



# Advanced *in situ* Diagnostic Techniques for Battery Materials

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Project ID: ES059

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# Overview

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## Timeline

- ▣ **Start: 10/01/2012**
- ▣ **Finish: 09/30/2016**

## Budget

- ▣ **Funding received in FY13**  
**DOE: \$415k**
- ▣ **Funding received in FY14**  
**DOE: \$415k**

## 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

- University of Massachusetts at Boston
- Argonne National Lab. (ANL)
- Pacific Northwest National Lab. (PNNL)
- Beijing Institute of Physics
- Korea Institute of Science and Technology
- GM R&D Center
- Oakridge National Lab. (ORNL)
- SUNY Stony Brook
- Korean Institute of Science and Technology (KIST)
- Beijing Institute of Physics
- Hydro-Québec (IREQ)

# Project Objectives

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

- ↳ to establish and investigate the structural origin of thermal instability of various cathode materials, especially the high voltage  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  materials
- ↳ to search new approaches on how to improve the thermal stability of cathode materials including surface modification techniques and the effectiveness of them.
- ↳ 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, voltage and power fading.***

- ↳ to develop *in situ* diagnostic techniques with surface and bulk sensitivity for studying the capacity, voltage, and powder fading mechanisms of Li-ion battery.
- ↳ to establish and investigate the capacity and power fading mechanisms of various cathode materials, especially the layer structured Li and Mn rich materials

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

# Milestones

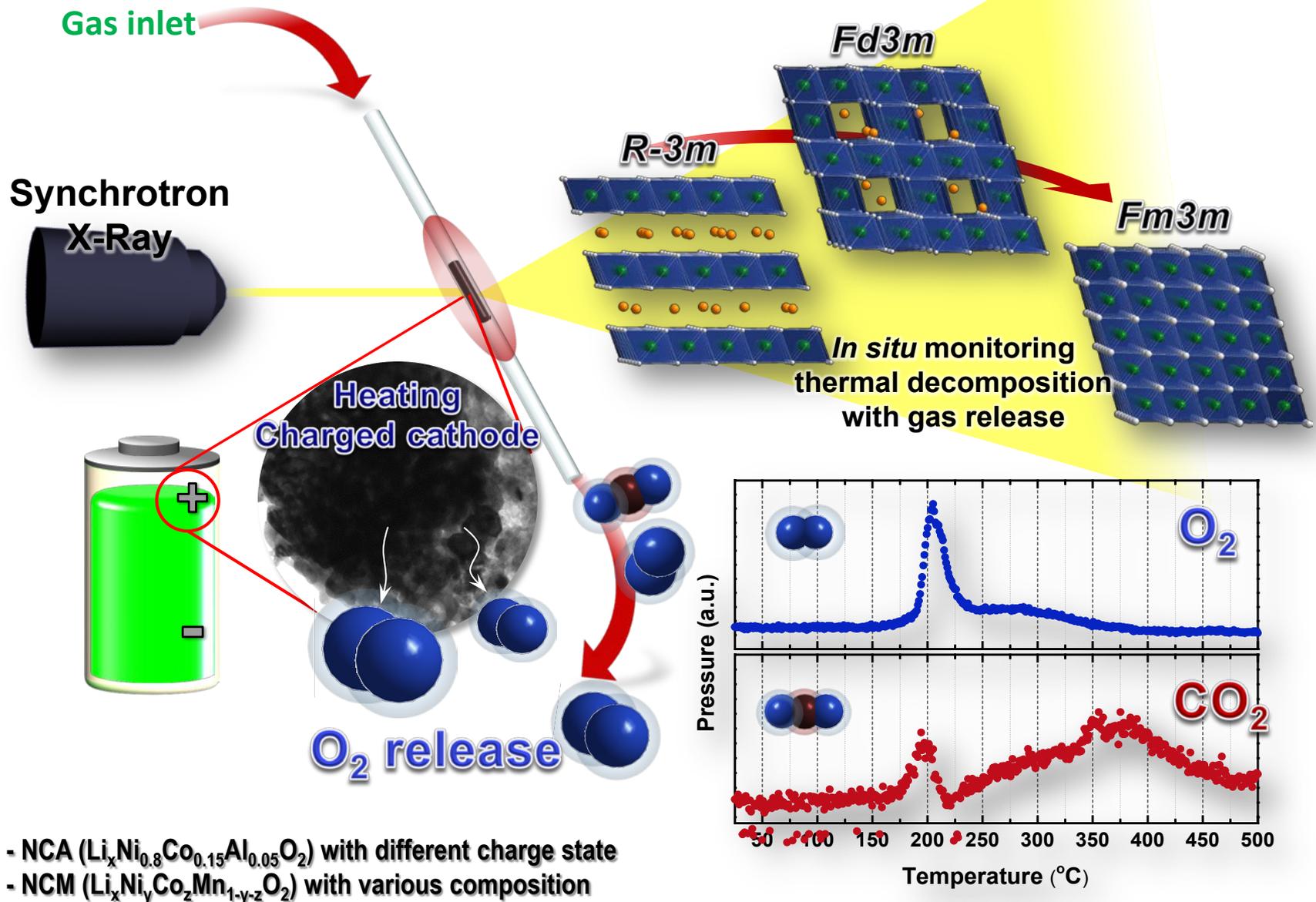
Month/Year	Milestones
Sep/13	Complete the <i>in situ</i> time resolve XRD and XAS studies of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode material with ordered ( $P4_332$ ) and disordered ( $Fd-3m$ ) spinel structure during heating. ↪ <b>Completed.</b>
Dec/13	Complete the studies of the kinetic properties of $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.1}\text{Mn}_{0.55}\text{O}_2$ high energy density cathode materials during constant current charge using x-ray absorption spectroscopy. ↪ <b>Completed.</b>
Mar/14	Complete the development of using quick x-ray absorption spectroscopy technique to study the kinetic properties of $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.1}\text{Mn}_{0.55}\text{O}_2$ high energy density cathode materials during constant voltage charge. ↪ <b>Completed.</b>
Jun/14	Complete the in situ x-ray diffraction studies of Fe substituted high voltage spinel during charge-discharge cycling. ↪ <b>On schedule.</b>
Sep/14	Complete the in situ x-ray absorption studies of Fe substituted high voltage spinel during charge-discharge cycling. ↪ <b>On schedule.</b>

