Diagnostic Studies to Improve Abuse Tolerance and Life of Li-ion Batteries

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ES034

BROOKHAVEN NATIONAL LABORATORY

Overview

Timeline

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

Budget

- Funding received in FY09
  DOE: $350k
- Funding received in FY10
  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

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/10	Complete in situ TEM and selected area electron diffraction studies of overcharged $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (G3) cathode materials during heating. ➥ *Completed.*
Sep/10	Complete the thermal stability study of surface modified (e.g., surface coating using ZrO_2, $AlPO_4$, and Al_2O_3 etc) G2 and G3 cathode materials using TR-XRD *and* in situ hard & soft XAS techniques during heating. ➥ *Completed.*
Apr/11	complete the in situ XRD studies during charge-discharge cycling for Cr and F doped $LiMn_2O_4$ spinel as high power cathode materials in collaboration with ANL. ➥ *Completed.*
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). ➥ *On schedule.*
Sep/11	Start in situ XAS and TR-XRD studies of Li_2MnO_3-LMO_2 type new cathode materials during cycling and heating. ➥ *On schedule.*

Approaches

1. Abuse Tolerance

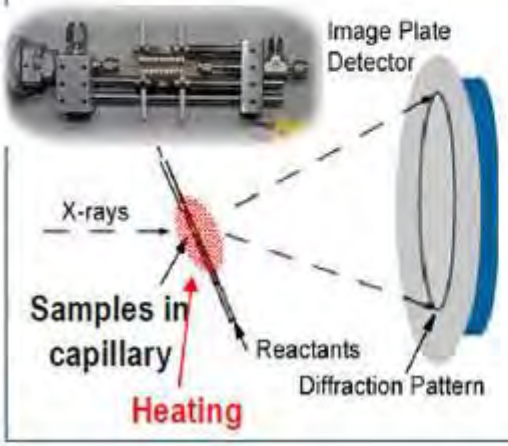
- A combination of time resolved X-ray diffraction (XRD), *in situ soft and hard* X-ray absorption (XAS), *in situ* transmission electron microscopy (TEM) techniques during heating to study the thermal stability of the electrode materials.
- Apply the atomic layer deposition (ALD) technique for the surface modification of new cathode materials, using time resolved X-ray diffraction (XRD) to study the effects of surface modification on the thermal stability.

2. Life of Li-ion batteries

- In situ XRD, soft and hard XAS studies of new electrode materials during charge-discharge cycling to understand the power and energy density fading mechanism for longer cycling life of Li-ion batteries.
- Extended collaboration with other US and international academic institutions and US industrial partners.

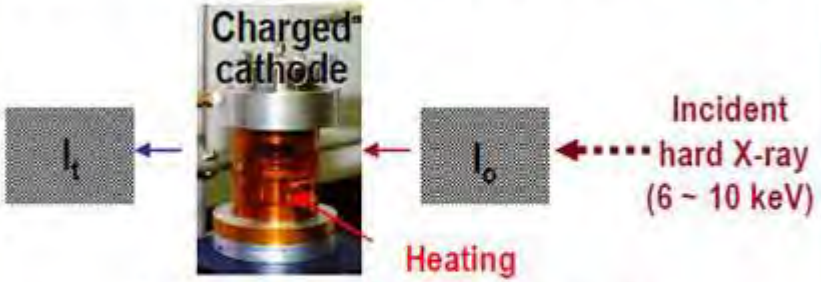
Approach I: *In situ* TR-XRD, XAS and TEM during heating of charged cathode materials (thermal stability study)

1. *Time-resolved XRD* of charged cathode



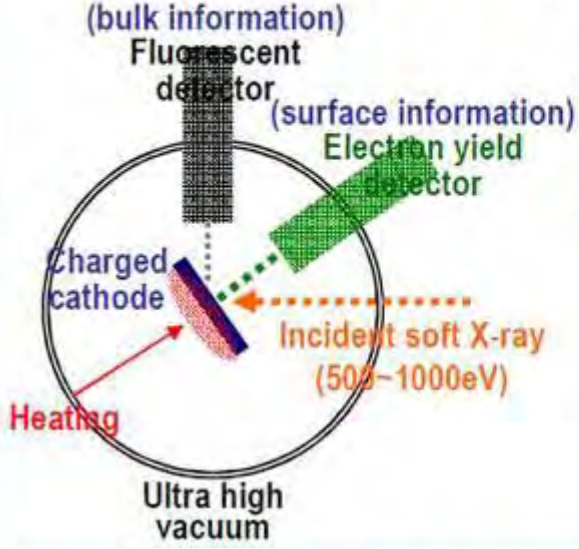
- Average structural information (long range order)

2. *In situ Hard XAS* of charged cathode



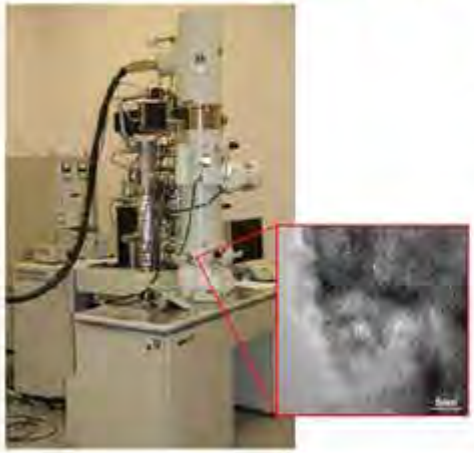
- Local electronic and structural information (bulk) in elemental-selective way

3. *In situ Soft XAS* of charged cathode



- Electronic structural information at the surface (~ 50Å) and in the bulk (~ 3000Å) in elemental-selective way

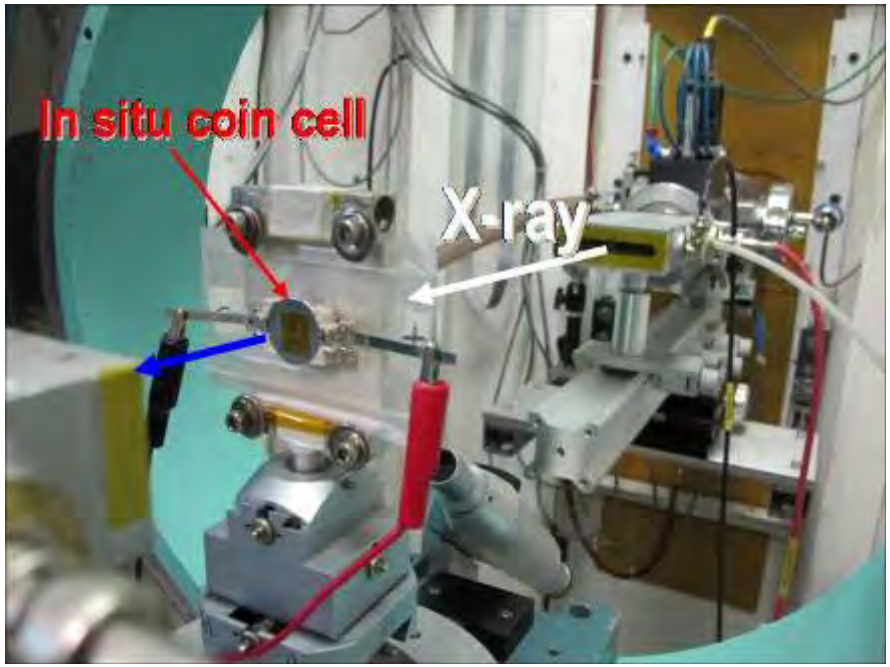
4. *In situ* TEM of charged cathode

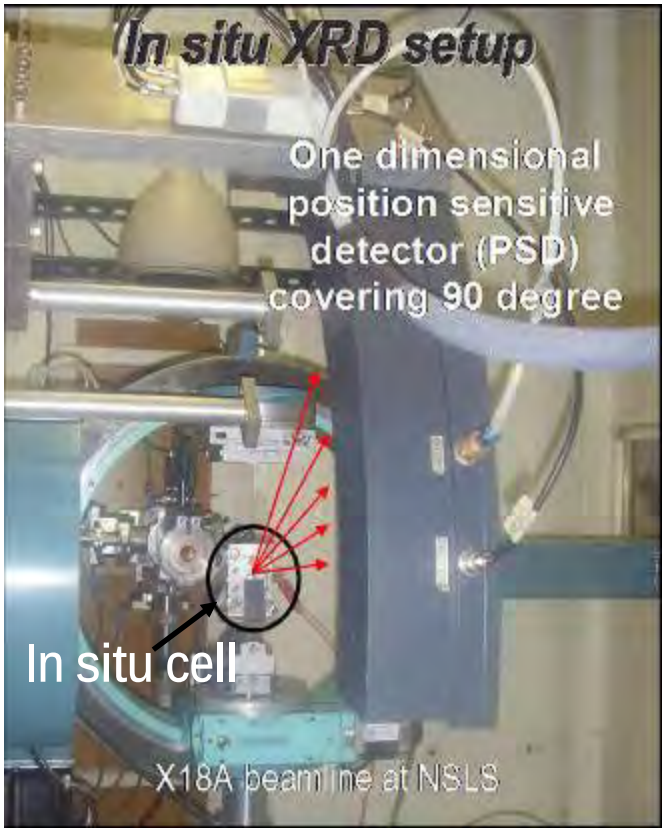


- Where and how the new structure nucleated and propagated with high location specification and spatial resolution (~ nm range)

Approach II: *In situ* XRD and XAS during charge-discharge cycling (Diagnostics study related to the life of Li-ion battery)

In situ XAS set up





- *In situ* high resolution X-ray diffraction : Crystalline structure change
- *In situ* X-ray absorption spectroscopy : Local and electronic structure change (up to ~10Å) (e.g., valance state, coordination number, bond length and disorder)

