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

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Washington, DC, May 9-13

ES059

Overview

Timeline

- ▣ Start: 10/01/2009
- ▣ Finish: continued
- ▣ Continued

Budget

- ▣ Funding received in FY10

  DOE: $650k

- ▣ Funding received in FY11

  DOE: $650k

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

Collaborators

- University of Massachusetts at Boston
- Dow Chemical
- GM R&D Center
- Oakridge National Lab. (ORNL)
- University of Tennessee
- Argonne National Lab. (ANL)
- SUNY Binghamton
- SUNY Stony Brook
- SUNY Buffalo
- 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 and high energy density materials such as Li_2MnO_3-$LiMO_2$ and $LiFe_{1-y}Mn_yPO_4$.
- ▣ To synthesize and characterize high voltage cathode and high voltage electrolytes for high energy density lithium batteries for plug-in hybrid electric vehicles (PHEV).
- ▣ To carry out fundamental studies of high energy density Li-Air batteries and gas diffusion electrode materials for Li-air batteries.
- ▣ To design, synthesize and characterize new electrolyte and electrolyte additives to increase the O_2 solubility and/or with capability to dissolve Li_2O and Li_2O_2 oxides for Lithium-air batteries.
- ▣ 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/11	Complete soft X-ray absorption spectroscopy (XAS) studies of $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ cathode materials during electrochemical cycling. ➥ Completed.
Apr/11	Complete the studies of carbon structure effects on the electro-catalysis performance of air cathode in Li-air cells. ➥ Completed.
Sep/11	Complete in situ X-ray diffraction studies of manganese doped lithium iron phosphate ($LiFe_{1-y}Mn_yPO_4$) cathode materials with mesoporous structure in comparison with large particle sized cathode during electrochemical cycling. ➥ On schedule.
Sep/11	Complete the studies of the effects on the improvement of discharge current density by increasing the solubility of oxygen in Li-Air electrolytes. ➥ On schedule.

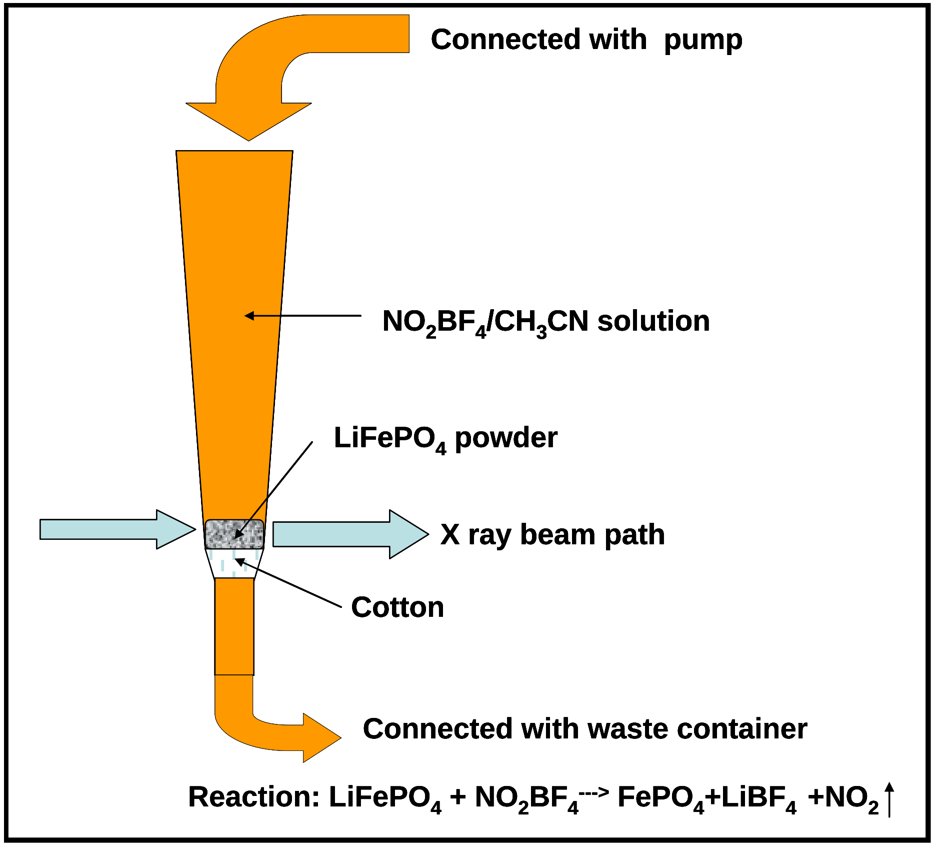
Approaches

- In situ XAS and XRD studies of new electrode materials such as $LiFe_{1-y}Mn_yPO_4$ and high capacity $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ during electrochemical cycling to carry out the diagnostic studies to improve the energy density and cycle life of Li-ion batteries.
- Soft XAS on the L-edges of Mn and Ni to distinguish the difference between the surface and the bulk structural changes caused by charge-discharge cycling for new cathode materials such as $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$.
- In situ and ex situ transmission electron microscopy (TEM) coupled with selected area electron diffraction (SAED) to study the structural changes of electrode materials with high location specification and spatial resolution.
- Electrochemical studies of gas diffusion electrode (GDE) for Li-Air batteries.
- Improve the performance of the GDE by surface modification.
- Develop new electrolyte with higher O_2 solubility to increase the discharge current density of Li-Air batteries.
- Design and synthesis of new electrolyte system with capability to dissolve Li_2O and Li_2O_2, and/or high solubility of O_2 for lithium-air batteries.

Technical Accomplishments

- Developed new in situ XRD to study cathode materials for Li-ion batteries during chemical delithiation.
- Completed combined in situ hard XAS and ex situ soft XAS studies on high energy $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ cathode materials during charge-discharge cycling. Important information about the roles of Mn cations was obtained.
- Completed in situ XAS and XRD studies on mesoporous $LiFe_{1-y}Mn_yPO_4$ $(0.0\leq y\leq 0.8)$ cathode materials during charge-discharge cycling. The effects of particle size and morphology on the phase transition behavior and performance of Li-ion cells have been studied.
- Modified the surface of carbon materials for gas diffuse electrode (GDE), which significantly improved the discharge capacity of the Lithium-Air cell.
- Developed novel new electrolyte which can increase the solubility of O_2 dramatically. The discharge rate of the Lithium-Air cell using this new electrolyte is increased more than one order of magnitude than the conventional electrolytes.
- Developed a family of new boron based additives with good SEI formation capability and anion receptor functionality for lithium battery electrolyte (US patents were filed in 2010). Designed and synthesized new solvents for lithium battery electrolytes.

New *in situ* XRD techniques during chemical delithiation



Connected with pump

NO_2BF_4/CH_3CN solution

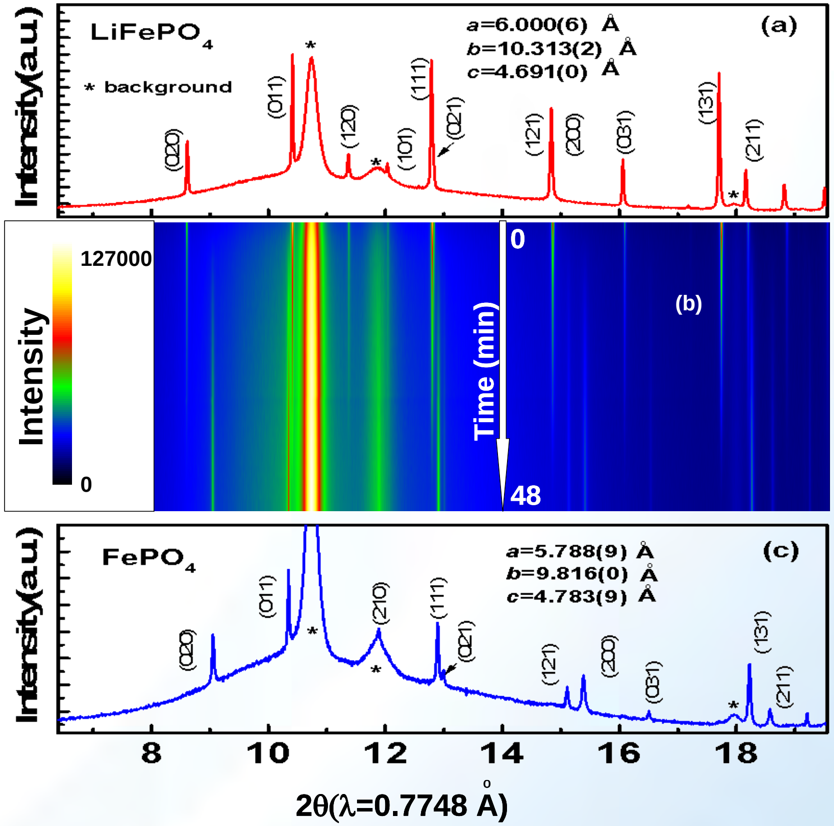
$LiFePO_4$ powder

X ray beam path

Cotton

Connected with waste container

Reaction: $LiFePO_4 + NO_2BF_4 \dashrightarrow FePO_4 + LiBF_4 + NO_2\uparrow$



Submitted to *Chemical Communications*

- New in situ XRD techniques during chemical delithiation have been developed to study the structural changes of electrode materials for lithium-ion batteries.
- Implication?

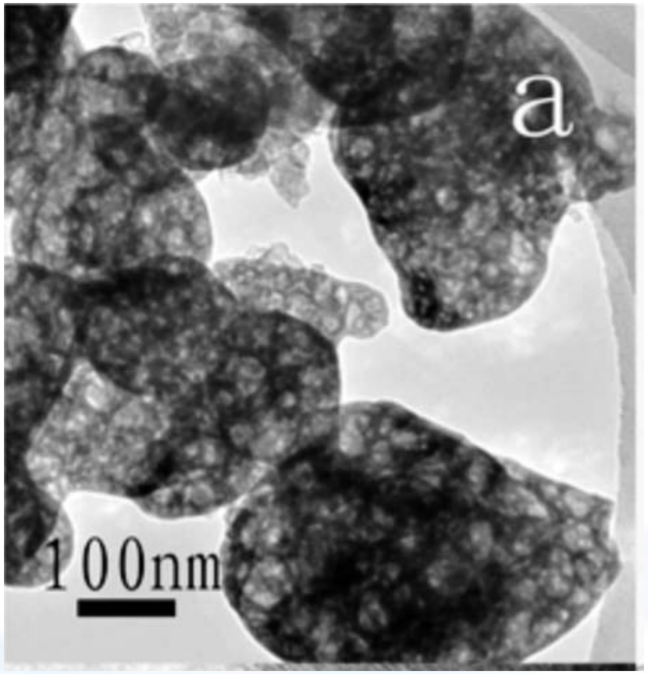
Mesoporous $LiFe_{1-y}Mn_yPO_4$ ($0 \leq y \leq 0.8$)

Motivation

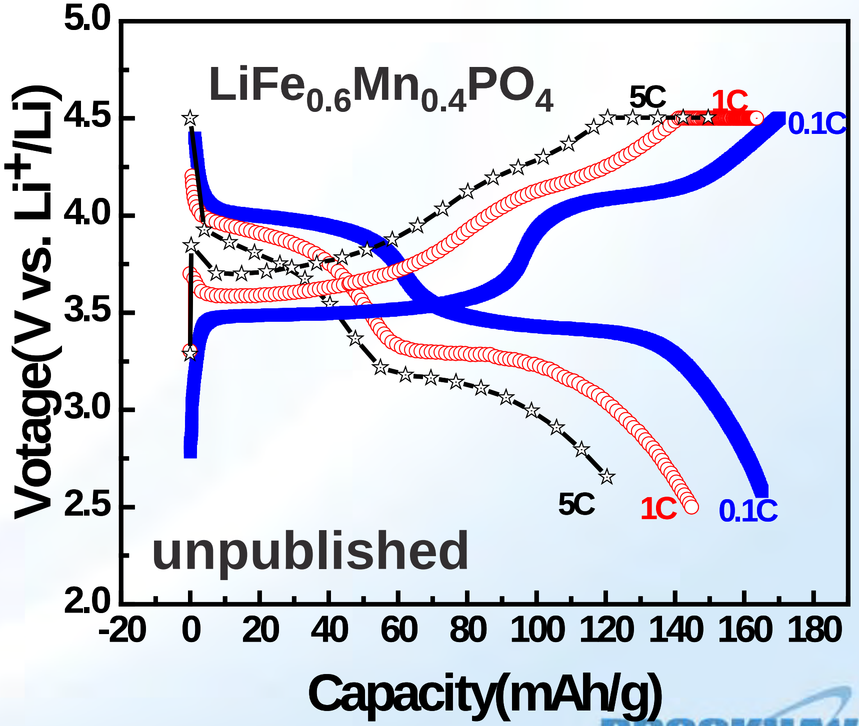
Higher energy density and lower cost cathode materials
The **phase transition** in **$LiFe_{1-y}Mn_yPO_4$** is not fully understood because it mainly depends on the **particle size**, **Mn** content et al.