# Approaches

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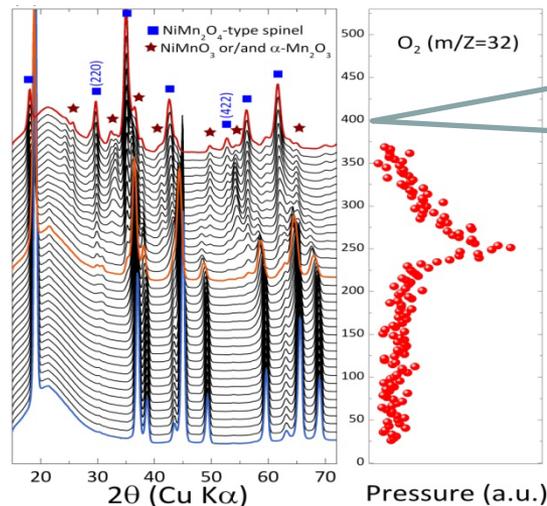
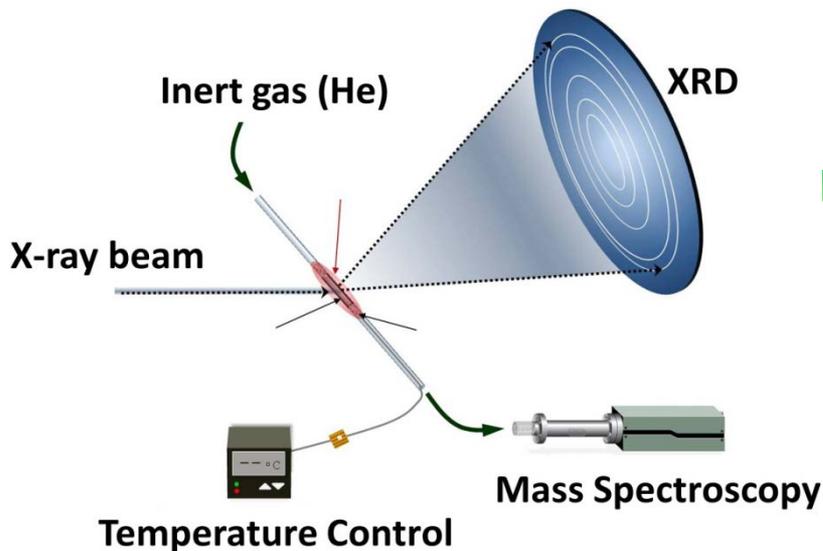
- A combination of **time resolved X-ray diffraction (TR-XRD)** and **mass spectroscopy (MS)**, together with *in situ* **soft and hard X-ray absorption (XAS)**, *in situ* **transmission electron microscopy (TEM)** techniques during heating to study the **thermal stability** of the electrode materials.
- 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) electrode materials during charge-discharge cycling for **longer cycling life** of Li-ion batteries.
- Using quick x-ray absorption spectroscopy technique to study the kinetic properties of  $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.1}\text{Mn}_{0.55}\text{O}_2$  high energy density cathode materials during constant voltage charge for **high rate capability** of Li-ion batteries.
- Extended collaboration with other US and international academic institutions and US industrial partners.

# Approach: using combined time-resolved XRD and mass spectroscopy



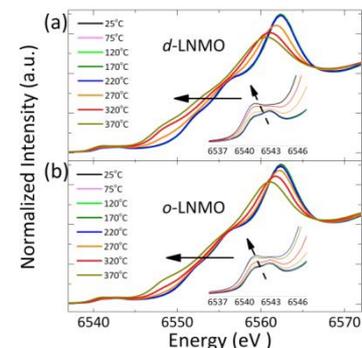
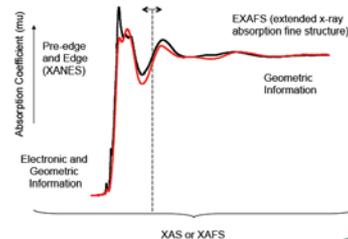
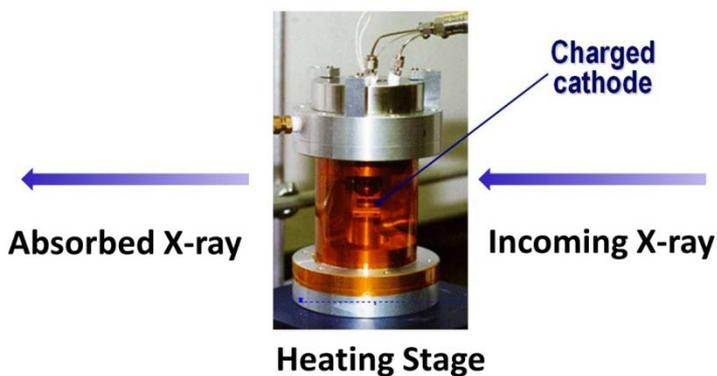
# In Situ Techniques to Address the Mechanism