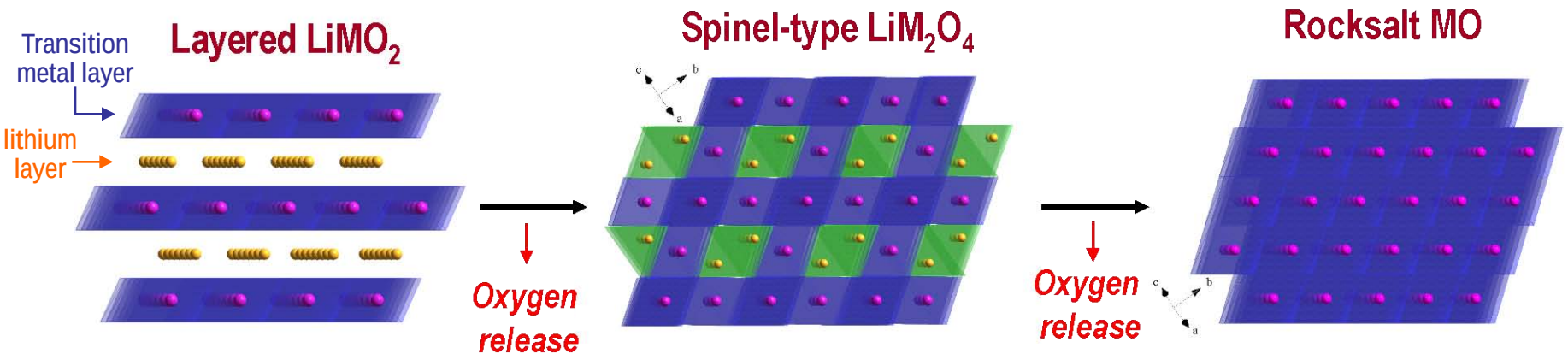
➥ *Combinations of various in situ X-ray techniques to better understand the structure-property relationship of lithium battery materials.*

Technical Accomplishments

- Completed *in situ* hard and soft X-ray absorption spectroscopy (XAS) study on charged $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (Gen2) and $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (Gen3) cathode materials during heating.
- Developed the combination of synchrotron based *in situ* XRD with high resolution TEM (HR-TEM) to study the overcharged cathode materials for Li-ion battery during heating aimed at the improvement of the thermal stability.
- Initiated the new studies to apply the atomic layer deposition (ALD) to improve the thermal stability of cathode.
- Working with GM, P&G (Duracell), and other collaborators, carried out diagnostic studies of new high energy density Li_2MnO_3-$LiMO_2$ (M=Ni, Co, Mn) and high voltage spinel ($LiNi_{0.5}Mn_{1.5}O_4$) cathode materials.
- Initiated the synthesis and characterization of new electrolytes for high voltage Li-ion batteries.
- Developed new *in situ* diagnostic tool using high resolution TEM (HR-TEM) during heating to study overcharged cathode materials such as $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (Gen2) and $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (Gen3). The formation and growth of rock-salt structure on the surface of Gen2 and the O1 type structure on the surface of Gen3 and their effects on thermal stability have been obtained.

Thermal stability study of layered cathode materials (safety related issue)

General scheme for thermal decomposition path of charged layered cathode materials



When x= 0.5 (50% of SOC) in Li_xMO_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!!*

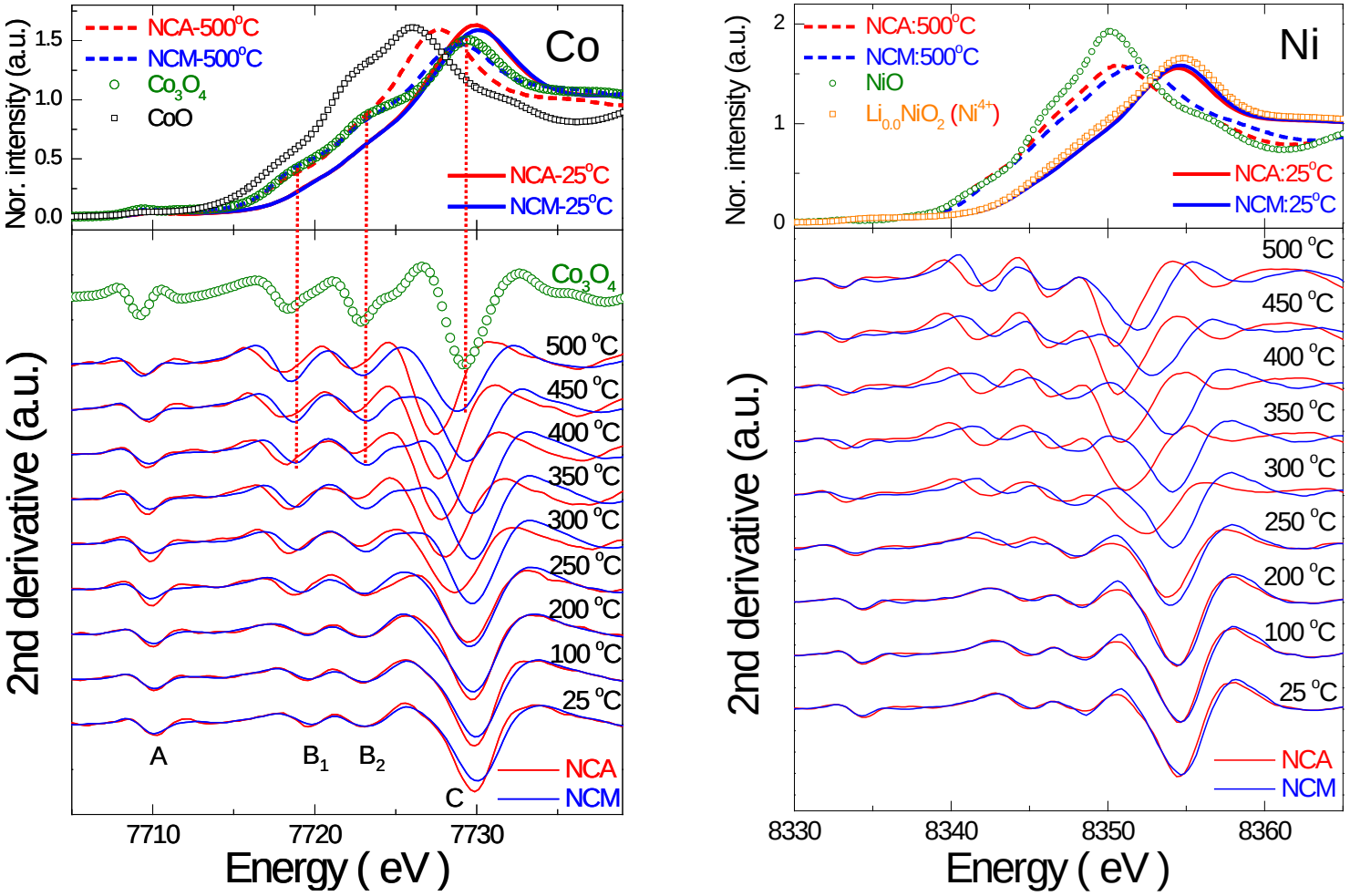
When x= 0.33 (67% of SOC) in Li_xMO_2

$Li_{0.33}M(^{3.67+})O_2$ (layered, *R-3m*) ⇨ $Li_{0.33}M(^{3.21+})_{1.0}O_{1.77}$ (disordered spinel, *Fd3m*) + 0.115 O_2 ; *oxygen release!!*

$Li_{0.33}M(^{3.21+})_{1.0}O_{1.77}$ (disordered spinel, *Fd3m*) ⇨ $Li_{0.33}M(^{2.33+})_{1.0}O_{1.33}$ (rock salt, *Fm3m*) + 0.22 O_2 ; *oxygen release!!*

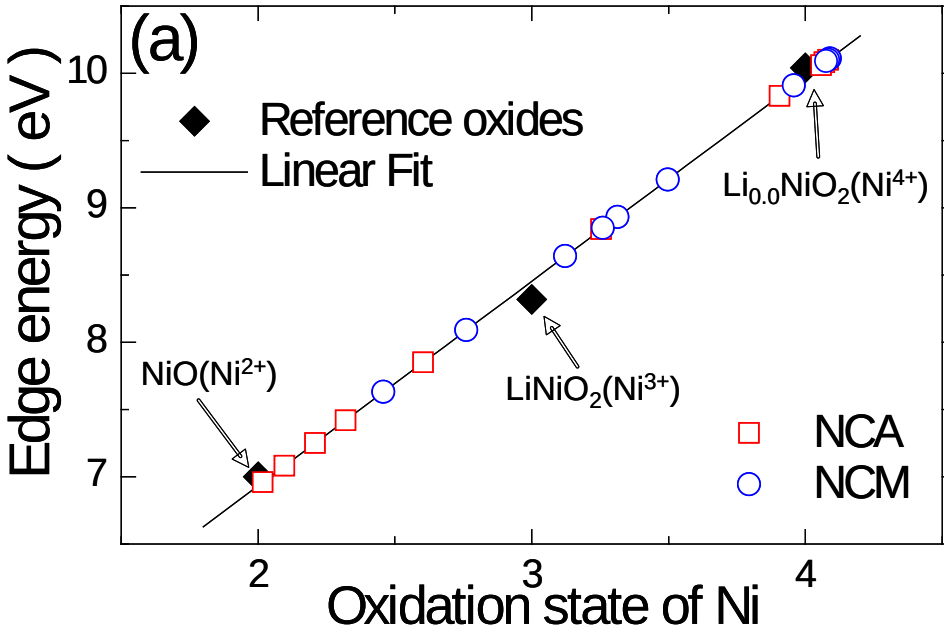
➥ *More deeper charged state, more thermally unstable.*
➥ *Released oxygen causes safety problems by reacting with flammable electrolytes. (e.g., thermal runaway)*