$LiFe_{1-y}Mn_yPO_4$: High speed ball milling and citric acid

Results

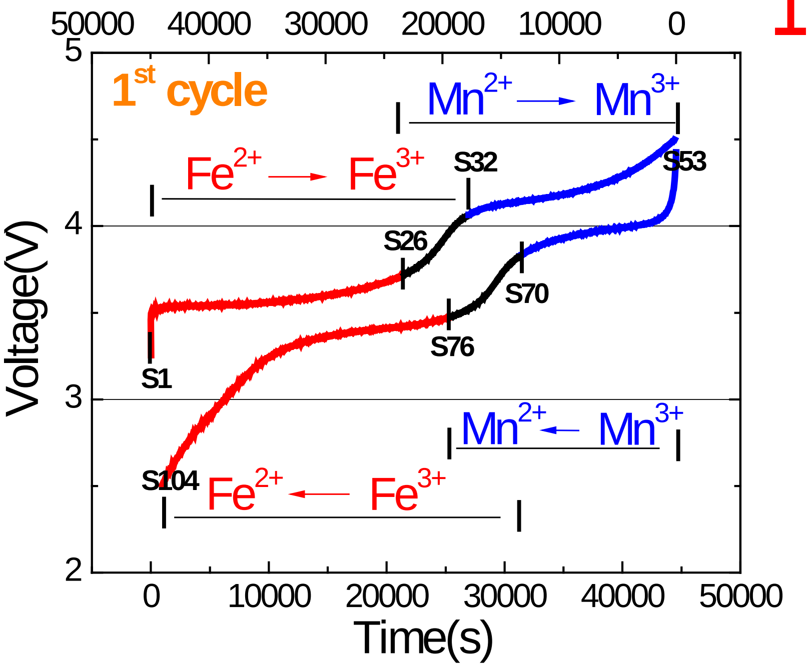


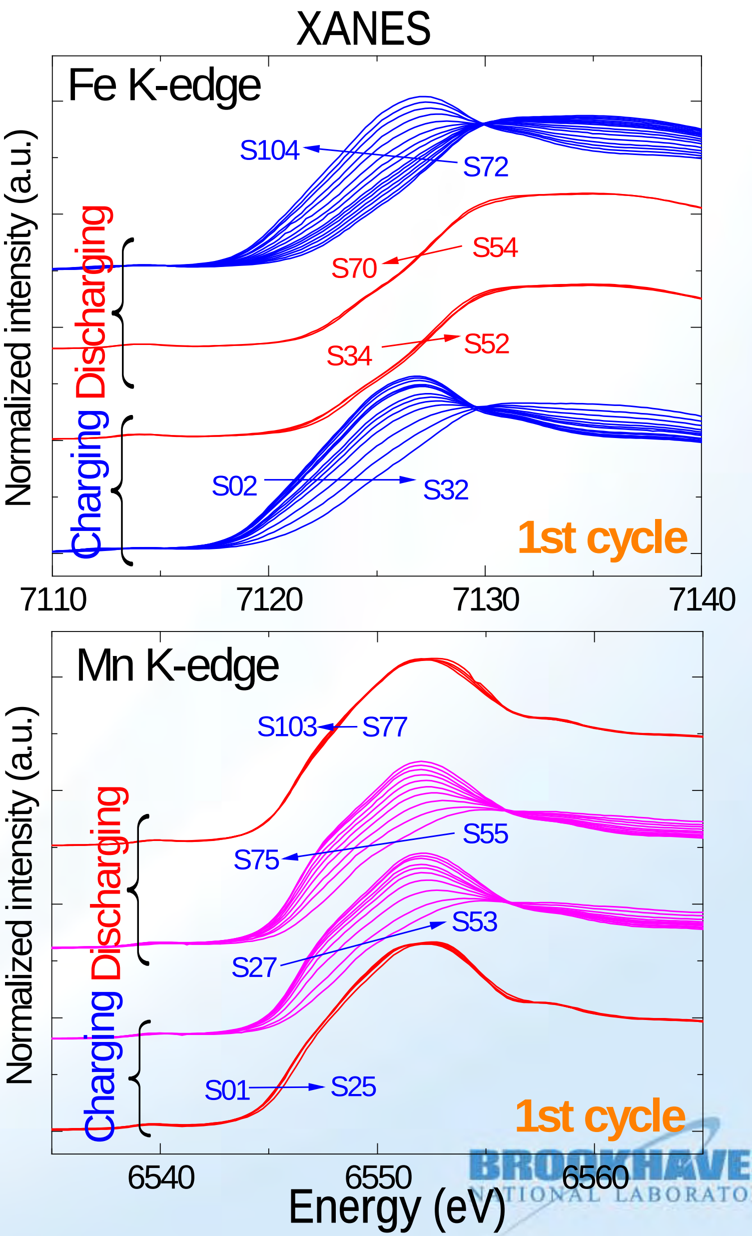
Typical TEM image



In situ XAS of mesoporous $Li_{1-x}Fe_{0.6}Mn_{0.4}PO_4$ during cycling

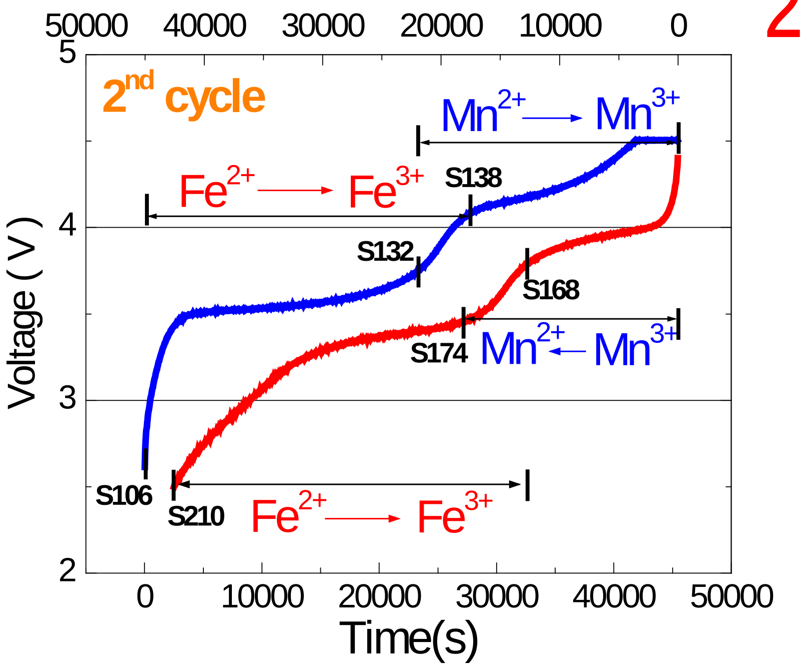
1^{st} cycle



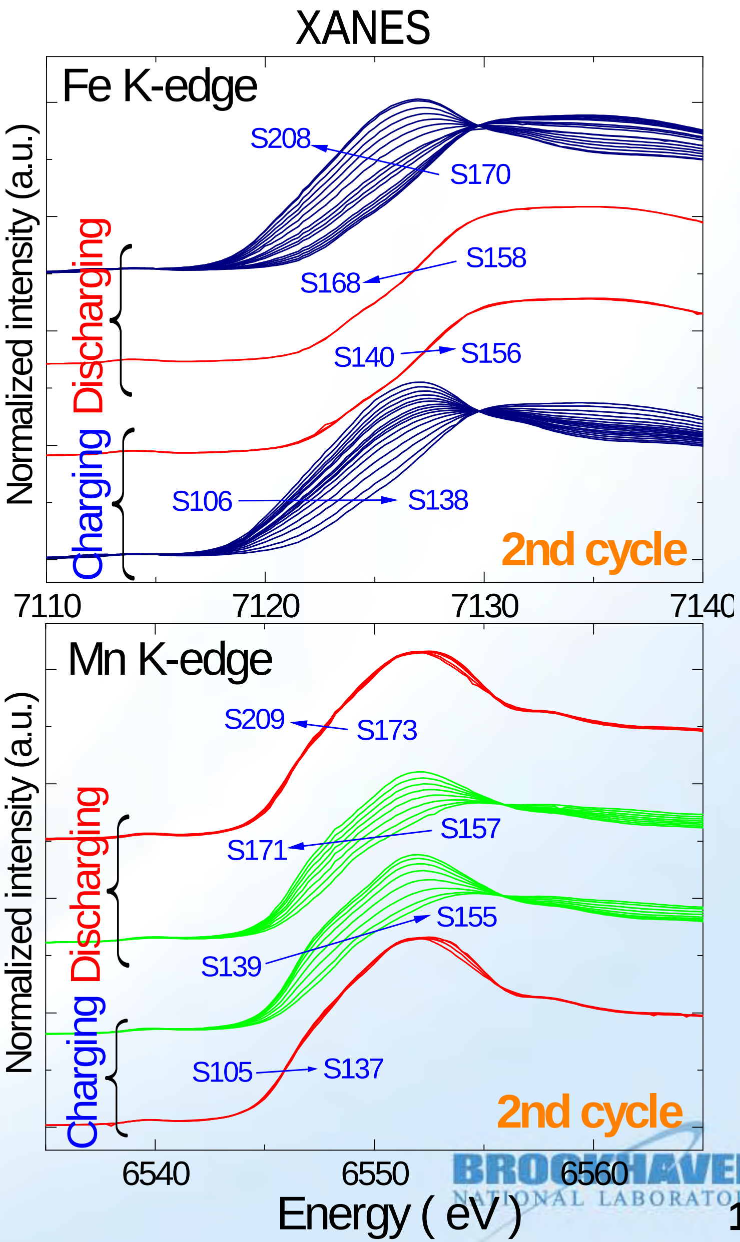


- Reversible redox reactions of Fe^{2+}/Fe^{3+} and Mn^{2+}/Mn^{3+} at low voltage (~3.5V) and high voltage (~4.0V) plateaus during 1^{st} cycle.
- Simultaneous Fe^{2+}/Fe^{3+} and Mn^{2+}/Mn^{3+} redox reactions at the sloppy voltage region (transition region). ☞ Related to the solid-solution (single phase) region.