## *In situ* XRD

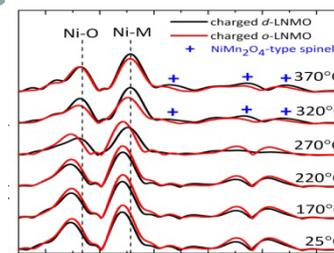


**Crystal Structure and Gas Evolution**

## *In situ* XAS



**Electronic Structure and Local Environment**



S.Bak et al, *Chem. Mater.* 2013

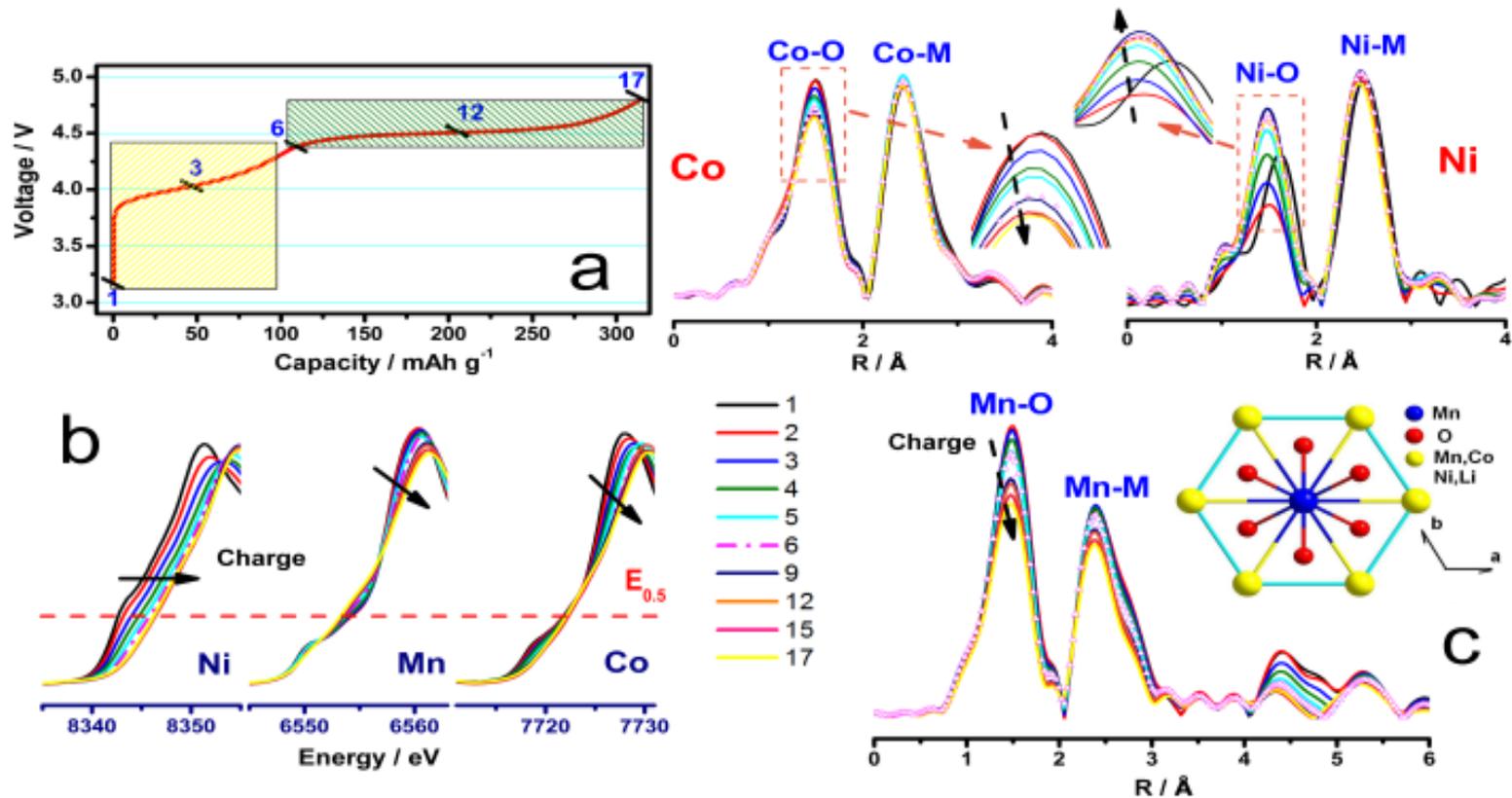
K.Nam et al, *Adv. Funct. Mater.* 2013

# Technical Accomplishments

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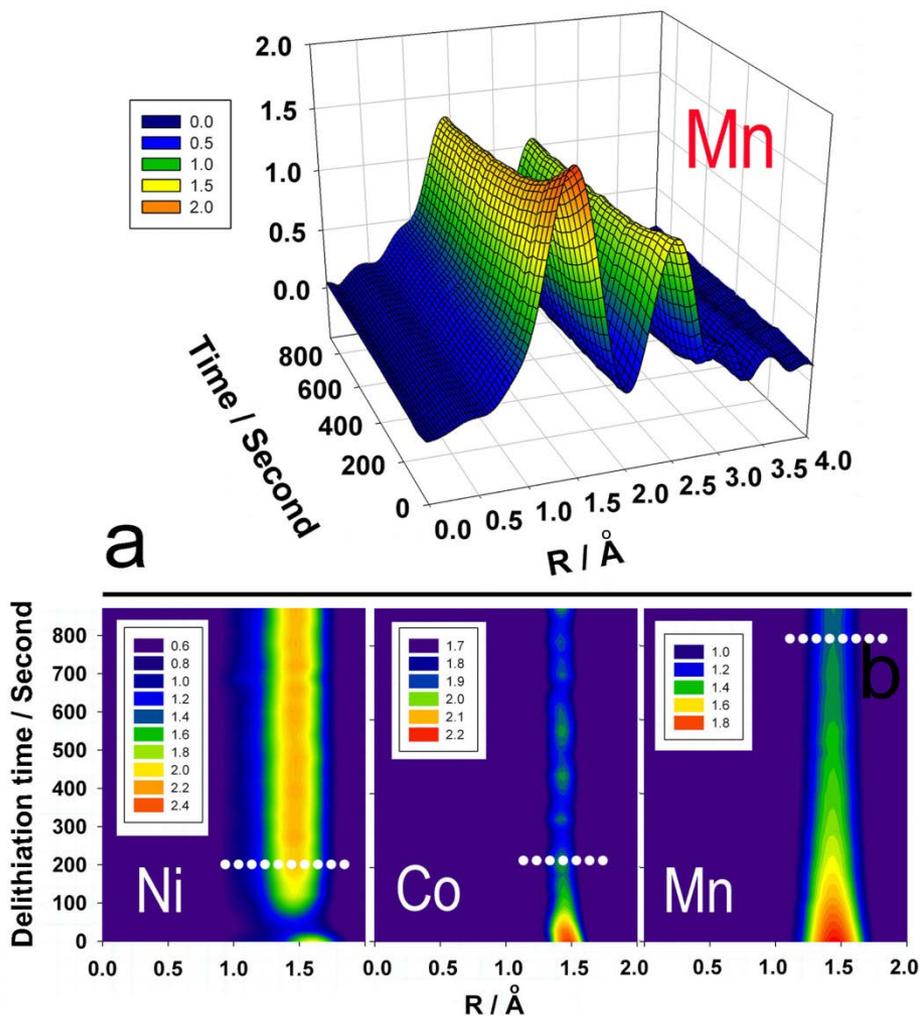
- By collaborating with Dr. Huiming Wu and Dr. Khal Amine, the elementally related delithiation kinetic behaviors studied by time-resolved XAS technique during 5V constant voltage charging show that the lithium extraction with a concomitant oxidation of  $\text{Ni}^{2+}$  to  $\text{Ni}^{4+}$  has fast reaction kinetic which is not much negatively affected by the irreversible structure change of the  $\text{Li}_2\text{MnO}_3$  component after initial delithiation process. In contrast much poorer delithiation kinetic was revealed in Mn region during and after the activation process.
- By collaborating with ANL, R&D Center of GM, and other collaborators, carried out diagnostic studies of new high energy density  $\text{Li}_2\text{MnO}_3\text{-LiMO}_2$  (M=Ni, Co, Mn, LMR-NCM) cathode materials. Some important structural origins of the voltage and capacity fading mechanism has been obtained.
- Using combination of time-resolved XRD and mass spectroscopy, it was found that Ordered  $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$  demonstrated better thermal stability than disordered counterpart. This can be explained by less rock salt impurity and ordering between Ni/Mn.

# In situ XAS spectra of $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.1}\text{Mn}_{0.55}\text{O}_2$ during constant current charging



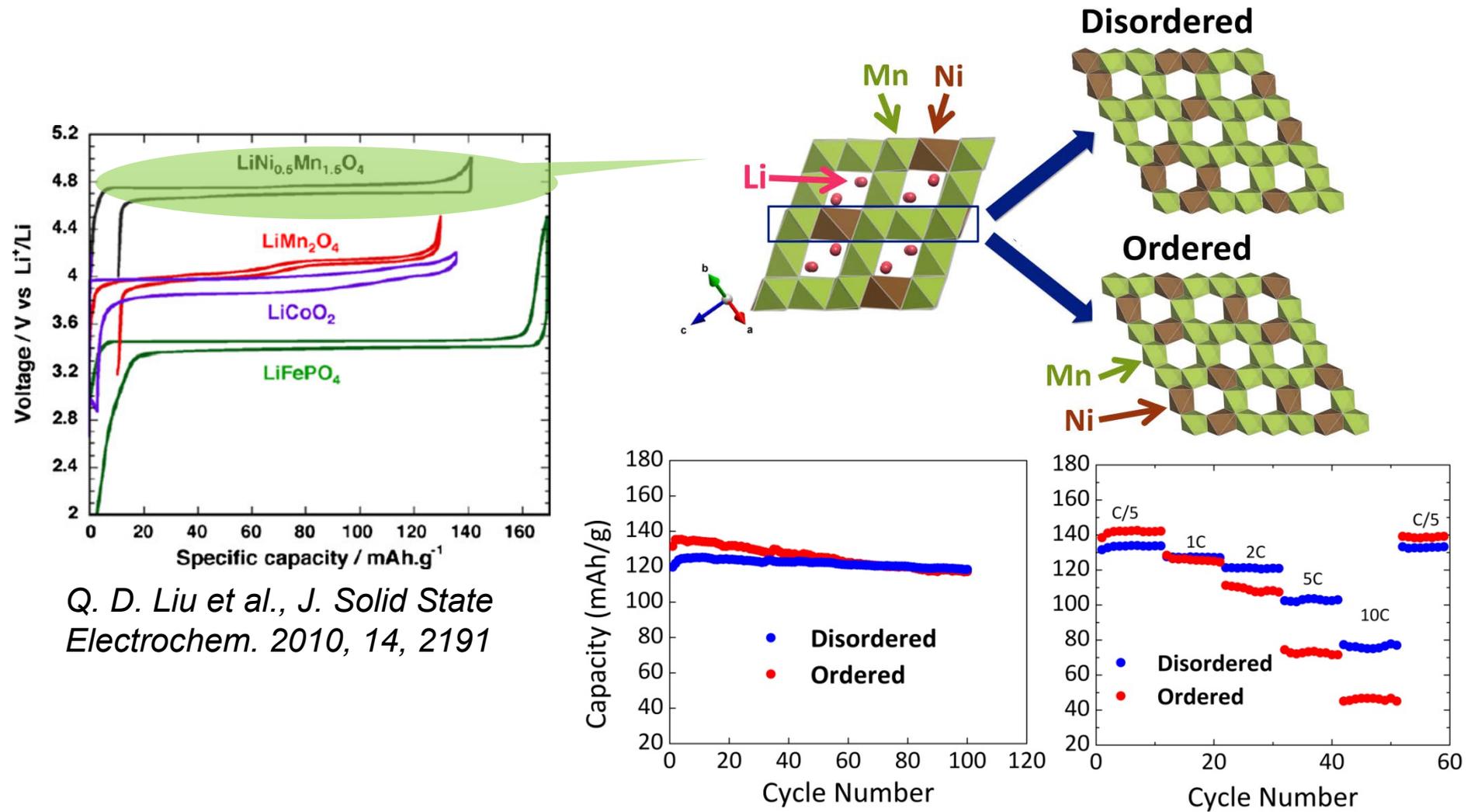
(a) The first charging curve of during *in situ* XAS experiment (under constant current), selected XAS scan numbers are marked on the charge curves; (b) Normalized XANES spectra and (c) Magnitude of Fourier transformed Mn, Co and Ni K-edge spectra of  $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.1}\text{Mn}_{0.55}\text{O}_2$  collected during initial charge. Inset is the schematic view of the coordination environment around transition metal ions.