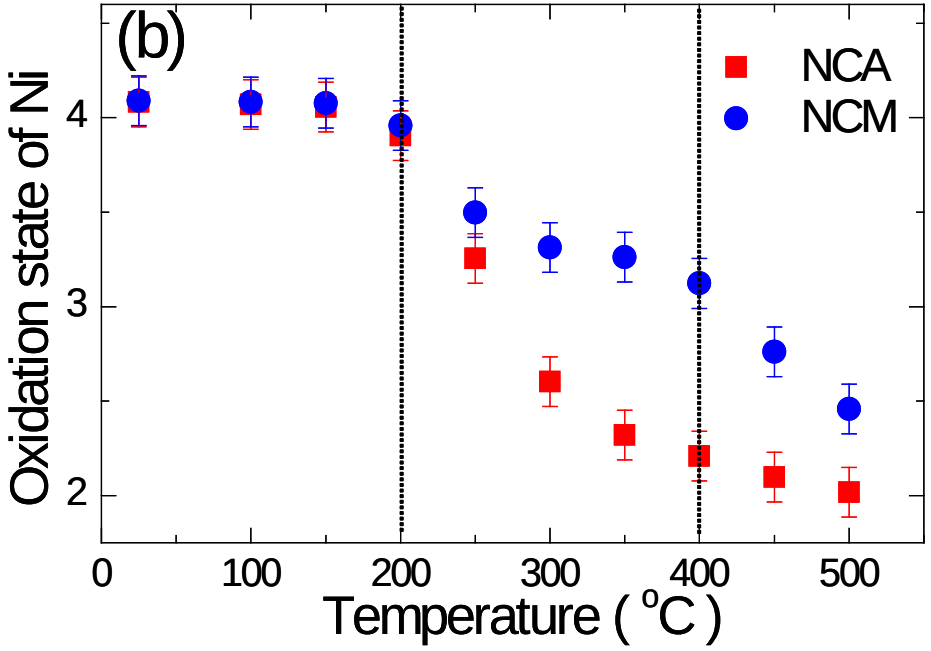
Co and Ni K-edge XANES of charged $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (Gen 2) and $Li_xNi_{1/3}Co_{1/3}Al_{1/3}O_2$ (Gen 3) during heating



➥Gen 3 shows much slower reduction (thermal decomposition) in both Co and Ni sites than Gen2 indicating much better thermal stability of Gen3 than Gen2.

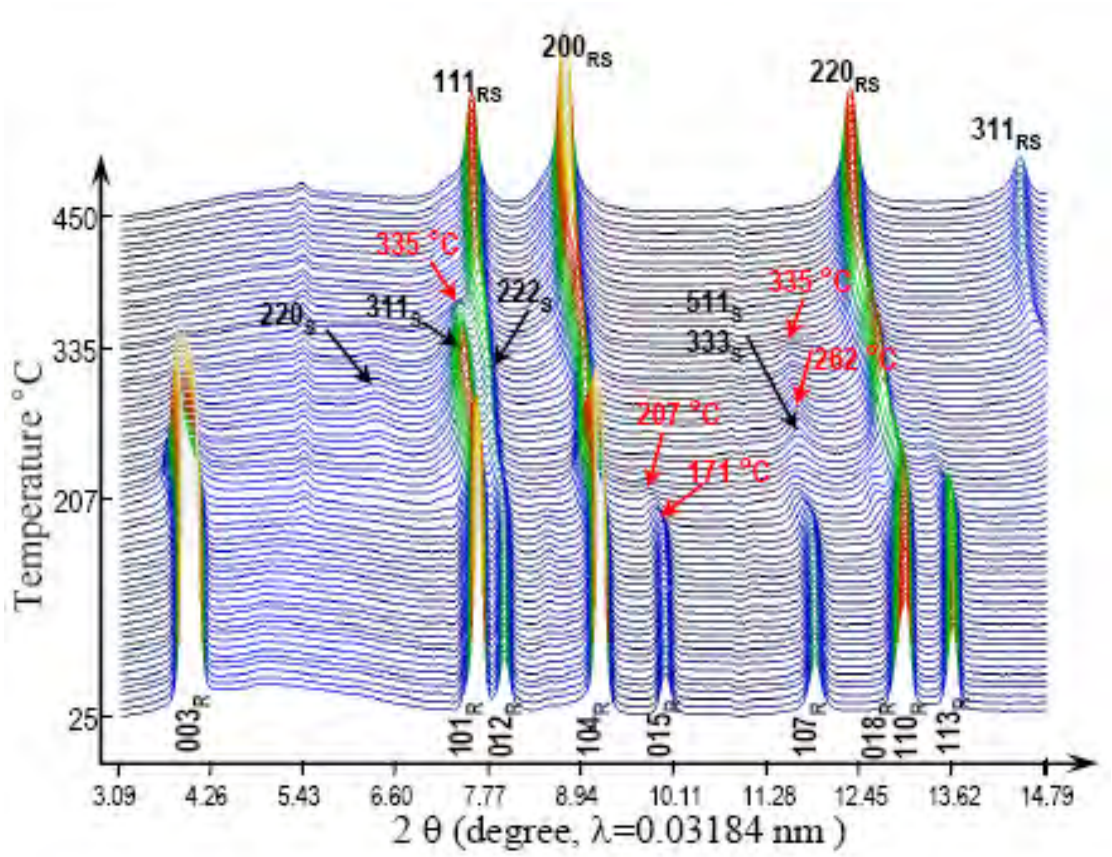
Estimation of oxidation state of Ni in charged $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (Gen 2) and $Li_xNi_{1/3}Co_{1/3}Al_{1/3}O_2$ (Gen 3) during heating by Ni K-edge XAS





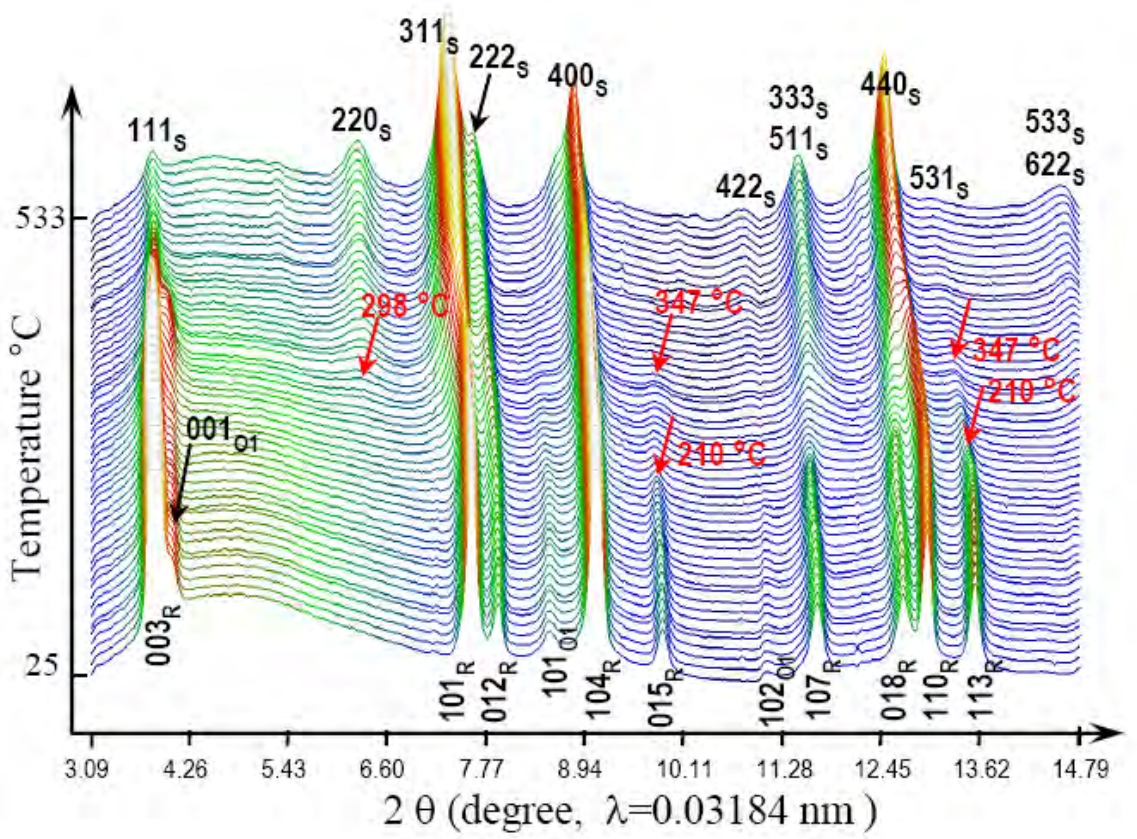
- Using standard materials which have known Ni oxidation state, oxidation state change of Ni in charged Gen2 and Gen3 cathodes was estimated during heating.
- Gen2 shows much faster reduction of Ni from 4+ to 2+ than Gen3 during heating.
- Considering Ni composition in Gen2(80%) and Gen3(33%), the calculated amount of oxygen release in Gen2 after heating at 500°C is 3.2 times of Gen3.
- Much better thermal stability of Gen3 than Gen2.

Time-resolved XRD patterns of overcharged $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (Gen 2) without electrolyte during heating



➥The phase transition from layered to spinel phase starts at about 171ºC and the phase transition from spinel to rock-salt phase starts at about 262 ºC.

Time-resolved XRD patterns of overcharged $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (Gen 3) without electrolyte during heating

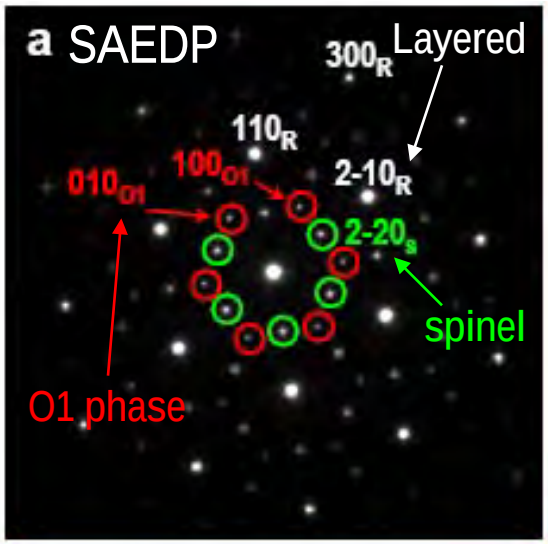


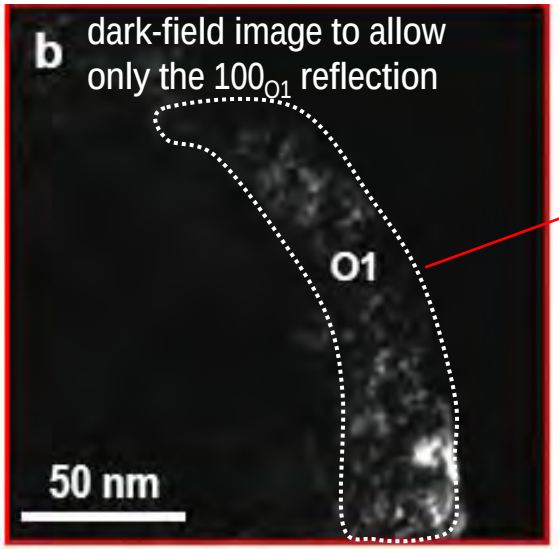
- Layered structure is still the dominant, but a new CdI_2-type O1 phase was also observed as a minor phase after overcharge at room temperature.
- The phase transition from layered to the $LiMn_2O_4$ type spinel phase starts at about 210ºC and the phase transition from $LiMn_2O_4$ type spinel to the Co_3O_4 type spinel phase starts at about 347 ºC.
- The formation of CdI_2-type O_1 phase and it's transformation to Co_3O_4 type spinel are the structural origins of the better thermal stability of Gen 3 than Gen 2 cathode material.

