Diagnostic Studies to Improve Abuse Tolerance and life of Li-ion batteries

Kyung-Wan Nam and Xiao-Qing Yang
Brookhaven National Lab. (BNL)

May 14-18, 2012

2012 DOE Hydrogen Program and Vehicle Technologies
Annual Merit Review and Peer Evaluation Meeting
Washington, DC, May 14-18, 2012

ES034

This presentation does not contain any proprietary, confidential, or otherwise restricted information

BROOKHAVEN NATIONAL LABORATORY

Overview

Timeline

- Start: 10/01/2010
- Finish: Continued
- Continued

Budget

- Funding received in FY10

  DOE: $350k

- Funding received in FY11

  DOE: $350k

Barriers addressed

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

Collaborators

- Argonne National Lab. (ANL)
- Oakridge National Lab. (ONL)
- University of Tennessee
- Beijing Institute of Physics
- Korea Institute of Science and Technology
- Hydro-Québec (IREQ)
- Duracell (P&G)
- Dow Chemical
- GM R&D Center
- Johnson Controls-Advanced Power solutions

Project Objectives

✓ ***Diagnostics study of thermal abuse tolerance (safety related issues).***

- ➥ to establish and investigate the structural origin of thermal instability of various cathode materials.
- ➥ to search new approaches on how to improve the thermal stability of cathode materials including surface modification.
- ➥ to provide valuable information about how to design thermally stable cathode materials for HEV and PHEV applications.
- ➥ to develop new in situ diagnostic techniques with surface and bulk sensitivity for studying the thermal stability of various cathode materials.

✓ ***Diagnostics study of the cell capacity and power fading.***

- ➥ to develop *in situ* diagnostic techniques with surface and bulk sensitivity for studying the capacity and powder fading mechanisms of Li-ion battery.
- ➥ to establish and investigate the capacity and power fading mechanisms of various cathode materials.

✓ ***Diagnostics study of electrode materials with lower cost potential.***

Milestones

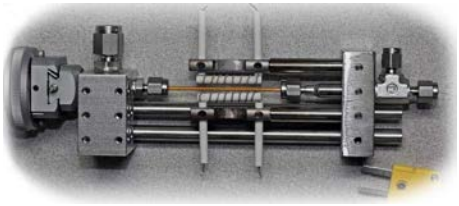
Month/Year	Milestones
Sep/11	Complete the results of in situ XRD studies of Cu or Ni doped $LiMn_2O_4$ spinel as high voltage cathode materials in collaboration with Duracell (P&G). ➥ *Completed.*
Apr/12	Complete the study of thermal decomposition of charged $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) cathode materials during heating using combined Time-Resolved XRD and Mass Spectroscopy ➥ *Completed.*
Apr/12	Complete the Time resolved X-ray diffraction (TRXRD) studies of ALD coated Al_2O_3 on $Li_{1.2}Ni_{0.17}Co_{0.07}Mn_{0.56}O_2$ new cathode material during heating. ➥ *Completed.*
Sep/12	Complete the study of charged $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) cathode material thermal decomposition during heating using combined Time-Resolved XRD and Mass Spectroscopy. ➥ *On schedule.*
Sep/12	Complete the in situ XRD studies of $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$ (Toda HE5050) cathode material during charge-discharge cycling. ➥ *On schedule.*

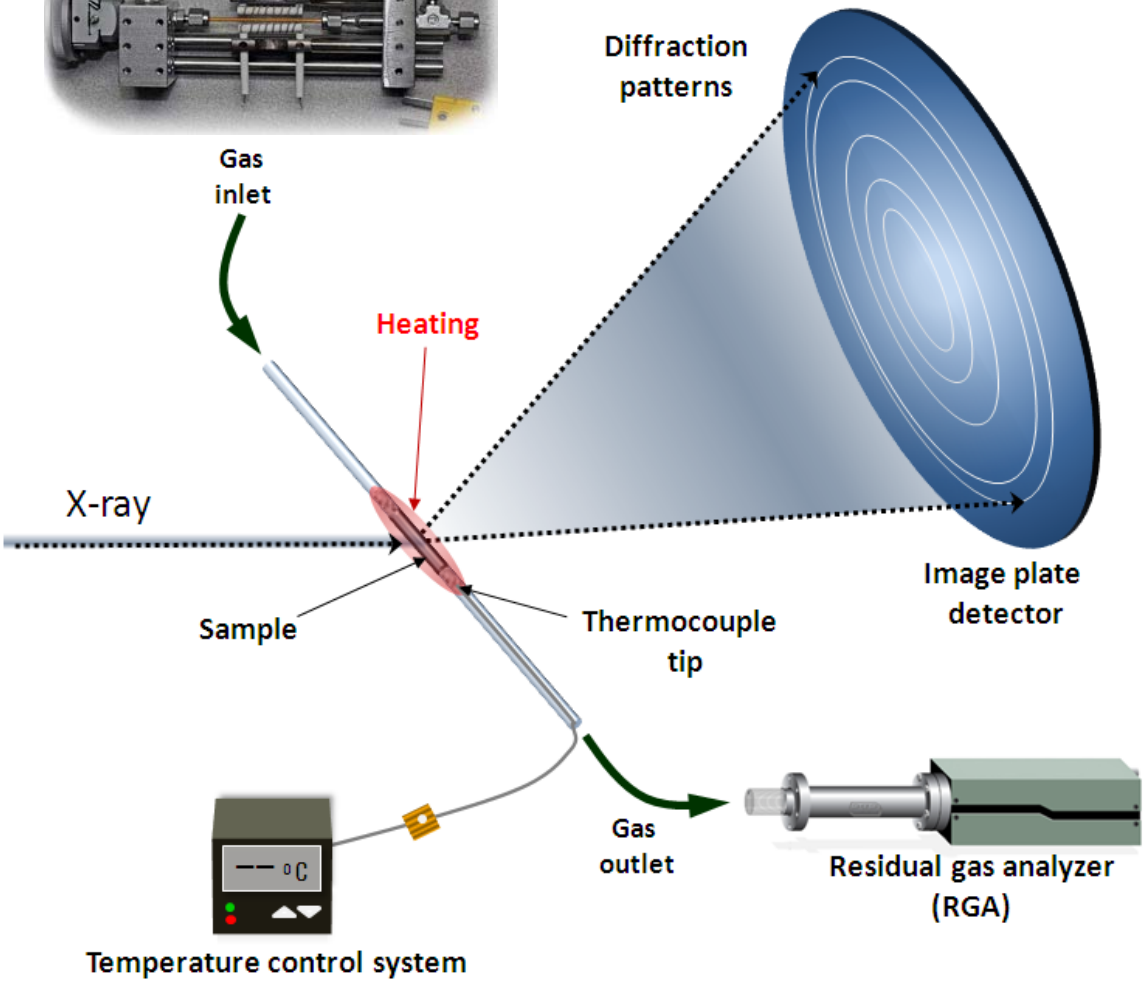
Approaches

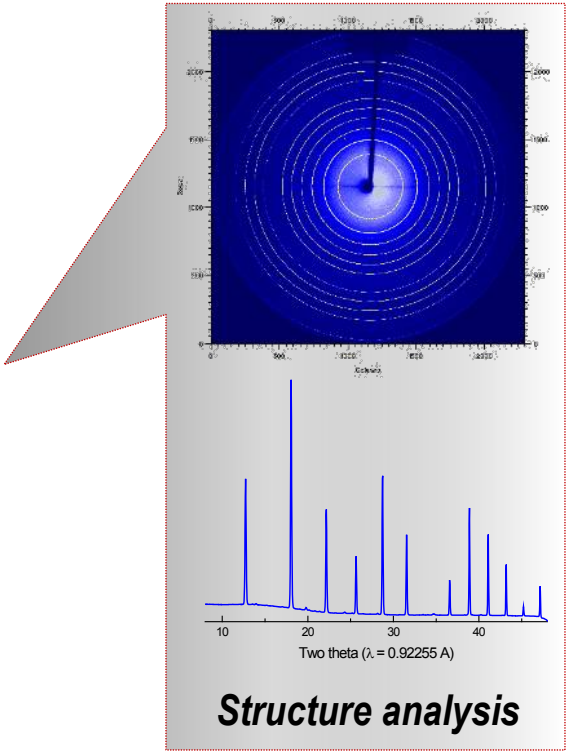
- A combination of time resolved X-ray diffraction (TR-XRD) and mass spectroscopy (MS), together with *in situ* soft and hard X-ray absorption (XAS), *in situ* transmission electron microscopy (TEM) techniques during heating to study the thermal stability of the electrode materials.
- Apply the atomic layer deposition (ALD) technique for the surface modification of new cathode materials, using time resolved X-ray diffraction (XRD) to study the effects of surface modification on the thermal stability.
- Using *in situ* XRD, soft and hard XAS to study the voltage and capacity fading mechanism of high energy density Li and Mn rich layer structured NCM (LMR-NCM) new electrode materials during charge-discharge cycling for longer cycling life of Li-ion batteries.
- Extended collaboration with other US and international academic institutions and US industrial partners.

