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

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BROOKHAVEN NATIONAL LABORATORY

# Overview

## Timeline

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

## 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)
- Lockheed Martin Space System
- TOYOTA Research Institute of North America (will be started)

# Project Objectives

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

- ➥ to develop new *in situ* diagnostic techniques with surface and bulk sensitivity for studying the thermal stability of various cathode materials.
- ➥ to establish and investigate the thermal decomposition mechanisms of various cathode materials.
- ➥ to provide valuable information about how to design thermally stable cathode materials for HEV and PHEV applications.

## ✓ *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.
- ➥ to provide valuable information about how to improve the cell capacity and power fading of Li-ion battery for HEV and PHEV applications.

# Milestones

| Month/Year | Milestones |
|---|---|
| Oct/09 | Complete time resolved X-ray diffraction (TR-XRD) and *in situ* soft & hard X-ray absorption spectroscopy (XAS) studies of charged $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (G3) cathode material during heating for thermal stability studies (safety related issues). ➥ *Completed.* |
| Apr/10 | Complete *in situ* TEM and selected area electron diffraction studies of overcharged $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (G2) cathode materials during heating. ➥ *Completed.* |
| 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. ➥ *On schedule.* |
| 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. ➥ *On schedule.* |
| Sep/10 | Complete TR-XRD study of $LiNi_xCo_yMn_zO_2$ (x+y+z=1) cathode materials during heating for thermal stability studies. ➥ *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.

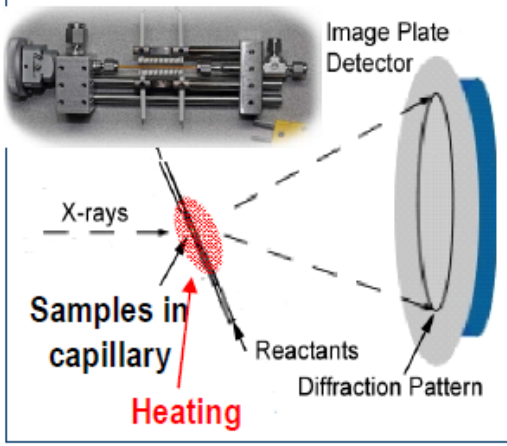
## 2. Life of Li-ion batteries

- 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.

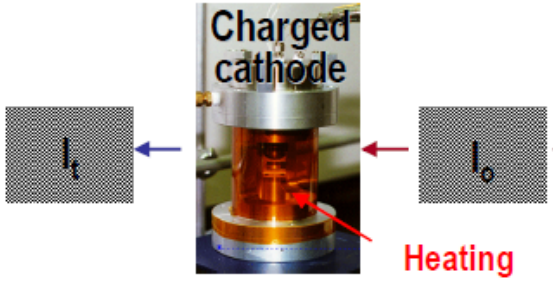
# Approach I: *In situ* TR-XRD, XAS and TEM during heating of charged cathode (thermal stability study)

## 1. *Time-resolved XRD* of charged cathode



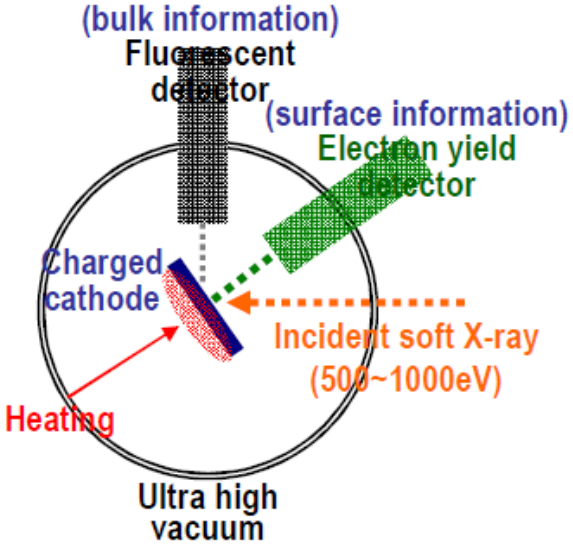

- Average structural information (long range order)

## 2. *In situ Hard XAS* of charged cathode



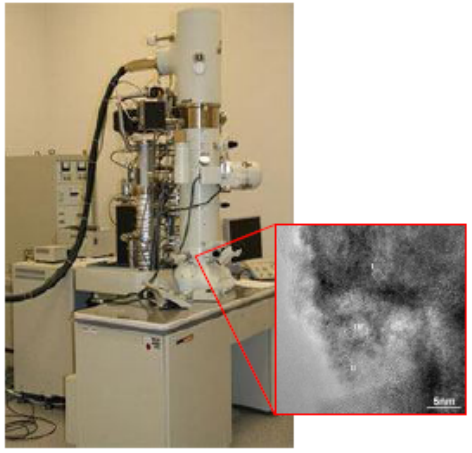

- Local electronic and structural information (bulk) in elemental-selective way

## 3. *In situ Soft XAS* of charged cathode



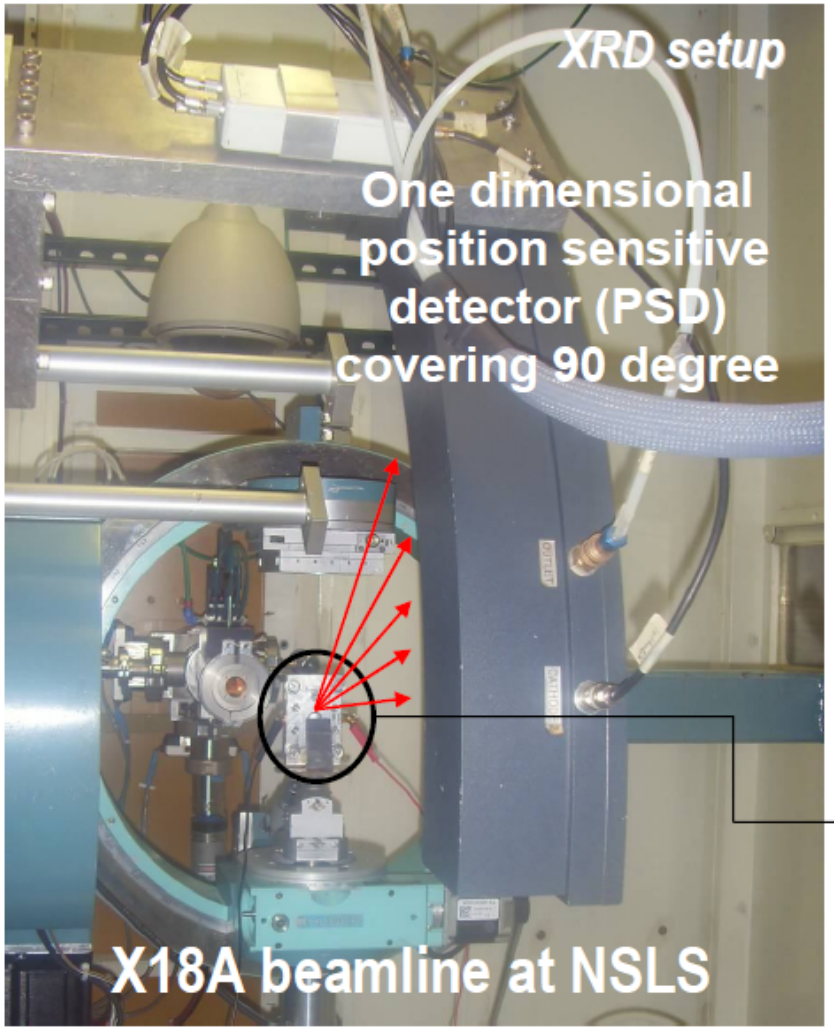

- Electronic structural information at the surface (~ 50Å) and in the bulk (~ 3000Å) in elemental-selective way

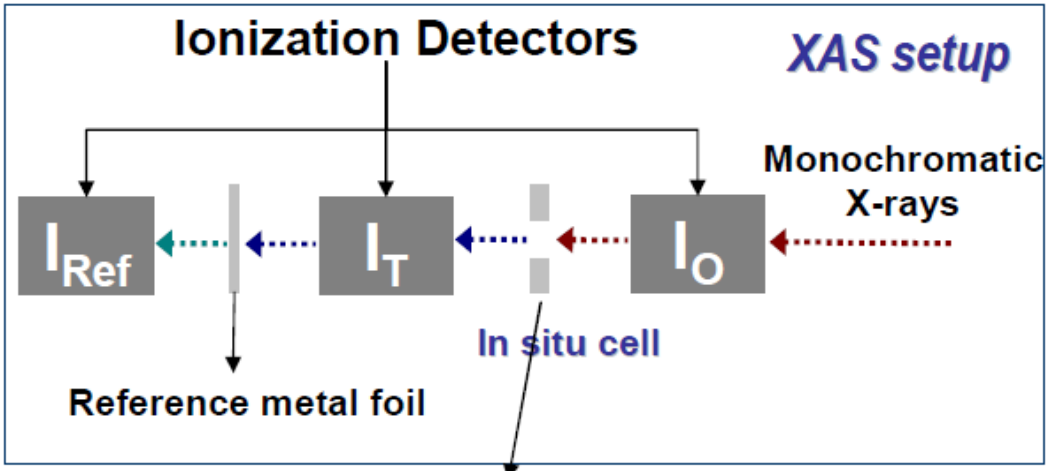
## 4. *In situ* TEM of charged cathode

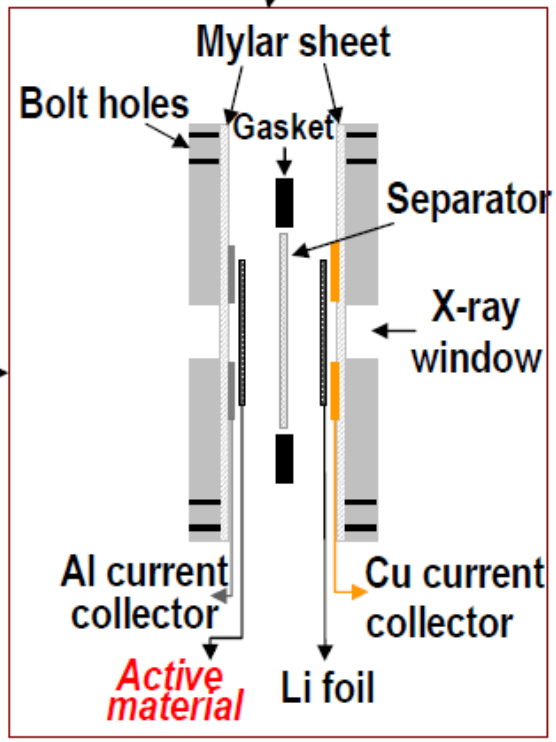


- Where and how the new structure nucleated and propagated with high location specification and spatial resolution (~ nm range)