# Time resolved XAS spectra of $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.1}\text{Mn}_{0.55}\text{O}_2$ during constant voltage charging at 5V



XAS spectra of  $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.1}\text{Mn}_{0.55}\text{O}_2$  during constant voltage charging at 5V. Ni, Co, Mn reacted simultaneously which was recorded by a time-resolved XAS technique. (a) Magnitude of Fourier transformed Mn K-edge spectra of  $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.1}\text{Mn}_{0.55}\text{O}_2$ ; (b) Projection view of corresponding Ni-O, Co-O, Mn-O peak magnitudes of the Fourier transformed K-edge spectra as functions of charging time. These results show that Mn sites have a much poorer reaction kinetics both before and after initial "activation" of  $\text{Li}_2\text{MnO}_3$ , comparing with Ni and Co, providing valuable guidance in designing various Li-rich layered materials with desired balance of energy densities and rate capabilities for different applications.

# Structure and performance of disordered and ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$

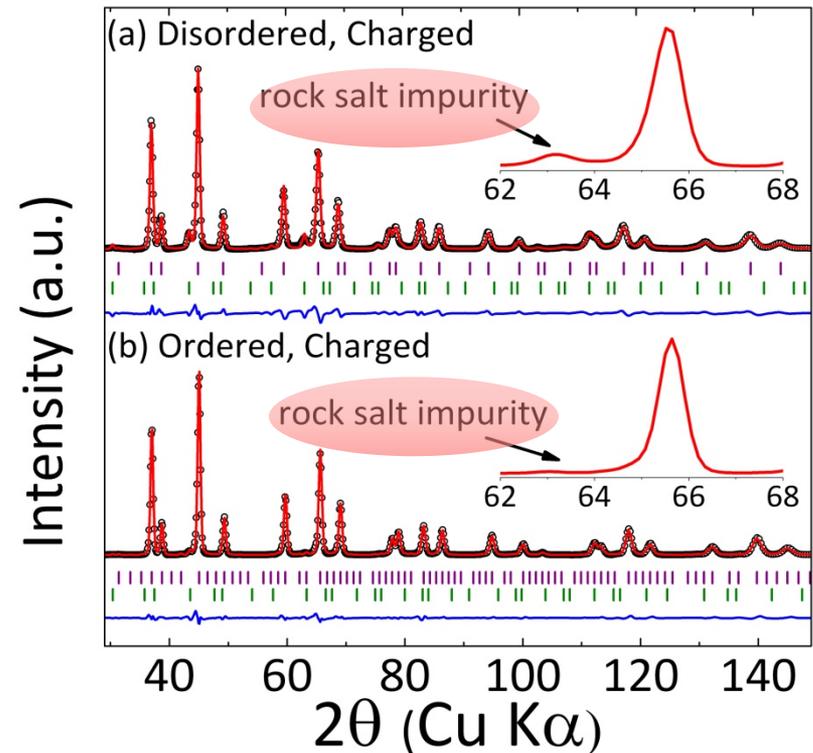
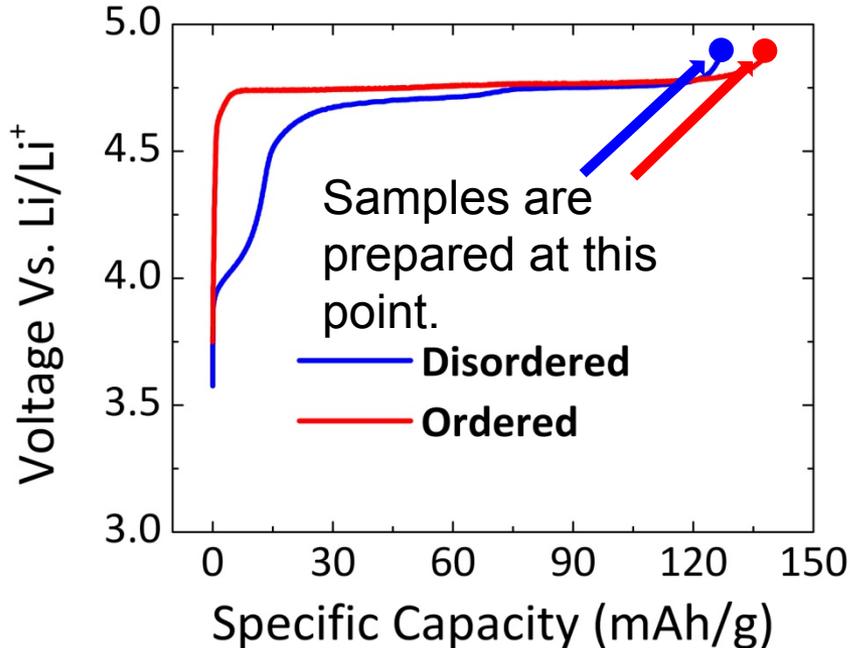


Q. D. Liu et al., *J. Solid State Electrochem.* 2010, 14, 2191

So disordered and ordered  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  differ in electrochemical performance.  
How about their **thermal stability**?