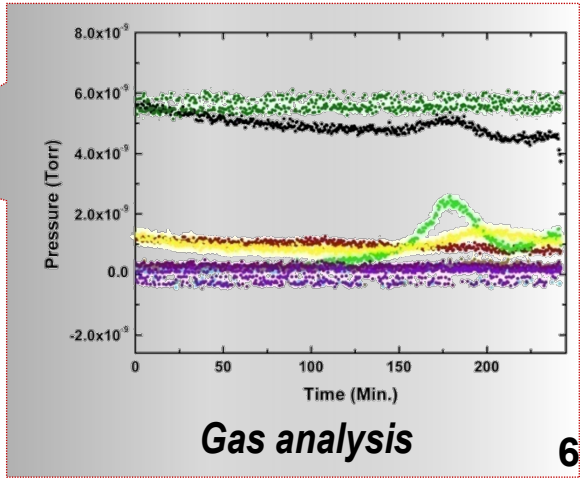
Approach: Develop and apply combined TR-XRD and mass spectroscopy

Experimental setup: in situ heating cell









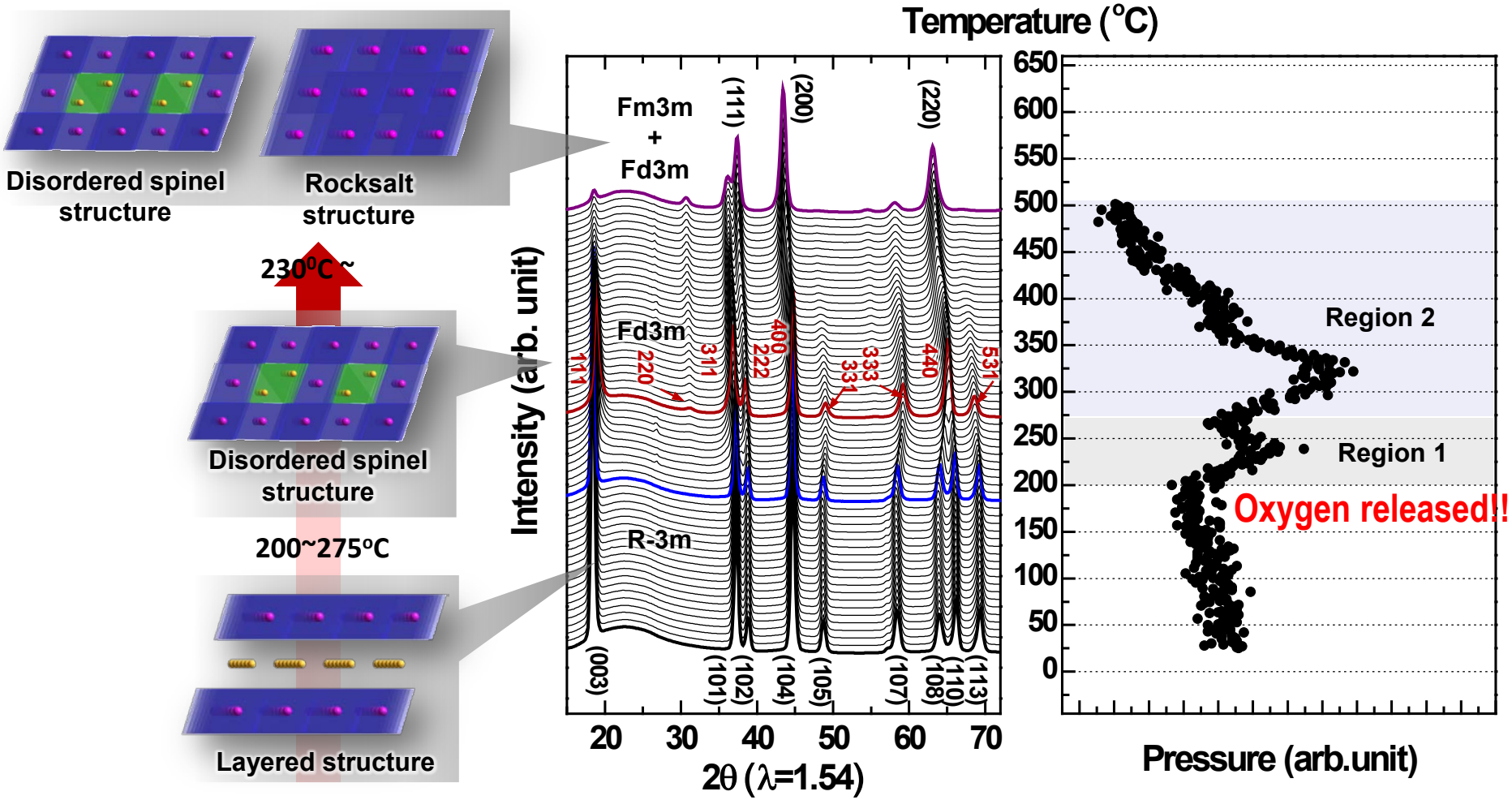
Technical Accomplishments

- Developed new *in situ* technique by combining the time resolved XRD (TR-XRD) with mass spectroscopy and applied it to study the overcharged $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ and $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode materials during heating. The co-relation between the structural changes and the oxygen release of these two type of materials were obtained.

- New studies on applying the atomic layer deposition (ALD) to improve the thermal stability of cathode during heating and structural stability during cycling were carried out.

- By collaborating Argonne National Lab., R&D Center of GM, and other collaborators, carried out diagnostic studies of new high energy density Li_2MnO_3-$LiMO_2$ (M=Ni, Co, Mn, LMR-NCM) cathode materials. Some important structural origins of the voltage and capacity fading mechanism are obtained.

Thermal behavior of charged cathode material ($Li_{0.5}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$, SOC=1/2)



When x= 0.5 (50% of SOC) in $Li_{1-x}MO_2$

$Li_{0.5}M(^{3.5+})O_2$ (layered, *R-3m*) ⇨ $Li_{0.5}M(^{3.5+})_{1.0}O_2$ (disordered spinel, *Fd3m*) ; no oxygen loss

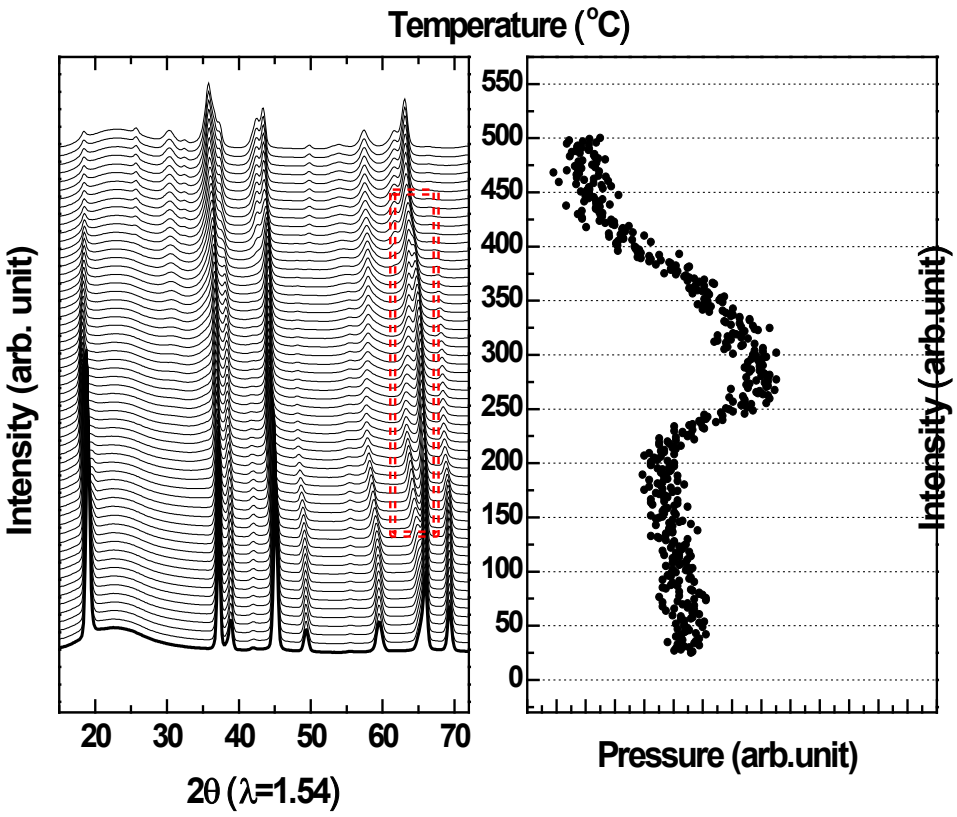
$Li_{0.5}M(^{3.5+})_{1.0}O_2$ (disordered spinel, *Fd3m*) ⇨ $Li_{0.5}M(^{2.5+})_{1.0}O_{1.5}$ (rock salt, *Fm3m*) + 0.25 O_2 ; *oxygen release!!*

- Oxygen released at 200~275°C (1st phase transition region, layered ⇨ disordered spinel)

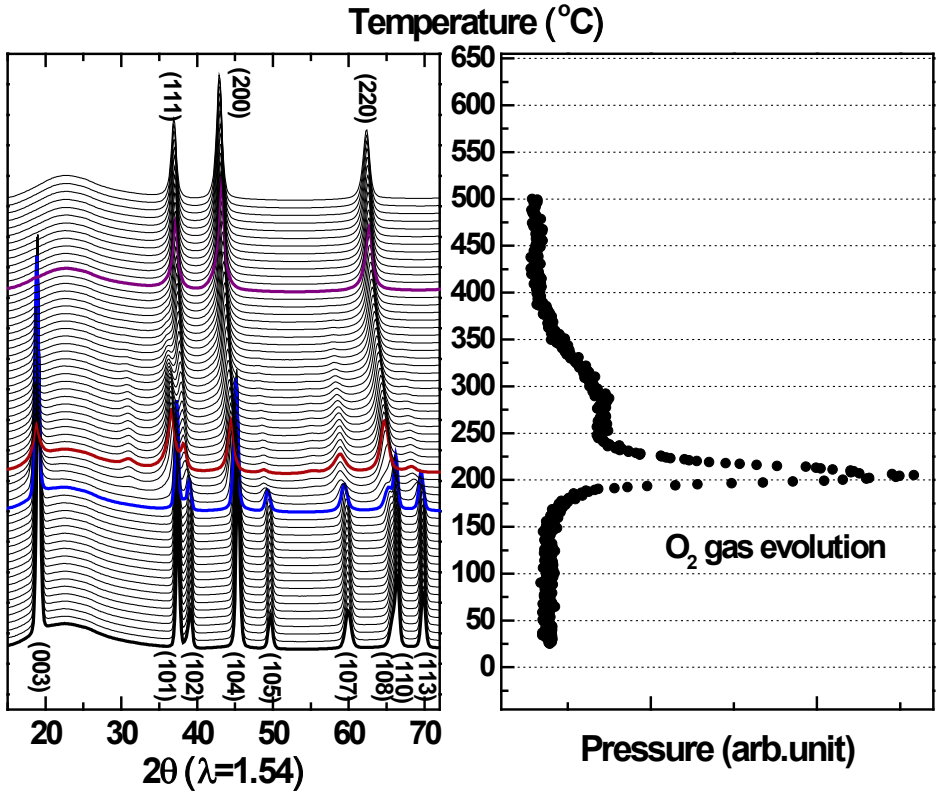
- Non-uniform Li delithiation during charging process