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



# 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.

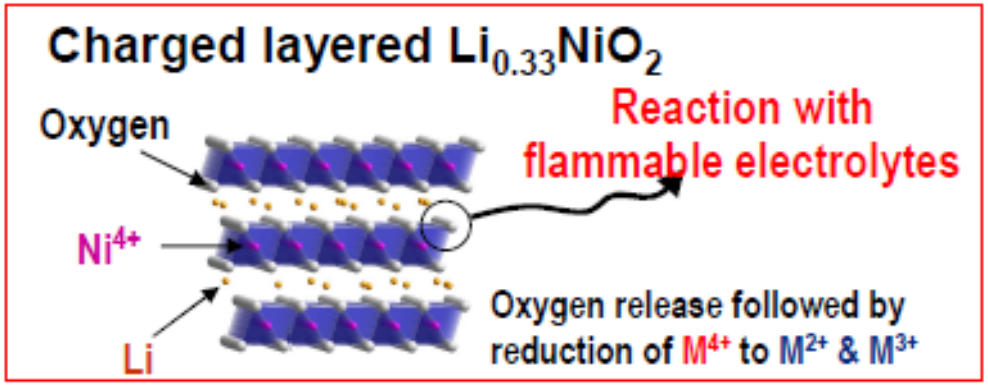
- Developed new *in situ* diagnostic tool using high resolution TEM (HR-TEM) during heating of charged cathode materials to study the thermal decomposition mechanism with high location specification and special resolution.

- Completed *in situ* HR-TEM study of overcharged $Li_{0.27}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ (Gen2) cathode material during heating and discovered the unstable rock salt phase formed at room temperature due to the overcharge condition.

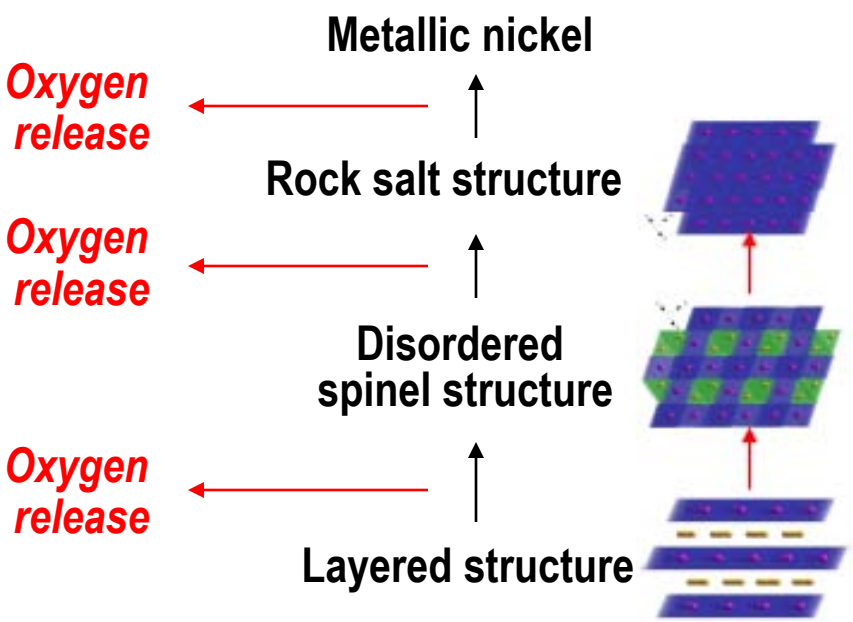
- Identified thermal decomposition mechanisms of charged Gen2 and Gen3 cathode materials and provided ideas how to improve the thermal stability of layered cathode materials.

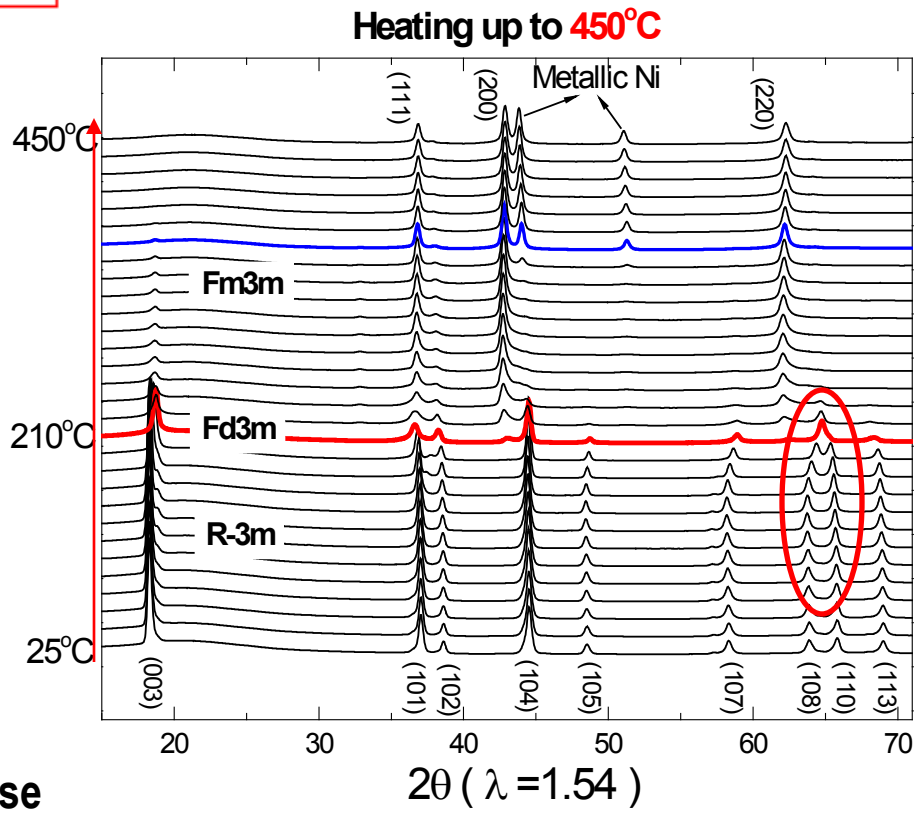
- Completed *in situ* XRD studies of new Cr and F doped $LIMn_{1-x}Cr_xO_{4-y}F_y$ spinel in collaboration with Argonne National Lab.

# TR-XRD study on thermal stability of $Li_{0.33}NiO_2$ with electrolyte (reference)




- $Li_{0.33}NiO_2$
  - ➥ A good road map for the structural changes of nickel-based cathode materials during heating.

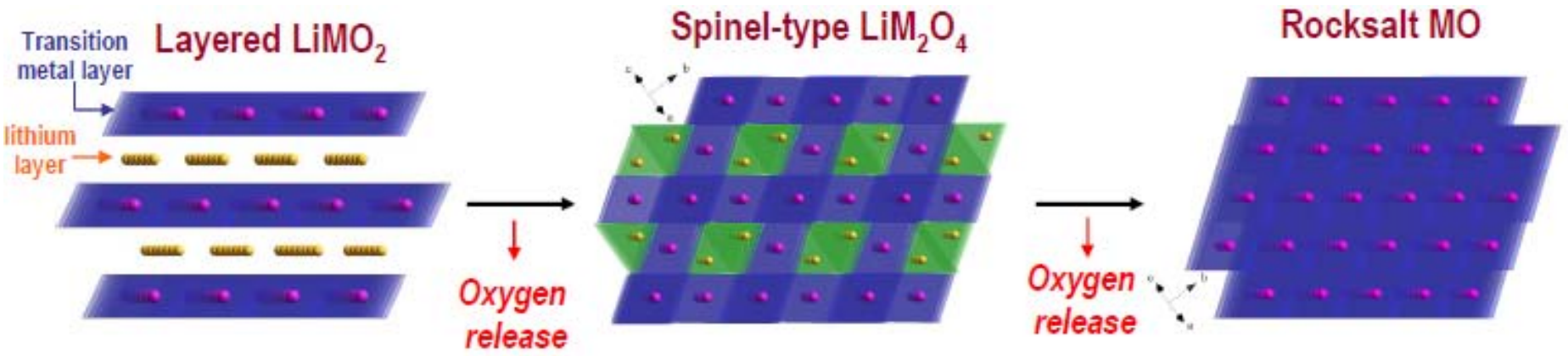



- ➥ $Li_{0.33}NiO_2$ goes through a whole series of phase transitions (i.e., thermal decomposition) when heated up to 450 °C.