In situ XAS of mesoporous $Li_{1-x}Fe_{0.6}Mn_{0.4}PO_4$ during cycling



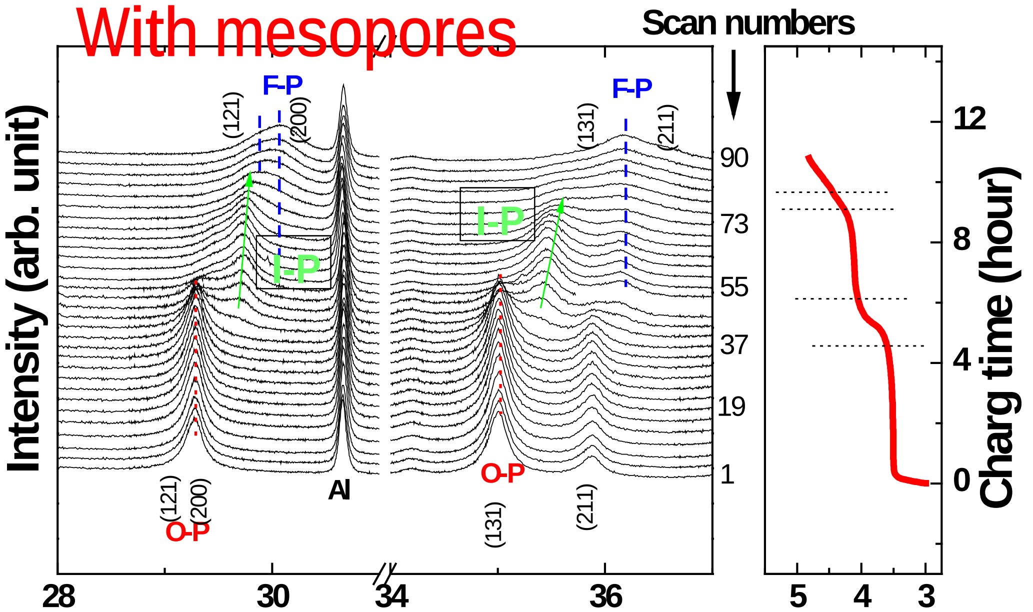
2^{nd} cycle



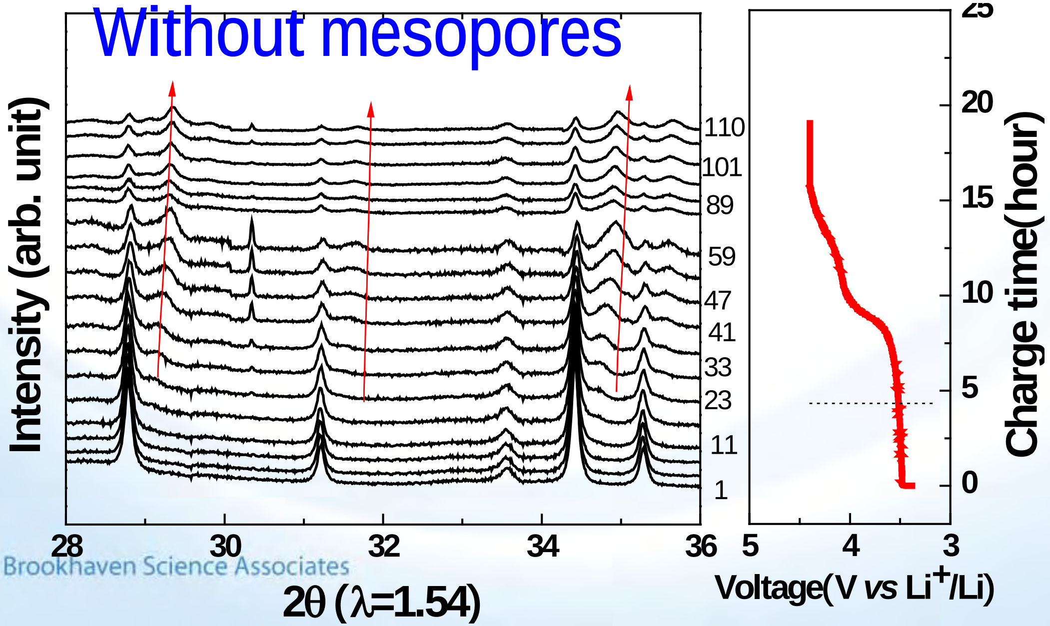
- ➥ Quite reversible Fe and Mn K-edge shifts at both low voltage (~3.5V) and high voltage (~4.0V) plateaus at 2nd cycle suggesting very reversible redox reactions of Fe^{2+}/Fe^{3+} and Mn^{2+}/Mn^{3+}.
- ➥ Well agreed with highly reversible Li extraction/ insertion behavior of the mesoporous $LiFe_{0.6}Mn_{0.4}PO_4$ during cycling.

  ☞ Good cyclability!

Comparative study of crystal structural changes of $Li_{1-x}Fe_{0.6}Mn_{0.4}PO_4$ with and without mesoporous structure by in situ XRD during *charge*

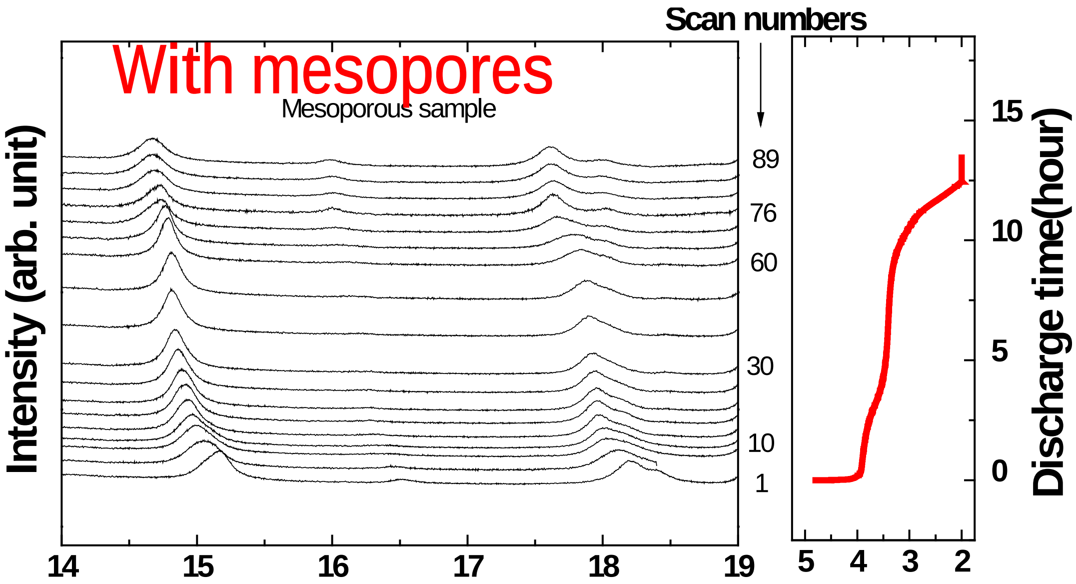


For the sample with mesoporous structure, a significant phase transition delay was observed: the second phase appear at the end of the plateau, rather than at the beginning. The transition to the third phase is almost completed at the end of charge at 5V.

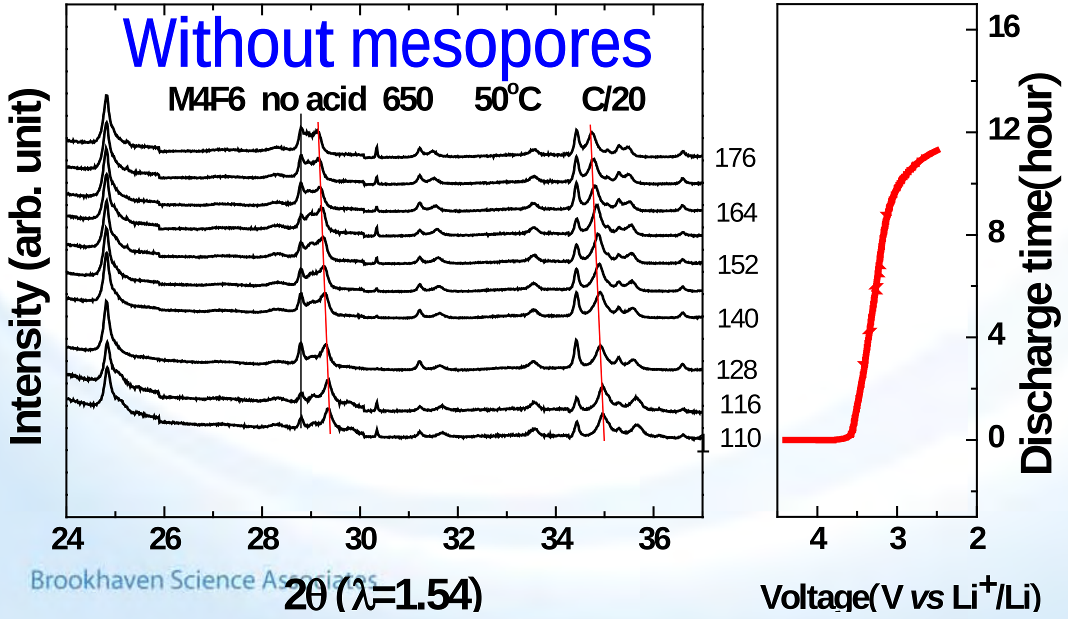


For the sample without mesoporous structure, no significant phase transition delay was observed: the second phase appear at the beginning of the plateau. The transition to the third phase is not completed at the end of charge at 5V.

Comparative study of crystal structural changes of $Li_{1-x}Fe_{0.6}Mn_{0.4}PO_4$ with and without mesoporous structure by in situ XRD during *discharge*

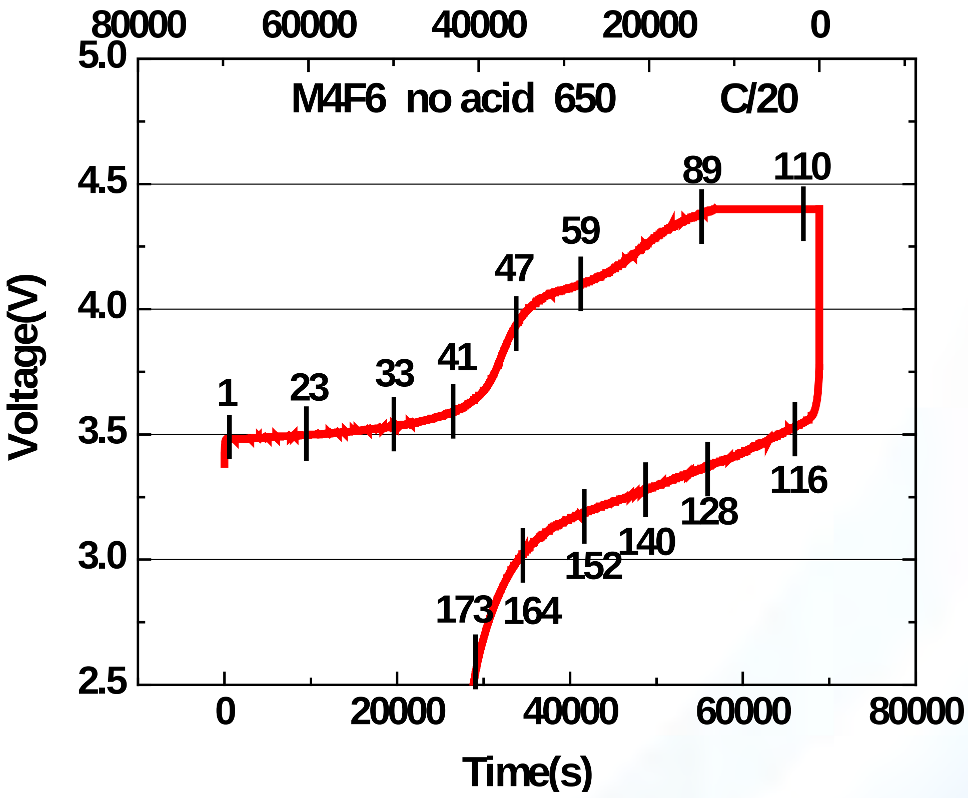


For the sample with mesoporous structure during discharge, the phase transition back to intermediate phase 2 and original phase 1 are quite reversible.



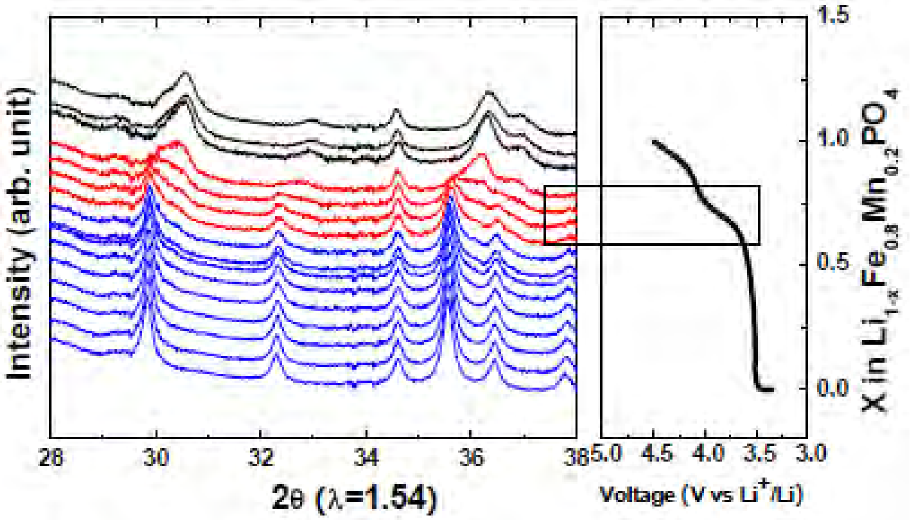
For the sample without mesoporous structure during discharge, the phase transition back to intermediate phase 2 and original phase 1 are not reversible at all. Large amount of sample still remain in the intermediate phase 2 at the end of discharge.