Thermal behavior of overcharged cathode material ($Li_{0.1}MO_2$, SOC=9/10)

$Li_{0.1}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$



$Li_{0.1}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$



- Broad oxygen evolution during heating (200~ 450 °C) for NCM

- Much better thermal stability (better safety property) of NCM than NCA

Li and Mn rich layered-layered oxide compound (LMR-NCM)

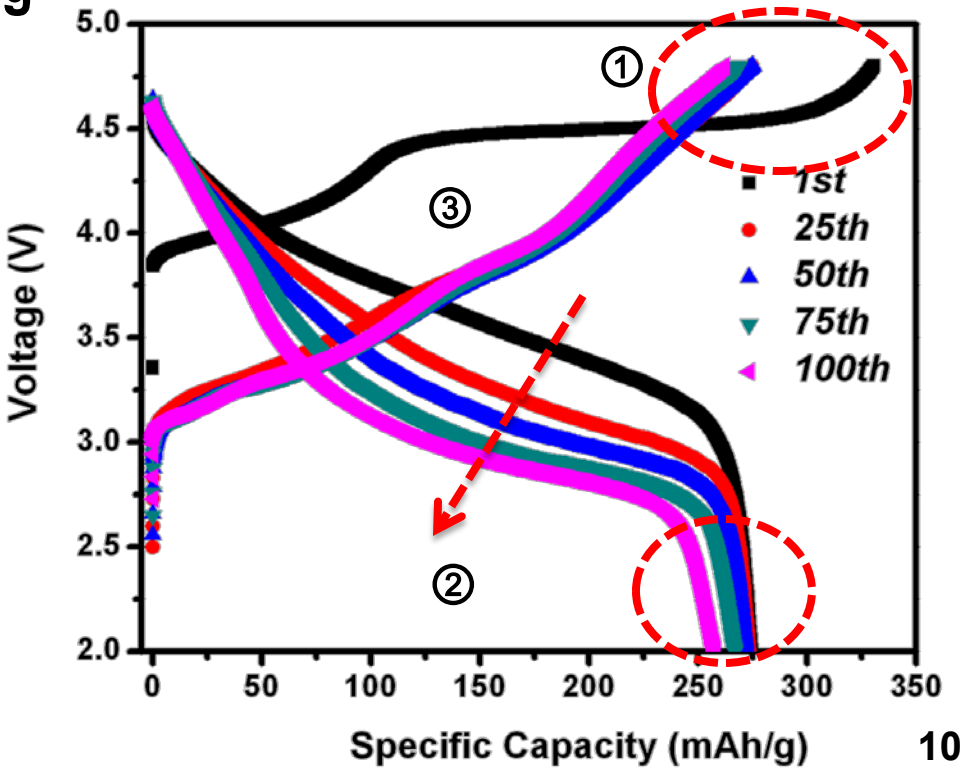
$Li_{1.2}Ni_{0.15}Co_{0.1}Mn_{0.55}O_2=0.5Li_2MnO_3\cdot0.5LiNi_{0.375}Co_{0.25}Mn_{0.375}O_2$

in collaboration with Argonne National Lab.

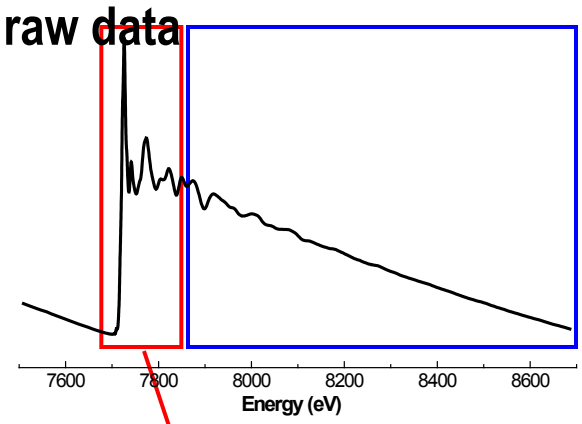
- High specific capacity (>250 mAh/g)
- Integration and interconnection of $LiMO_2$-like (rhombohedral) and Li_2MnO_3 (monoclinic) structures at atomic level
- Activation of Li_2MnO_3 during the 1st charge process
- Structure changes during cycling

Issues to be addressed:

1. Large irreversible capacity loss during first charge
2. Voltage and capacity fading during cycle
3. Rearrangement of TM ions
4. Role of Surface coating



X-ray absorption spectroscopy: XANES and EXAFS

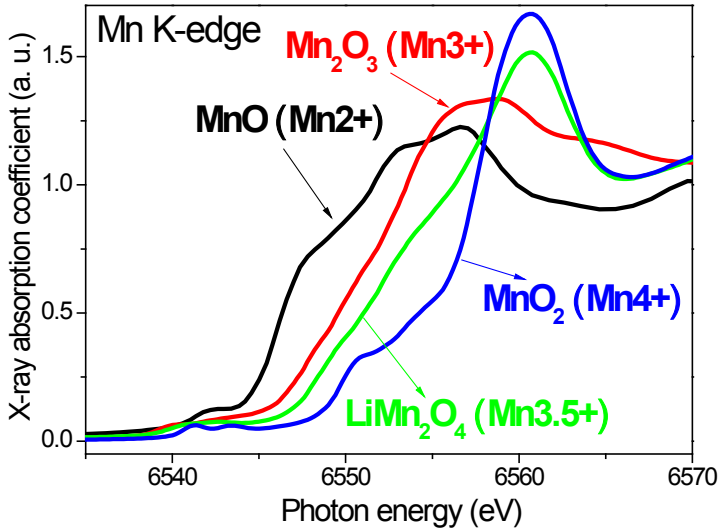


Extended X-ray Absorption Fine Structure (EXAFS)

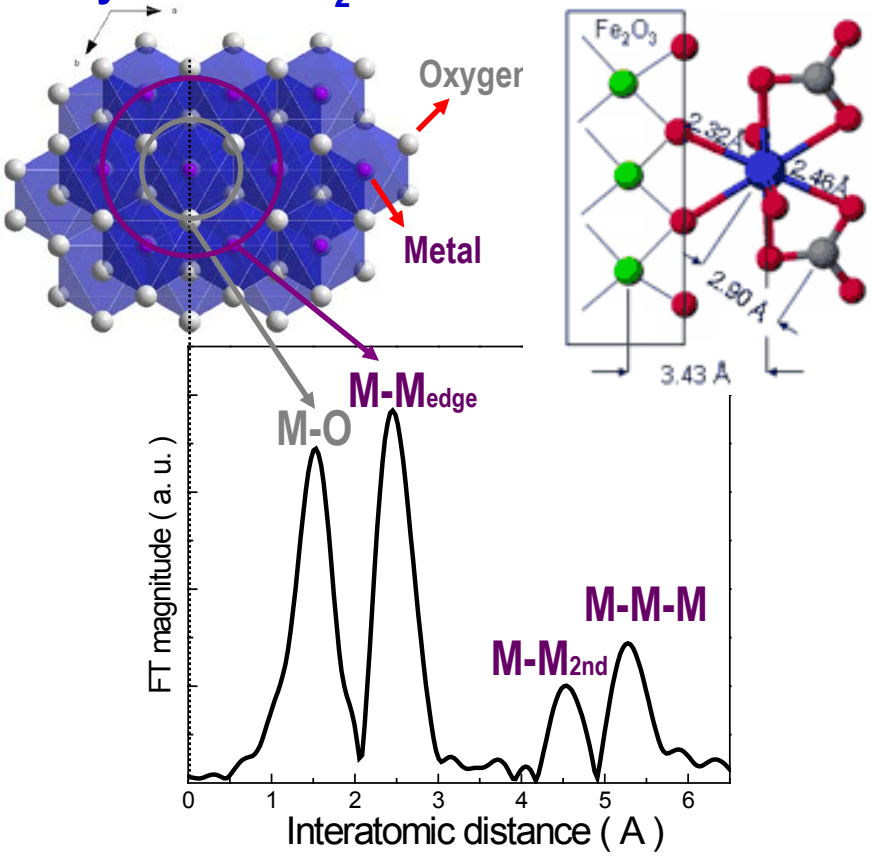
; Local structural information like bond distance, coordination number, degree of disorder

X-ray Absorption Near Edge Structure (XANES)

