- Heat treatment of the MnO_2/CNT nanocomposite electrodes improved the cyclability (i.e. reversibility) in organic electrolytes which confirmed by *in situ* XAS study.

S. B. Ma, K. W. Nam, X. Q. Yang et al, Electrochemistry Communications, 9 (2007) 2807 & Journal of Power Sources, 178 (2009) 483.

Planned work for FY 2009 and FY2010

- ▣ Complete the *in situ* XRD 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. (milestone for Sep. 2009)

- ▣ Further development of *in situ* 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, lithium metal cells and lithium-air cells in collaboration with MER Corp. and Army Research Lab (ARL).

- ▣ In collaboration with UMASS at Boston, continue on the efforts to develop gas diffusion electrode for Li-air batteries using organic electrolytes. The key issue is to increase the solubility of oxygen to overcome the oxygen deficiency in organic electrolytes.

Summary

- *In situ* XRD and XAS techniques have been developed at NSLS and made available to battery research community (SUNYSB, ANL, Yardney, and Duracell (P&G)).

- In collaboration with ANL, $Li_{1+x}(Ni_{0.5}Mn_{0.5})_{1-x}O_2$ new cathode materials have been studies using in situ XRD and XAS. The results of these studies provide useful information for improving the energy density and cycleability of Li-ion batteries.

- In collaboration with Institute of Physics in China, $Li_{1-x}Fe_{1/4}Mn_{1/4}Co_{1/4}Ni_{1/4}PO_4$ cathode material has been studied. Clear K-edge shifts to higher energies for Fe, Mn, and Co were observed corresponding to the voltage plateaus at ~3.5 (Fe^{2+} to Fe^{3+}), ~4.1 (Mn^{2+} to Mn^{3+}), and ~4.8 V (Co^{2+} to Co^{3+}). An intermediate phase and solid solution regions for all three phases were clearly observed during charge in the *in situ* XRD patterns. This is quite different than the unsubstituted $LiFePO_4$. These results are quite important for synthesis high voltage (high energy density) cathode materials with olivine structures.

- 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.