High-Resolution (HR) TEM with selected area electron diffraction pattern (SAEDP) study of overcharged $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (Gen3) particle before heating

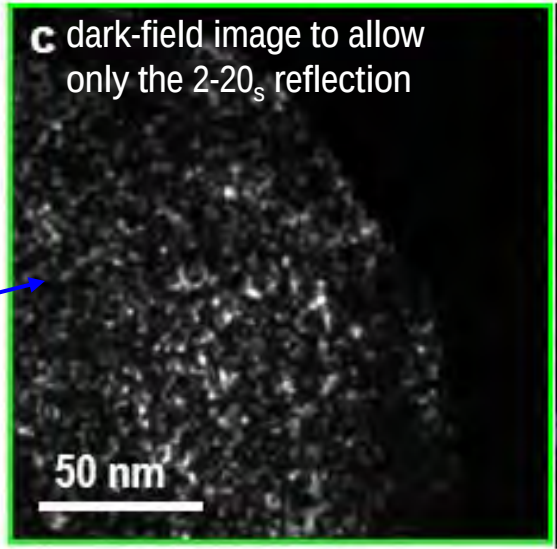
- No trace of the rock-salt structure at the surface.

- Layered (major), spinel (2nd major), and O1 (minor) phases coexist.

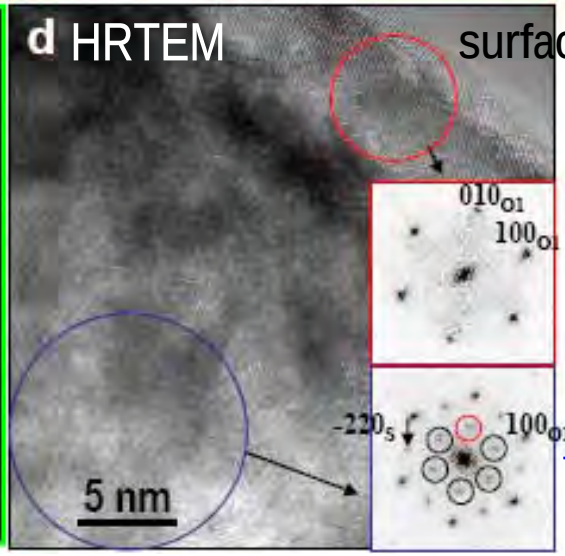




O1 phase (bright area) is located at the surface!



Spinel phase (bright area) is located slightly off the surface.

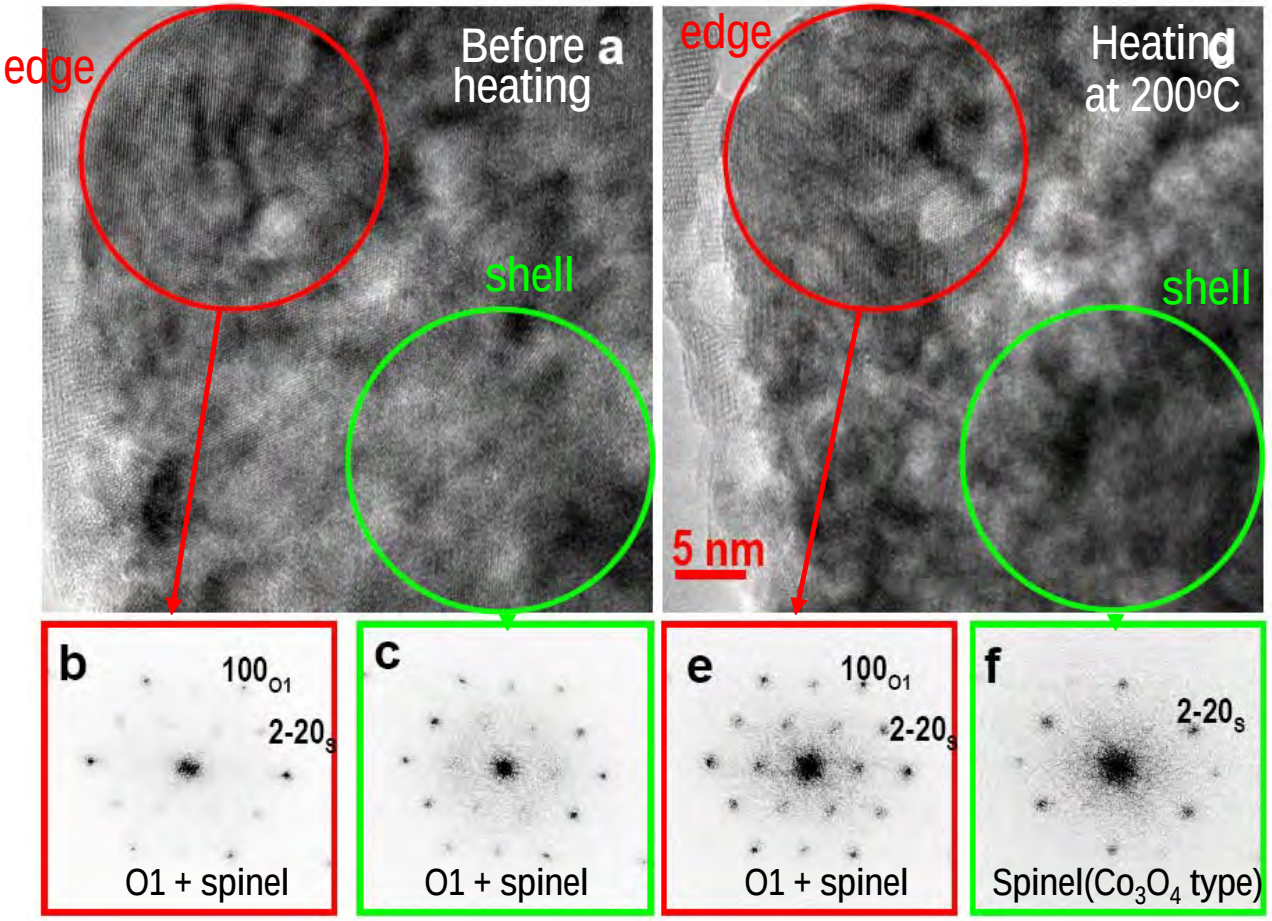


O1 phase at the surface.

Mixed spinel and O1 phases at the inner shell.

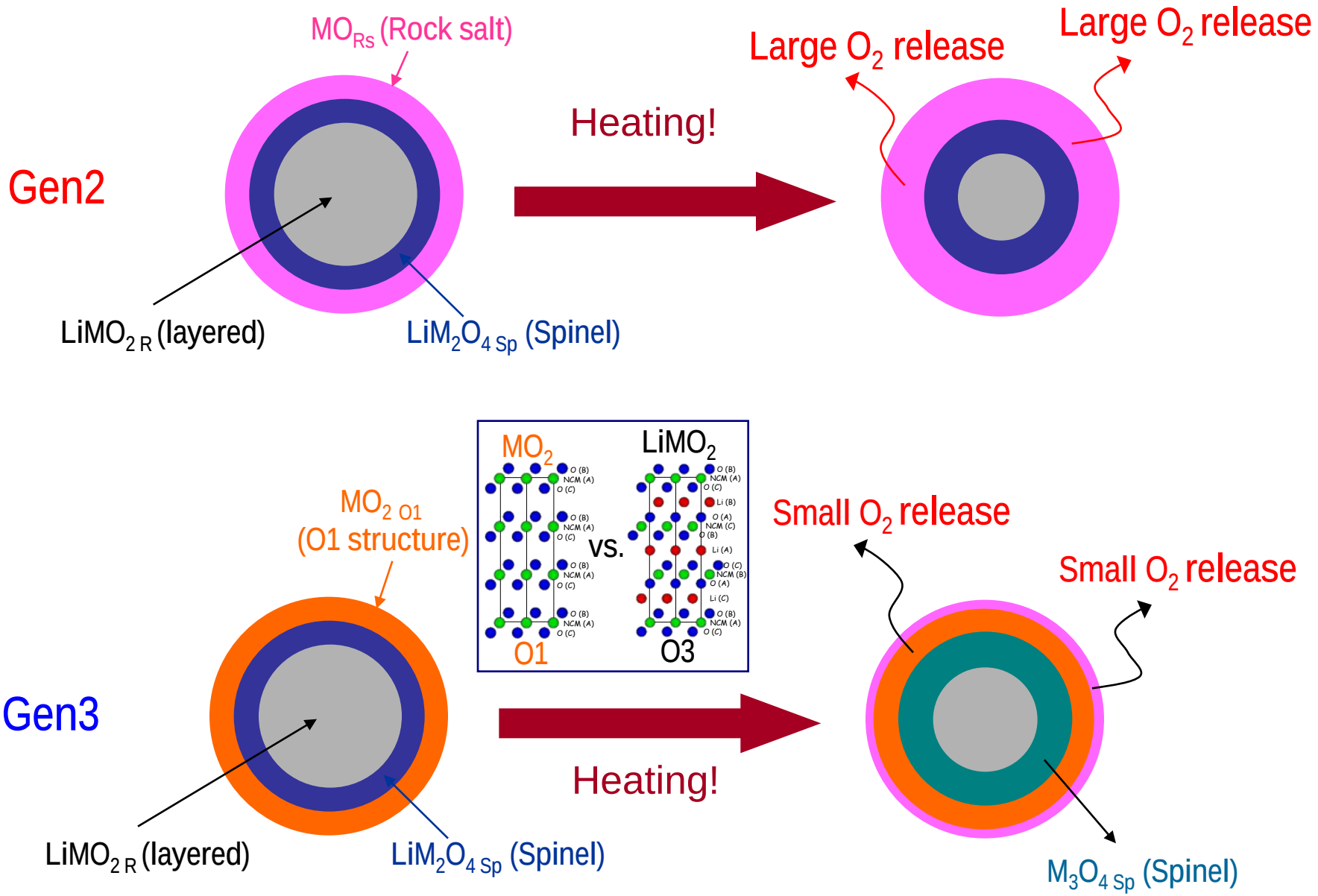
➥ These results show clearly that the O1 phase observed by TR-XRD had been formed at the surface of the particles at room temperature after overcharge!