# 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!!*

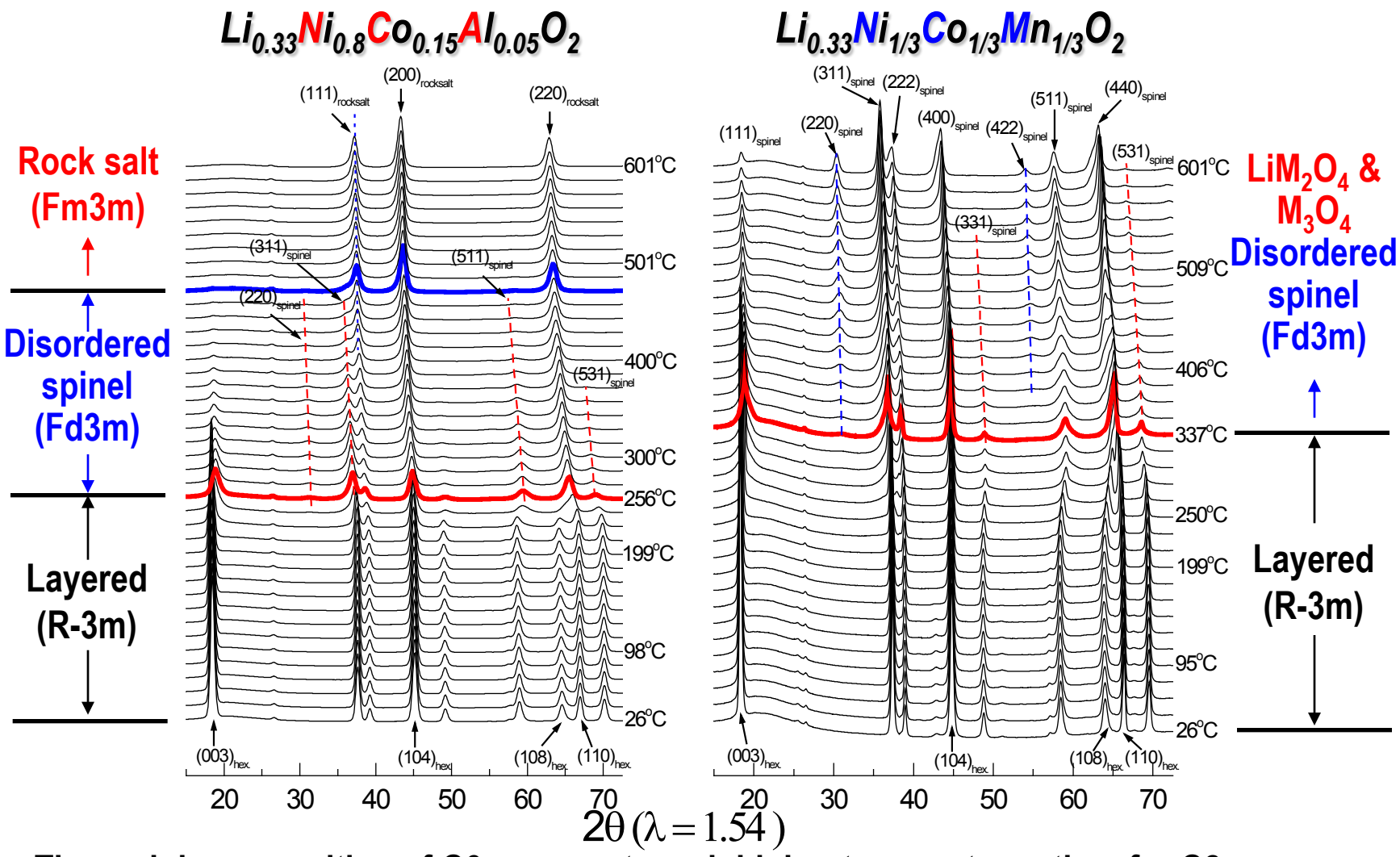
***When x= 0.33 (67% of SOC) in $Li_xMO_2$***

$Li_{0.33}M(^{3.67+})O_2$ (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)*

# TR-XRD of charged $Li_{0.33}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ (G2) and $Li_{0.33}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ (G3) without electrolyte

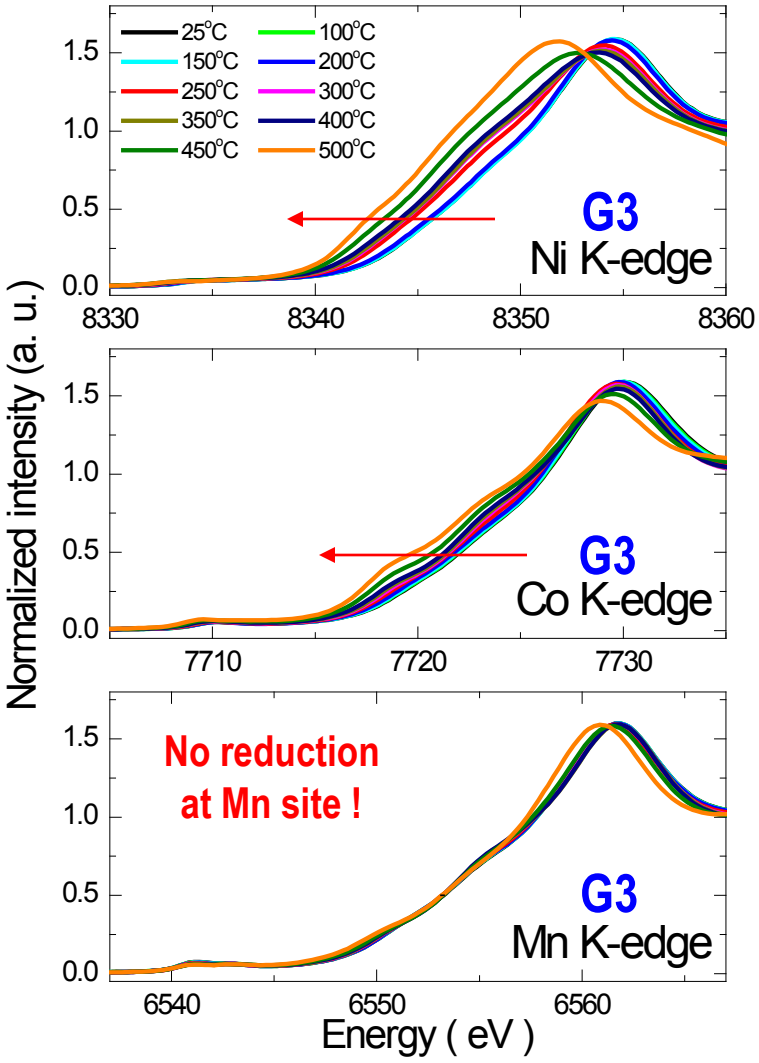


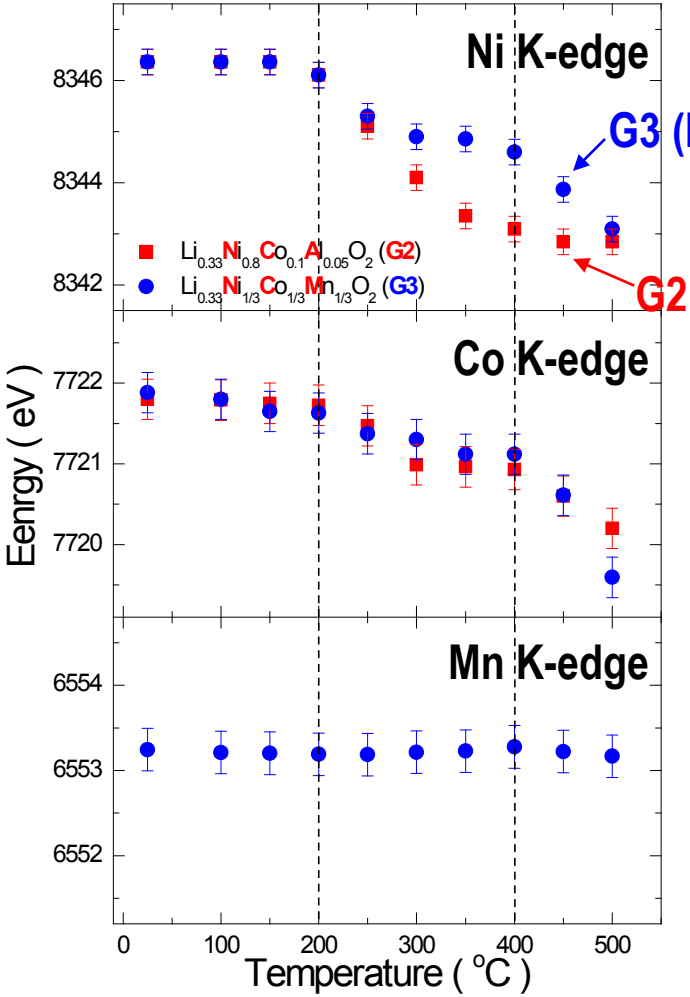

➥Thermal decomposition of G3 occurs at much higher temperatures than for G2.

➥G3 shows much wider temperature range for the disordered spinel region.