# In Situ XRD-MS I: Sample Preparation

1. Samples are prepared at charged state
2. XRD of prepared samples

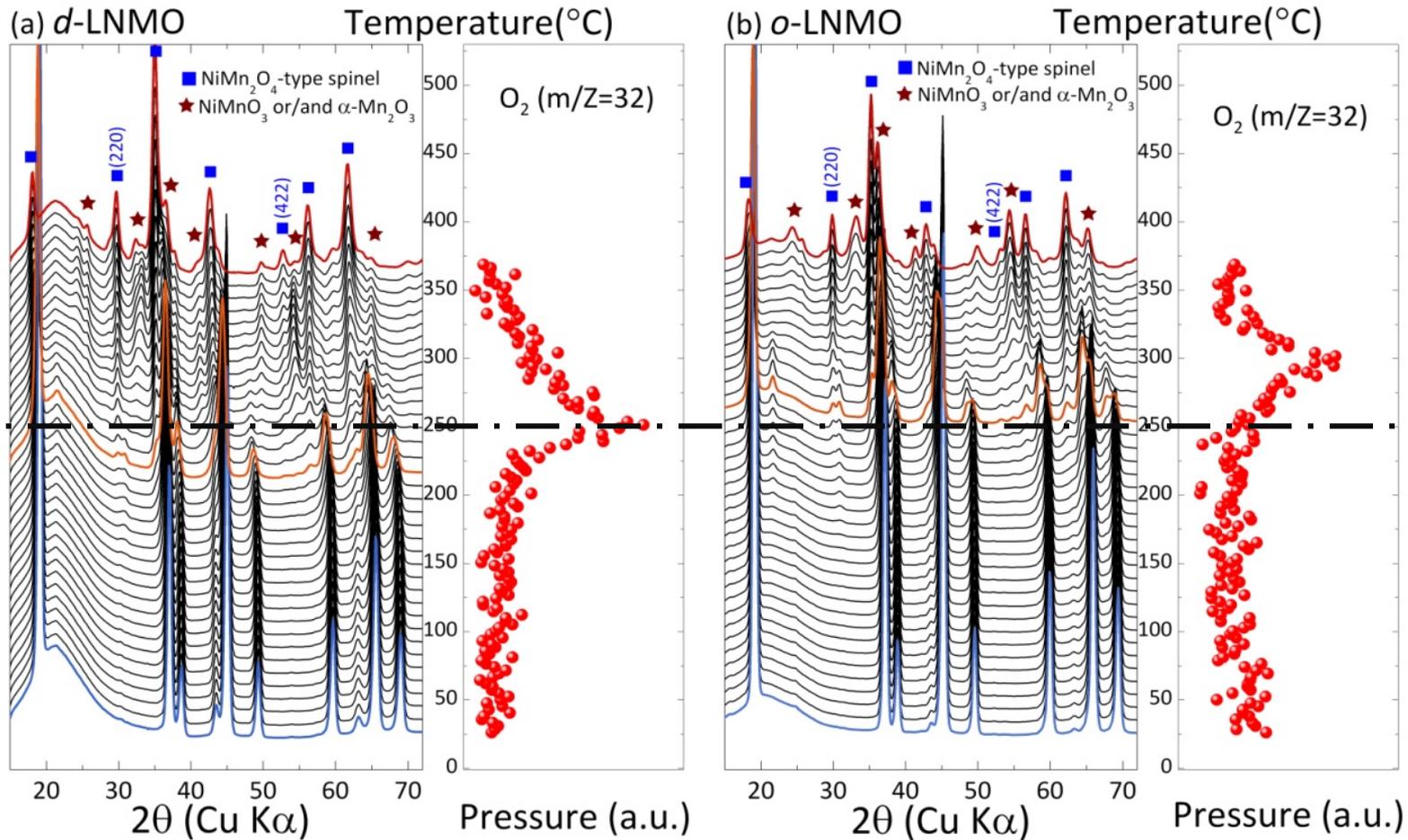


## Rock salt impurity

1. Ni-rich (Ni exists in  $\text{Ni}^{2+}$  form);
2. Formed from high temperature calcination and very difficult to totally eliminate;
3. Disordered sample has more rock salt impurity (around 5% Vs. 1%);
4. It's electrochemically inactive.

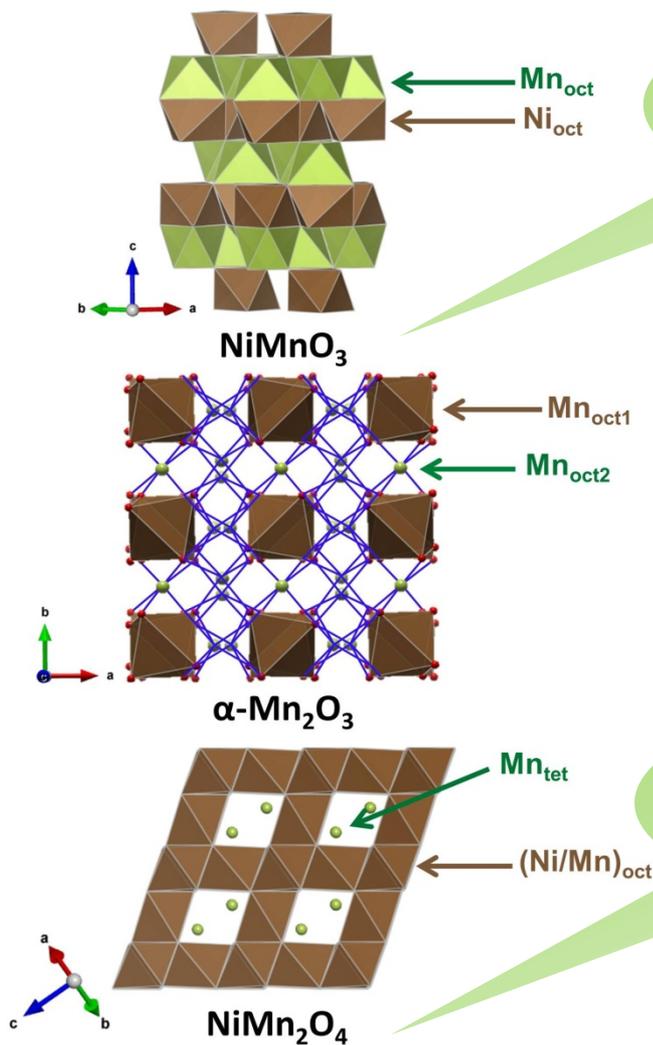
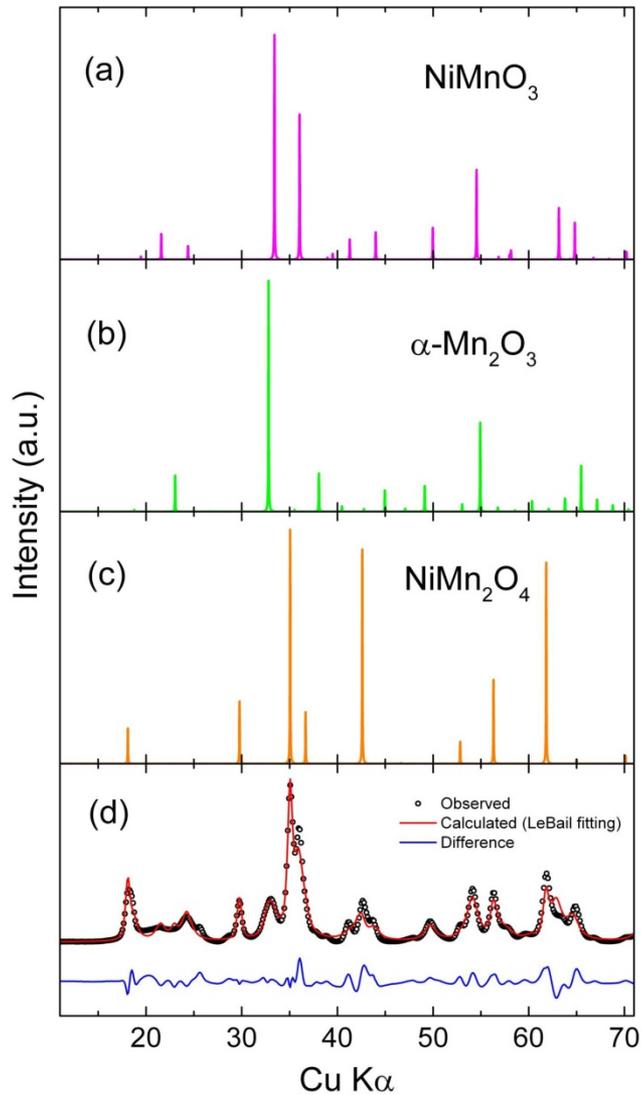
# In Situ XRD-MS II: In situ Data Analysis