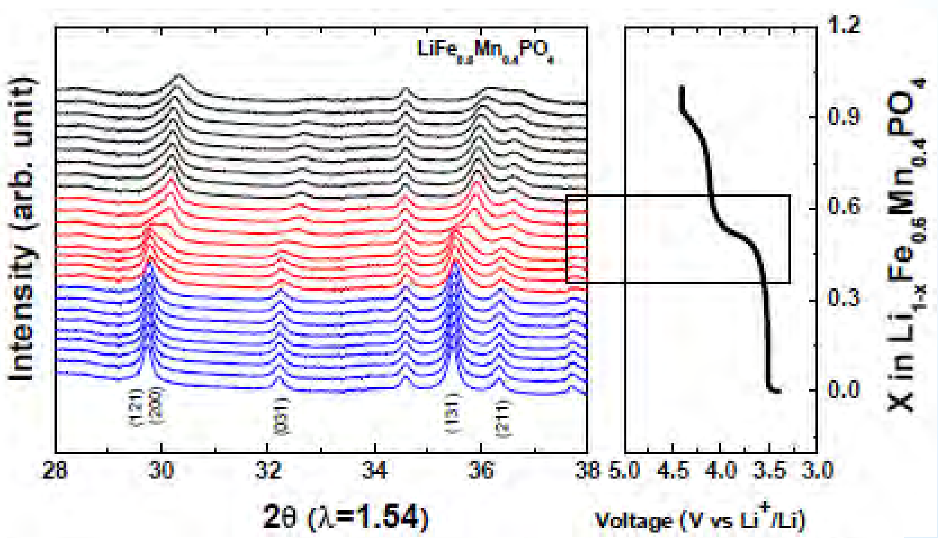
1st charge-discharge curves of $Li_{1-x}Fe_{0.6}Mn_{0.4}PO_4$ without mesoporous structure

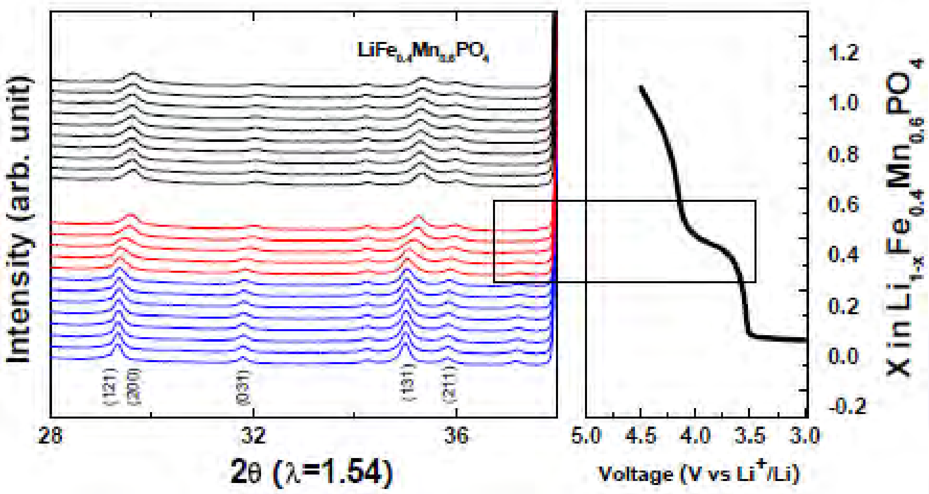


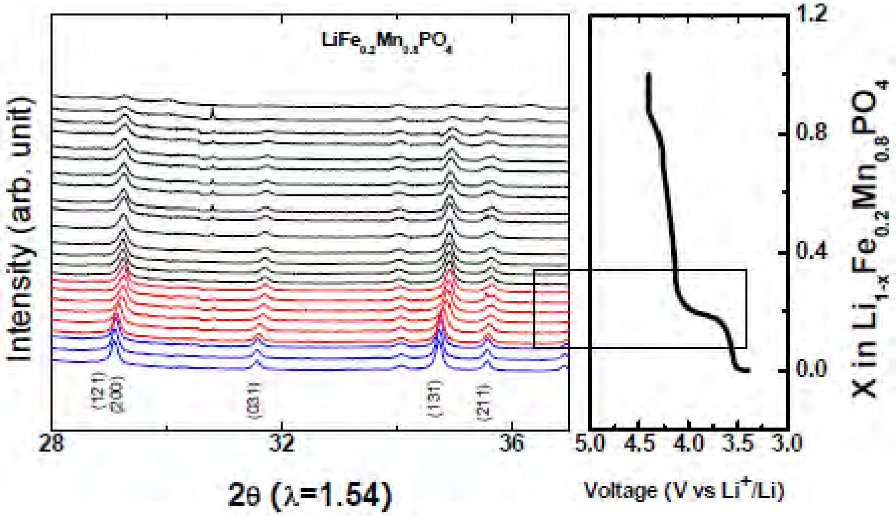
- Comparing with the $Li_{1-x}Fe_{0.6}Mn_{0.4}PO_4$ with mesoporous structure created by citric acid during synthesis, the $Li_{1-x}Fe_{0.6}Mn_{0.4}PO_4$ sample without mesoporous structure showed quite poor voltage profile and discharge capacity, indicating the low utilization of the active material during both charge and discharge.

For $LiFe_yMn_{1-y}PO_4$, with **y=0.2, 0.4, 0.6, 0.8**, two plateaus are observed and the length of second plateau increases with increasing y. Every second phase starts appearing at the end of the first plateau, where the voltage is rising rapidly. (cut off voltage = 4.5V)

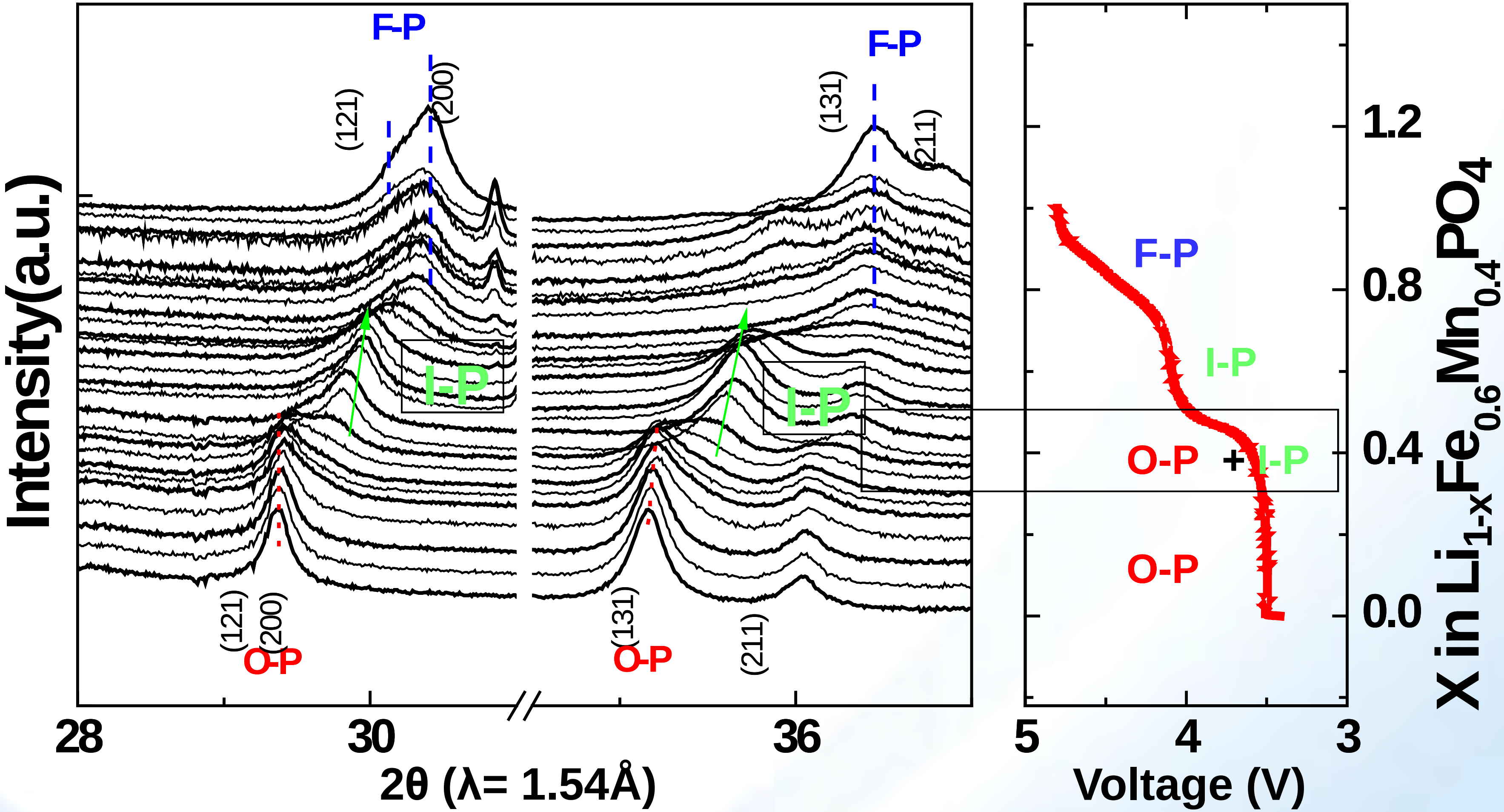








In situ XRD of mesoporous $Li_{1-x}Fe_{0.6}Mn_{0.4}PO_4$ with increased cut off voltage to ~ 5.0V



- By increasing charge voltage to 4.8 V, the third final phase (FP) was observed. In our early studies, only the original phase OP (original phase) and intermediate phase IP (Intermediate phase) were observed. `

Phase transition behaviors in mesoporous $LiFe_{1-y}Mn_yPO_4$ (0≤y≤0.8) during charge