High-Resolution (HR) TEM with selected area electron diffraction pattern (SAEDP) study of overcharged $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (Gen3) particle after heating at 200°C

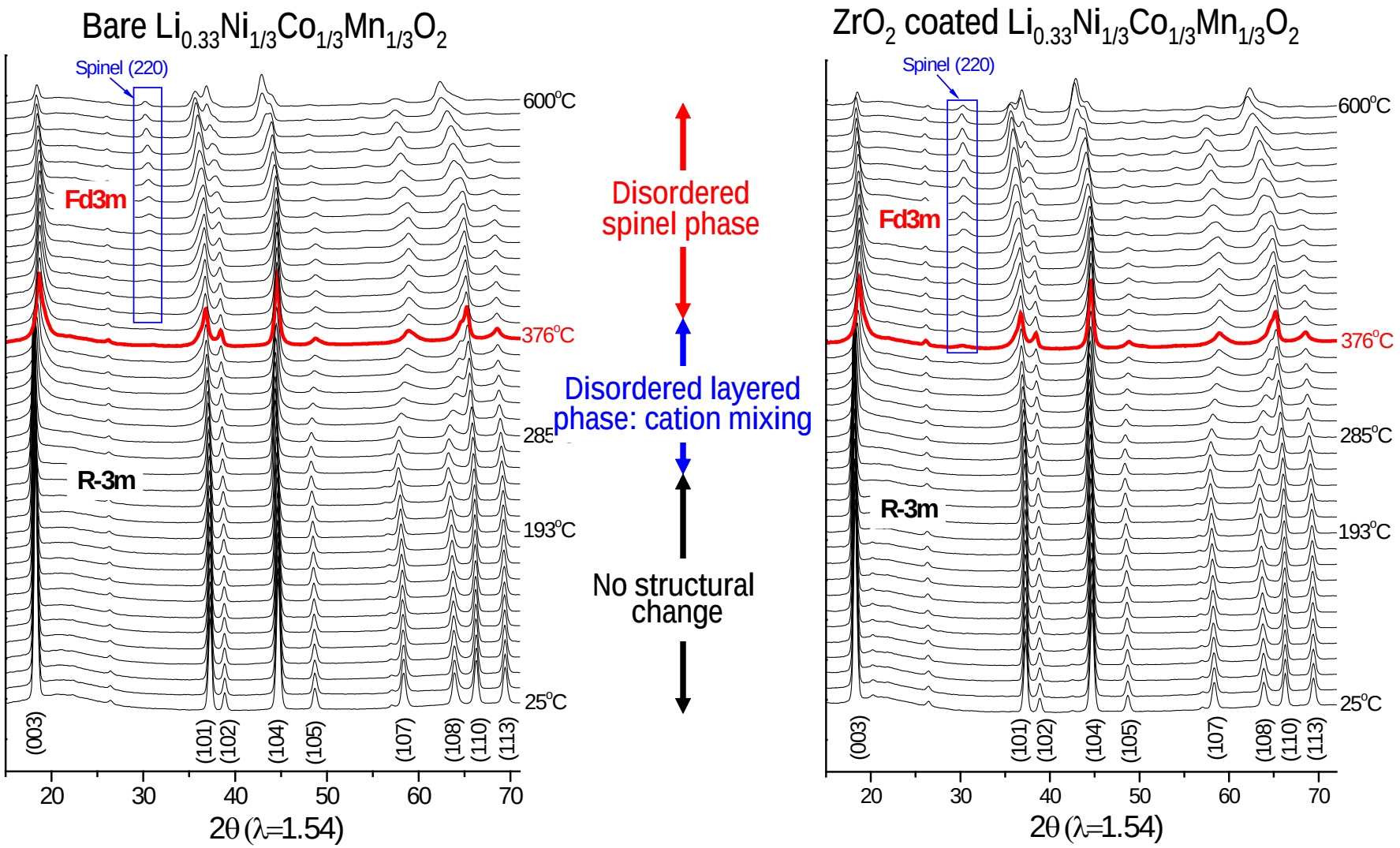


- After heating at 200 °C, the structure changes. The green-circled area has transformed from the mixed O1 and spinel structure to the Co_3O_4-type spinel structure, as evidenced by the disappearance of the diffraction spots of the O1 in the diffractogram.
- The formation of the O1 phase, rather than the rock-salt structure at the surface of the particle is crucial in protecting the particle from losing oxygen.

Thermal decomposition mechanism of overcharged $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (Gen 2) and $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (Gen3) particles during heating



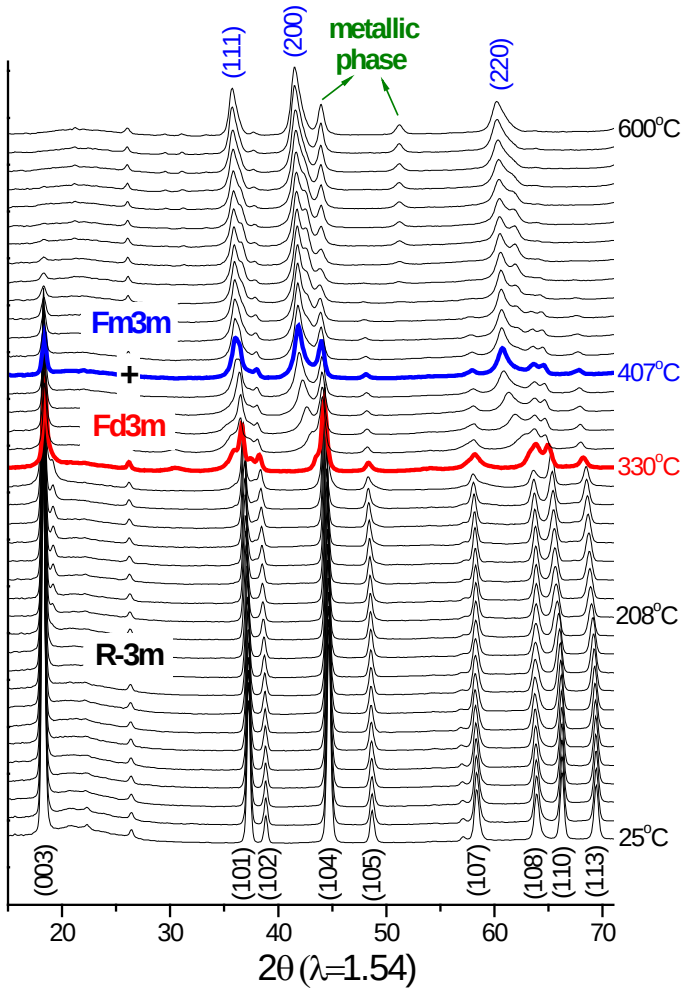
TR-XRD of bare and ZrO_2 coated $Li_{0.33}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$: no electrolyte



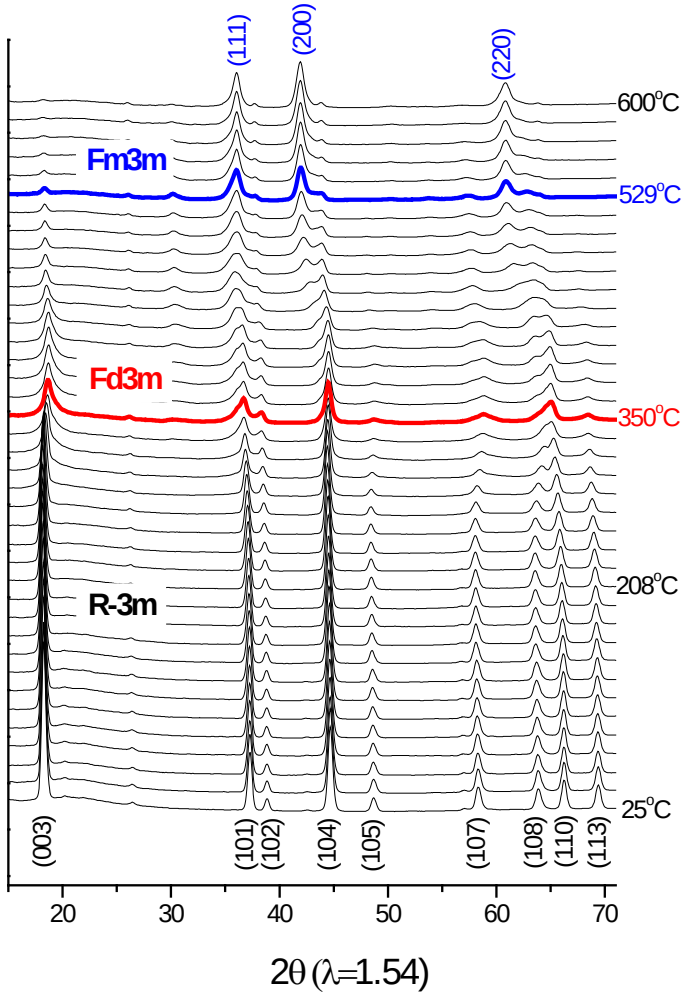
➥ The improvement of thermal stability by ZrO_2 coating is not significant for the sample without electrolyte.