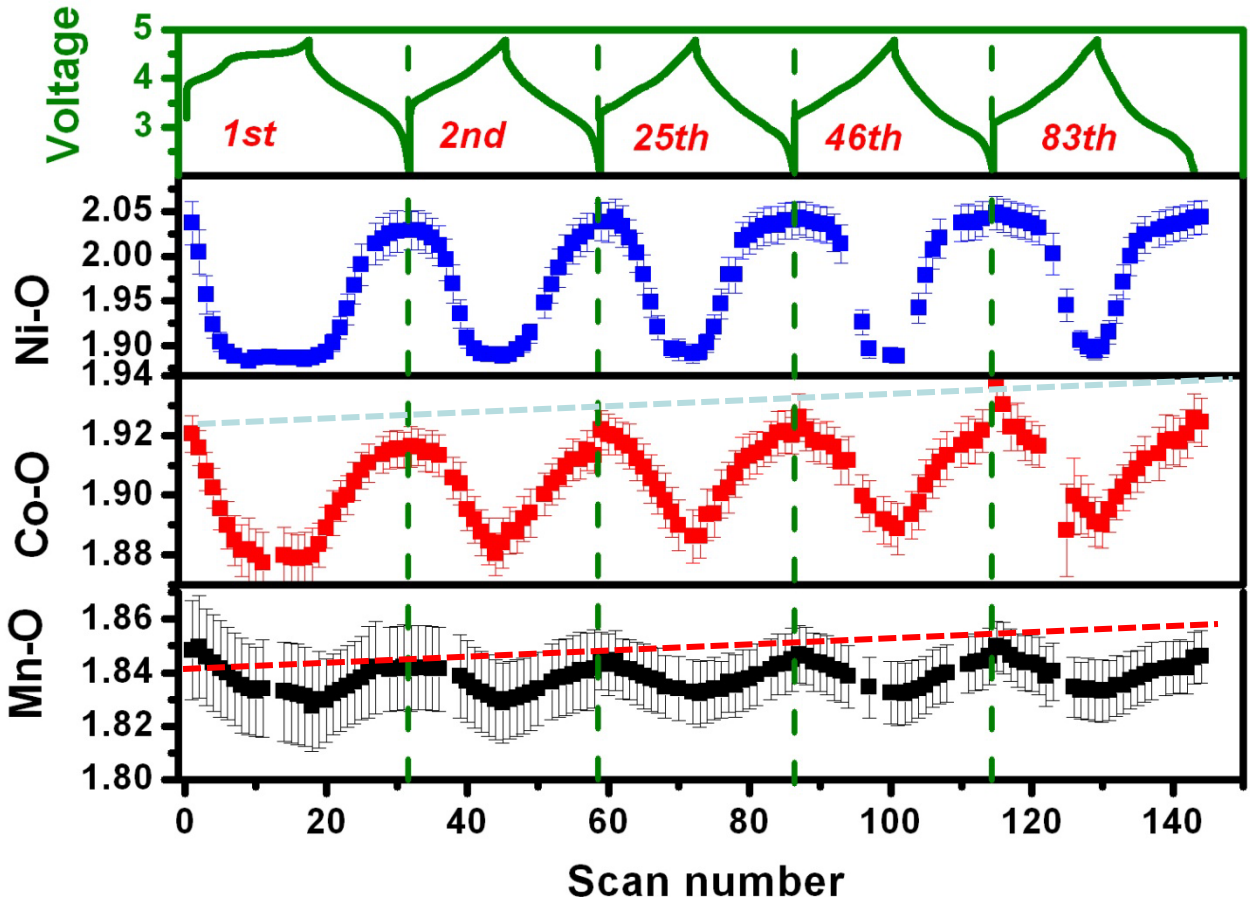
; Oxidation state, site symmetry, covalent bond strength

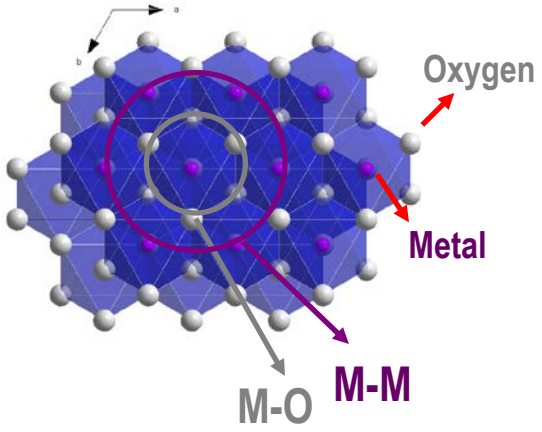


Layered $LiMO_2$ structure



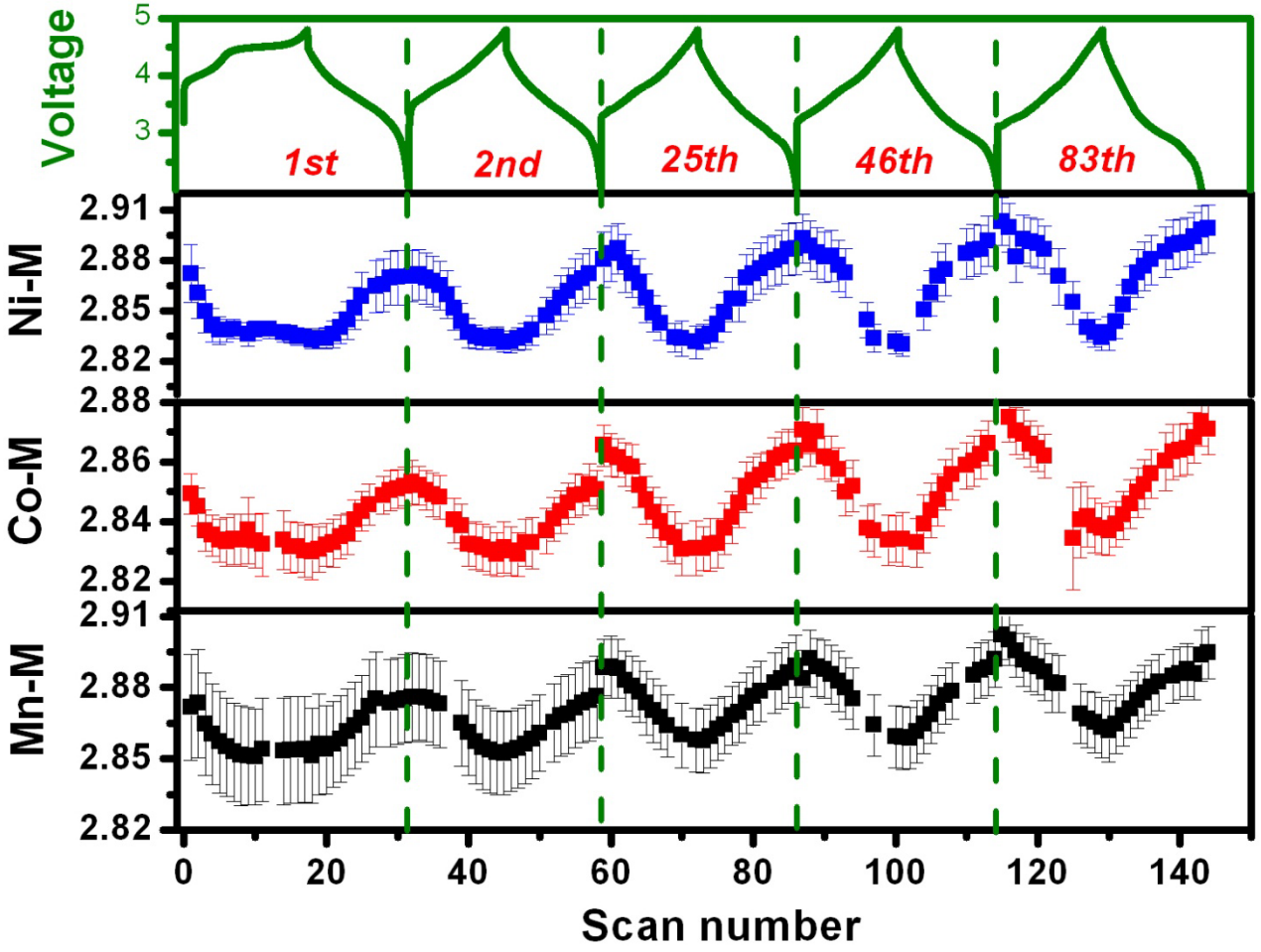
Metal-Oxygen bond length using K-edge EXAFS data for Ni, Co, Mn

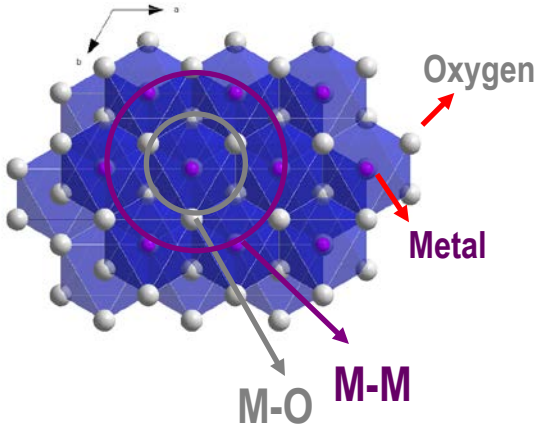




- Both Co and Mn are more reduced at the end of discharge during cycling
- Gradual structure change may contribute to the voltage drop