🟦

Final Phase

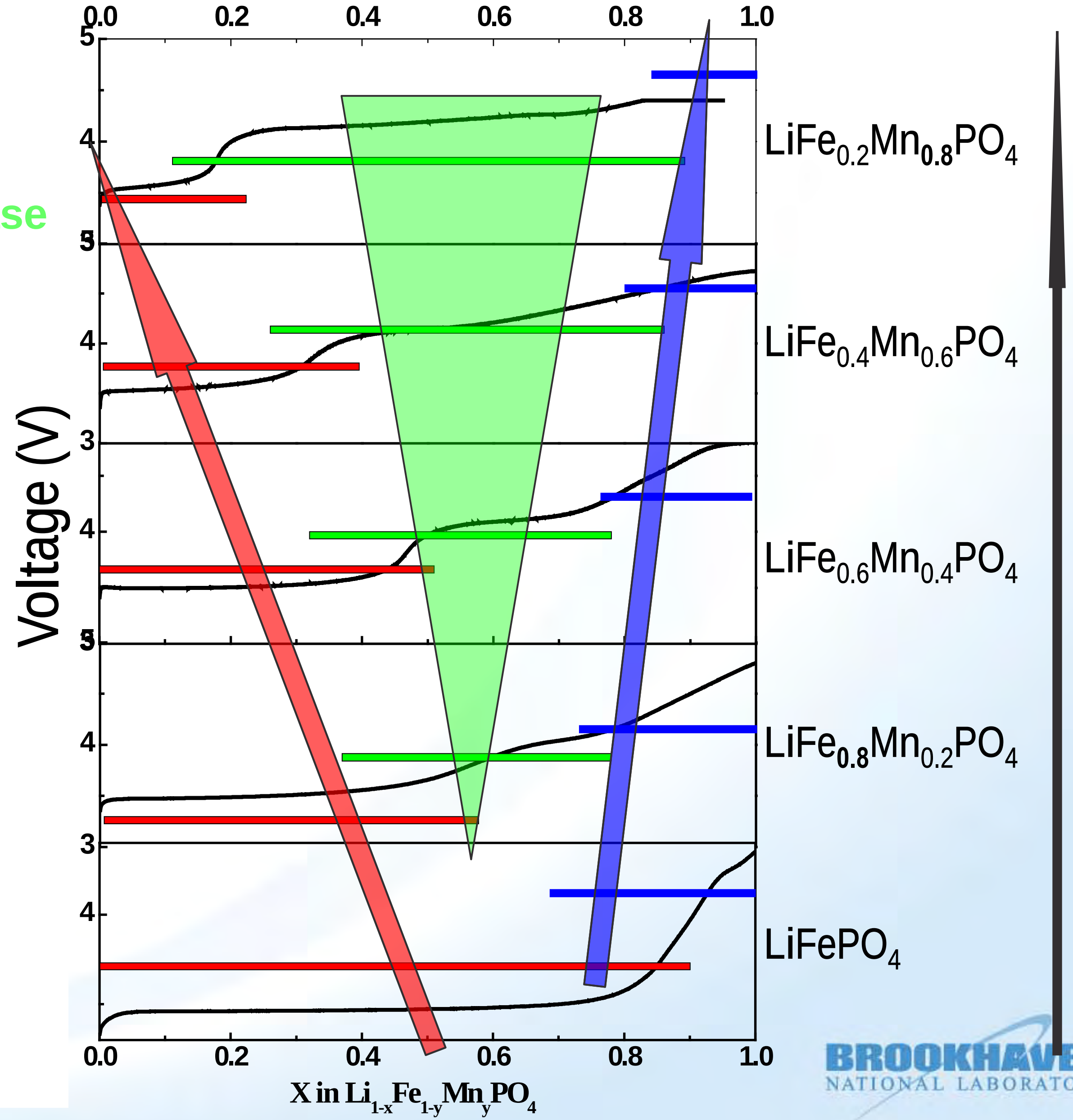
🟩

Intermediate Phase

🟥

Original Phase

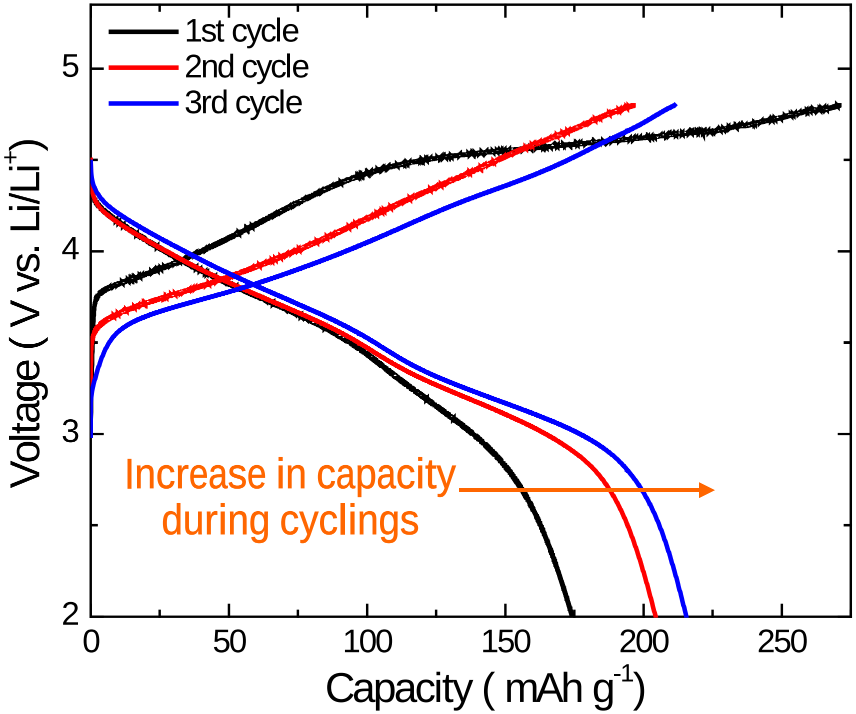
- Both the intermediate phase and the final phase appeared a delay to the charge curve.
- Their appearance is related to the regions where the voltage moves up sharply.
- The higher the content of Mn, the wider the range of the intermediate phase

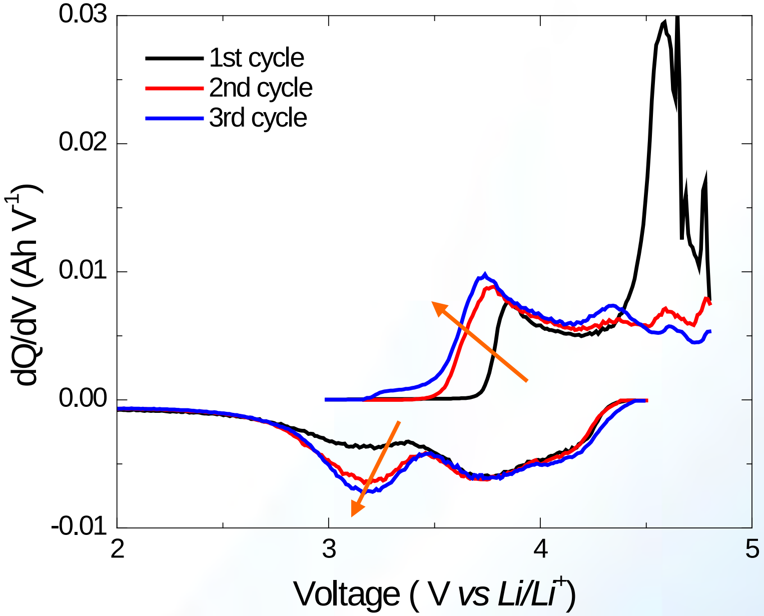


In situ XAS study of high energy Li$_{1.2}$Ni$_{0.2}$Ni$_{0.6}$O$_2$ cathode material

Charge-discharge curves
During in situ experiment

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





- ➥ Charge-discharge current density = 0.11 mA/cm^2 at room temp.
- ➥ Increase in the capacity Li$_{1.2}$Mn$_{0.6}$Ni$_{0.2}$O$_2$ cathode during initial a few cyclings. ➥ Why?

☞Combined in situ Ni & Mn K-edge and ex situ Mn L-edge XAS was used to study the charge compensation mechanism and increasing capacity during initial cyclings.

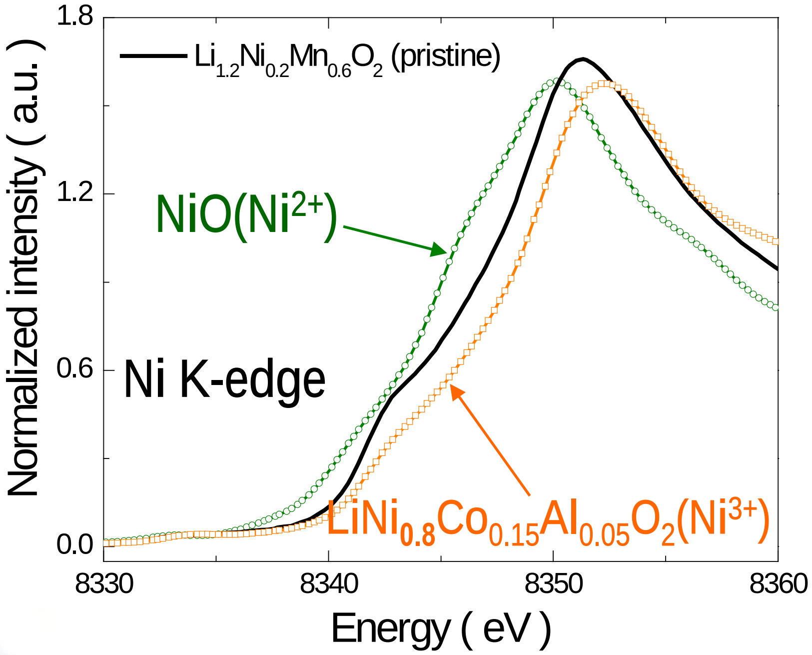
In situ XAS study of high energy $Li_{1.2}Ni_{0.2}Ni_{0.6}O_2$ cathode material

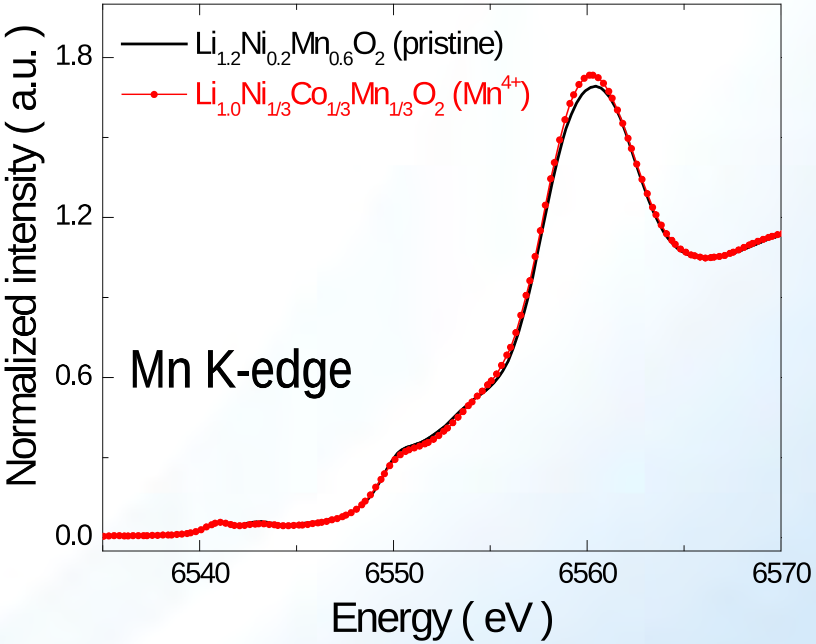
In collaboration with Dr. Kang
at Argonne Nat'l Lab.

$Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$
$= 0.5Li_2MnO_3 \bullet 0.5LiNi_{0.5}Mn_{0.5}O_2$ (ideally Ni^{2+}, Mn^{4+})

However, valance of Ni is slightly over 2+.

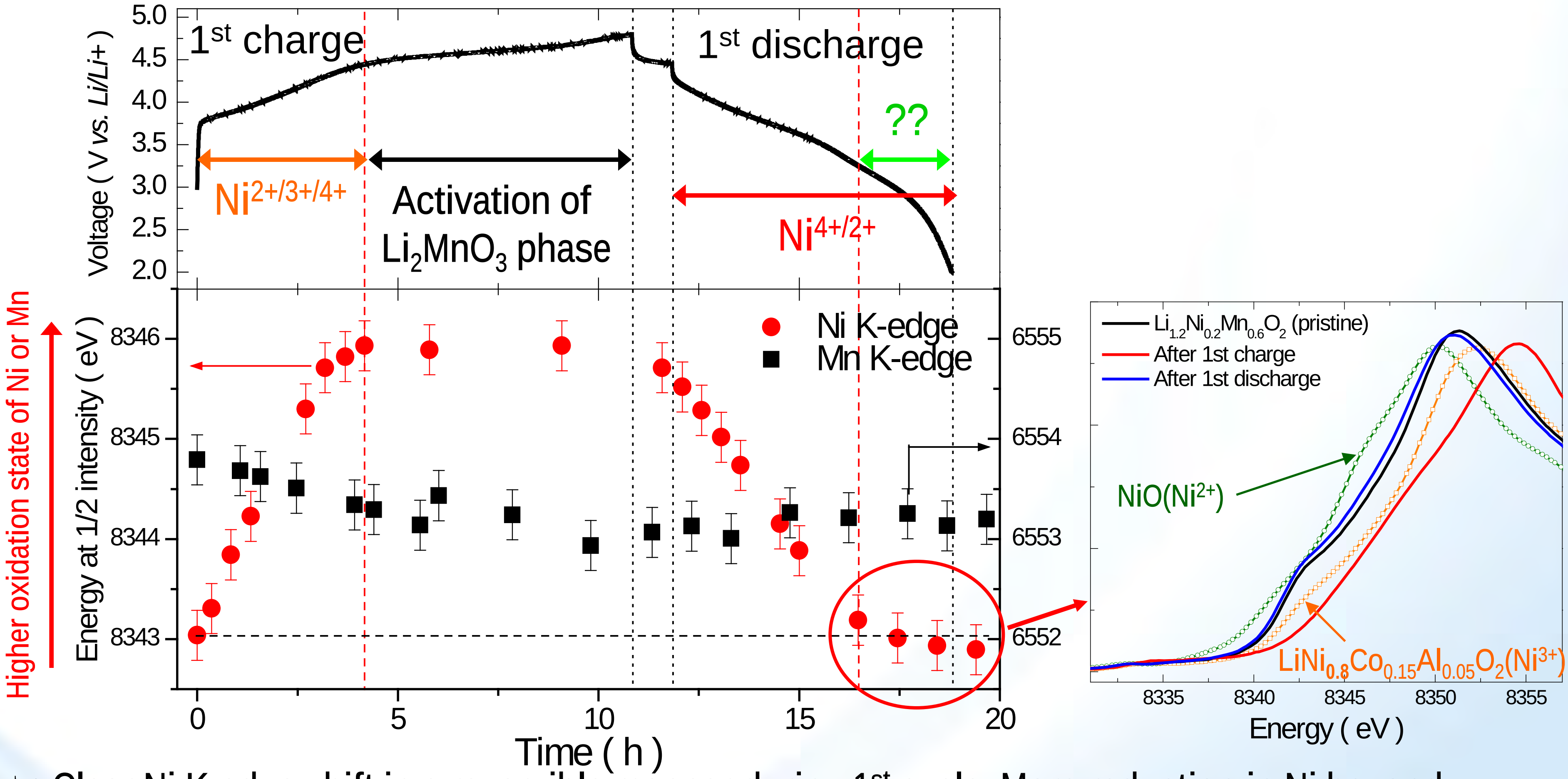
Mn valance = 4+.