## 2. In situ XRD-MS



**Earlier oxygen  
release of *d*-LNMO**

# Identification of phases at high temperature

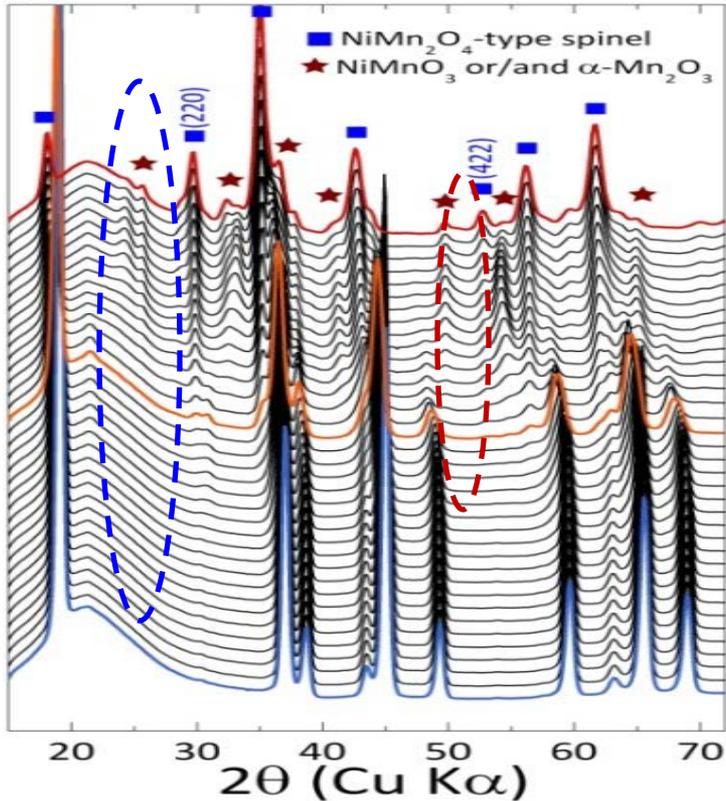


Ni exists in  $\text{Ni}^{2+}$  form

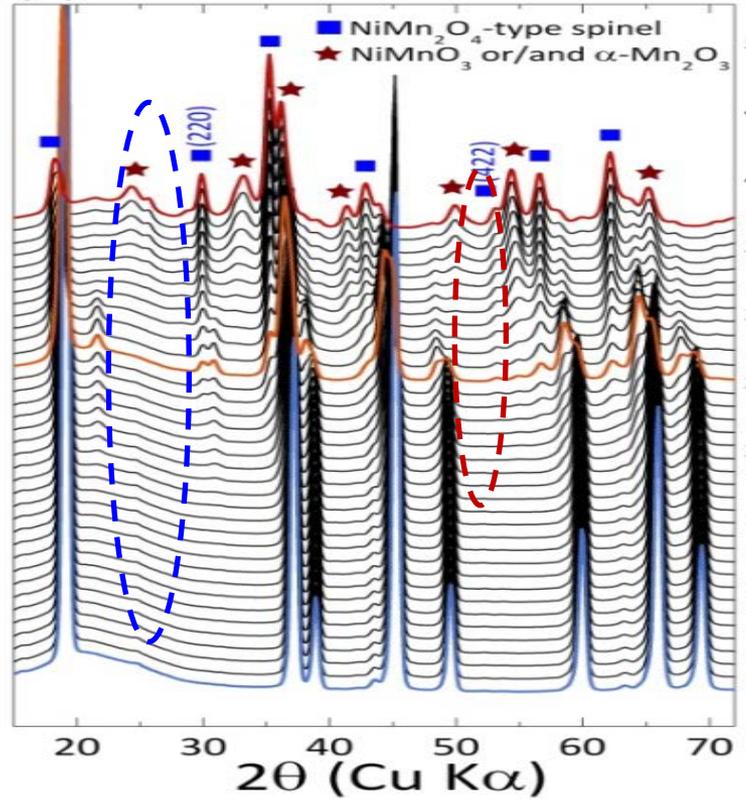
Spinel framework is maintained

# Unraveling phase transition paths

(a) *d*-LNMO



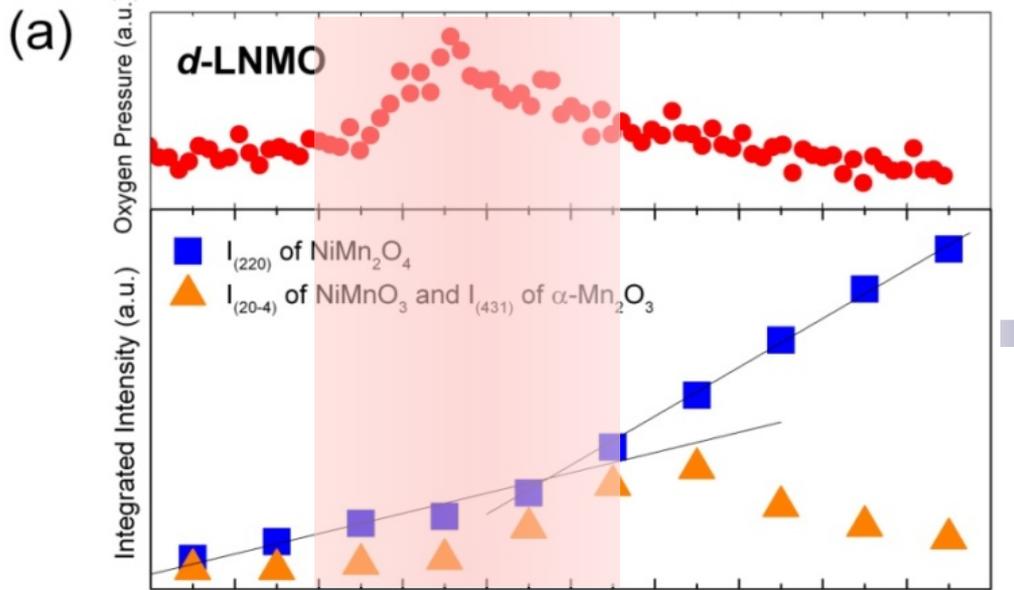
(b) *o*-LNMO



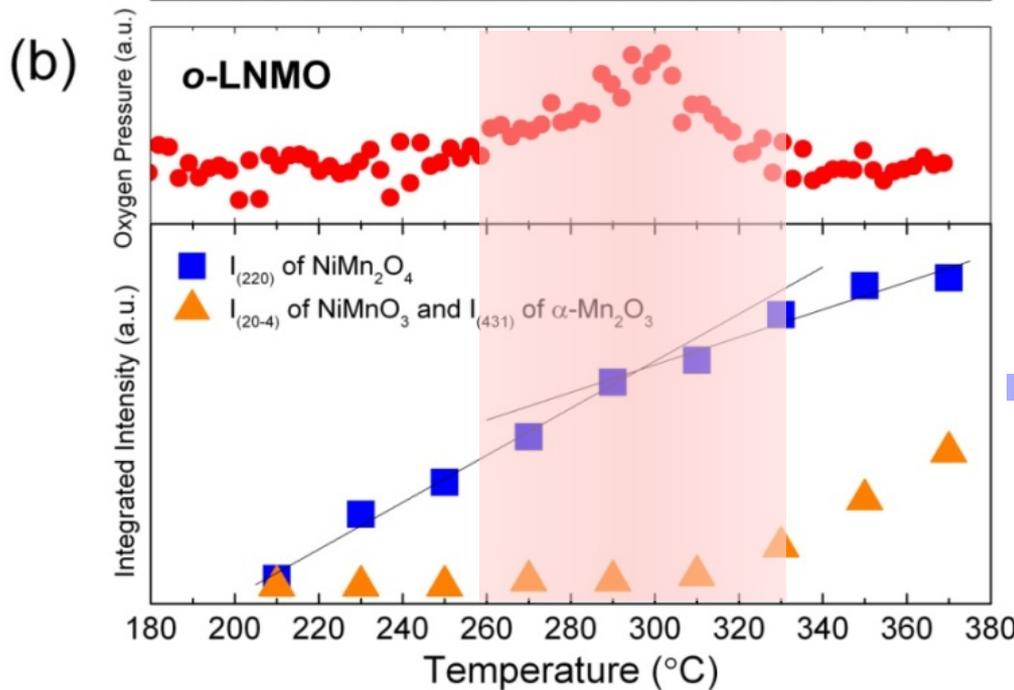
Despite that they formed similar phase at the end, their reaction pathways are different.