⇨ *much better thermal stability of G3!! Why? ☞ In situ XAS and TEM !*

# *In situ* XANES spectra of $Li_{0.33}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ (G2) & $Li_{0.33}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ (G3) during heating



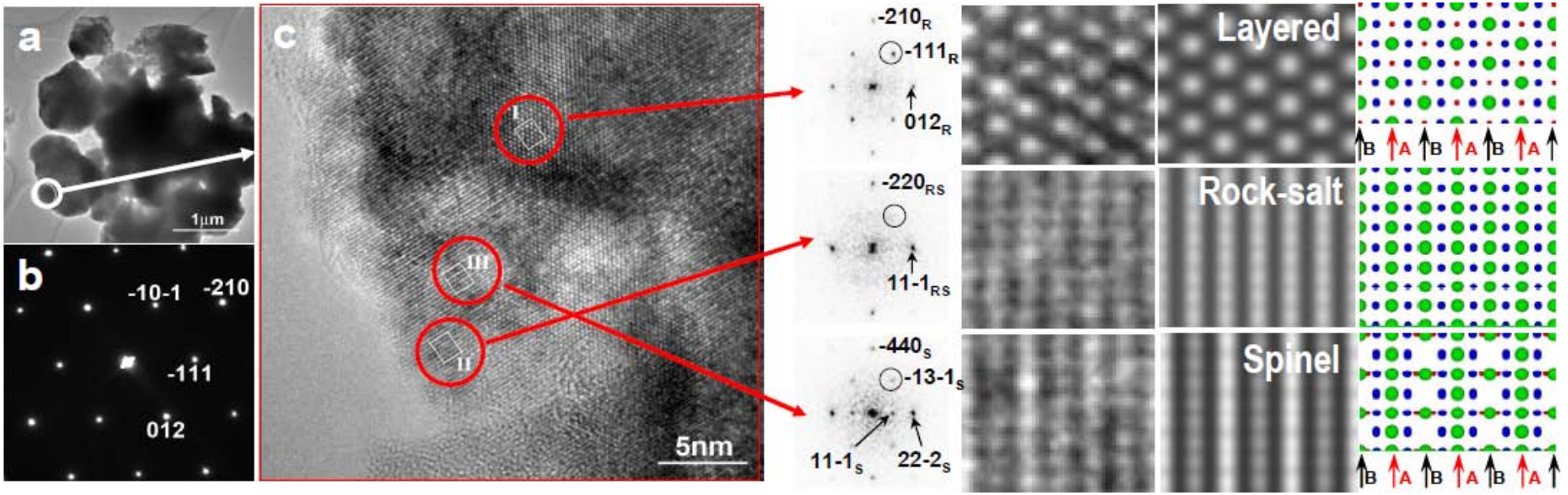




**Edge position at half height (i.e., intensity = 0.5) with heating temperature**

➥During heating, reduction occurs first at Ni and Co sites, but no reduction at Mn site.

➥ Much better thermal stability of G3 attributed to the existence of Mn.

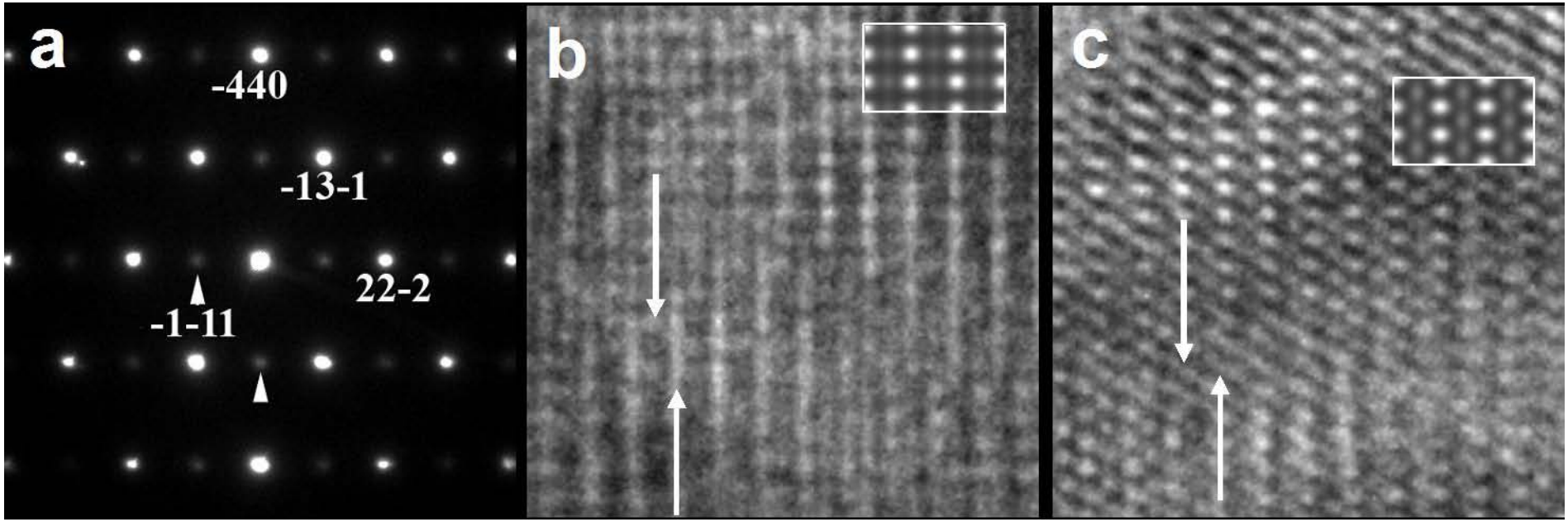
# TEM study of overcharged $Li_{0.27}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ (G2) at room temperature




(a) Bright-field image from overcharged $Li_{0.27}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ particles.
(b) Selected area electron diffraction.
(c) HR-TEM image from the circled area in (a).

- Distinguishable high resolution TEM (HR-TEM) patterns for all three phases, the layered, spinel, and rock-salt structures have been identified, providing a road map for further studies.
- All of the above three structures were observed from the overcharged samples at room temperature, showing the seeding formation of "high temperature phases" (spinel and rock-salt) by overcharge.

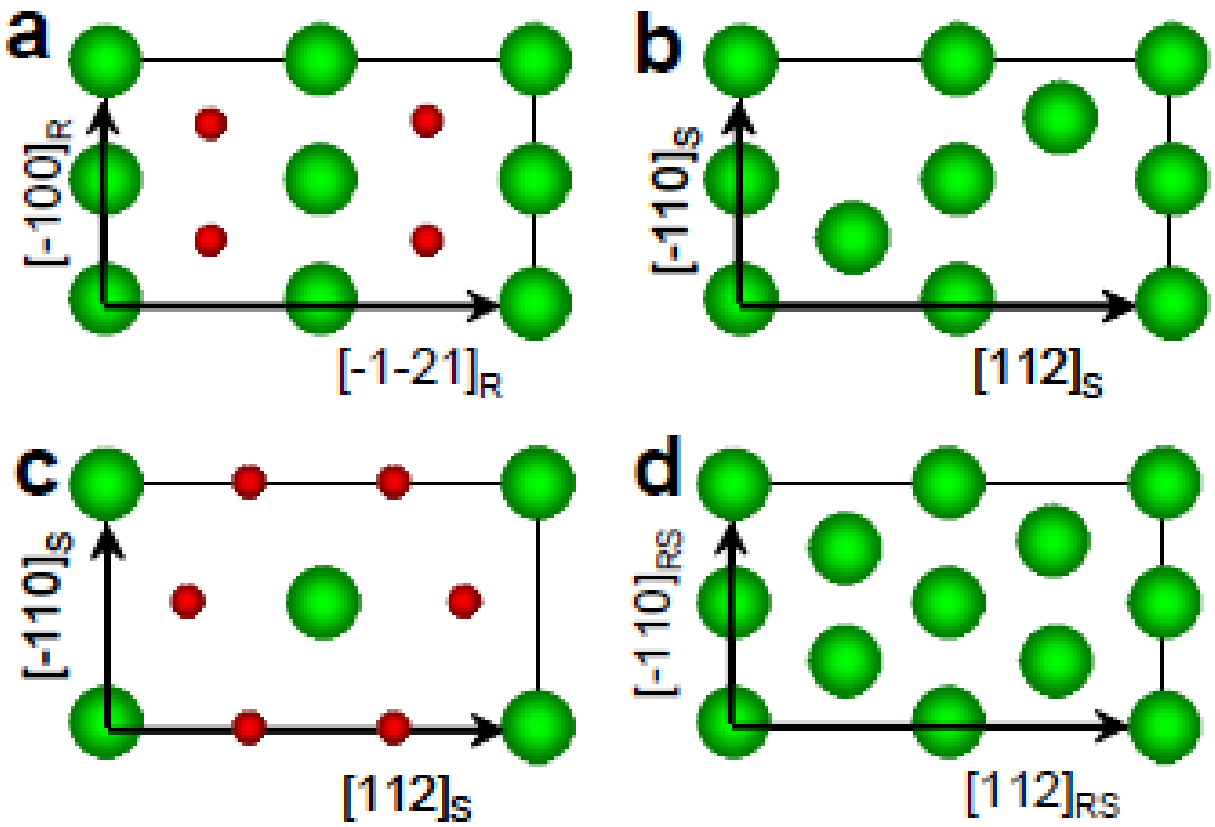
# TEM study of overcharged $Li_{0.27}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ (G2) at room temperature




(a) Sellected area electron diffraction pattern (SAEDP) from the thin area of a as-overcharged particle. The SAEDP can be indexed as [112] zone pattern of the spinel structure.
(b-c) HRTEM images from the thin area of the same particle of (a). The insets in (b) and (c) are the calculated images with thickness=12nm and defocus=3nm, and thickness=16nm and defocus=16nm, respectively. The antiphase domains were observed in both images as indicated by the arrows.

- ➥ In the thin area of the over charged sample, the spinel "high temperature" phase was observed by HR-TEM and confirmed by SAEDP.
- ➥ The antiphase domains were also observed.