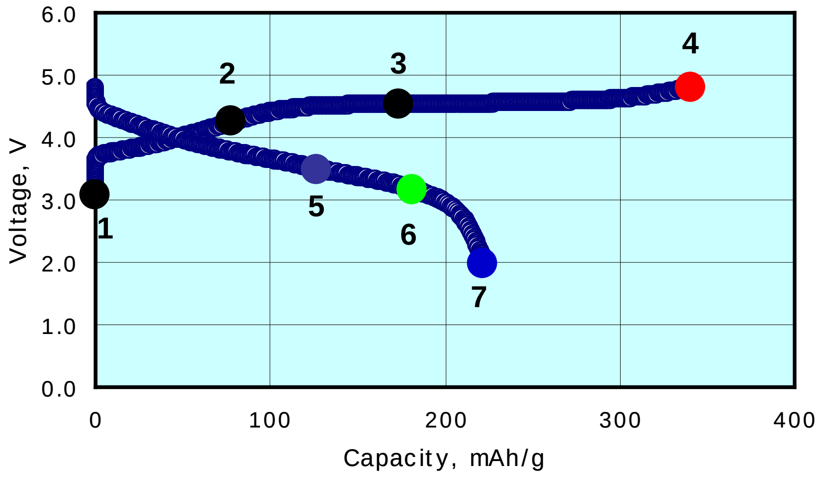
- Ni valance in pristine $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ is slightly over 2+.
- Mn valance in pristine $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ is 4+.

In situ XAS study of high energy $Li_{1.2}Ni_{0.2}Ni_{0.6}O_2$ cathode material

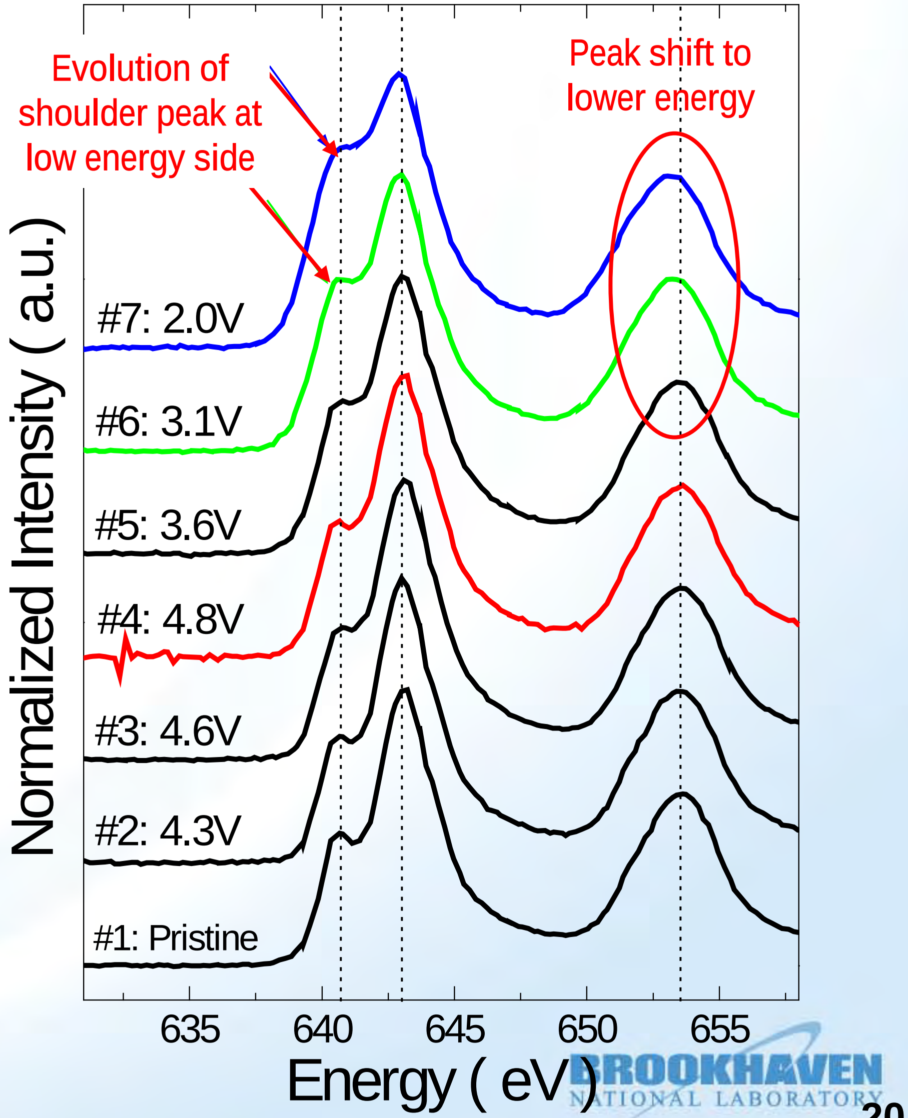


- Clear Ni K-edge shift in a reversible manner during 1st cycle. More reduction in Ni beyond pristine state close to Ni^{2+} after 1st discharge.
- However, Mn contribution to the charge compensation reaction after 1st charge remains unclear. ☞ Mn L-edge soft XAS to look at the surface!

Ex situ Soft XAS study of $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ during 1st cycle



Mn L-edges (EY detector) : Surface !!



Evolution of shoulder peak at low energy side

Peak shift to lower energy

- Pristine spectrum is identical to the Li_2MnO_3 (Mn^{4+}) spectrum.
- Mn^{4+} ions remain unchanged during 1st charge and then start to reduce slightly to Mn^{3+} below ~ 3.6V during 1st discharge.
- Surface of particle is reduced from $Mn(^{4+})O_2$ to $LiMn(^{3+})O_2$ and participate in charge compensation reaction during 1st discharge.

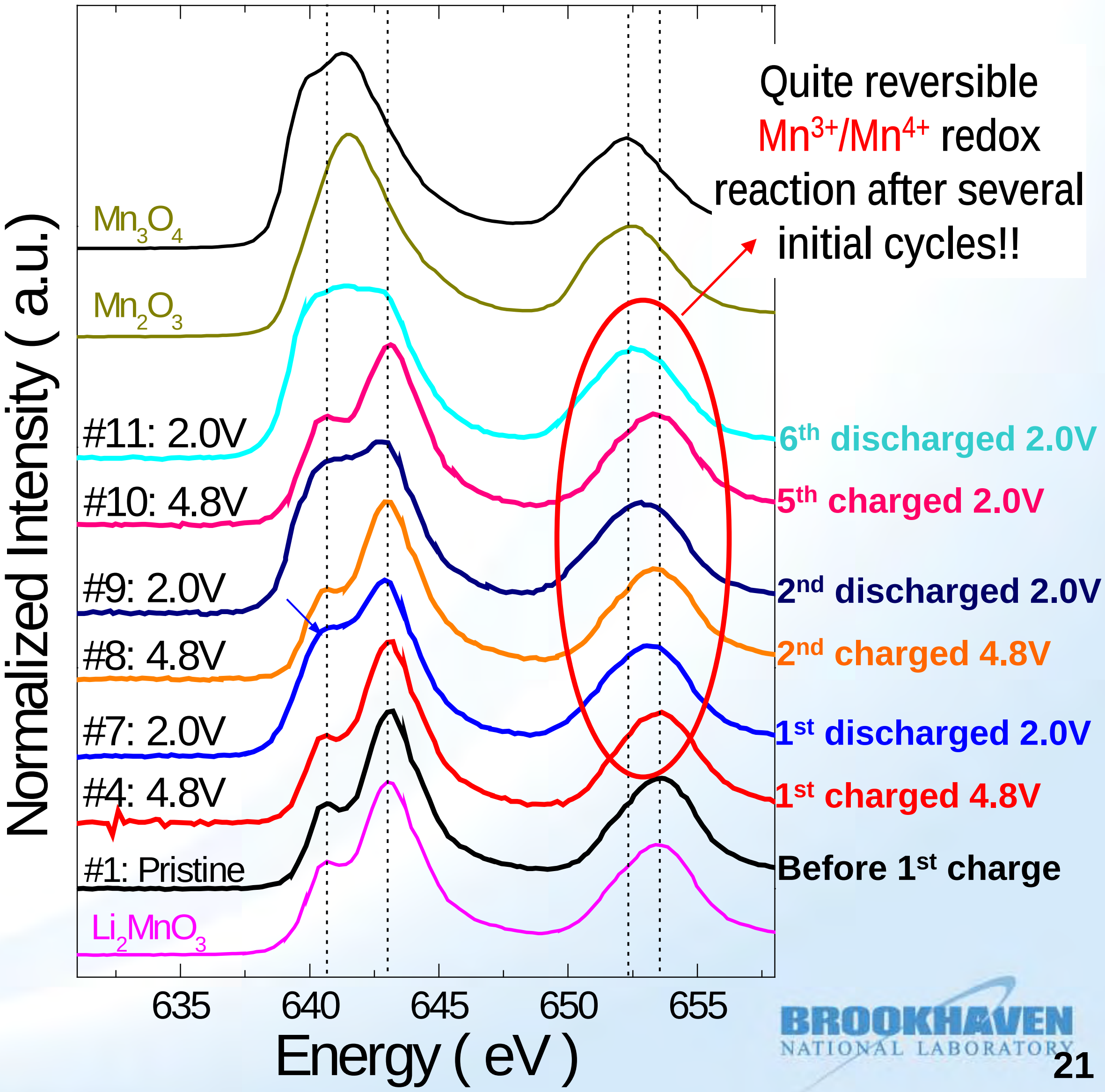
☞ 1st spectroscopic evidence !!

Ex situ Soft XAS study of $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ during cycling

- Quite reversible Mn^{3+}/Mn^{4+} redox reaction becomes more pronounced especially at the surface of $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ during further cyclings.

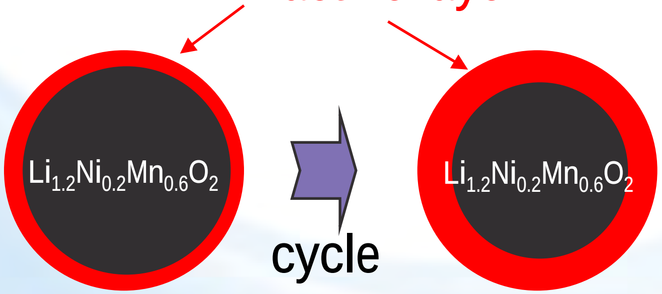
- Activation of Mn site at the surface occurs during initial cyclings.
  - ☞ can explain increase in capacity during cycling in part.

Mn L-edges (EY detector) : Surface !!