TR-XRD of bare and ZrO_2 coated $Li_{0.33}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$: with electrolyte

Bare $Li_{0.33}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$

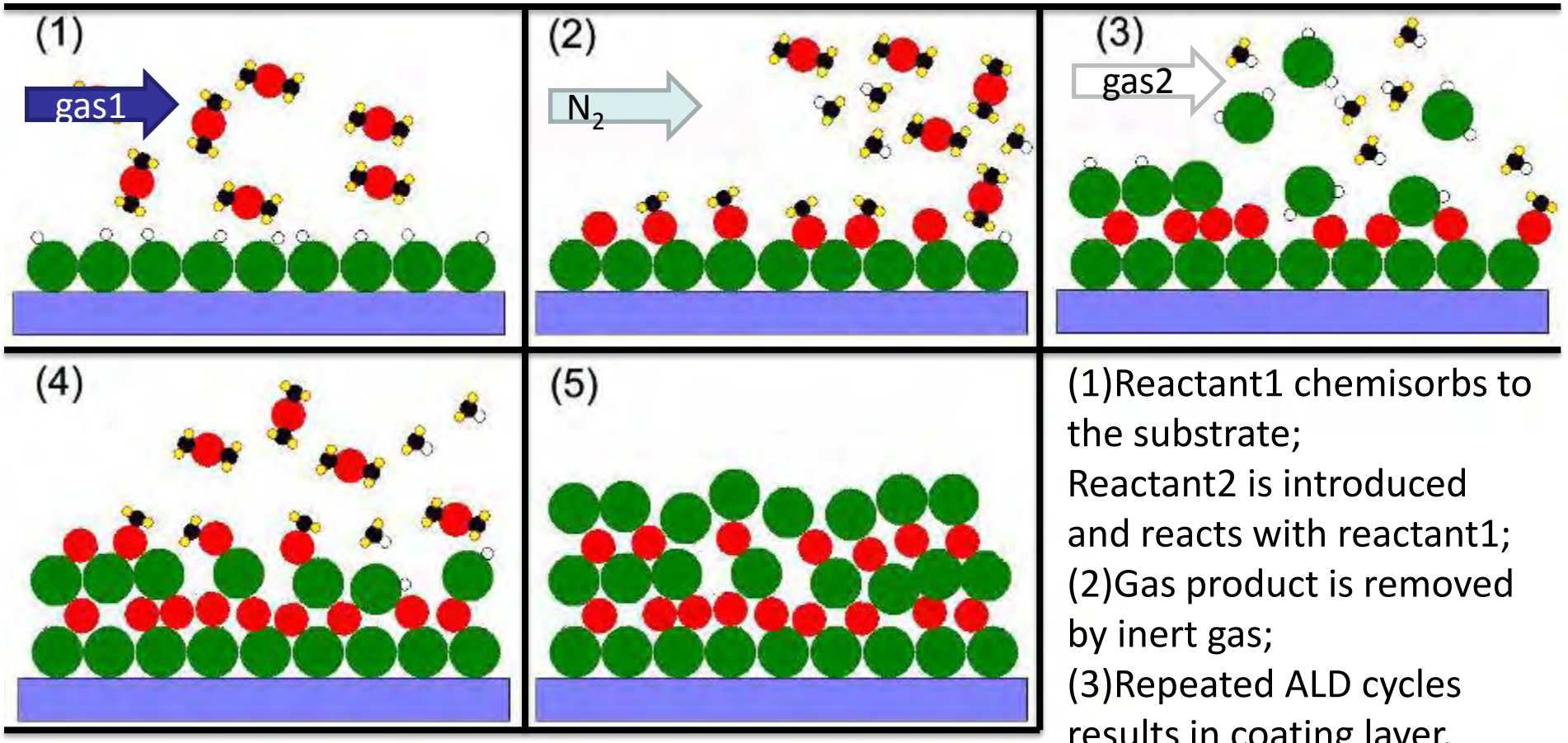


ZrO_2 coated $Li_{0.33}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$



➥ The improvement of thermal stability by ZrO_2 coating is much more pronounced. (increased temperature to the rock-salt Fm3m phase in the presence of electrolyte)

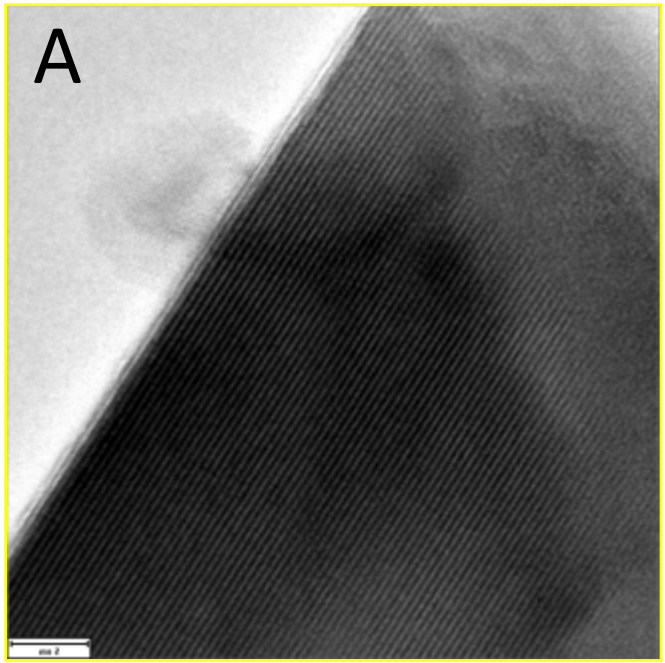
Mechanism of atomic layer deposition (ALD) technique

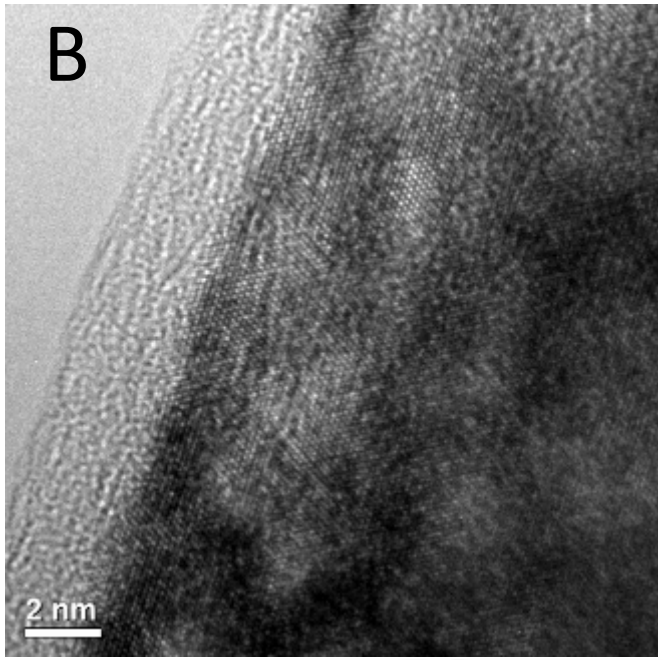


(1)Reactant1 chemisorbs to the substrate; Reactant2 is introduced and reacts with reactant1;
(2)Gas product is removed by inert gas;
(3)Repeated ALD cycles results in coating layer.

e.g. Al_2O_3 : $TMAl+H_2O=Al_2O_3+CH_4$
(TMAl: trimethylaluminum)

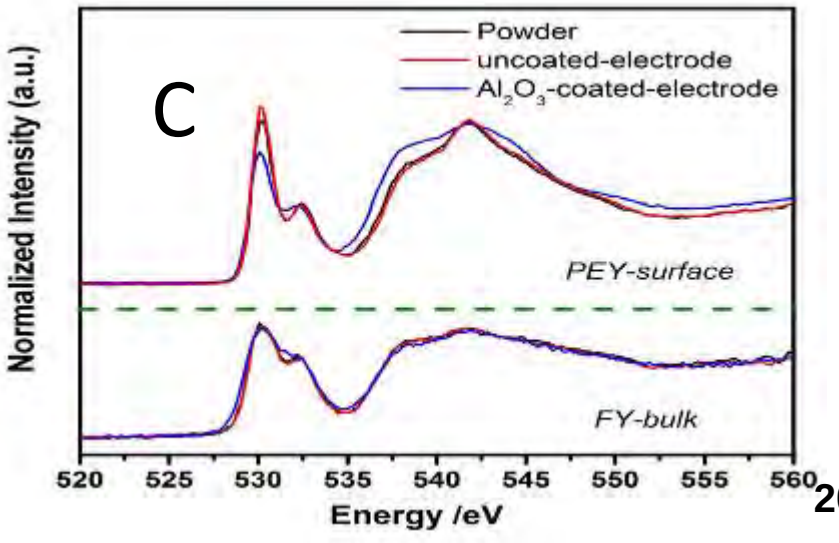
Al_2O_3 coated $Li_{1.2}Ni_{0.13}Co_{0.07}Mn_{0.6}O_2$ electrode studied at BNL in collaboration with Institute of Physics, CAS