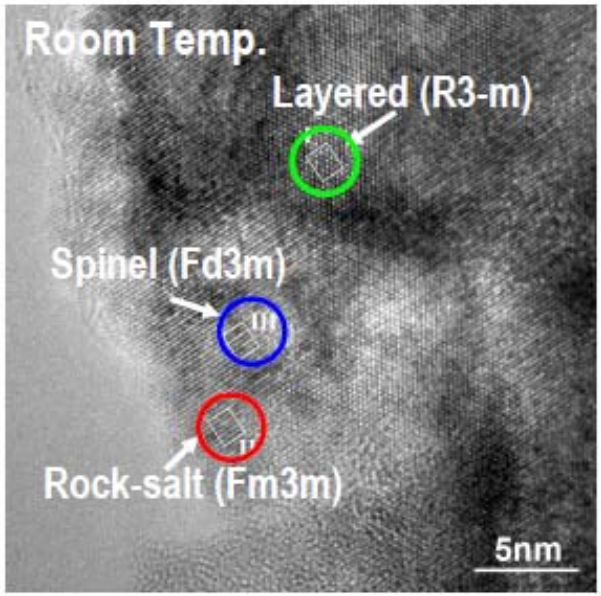
# TEM study of overcharged $Li_{0.27}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ (G2) at room temperature

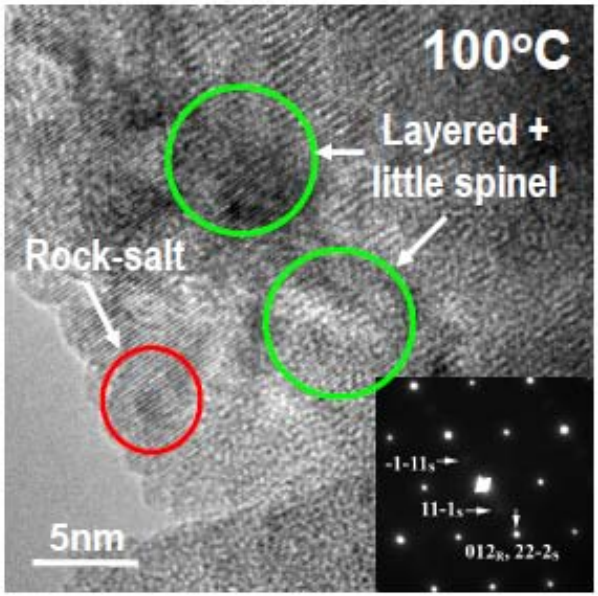


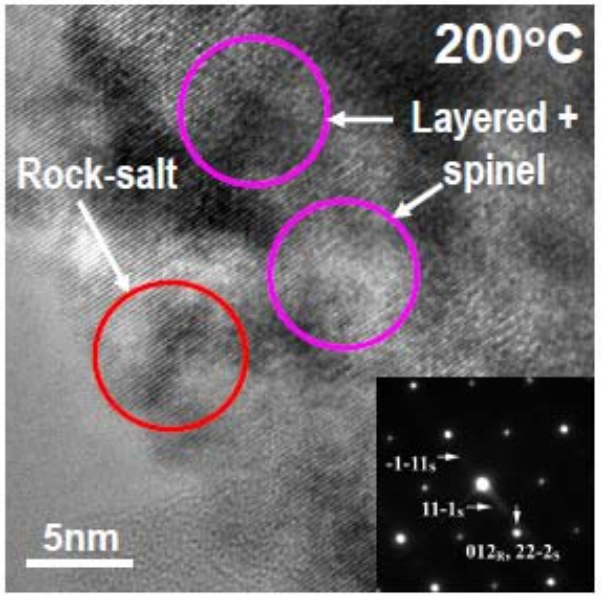

(a) (012) Ni-Li plane of the *layered* structure.
(b, c) (11-1)s Ni-Li plane of the *spinel* structure at (b) z=0 and (c) z=1/6[11-1] position.
(d) $(11\text{-}1)_{RS}$ Ni plane of the *rock-salt* structure.

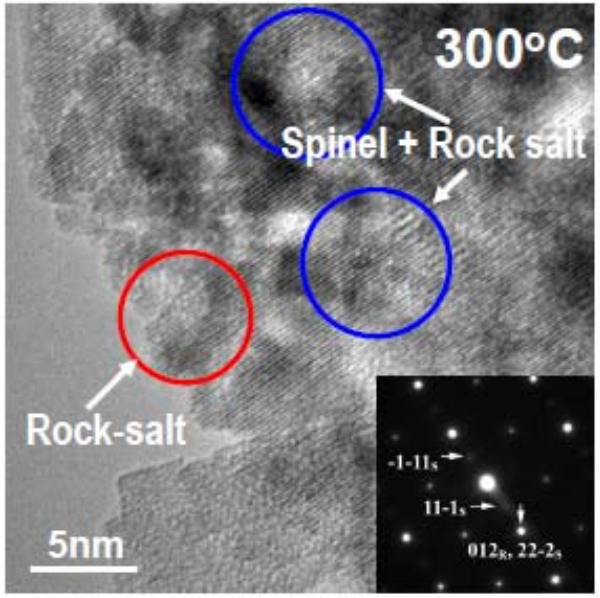
➥ The alternative (11-1) plane stacking with alternative high and low density of transition metal cations is the origin of the alternative bright and dark stripes in HR-TEM image.

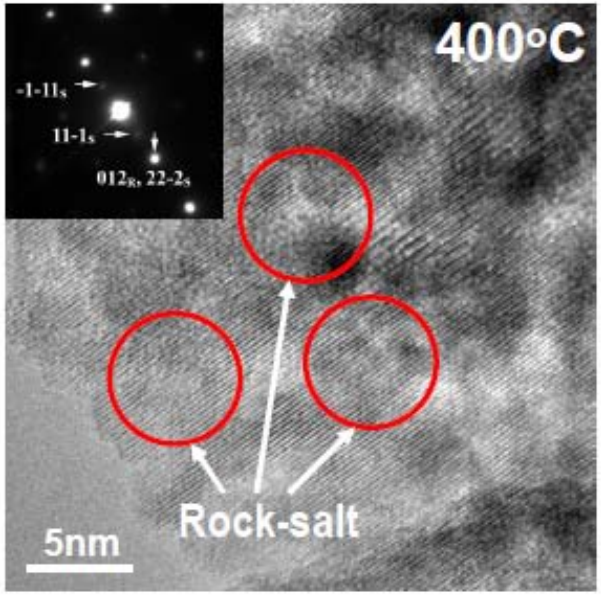
# *In situ* TEM study of charged $Li_{0.27}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ (G2) during heating




➥During heating, the layered structure is changing to the spinel and the spinel is changing to rock-salt structure.

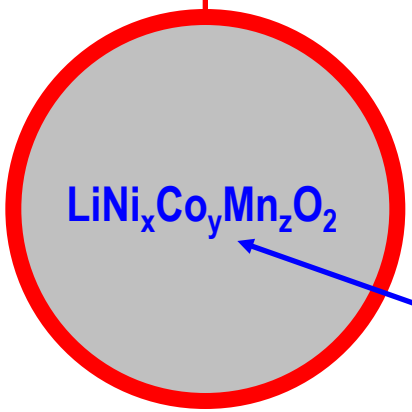
➥*The rock-salt structure continues to grow from the surface and edge into the core parts of the sample* and becomes the dominating phase at 400°C.

# How to improve thermal stability of $LiNi_xCo_yMn_zO_2$ (x+y+z=1) cathode?

For thermal stability (safety) : Mn > Co > Ni

For high capacity (energy) : Ni > Co > Mn

## Proposed approaches to improve the thermal stability of cathode materials



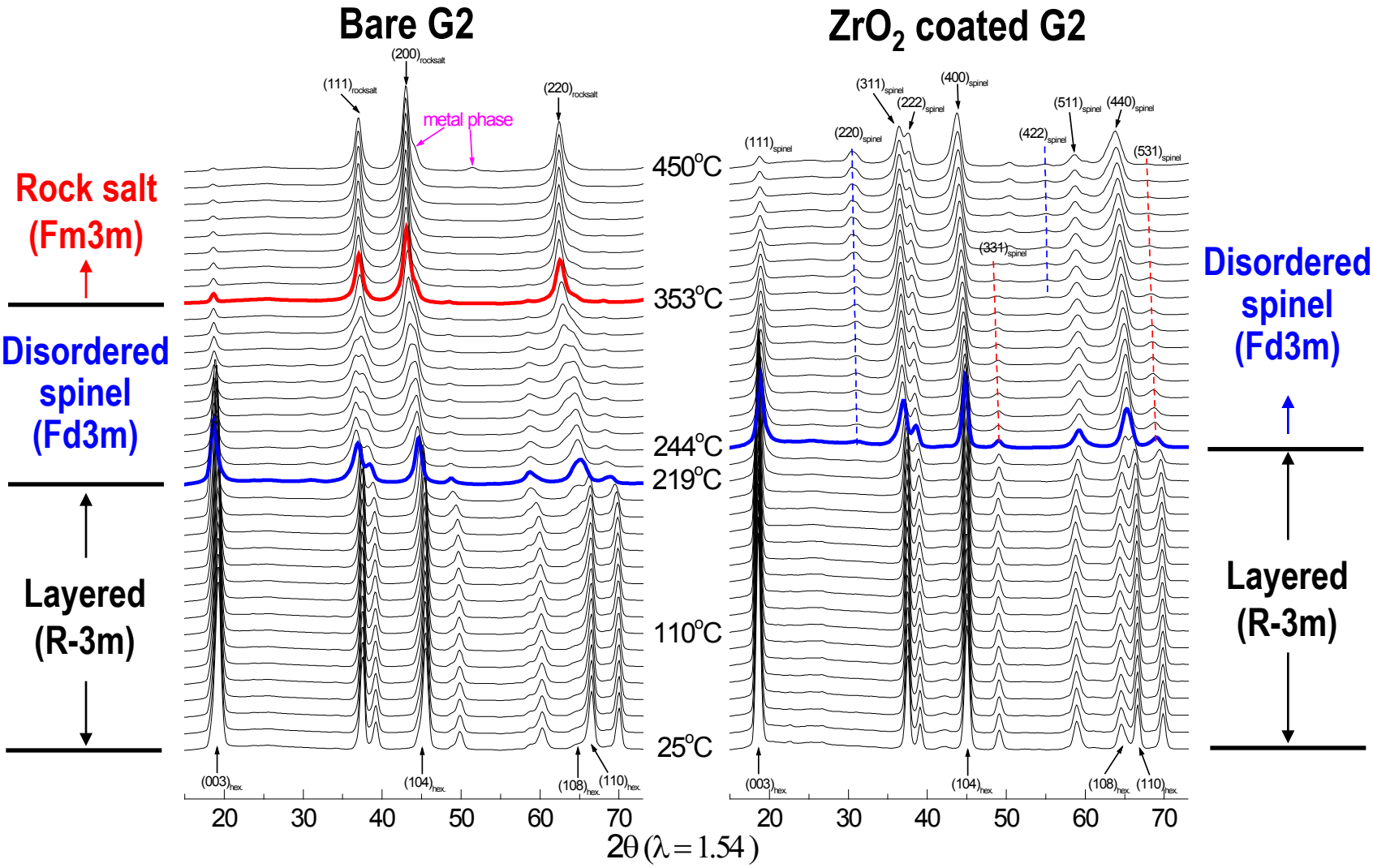

**Surface**

coating with thermally stable materials in nm scale (e.g., $ZrO_2$, $AlPO_4$, $Al_2O_3$ etc)