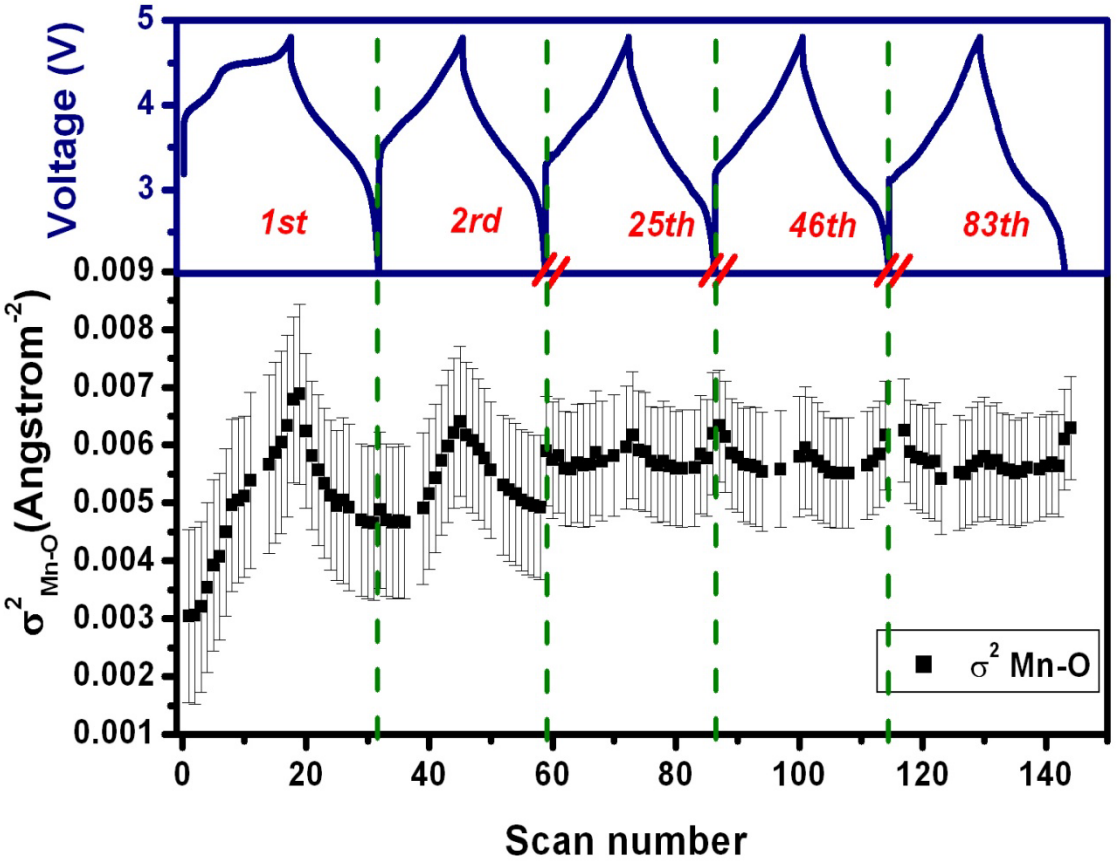
Metal-Metal bond length using K-edge EXAFS data for Ni, Co, Mn

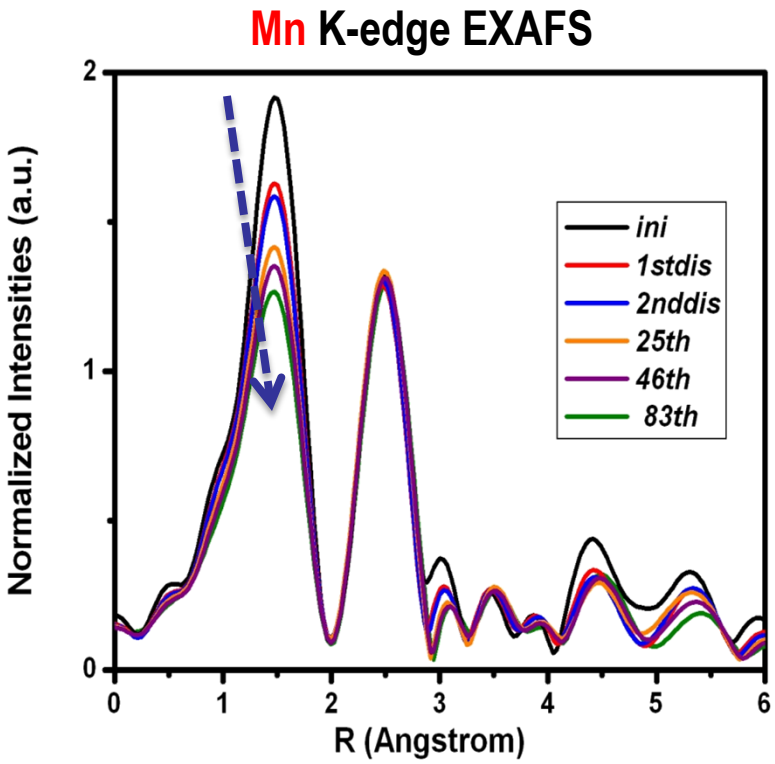




- Increased metal-metal bond length at the same fully charged or fully discharged state during cycling indicates expansion of a-b plane.

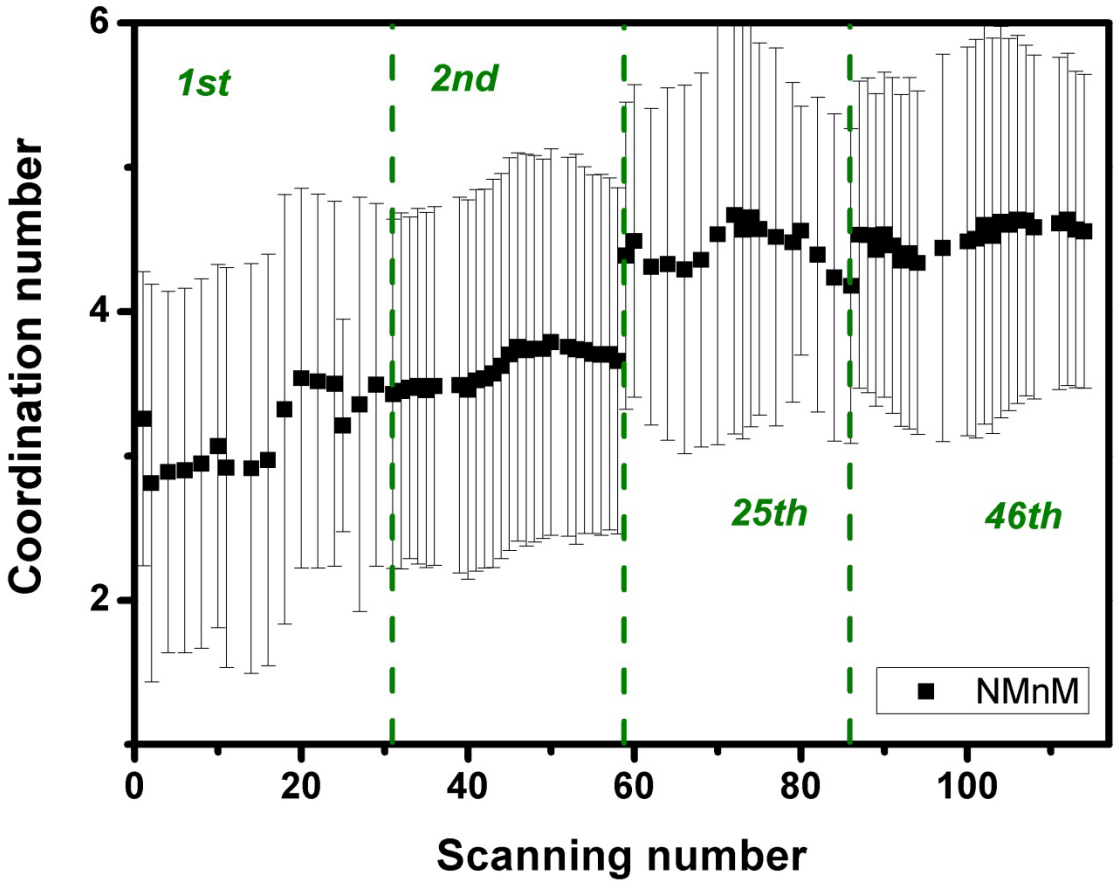
Local structure change of 1st shell (Mn-O)

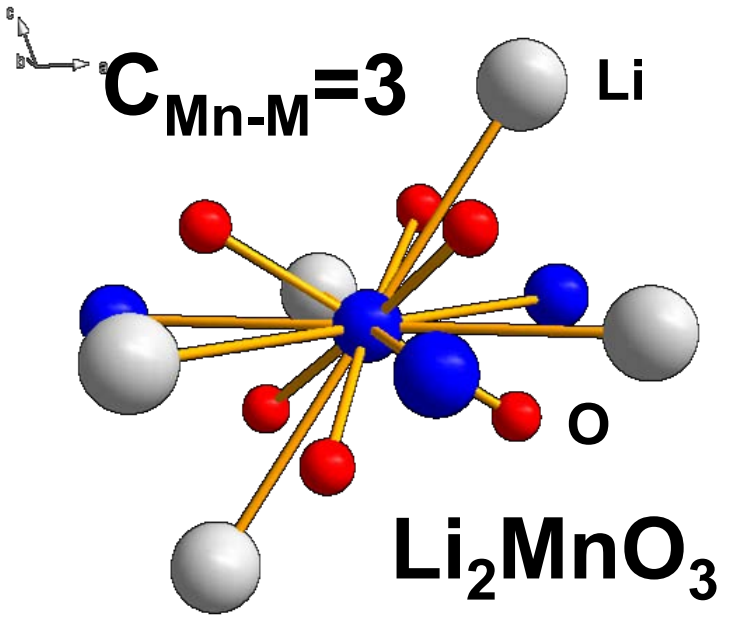


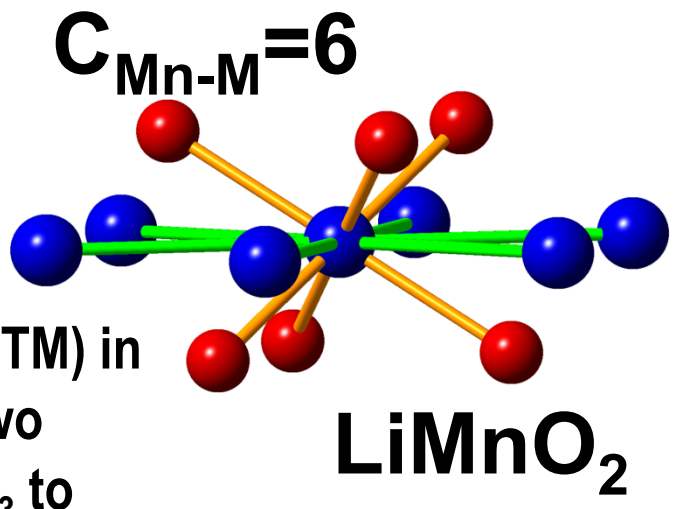


- Debye-Waller factor (σ^2) represents degree of disorder around absorbing Mn atoms
- Significant change of $\sigma^2_{Mn\text{-}O}$ during the 1st and 2nd cycle is due to the oxygen release from Li_2MnO_3 component.