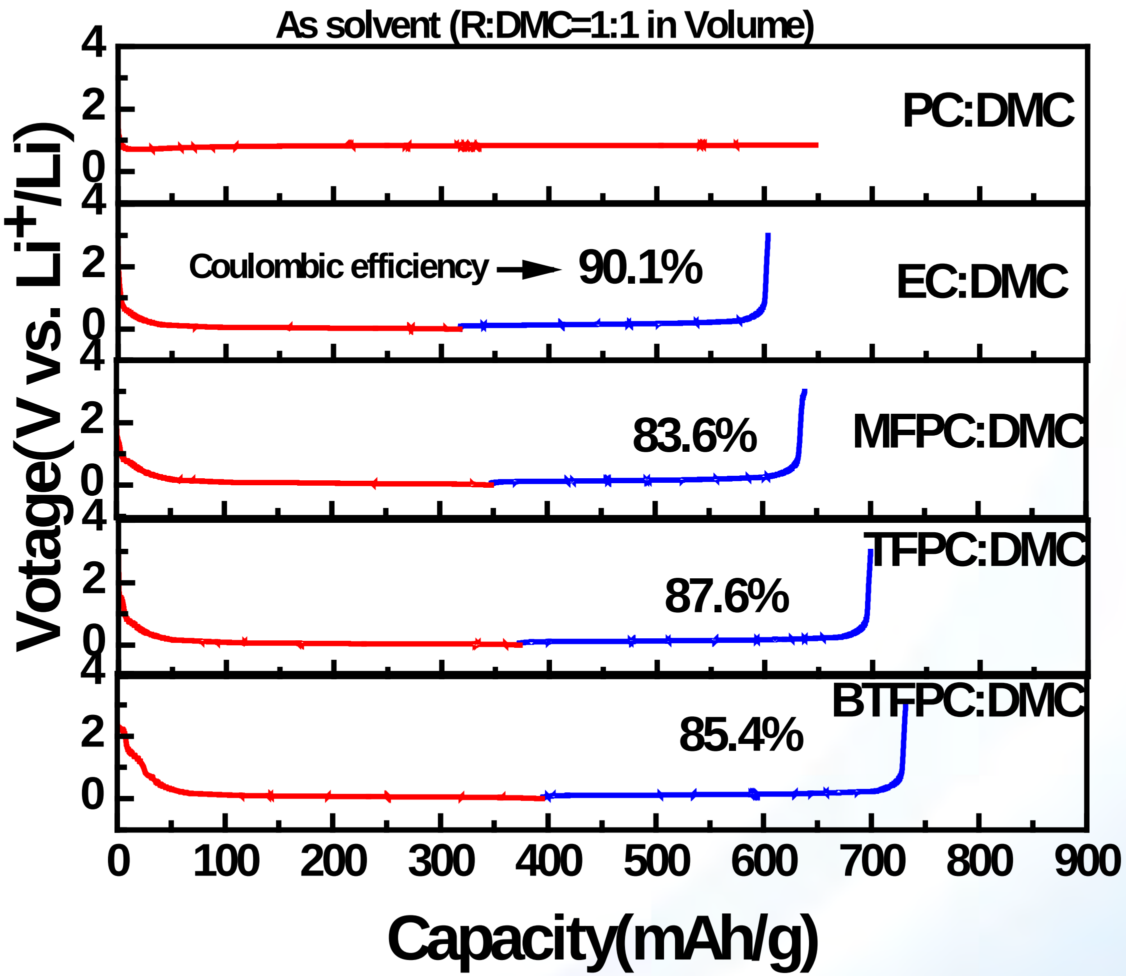


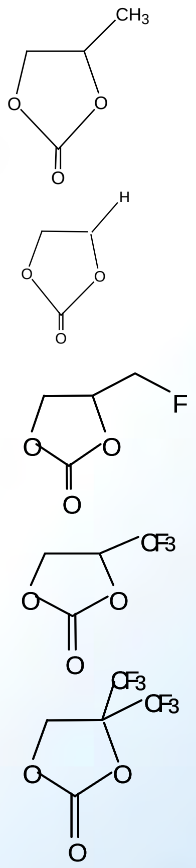
Quite reversible Mn^{3+}/Mn^{4+} redox reaction after several initial cycles!!

$Mn^{3+/4+}$ active layer

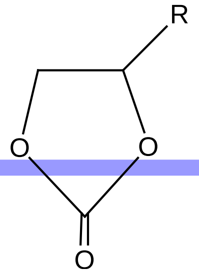


New solvents synthesized and studied to understand the effects of substitution groups on the SEI formation capability

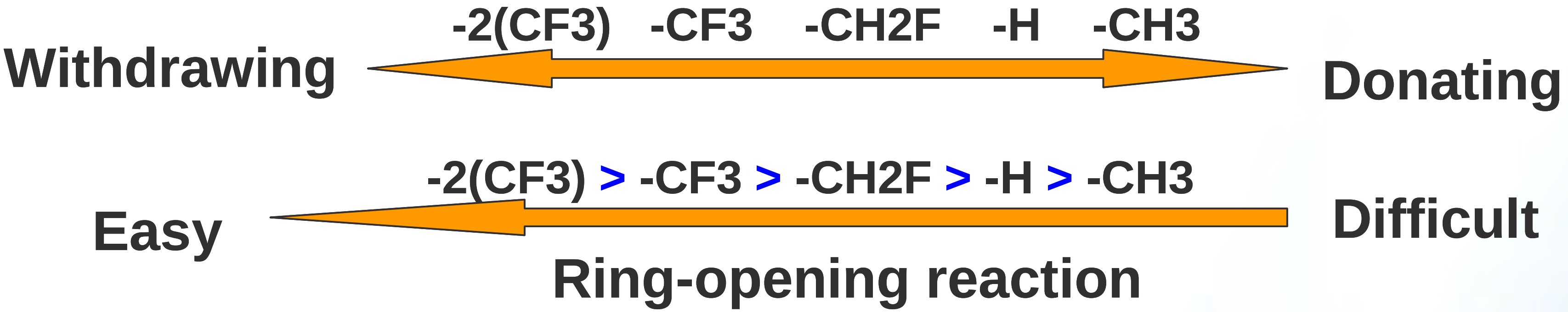




- When H in EC is replaced by the electron donating group CH_3 in PC, the electrolyte lost SEI formation capability.
- When the CH_3 is replaced by electron withdrawing group CF_3, the SEI formation capability is increased.



Electron withdrawing on ring opening



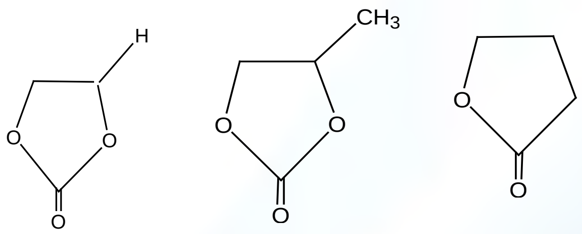
-2(CF3) -CF3 -CH2F -H -CH3

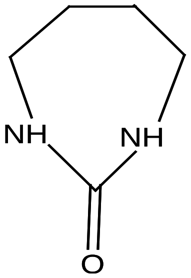
Withdrawing **Donating**

-2(CF3) > -CF3 > -CH2F > -H > -CH3

Easy **Difficult**

Ring-opening reaction





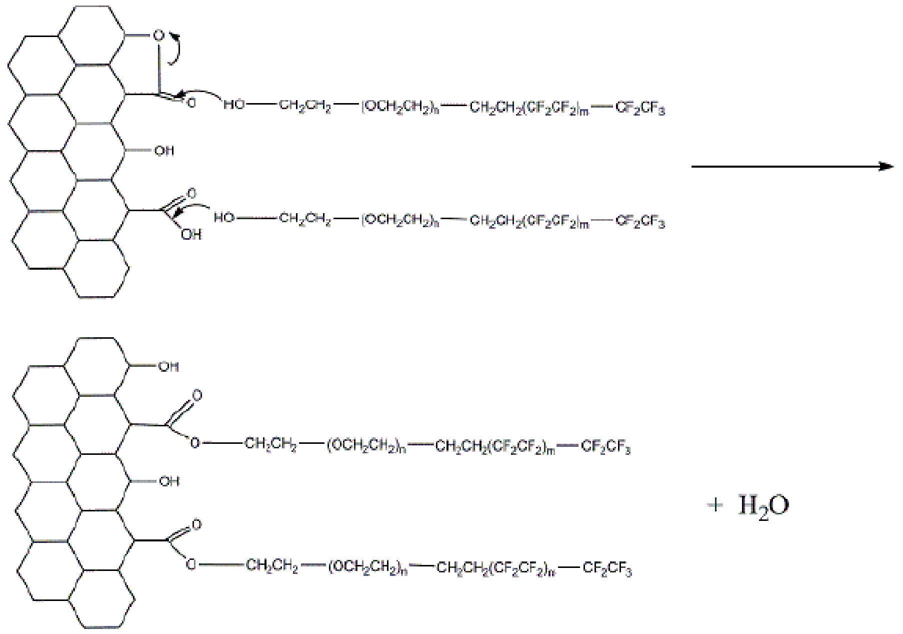
Tetramethylene Urea (TeU)

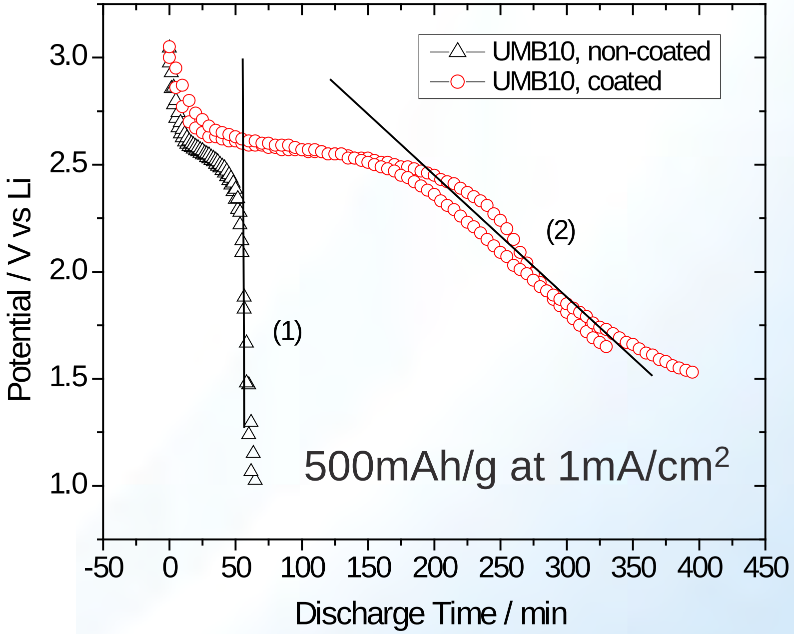
EC>> PC ~ γ-BL

Macromolecules **2004,** *37,* 6755-6762

Approaches and achievements on Li-air battery research

- ☐ Li_2O and Li_2O_2 deposition on the carbon electrode and filling up pores causing the premature passivation of the gas-diffusion-electrode . ☞ Surface modification.
- ☐ Solubility of Li oxides. ☞ New additives.
- ☐ Oxygen solubility in non-aqueous electrolytes. ☞ New electrolytes.



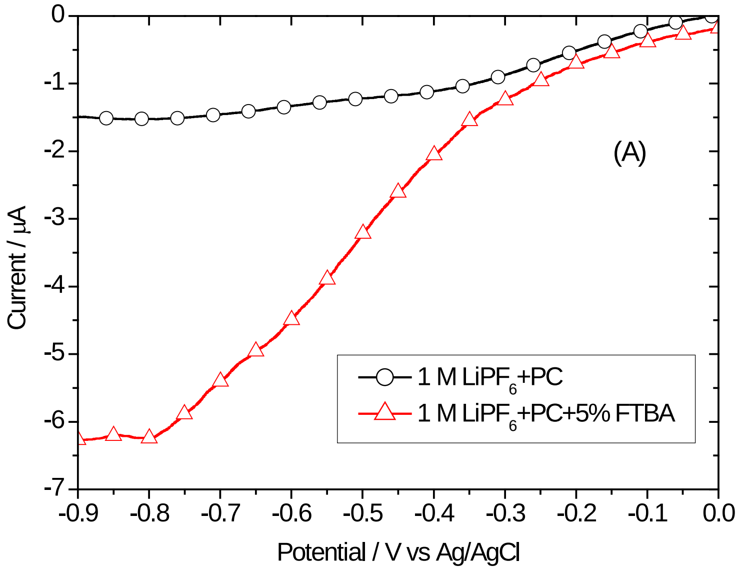


Submitted to Carbon

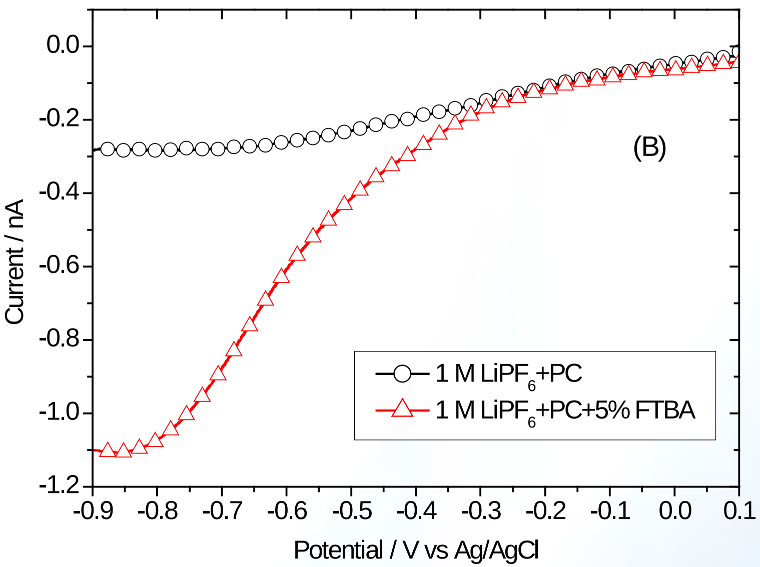
➥ Formation of the Compact and dense surface Li oxides passivation film can be delayed by modifying the carbon surface with long chain functional groups.