**Bulk structure**

Doping of structure with structure stabilizing element (Al, Cr etc) and optimization of $LiNi_xCo_yMn_zO_2$ chemistry

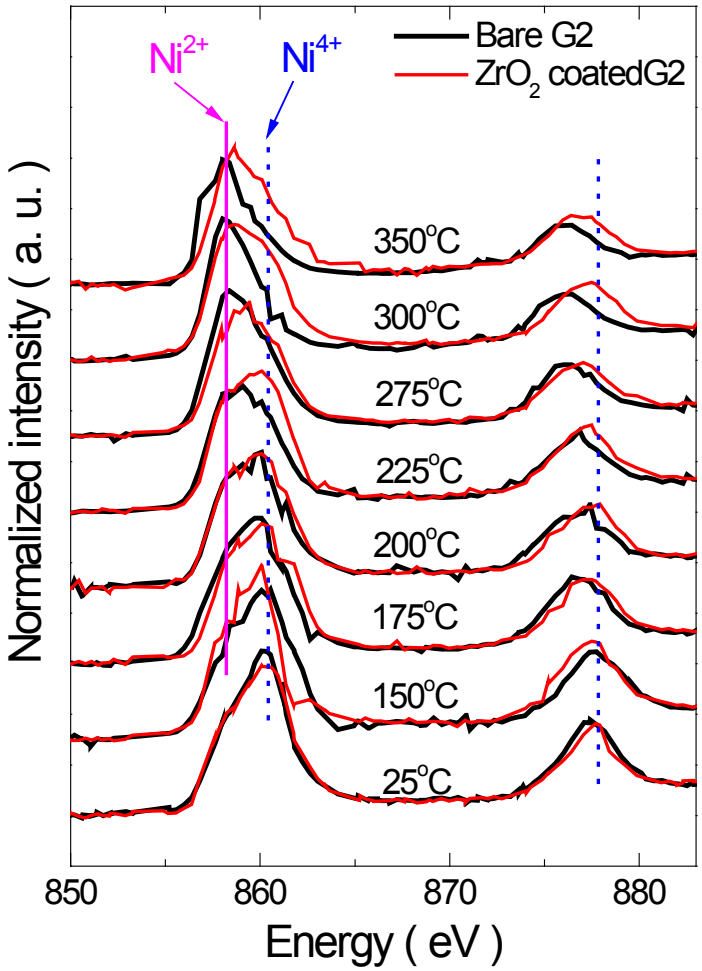
# Preliminary TR-XRD results of bare and $ZrO_2$ coated overcharged $Li_{0.1}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ (G2) during heating (collaboration with KIST, Korea)



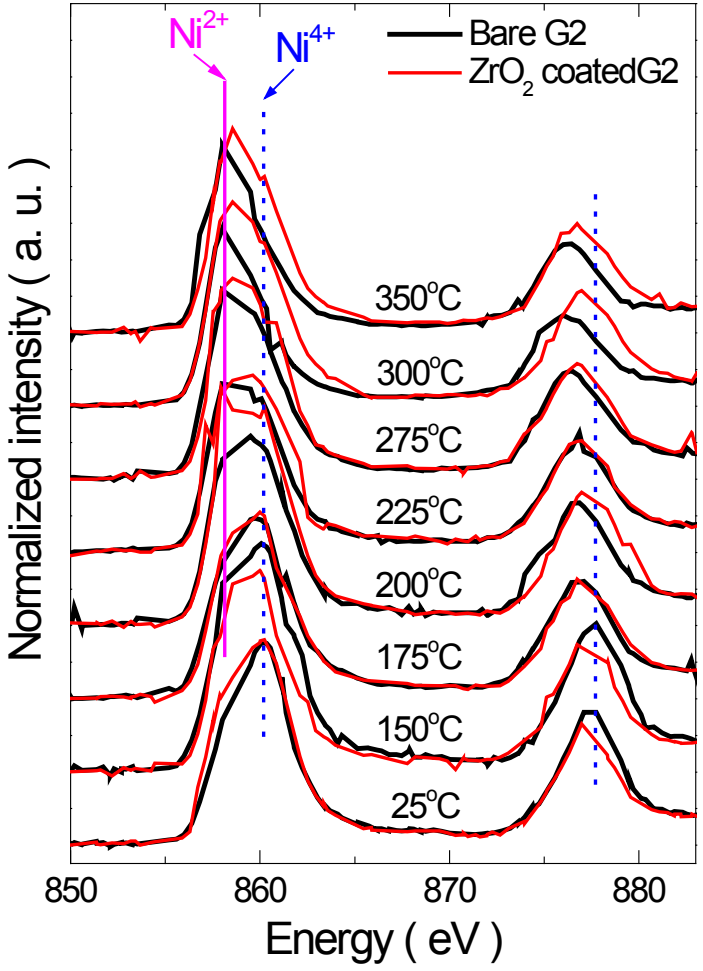

➥ Improved thermal stability of charged G2 cathode by surface modification (i.e., 1wt% $ZrO_2$ coating).

# Preliminary *In situ* soft XAS results of bare and $ZrO_2$ coated charged $Li_{0.33}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ (G2) during heating

## Electron yield: Surface



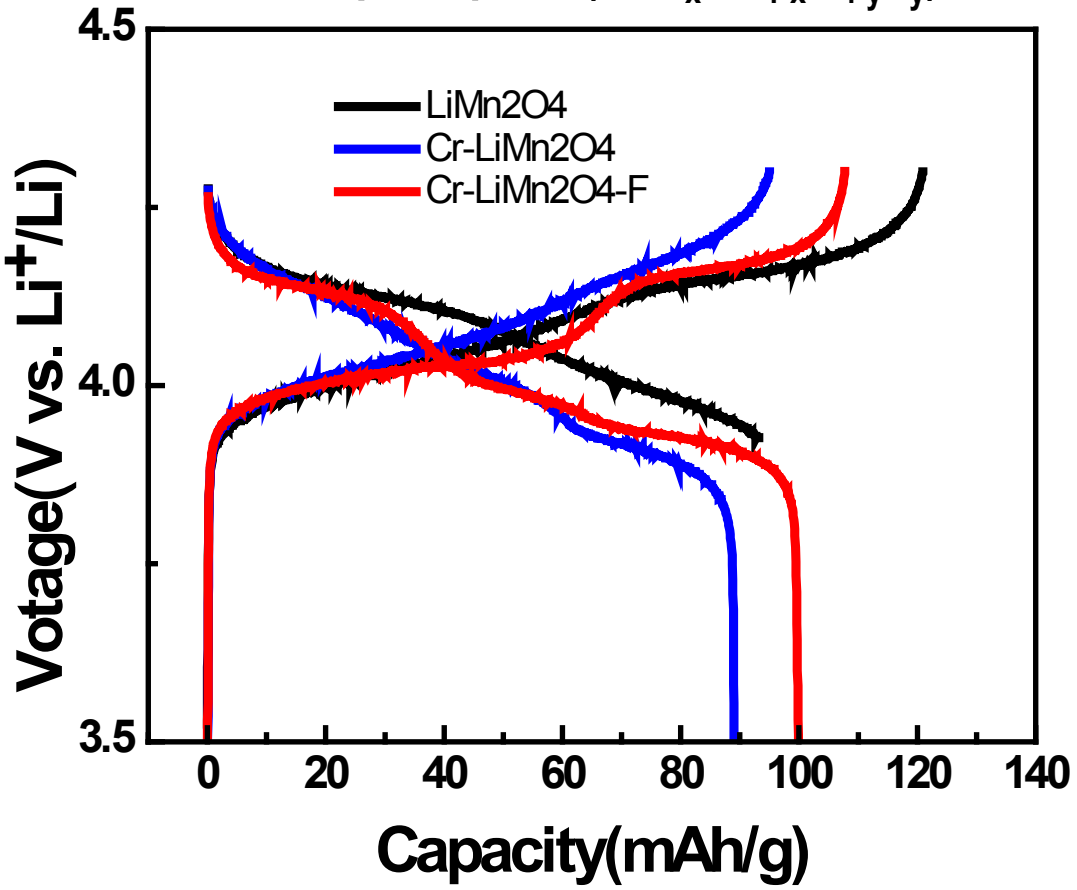

## Fluorescence yield: Bulk




➥ **Improved thermal stability at the surface as well as in the bulk for the charged G2 cathode by surface modification (i.e., 1wt% ZrO2 coating).**

# *In situ* XRD study of Cr and F doped spinel ($LiCr_xMn_{1-x}O_{4-y}F_y$) cathode in collaboration with Argonne National Lab (samples obtained from Tronox)