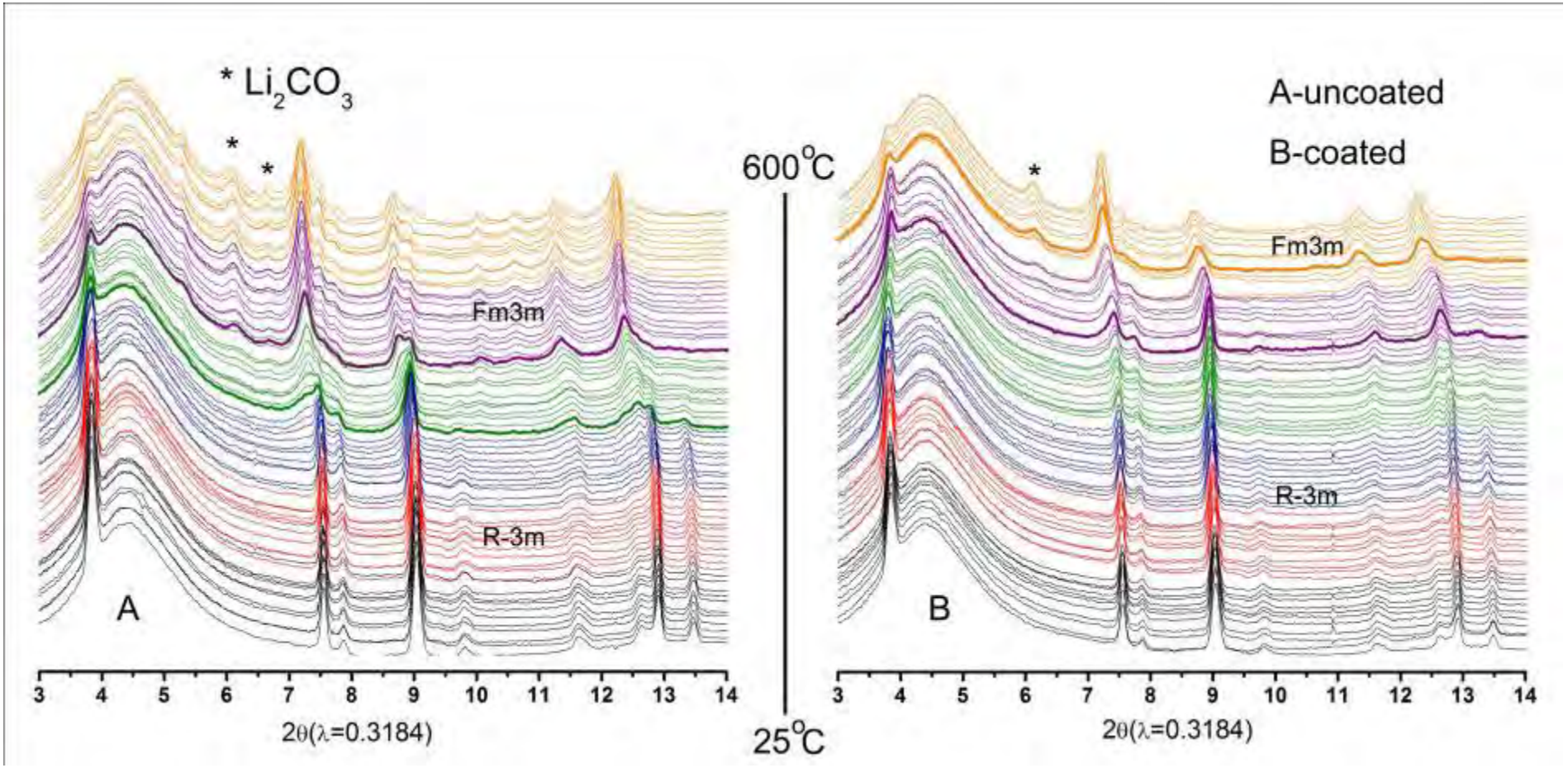


(A) HRTEM image of bare electrode
(B) HRTEM image of Al_2O_3 coated electrode
(C) PEY and FY spectra at O-k edge for bare and coated electrodes

1. ALD coating layer: dense, uniform and nano-thickness
2. Differences between O K-edge PEY spectra indicate different surface status of Al_2O_3 coated electrode.

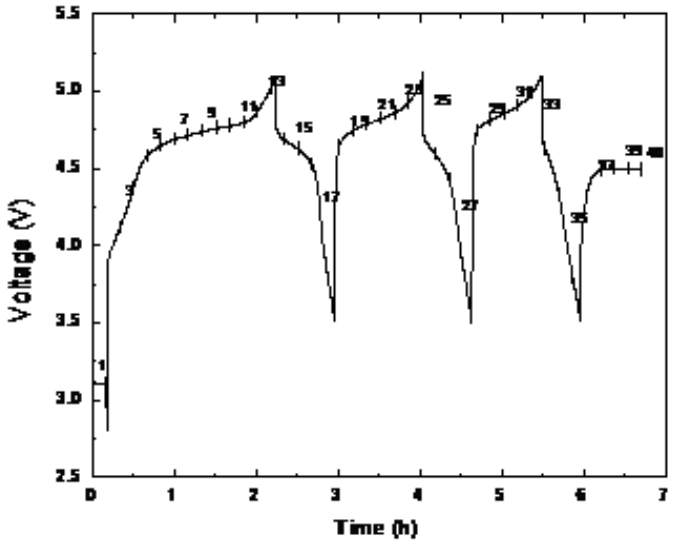


Thermal stability study of fully charged $Li_{1.2}Ni_{0.13}Co_{0.07}Mn_{0.6}O_2$ electrode with and without ALD coated Al_2O_3



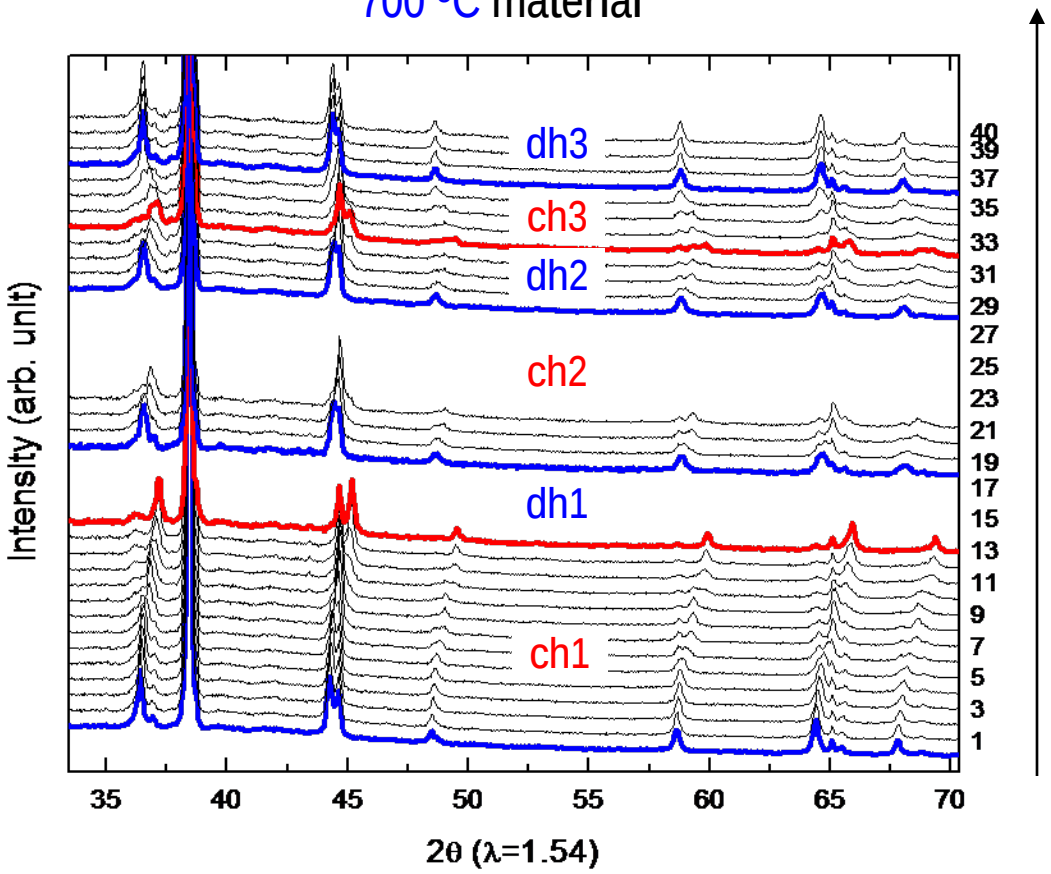
- Significant improvements of the thermal stability was obtained for the fully charged $Li_{1.2}Ni_{0.13}Co_{0.07}Mn_{0.6}O_2$ electrode with ALD coated Al_2O_3 in comparison with the uncoated electrode.
- The phase transition temperature to Fm3m phase is increased by almost 100 °C.

In situ XRD of high voltage $LiMn_{1.5}Ni_{0.5}O_4$ spinel cathode during cycling in collaboration with P&G (*Duracell R&D*)



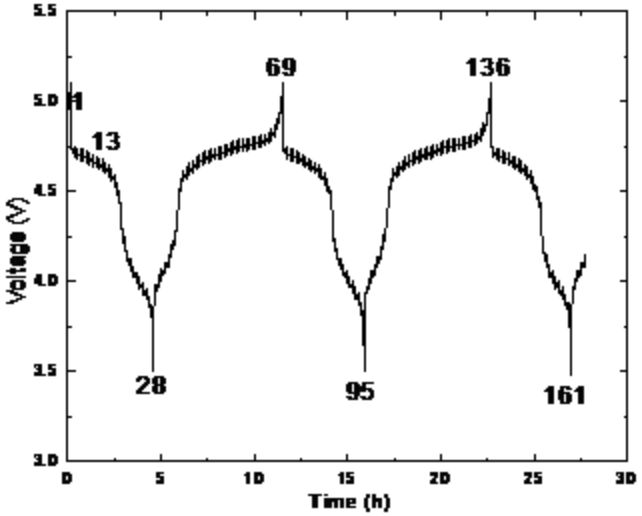
Charge-discharge curves during in situ XRD for the 700 ºC material

700 ºC material

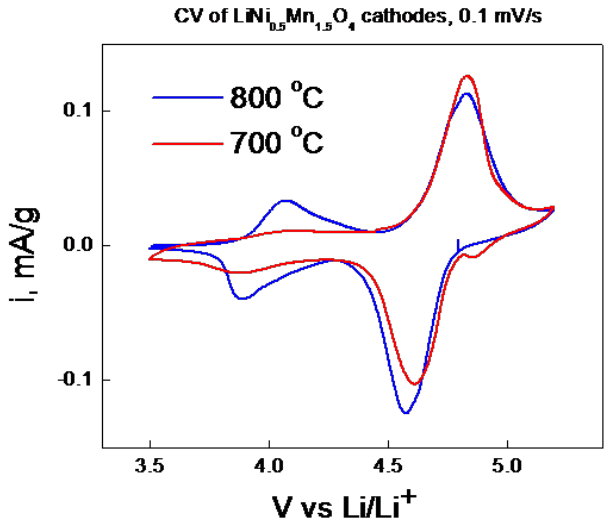


- Decomposition/phase separation upon delithiation at 4.7 V.
- With repeated cycles, likely amorphous phase formation as decomposition product loss of reversibility.
- Distinction between the low voltage plateau and the main high voltage plateau disappears.