Coordination changes of Mn to transition metal ions

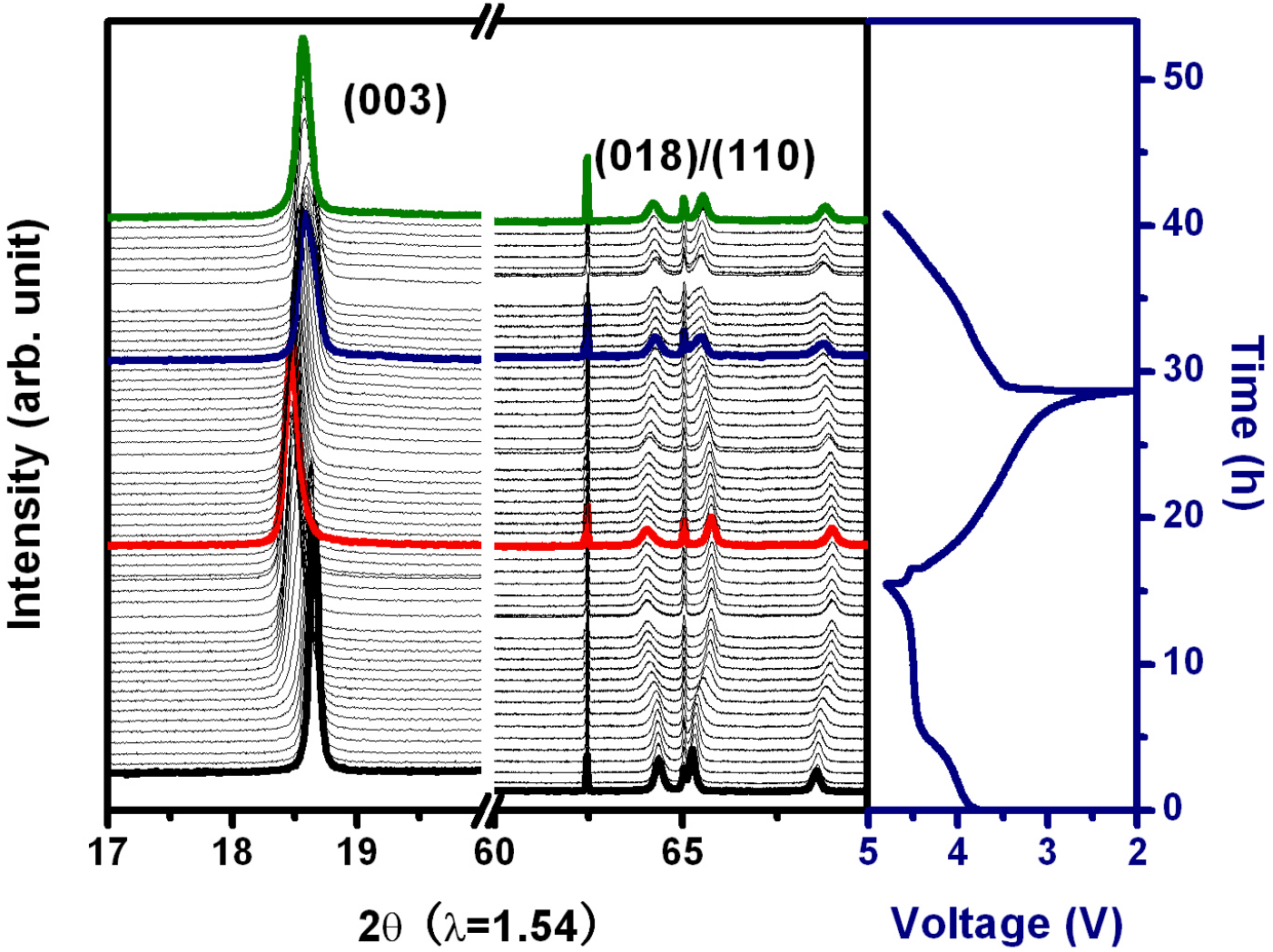






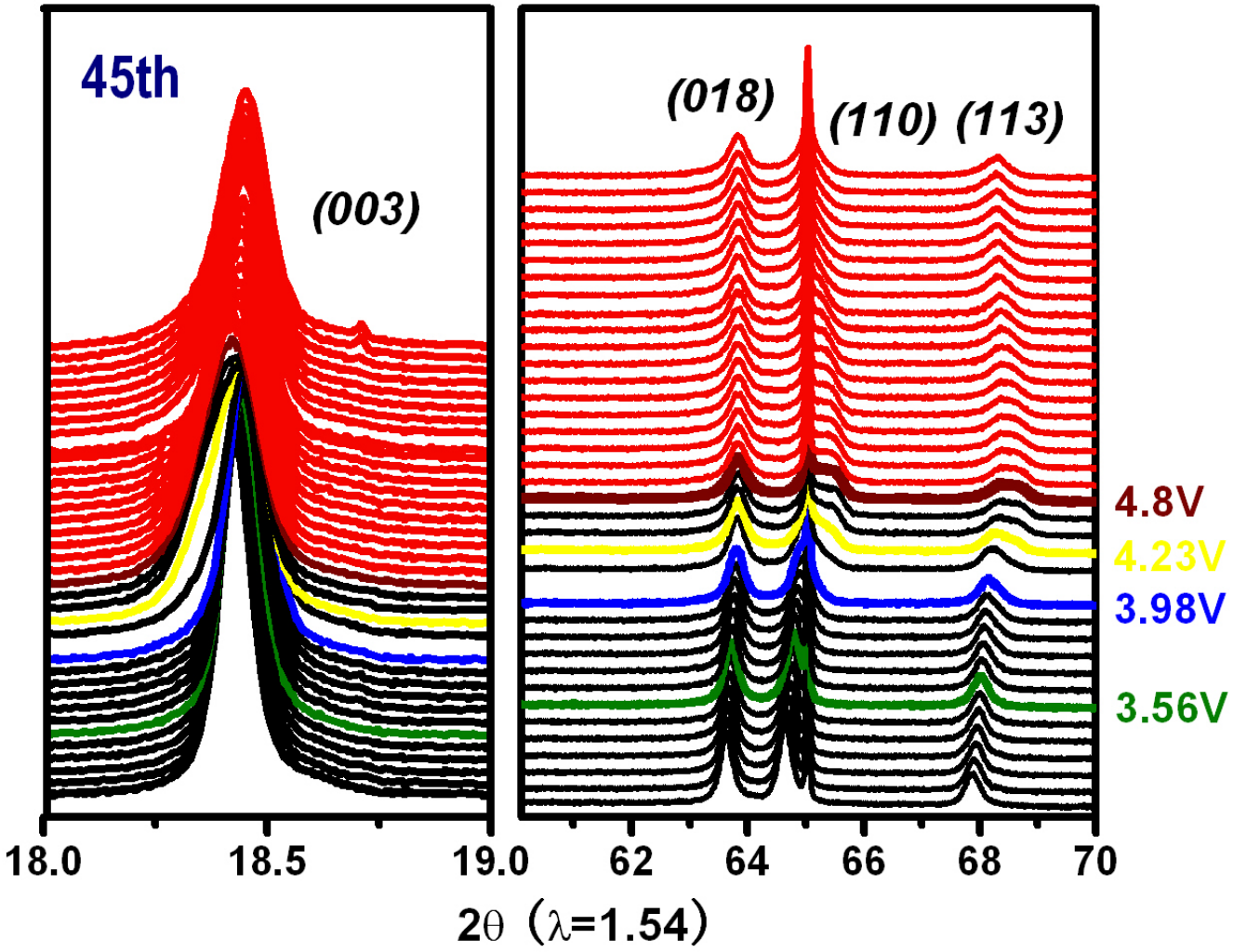
The coordination number of Mn to transition metals (TM) in the second shell significantly increased in the first two cycles, indicating the structural change from Li_2MnO_3 to MO_2 type during the formation cycling.

In-situ XRD: 1st and 2nd cycle



◆ Phase transition behavior is similar to the normal layered material at the 1st cycle.