Understanding their pathways may help us understand their difference in thermal stability.

# Unraveling phase transition paths



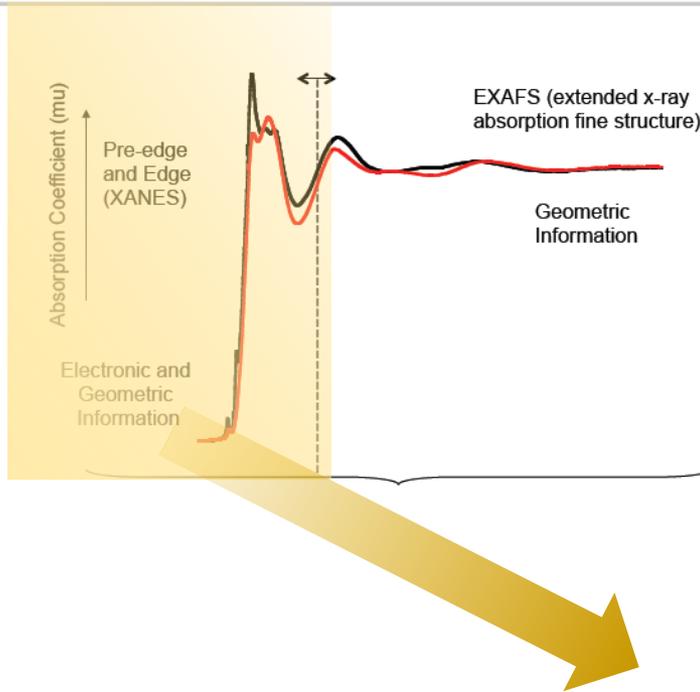
NiMnO<sub>3</sub> and  $\alpha\text{-Mn}_2\text{O}_3$  grow fast during oxygen release



$\text{NiMn}_2\text{O}_4$  phase grows fast during oxygen release

# In situ x-ray absorption: which element is **reduced** more during heating can be studied by XANES

X-ray Absorption Spectrum (XANES + EXAFS Region)

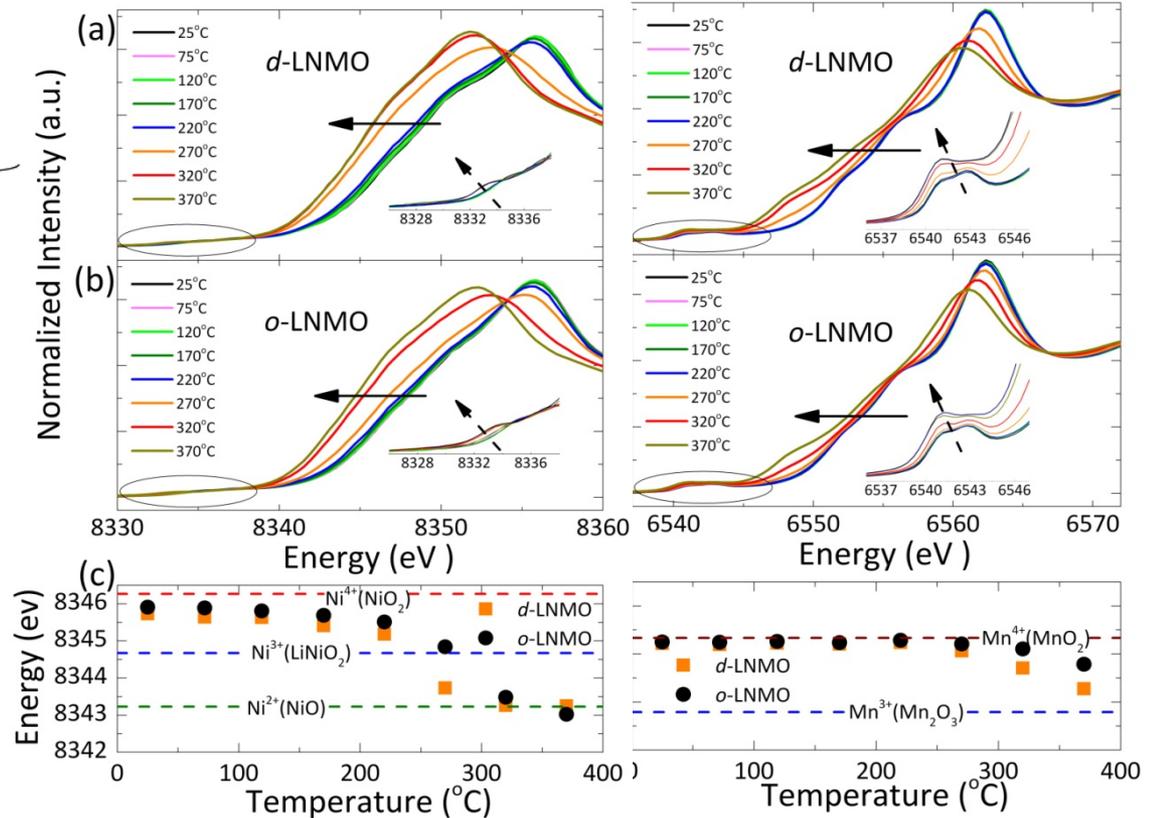


↳ Violent Ni reduction;

↳ Mn is responsible for tetrahedral site occupation.