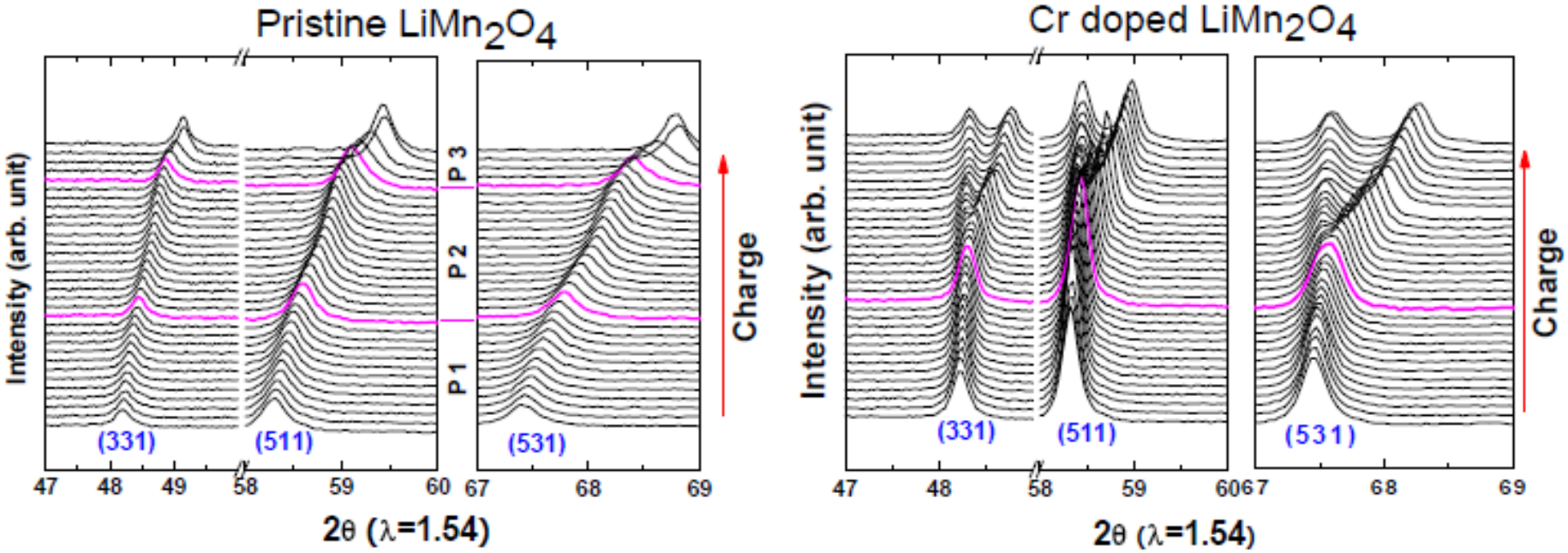
**Charge-discharge curves of Pristine and Cr doped $LiMn_2O_4$, as well as the Cr and F doped spinel ($LiCr_xMn_{1-x}O_{4-y}F_y$) cathode.**




- The Cr doped sample has better thermal stability and cyclability, but lower capacity.
- Both Cr and F doped sample restored most of the lost capacity.

# *In situ* XRD study of Cr and F doped spinel ($LiCr_xMn_{1-x}O_{4-y}F_y$) cathode

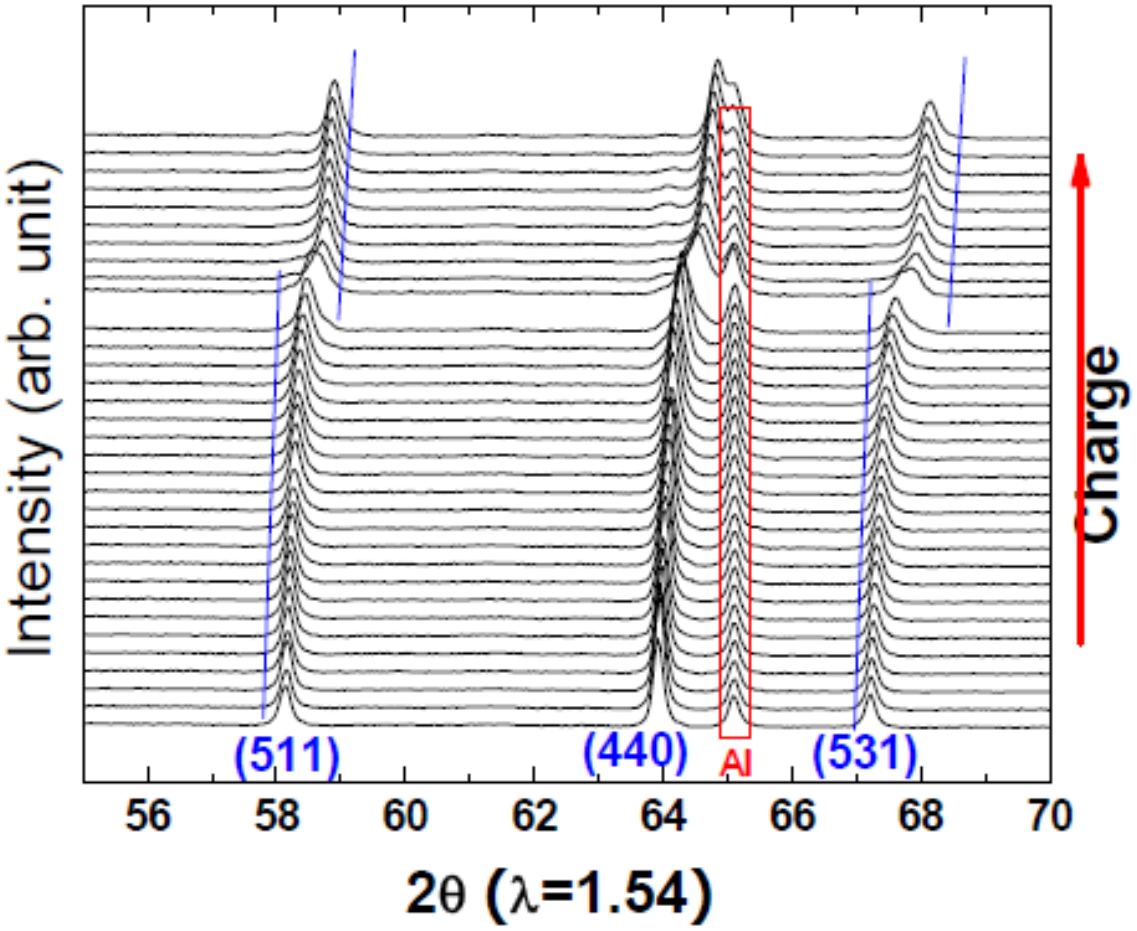
**In situ XRD patterns of Pristine and Cr doped $LiMn_2O_4$ during first charge.**




- Three cubic phases were observed in the pristine LiMn2O4 sample.
- In the Cr doped $LiMn_2O_4$ sample, a large amount of sample was not fully utilized reflected by the very small change of the lattice parameter (the 2 theta angles in the XRD pattern).

# *In situ* XRD study of Cr and F doped spinel ($LiCr_xMn_{1-x}O_{4-y}F_y$) cathode

*In situ* XRD patterns of both Cr and F doped spinel ($LiCr_xMn_{1-x}O_{4-y}Fy$) during first charge.

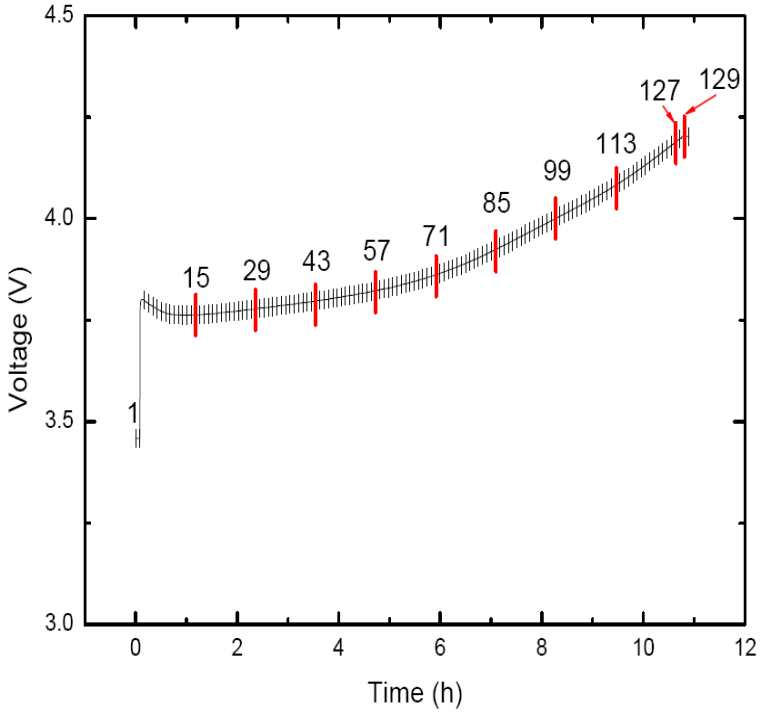



➥ The typical three cubic phases as observed in the pristine $LiMn_2O_4$ sample were restored.