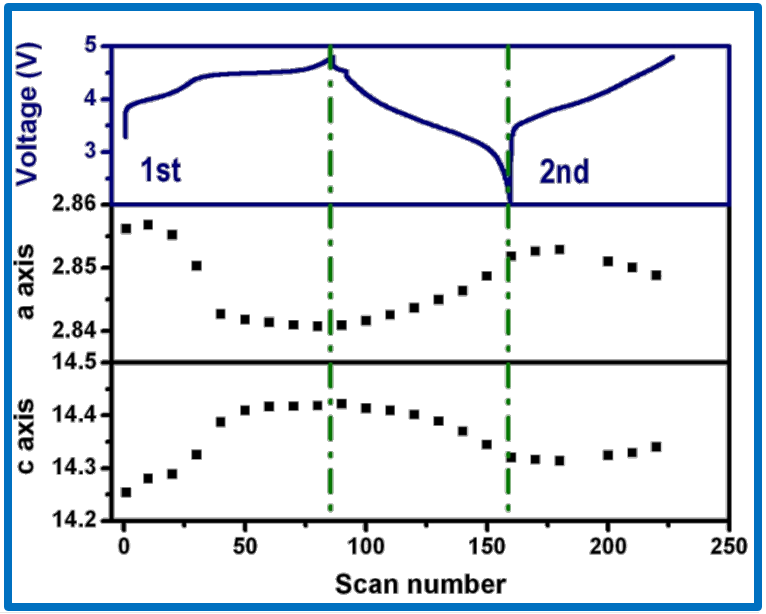
In-situ XRD: after 45 cycles

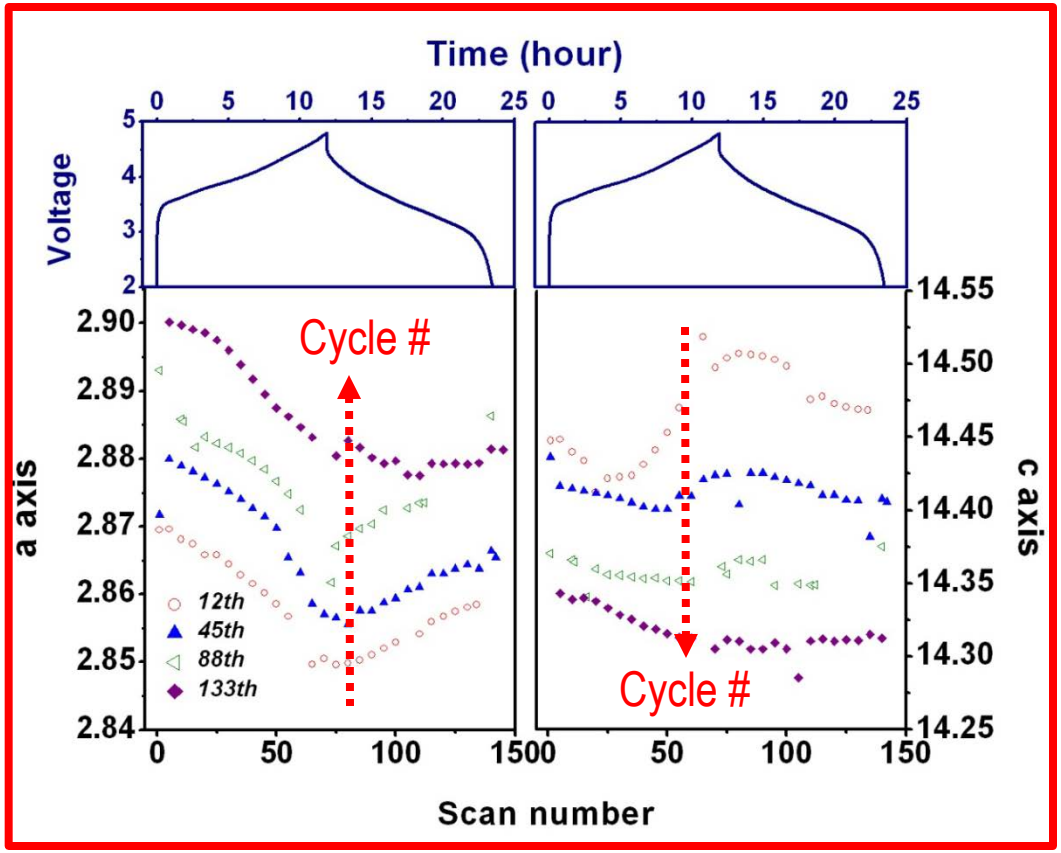


Spinel-like phase transition behavior after 45 cycles

Please note the peak position of (110) in comparison with first cycle

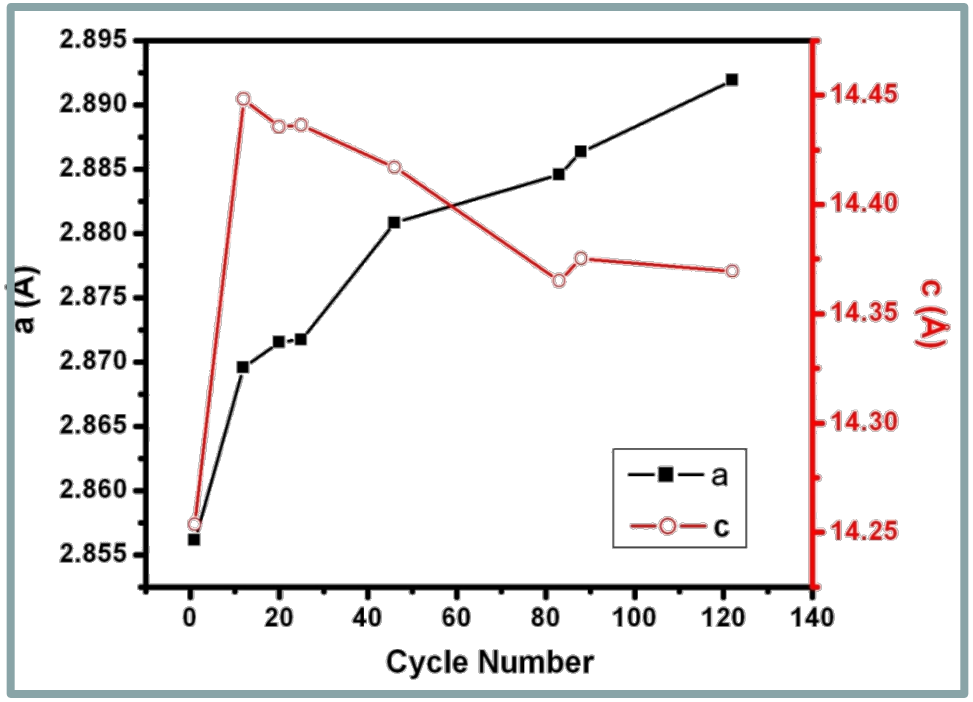
Lattices parameter changes with cycling numbers

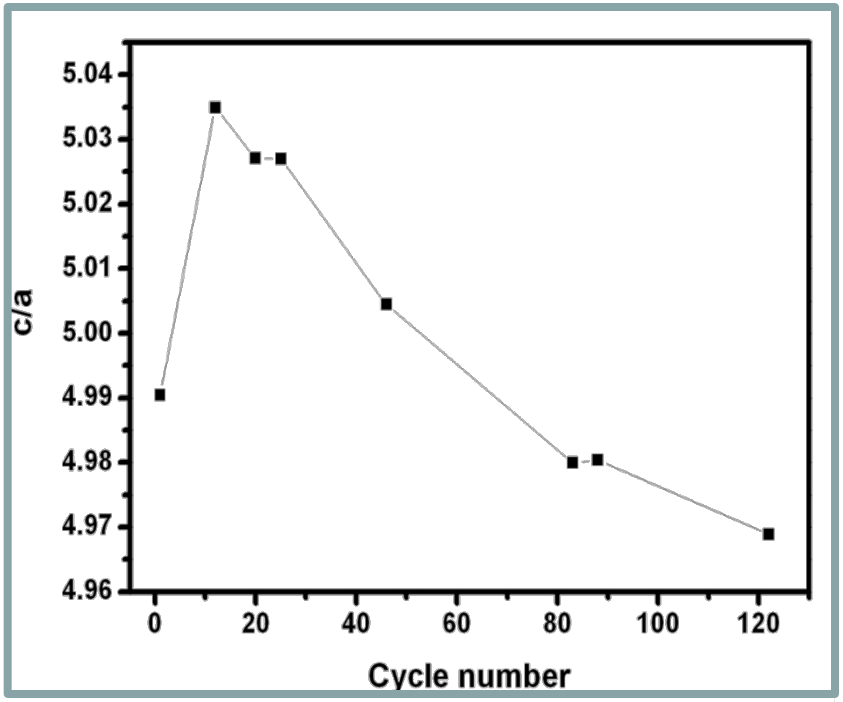




- Increased lattice parameter "*a*" with cycling number indicates the expansion of a-b plane, in good agreement with increased metal-metal bond length as obtained in XAS;
- Spinel-like phase transition behavior after 45 cycles.

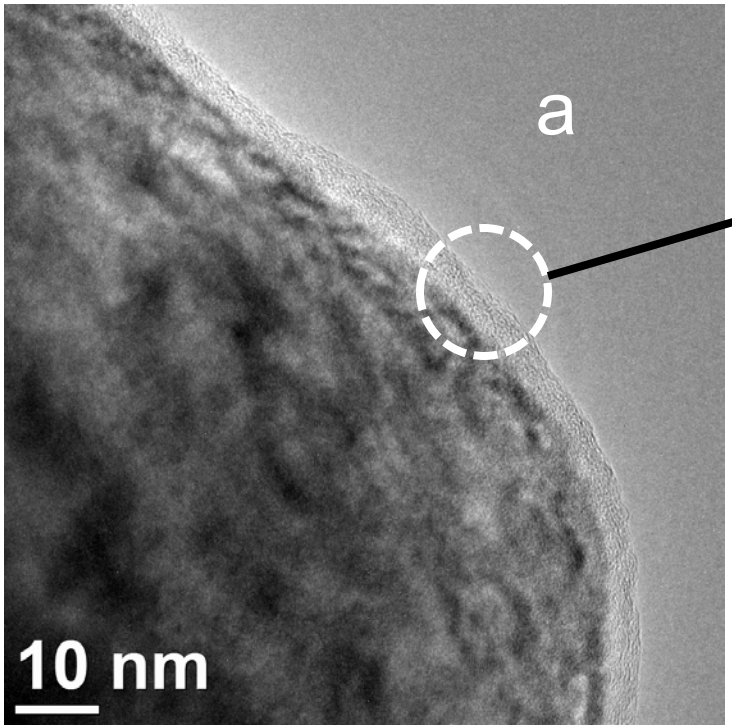
Changes of *lattices parameters* at discharged state during cycling