Comparison of O_2 reduction on Pt RDE and Pt micro disk electrode (with the great advantage in outside of the glove box operation)

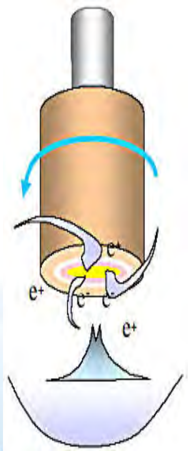
☞ 5 times increase of O_2 solubility was observed on both electrodes.

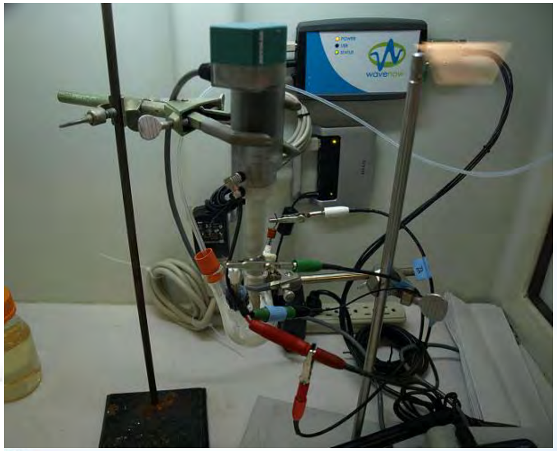


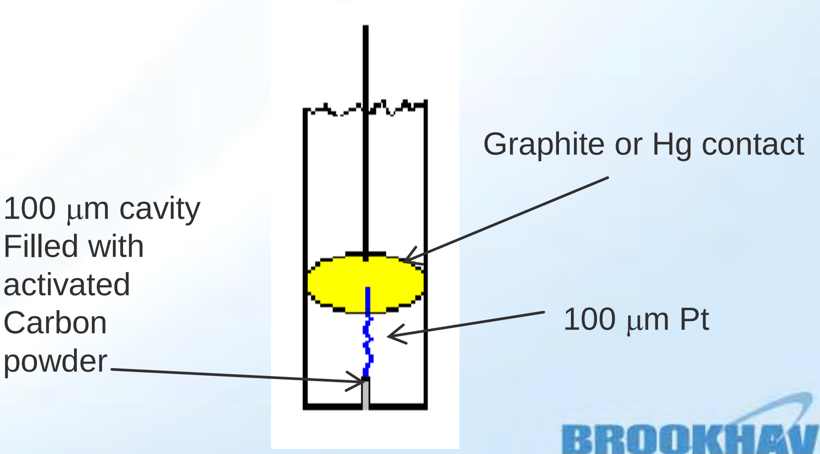
On Pt RDE



On Pt micro electrode





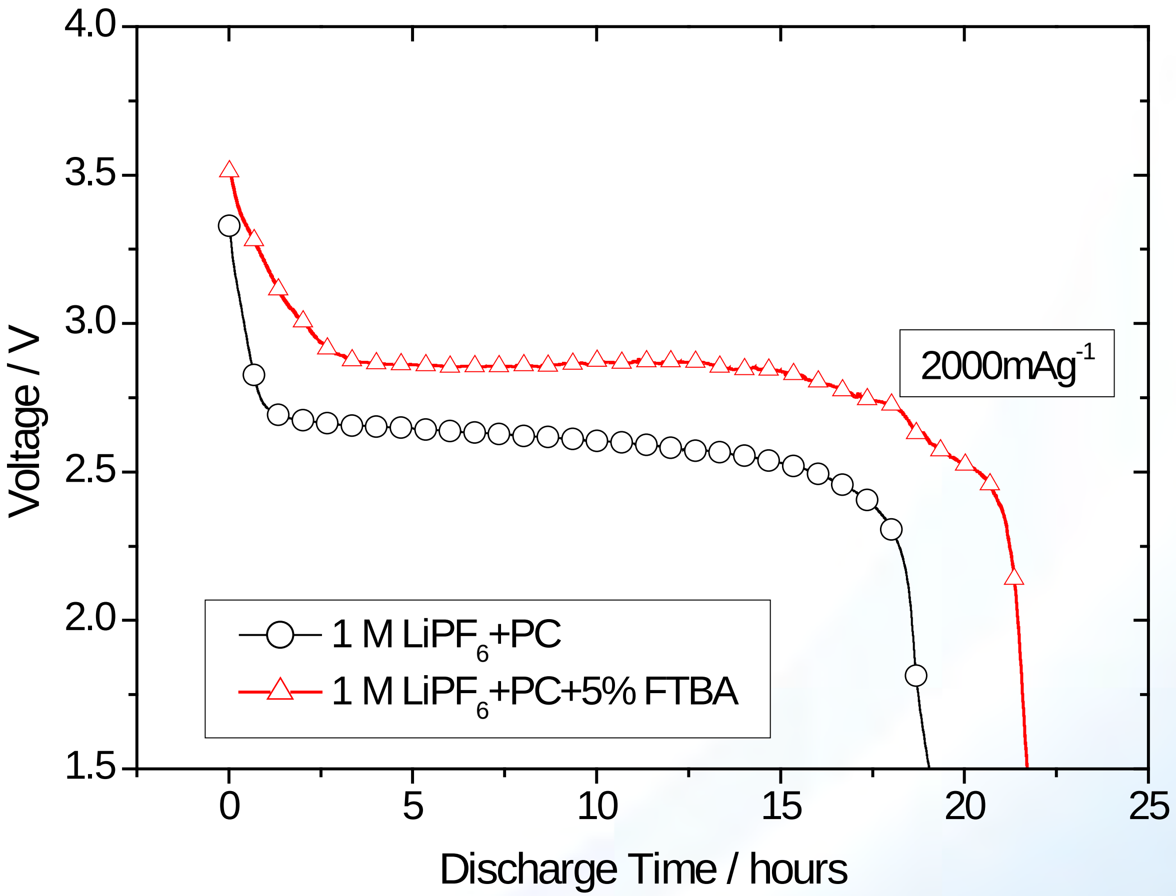


Graphite or Hg contact

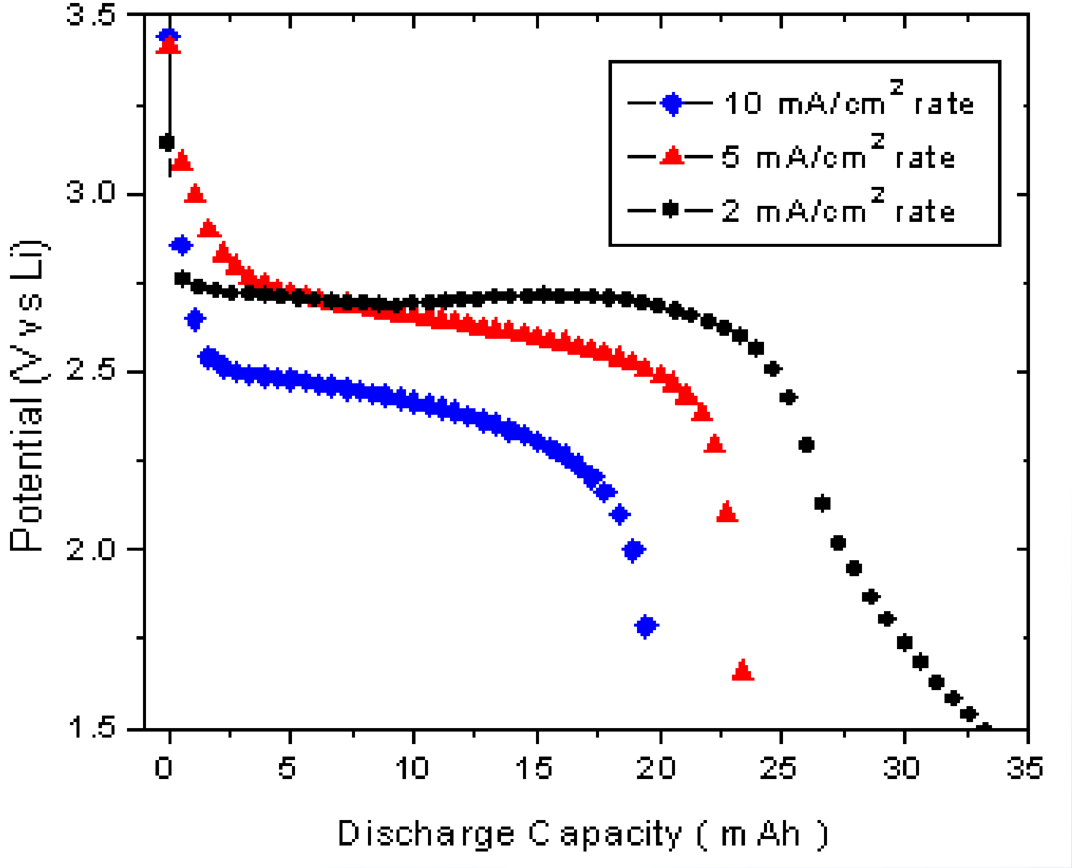
100 μm cavity
Filled with
activated
Carbon
powder

100 μm Pt

The performance of Li-air cell with new electrolyte is significantly improved.



Up to now, the discharge rate of Li-air cell is too low (about 0.1 mA/cm^2). Using our new electrolyte with increased O_2 solubility and mobility, almost 100 time higher discharge rate has been achieved, making it closer to the Li-ion battery level, which is feasible for practical application.



Electrode weight: 0.05 g (carbon)

Collaborations with Other Institutions and Companies

- University of Massachusetts
  - Lithium air battery.
- Argonne National Lab. (ANL)
  - *In situ* XAS study of high energy $Li_{1.2}Ni_{0.2}Mn_{0.2}O_2$ cathode material.
- Oakridge National Lab. (ONL) & University of Tennessee
  - *In situ* XRD technology development for Li-ion battery material research at NSLS.
- Dow Chemical Corp.
- General Motor Corp.
- 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 2011 and FY2012

- Complete soft and *in situ* hard XAS study of high energy Li_2MnO_3-$LiMO_2$ (M=Ni, Co, Mn, Fe) cathode materials during activation charge and multiple cycling.
- Complete comparative *in situ* XRD and XAS studies of $LiFe_{1-x}Mn_xPO_4$ (x=0 to 1) cathode materials with different particle size and morphology during chemical and electrochemical delithiations.
- Develop and test the atomic layer deposition (ALD) surface coating on new cathode materials.
- Using time resolved XRD to study the thermal stability of ALD surface coated Li_2MnO_3-$LiMO_2$ (M=Ni, Co, Mn, Fe) cathode materials during heating.
- 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 (GDE) with MnO_2 catalyst for Li-air batteries. Start the preliminary studies of the rechargeable lithium-air cells and in situ XRD and XAS on the GDE.
- Develop new electrolyte systems to increase the solubility and mobility of O_2 in the electrolyte in order to increase the discharge rate of lithium air cells.

Summary

- In the Multi Year Program Plan (MYPP) of VTP, the goals for battery were designed as: “Better energy storage systems are needed to expand the commercial markets for HEVs and to make PHEVs and EVs commercially viable. Specifically, lower-cost, abuse-tolerant batteries with higher energy density, higher power, better low-temperature operation, and longer lifetimes are needed for the development of the next-generation of HEVs, PHEVs, and EVs.” This ES059 program has been making progress towards these goals and will plan future works to achieve these goals.

- In collaboration with ANL, and GM R&D Center, Li_2MnO_3-$LiMO_2$ (M=Ni, Co, Mn) type high energy density cathode materials have been studied using combined *in situ* hard XAS and *ex situ* soft XAS. The results of these studies provide useful information for improving the energy density and cycleability of high energy density Li-ion batteries.

- In collaboration with Institute of Physics, CAS, the mesoporous $LiFe_{0.6}Mn_{0.4}PO_4$ cathode material are being studied by *in situ* XRD and XAS in comparison with the same composition without mesoporous structure. The results of these studies provide important information about the effects of meso-pores on the phase transition behavior and performance of this new cathode materials with low cost potential.

Summary (cont'd)

- Developed new in situ XRD to study cathode materials for Li-ion batteries during chemical delithiation.
- Modified the surface of carbon materials for gas diffuse electrode (GDE), which significantly improved the discharge capacity of the Lithium-Air cell.
- Developed novel new electrolyte which can increase the solubility of O_2 dramatically. The discharge rate of the Lithium-Air cell using this new electrolyte is increased almost 100 times than the conventional electrolytes.
- Developed a family of new boron based additives with good SEI formation capability and anion receptor functionality for lithium battery electrolyte (US patents were filed in 2010). Designed and synthesized new solvents for high voltage lithium battery electrolytes.
- Collaborations with US industrial partners such as Dow chem. and GM, as well as with US and international research institutions (IOP in China, KIST in Korea) have been established. The results of these collaborations have been published or presented at invited talks at international conferences.