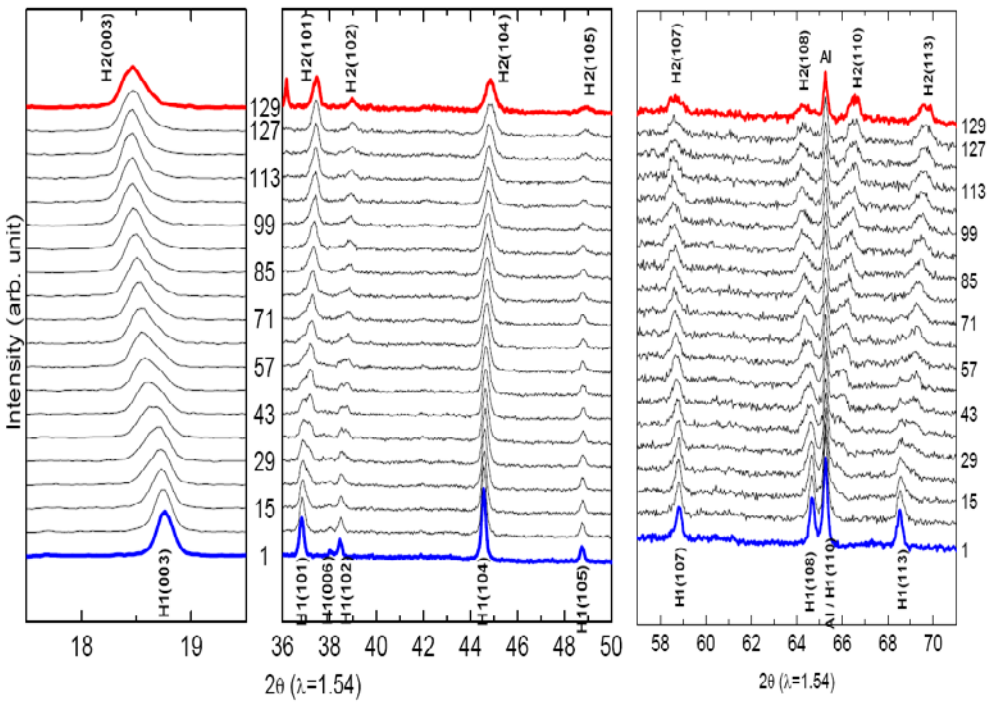
➥ The more detailed relationship between the structural changes and the capacity of this series of cathode materials will be further studied.

# *In situ* XRD and XAS study of high energy nickel based cathode materials In collaboration with *Lockheed Martin Space System*

## Charge Voltage



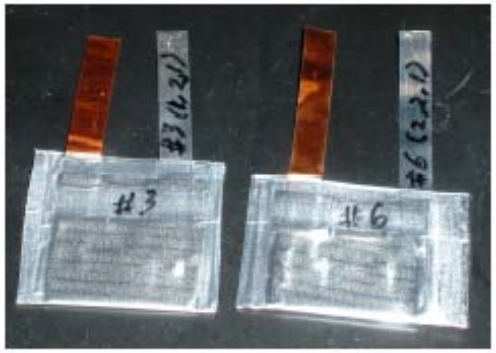

## In-situ XRD



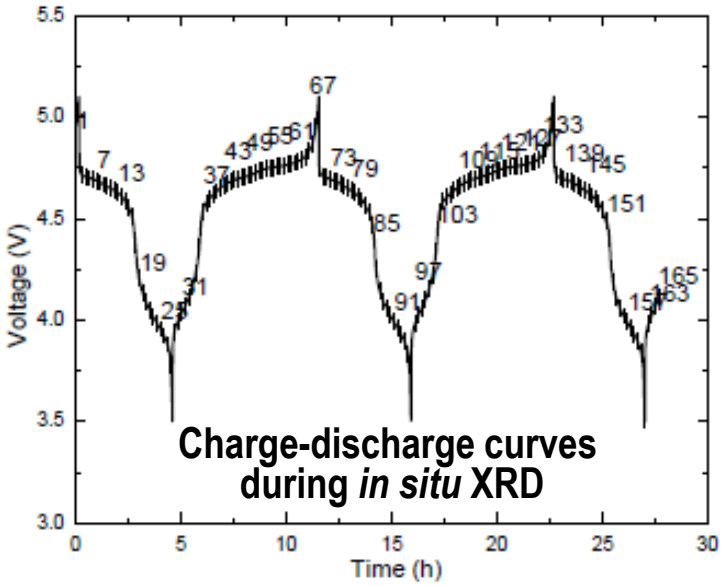

**Note: Data is for cycled cell**

***In situ* XRD and XAS currently underway at Brookhaven Nat'l Lab**

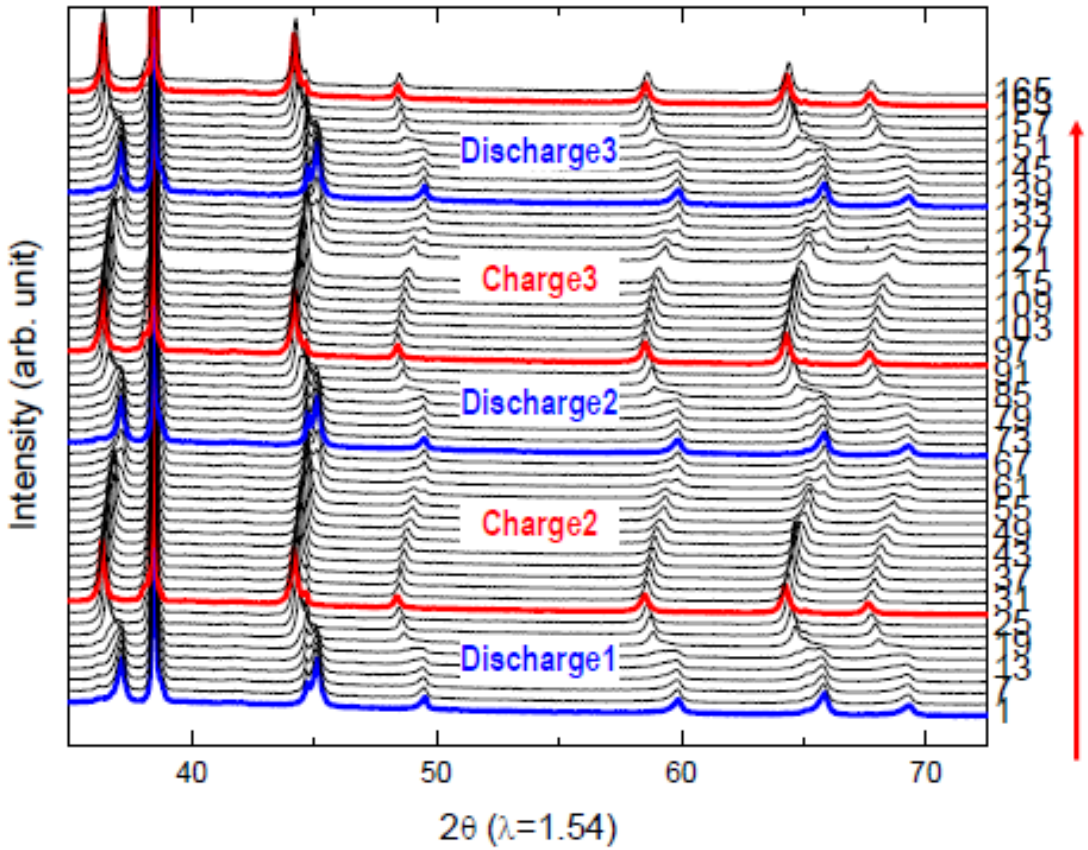
# *In situ* XRD of high voltage spinel during cycling in collaboration with P&G (*Duracell R&D*)




Pouch cells
(Duracell R&D)




Charge-discharge curves during *in situ* XRD




➥ **Providing valuable information about relationship between phase transition behavior and cycle life of high voltage spinel cathode materials.**

# Collaborations with Other Institutions and Companies

- **Argonne National Lab. (ANL)**
  - ➥ *In situ* XRD study of Cr and F substituted spinel ($LiCr_xMn_{1-x}O_{4-y}F_y$) cathode material.
- **Oakridge National Lab. (ONL) & University of Tennessee**
  - ➥ *In situ* XRD technology development for Li-ion battery material research at NSLS.
- **Beijing Institute of Physics**
  - ➥ Olivine structured $LiMPO_4$ 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.
- **Hydro-Québec (IREQ)**
  - ➥ Olivine structured $LiMPO_4$ cathode materials.
- **Duracell (P&G)**
  - ➥ *In situ* XRD and XAS study for high voltage spinel cathode material R&D.
- **Lockheed Martin Space System**
  - ➥ *In situ* XRD and XAS study for high energy nickel based cathode materials.
- **TOYOTA Research Institute of North America (will be started)**

# Planned work for *FY 2010* and *FY2011*

- Complete the *in situ* TEM studies on the thermal stability of layer structured Gen2 and Gen3 cathode materials.
- Thermal stability study of surface modified (e.g., surface coating using $ZrO_2$, $AlPO_4$, and $Al_2O_3$ etc) Gen2 and Gen3 cathode materials using TR-XRD *and in situ* hard and soft XAS techniques during heating.
- *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.
- Apply this new techniques 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.
- Expand the collaborative research with US and International academic research institutions and US industrial partners.
- Provide technical support to the development of setting up Li-ion battery manufacturing in the US.

# Summary

- Thermal decomposition mechanism of the charged $Li_{1-x}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode material during heating has been studied using combined *in situ* TEM and hard & soft XAS techniques.
- The overcharged $Li_{1-x}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ particle at room temperature has core-shell structure with the rhombohedral structure in the core, the spinel structure in the shell and the rock-salt structure at the surface. By heating the sample in the microscope, the spinel phase propagates toward the core of the particle while the rock-salt phase grows at the shell of the spinel phase. This result agrees quite well with the previous *in situ* soft XAS result during heating which showed that the thermal decomposition occurs at the surface much earlier than in the bulk.
- Combined *in situ* TEM and hard & soft XAS study during thermal decomposition (i.e., heating) clearly shows where and how the new structure nucleated and propagated with high location specification and special resolution as well as the structural changes at the surface and in the bulk in an elemental selective way. This *in situ* study provides new insight into the thermal decomposition mechanism of charged cathode materials and valuable information how to design thermally stable cathode materials of lithium ion battery for the vehicle applications.

# Summary (Cont'd)

- The preliminary *In situ* XRD studies of Cr and F doped spinel provide structural change origin for the decreased capacity due to the Cr doping and the restored capacity due to F doping.

- *In situ* XRD and XAS techniques developed at BNL are being used in collaboration with scientists at national Labs ANL, ORNL, PNNL, as well industrial partners like Duracell , Yaderney,  and Lockheed Martin Space System.