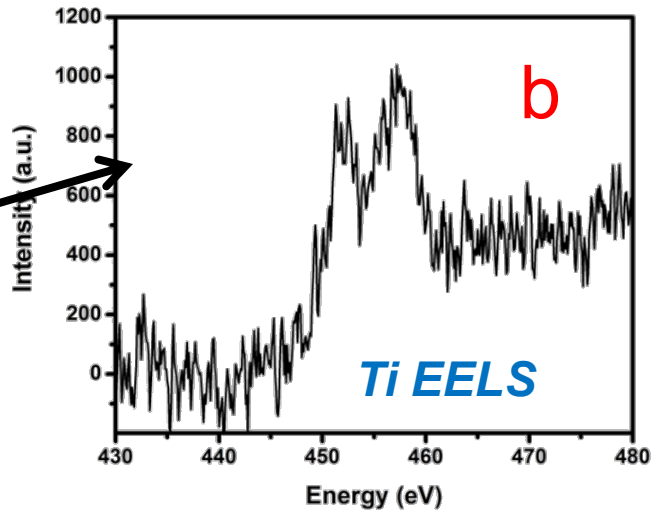




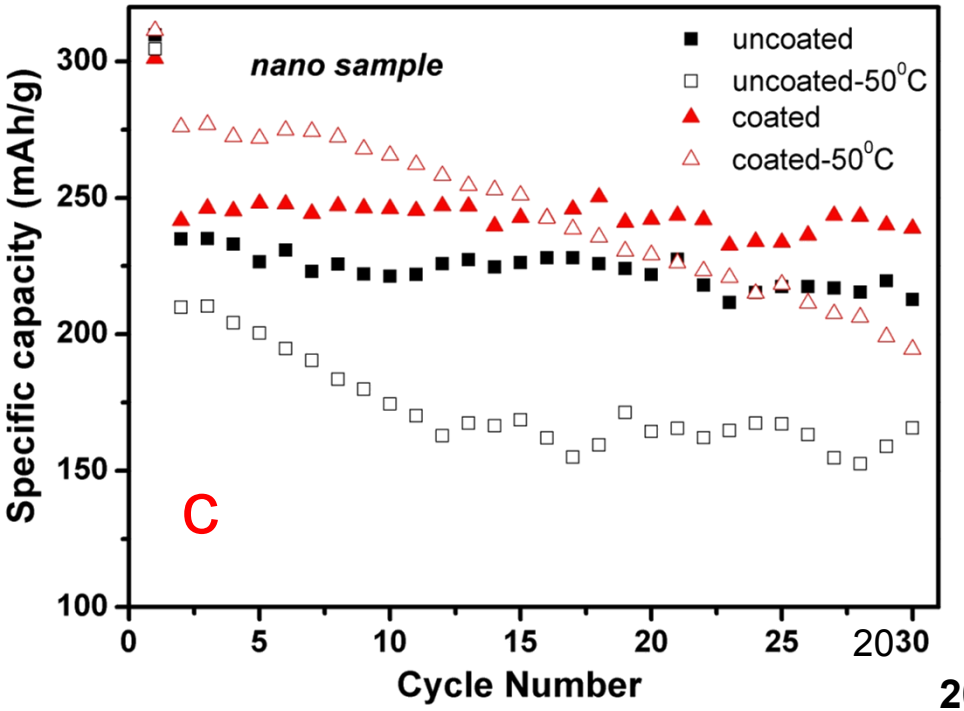
- Increased lattice parameter "*a*" during cycling indicates expansion of a-b plane, in good agreement with increased Metal-metal bond length as obtained in XAS
- Value of c/a is decreased towards the 4.899 value for cubic symmetry, indicating the structure is changing to more and more spinel like.

Amorphous TiO_2 ALD coating on the surface of $Li_{1.2}(Ni_{0.13}Co_{0.13}Mn_{0.54})O_2$

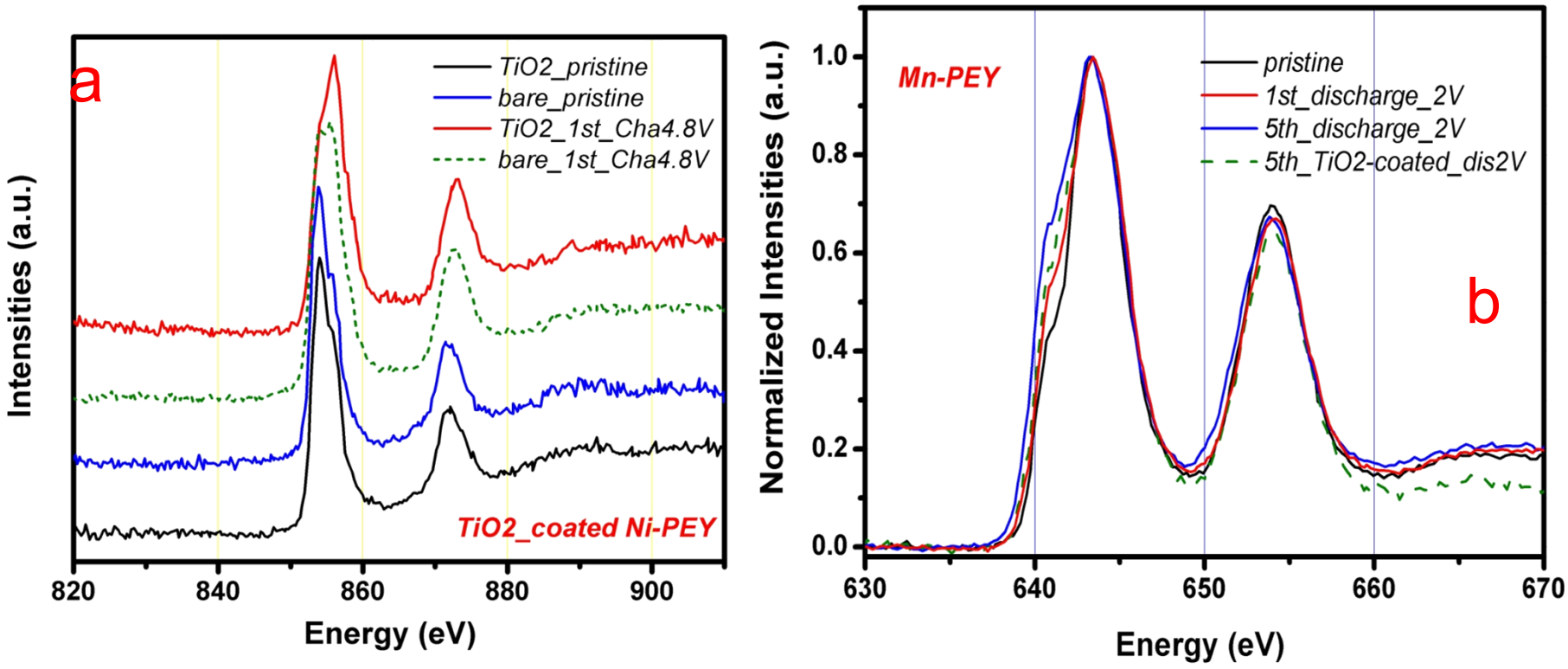




- ALD is a well established method to coat thin films on high-surface area tortuous materials
- TiO_2 coated sample show better cyclic performance



TiO_2 ALD coating partially suppressed the Ni and Mn reduction at surface



- Surface coating partially isolates the surface of the material from the electrolyte, supressing the chemical reduction of Ni^{4+}
- Surface coating may suppress the surface structure change and prevent the dissolution of Mn^{2+}.

Collaborations with other institutions and companies

- **Argonne National Lab. (ANL)**
  - ➥ *In situ* XRD and XAS study of high energy density Li_2MnO_3-$LiMO_2$ composite (LMR-NCM)
    LMR-NCM sample preparation and distribution by the "post-testing facility" at ANL

- **Oakridge National Lab. (ONL) & University of Tennessee**
  - ➥ *In situ* XRD technology development for Li-ion battery material research at NSLS.

- **Beijing Institute of Physics**
  - ➥ ALD surface coated cathode materials and new electrolyte additives.

- **Korea Institute of Science and Technology (KIST)**
  - ➥ Surface coated (e.g., ZrO_2, $AlPO_4$, and Al_2O_3) layered cathode materials.

- **Johnson Controls- Advanced Power Solutions**
  - ➥ Layer structured $LiNi_xCo_yMn_zO_2$ (x+y+z=1) cathode materials.

- **Duracell (P&G)**
  - ➥ *In situ* XRD and XAS study for high voltage spinel cathode material R&D.

- **GM R&D Center**
  - ➥ *In situ* XRD and XAS study for high energy density Li_2MnO_3-$LiMO_2$ composite.

Planned work for *FY 2012* and *FY2013*

- Complete the studies using *in situ* TR-XRD combined with MS on the thermal stability of layer structured $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ and $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode materials.
- Thermal stability study of surface modified high energy density Li_2MnO_3-$LiMO_2$ (LMR-NCM) composite cathode materials by atomic layer deposition (ALD) coating (e.g., Al_2O_3, AlF_3, and TiO_2 coating): TR-XRD *and in situ* hard and soft XAS studies during heating.
- Using *in situ* XRD, XAS and TEM to study the voltage and capacity fading mechanism of high energy density Li_2MnO_3-$LiMO_2$ (LMR-NCM) composite cathode materials with and without surface coating
- *In situ* XRD, TR-XRD, hard and soft XAS study of $LiNi_xCo_yMn_zO_2$ $(x + y + z = 1)$ cathode materials to identify the effect of Ni, Co, and Mn composition on the thermal stability, capacity and power fading during heating and/or charge-discharge cycling.
- Expand the collaborative research with US and international academic research institutions and US industrial partners.

Summary

- Through diagnostic studies and collaborations with US industries and international research institutions, progress has been made by this ES034 project to achieve the goals of developing next generation of batteries for HEV, PHEV, and EV of USDOE.
- New *in situ* diagnostic tools using the combination of time resolved x-ray diffraction (TR-XRD), mass spectroscopy and TEM during heating have been developed and applied to study the overcharged cathode materials such as $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ and $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ in parallel with *in situ* soft and hard XAS. The formation of rock-salt structure on the surface of $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ and their effects on oxygen release during heating (by MS) are thoroughly studied in comparison with $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, which has O1 structure formed at the surface during overcharge and has much less oxygen release during heating.
- *In situ* XRD and XAS were used to study the voltage and capacity fading mechanism of high energy density Li_2MnO_3-$LiMO_2$ (LMR-NCM) composite cathode materials with and without surface coating. The results of these studies show that this material forms more and more spinel like structure during cycling accompanied with reduction of oxidation state of Co and Mn, and oxygen loss, suggesting the intrinsic structural instability of this material.
- Large local structure changes during 1st and 2nd cycle due to the decomposition of the Li_2MnO_3, which causes large irreversible capacity at the 1st cycle were studied. The transition metal cations are rearranged in the structure during cycling, especially in the first several cycles.
- TiO_2 coated sample showed better cyclic performance attributed to the surface stabilization of the coating layer.