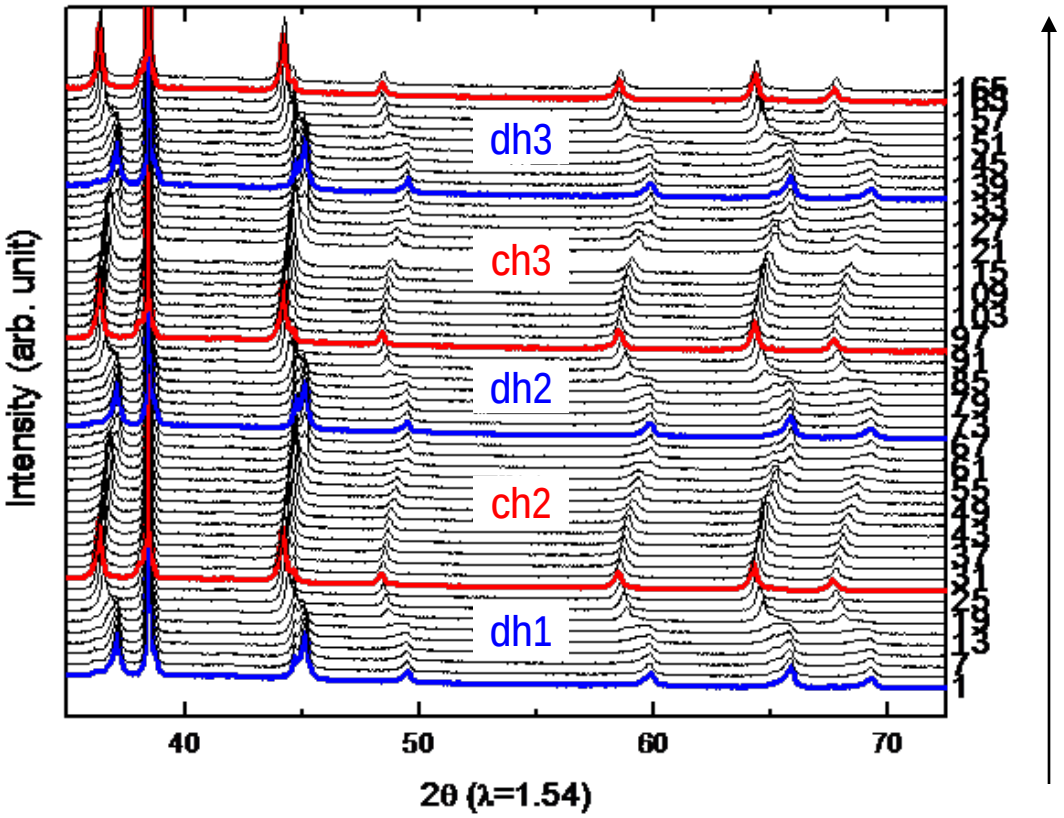
In situ XRD of high voltage $LiMn_{1.5}Ni_{0.5}O_4$ spinel cathode during cycling in collaboration with P&G (*Duracell R&D*)



Charge-discharge curves during in situ XRD for the 800 °C material

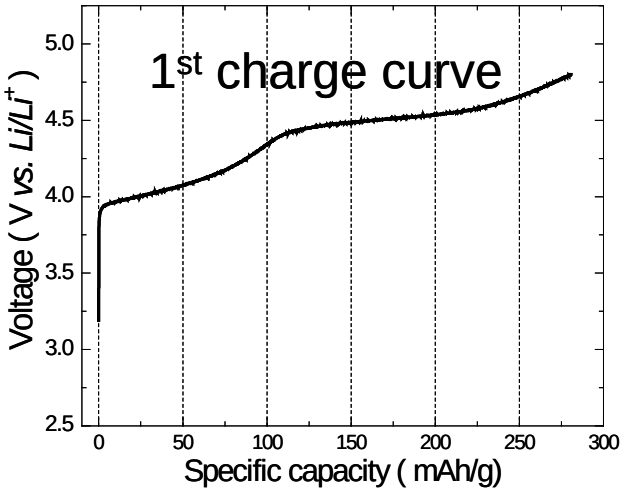


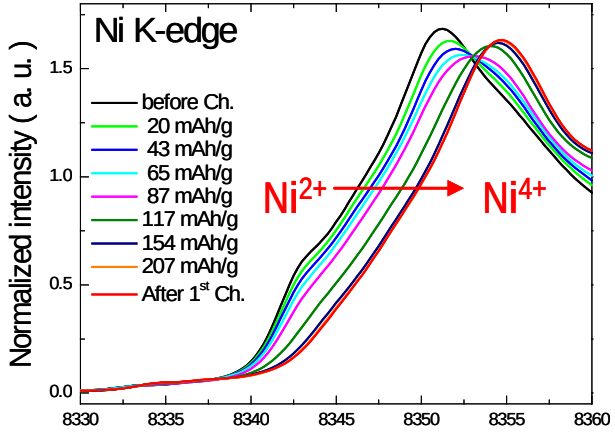
800 °C material

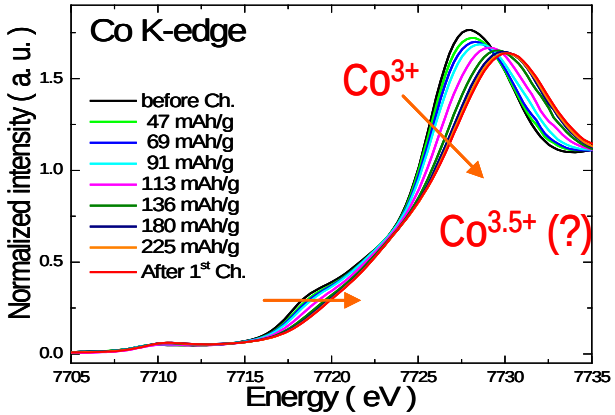


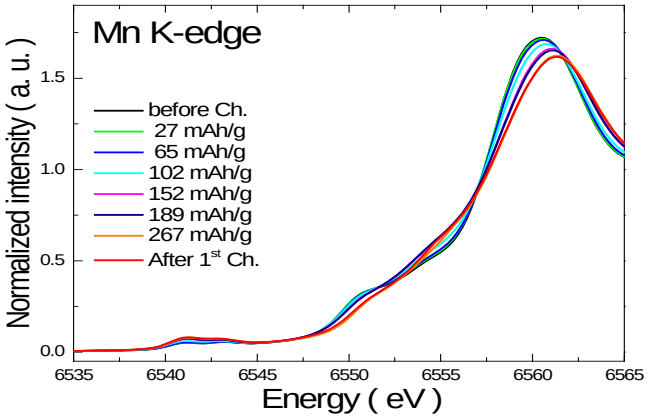
- Stays as a single phase. Lattice contracts and expands as charged and discharged, respectively.
- The materials synthesized at 800 °C has much better performance than that at 700 °C.

In situ XAS study of High Capacity Li_2MnO_3-$LiMO_2$ (M = Ni, Co, Mn) during 1st charge, In collaboration with Dr. Wu and Dr. Yang at GM









- Ni K-edge X-ray absorption near edge structure (XANES) spectra clearly show oxidation from Ni^{2+} to Ni^{4+} indicating charge compensation occurs mostly at the Ni sites during the early state of charge below 4.5V
- Co K-edge XANES spectra show small edge shift during charge suggesting that the possible oxidation from Co^{3+} to $Co^{3.5+}$
- Mn K-edge XANES result suggests that Mn valance (Mn^{4+}) does not change during 1st charge.

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.
- 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.
- Dow chemical
  - ➥ Olivine structured $LiFe_xMn_{1-x}PO_4$ 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 2011* and *FY2012*

- Complete the in situ TEM studies on the thermal stability of layer structured Gen2 and Gen3 cathode materials.
- Thermal stability study of surface modified high energy density Li_2MnO_3-$LiMO_2$ composite cathode materials by atomic layer deposition (ALD) coating (e.g., TiO_2 and SnO_2 coating): TR-XRD *and* in situ hard and soft XAS studies during heating.
- Using in situ TEM to study the thermal stability improvement by surface modification of atomic layer deposition (ALD) on high energy density Li_2MnO_3-$LiMO_2$ composite cathode materials.
- 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

- In the Multi Year Program Plan (MYPP) of VTP, the goals for battery were described as: “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.” In this ES034 project, progress has been made to achieve these goals through diagnostic studies and collaborations with US industries and international research institutions.
- New *in situ* diagnostic tools using high resolution TEM (HR-TEM) during heating have been developed and applied to study the overcharged cathode materials such as $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (Gen2) and $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (Gen3) in combination with time resolved XRD, soft and hard XAS. The formation and growth of rock-salt structure on the surface of Gen2 and the O1 type structure on the surface of Gen3 and their effects on thermal stability have been obtained.
- The results provide valuable information about the role of each transition metal (Ni, Co, and Mn) on the thermal- and structural-instability of the materials during overcharging and heating and are applicable to the development of new cathode materials with a similar layered structure and high capacity and thermal stability.

Summary (Cont'd)

- New studies to apply the atomic layer deposition (ALD) of Al2O3 on surface of Li2MnO3-LiMO2 type cathode materials have been initiated and significant improvement for the thermal stability has been obtained. Other type of surface modifications and their effects on the capacity retention during cycling are underway.

- In collaboration with GM R&D Center, diagnostic studies using *in situ* XAS for high energy density Li_2MnO_3-$LiMO_2$ (M=Ni, Co, Mn) type new cathode materials have been carried out. More *in situ* XRD studies will be followed.

- In collaboration with P&G (Duracell), diagnostic studies using *in situ* XRD for high voltage spinel ($LiNi_{0.5}Mn_{1.5}O_4$) type of new cathode materials have been carried out. *In situ* XAS studies will be followed.