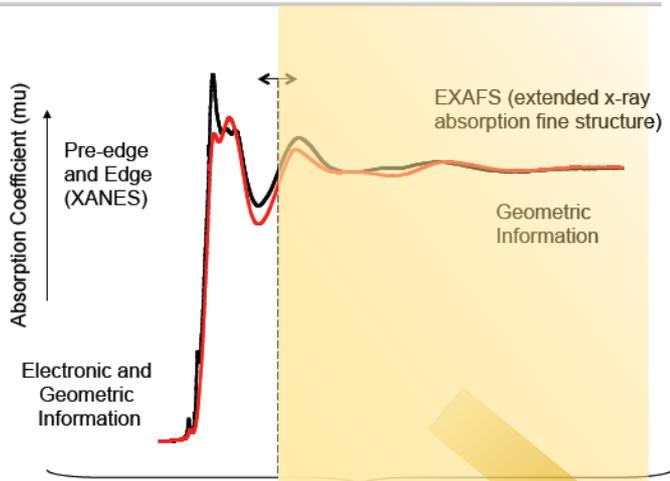
**Ni K-edge**

**Mn K-edge**



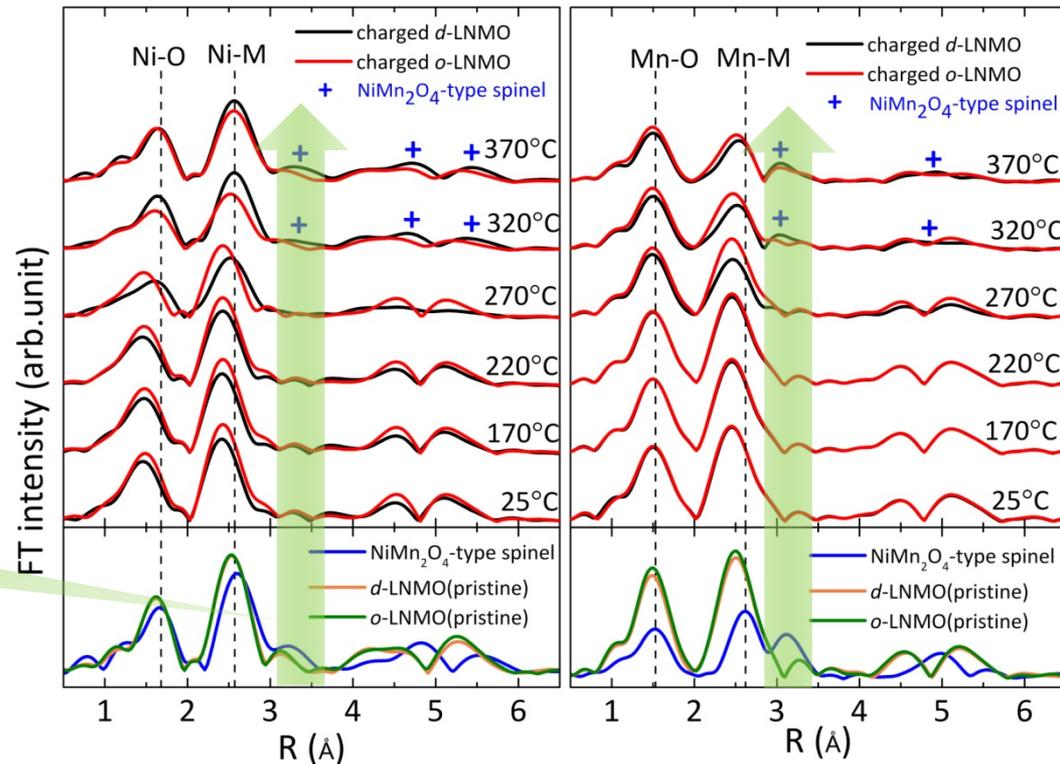
# In situ EXAFS at Ni and Mn k-edge during heating

X-ray Absorption Spectrum (XANES + EXAFS Region)



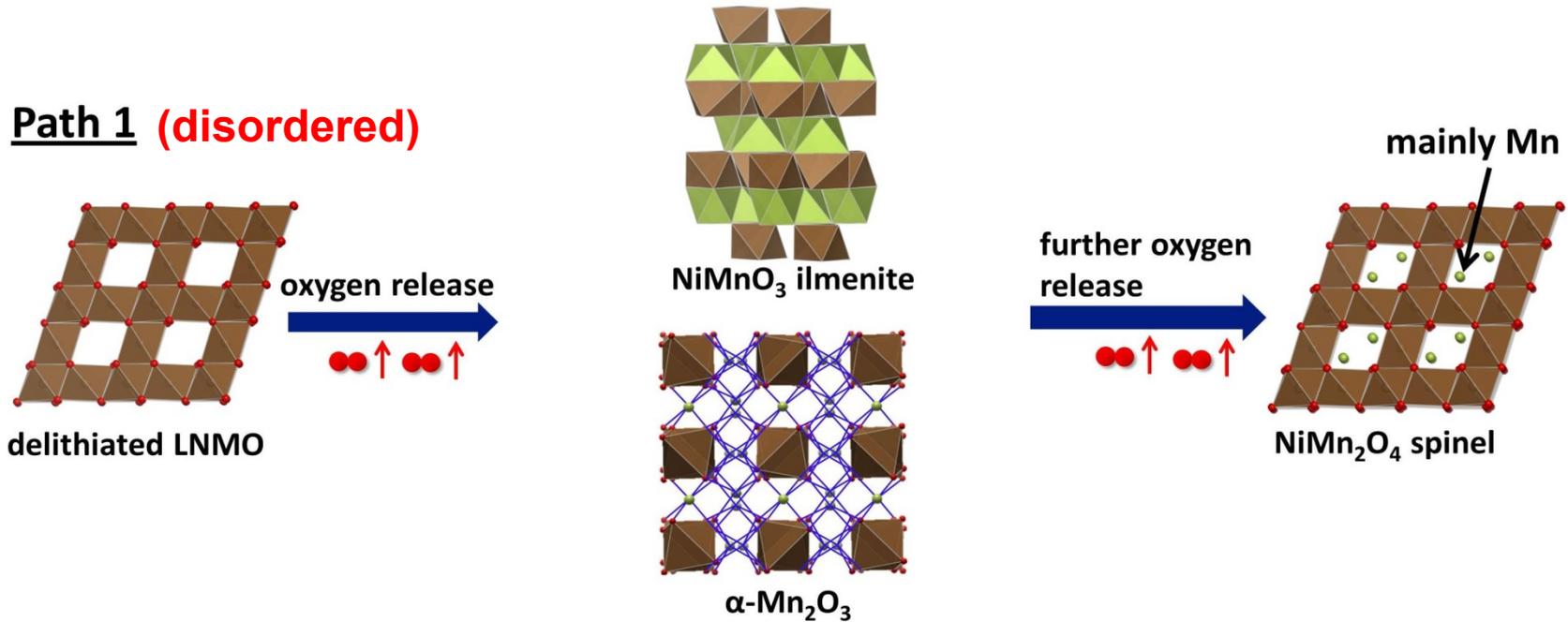
→ Formation of  $\text{NiMn}_2\text{O}_4$  is further confirmed.

characteristic of  $\text{NiMn}_2\text{O}_4$

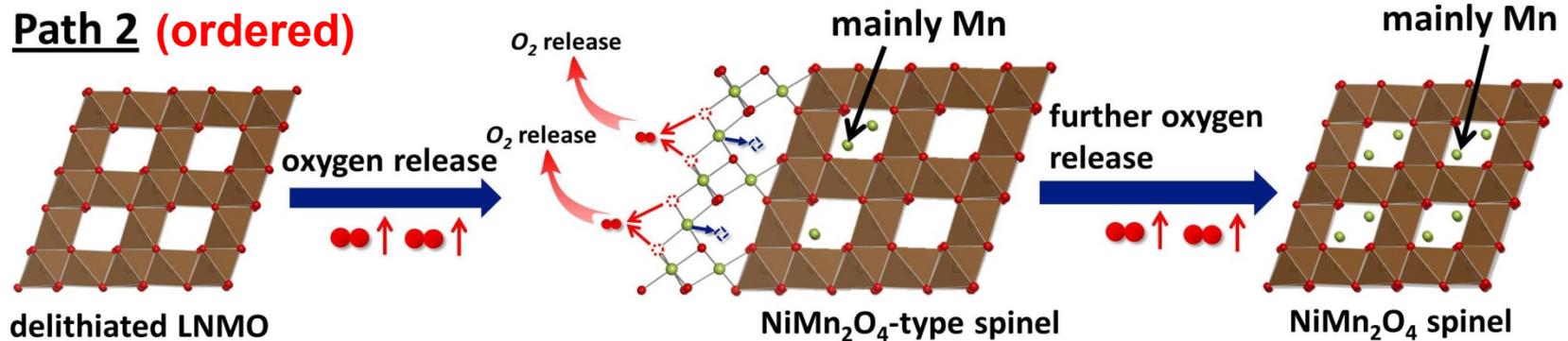


# Summary of reaction mechanism and phase transition paths

## Path 1 (disordered)

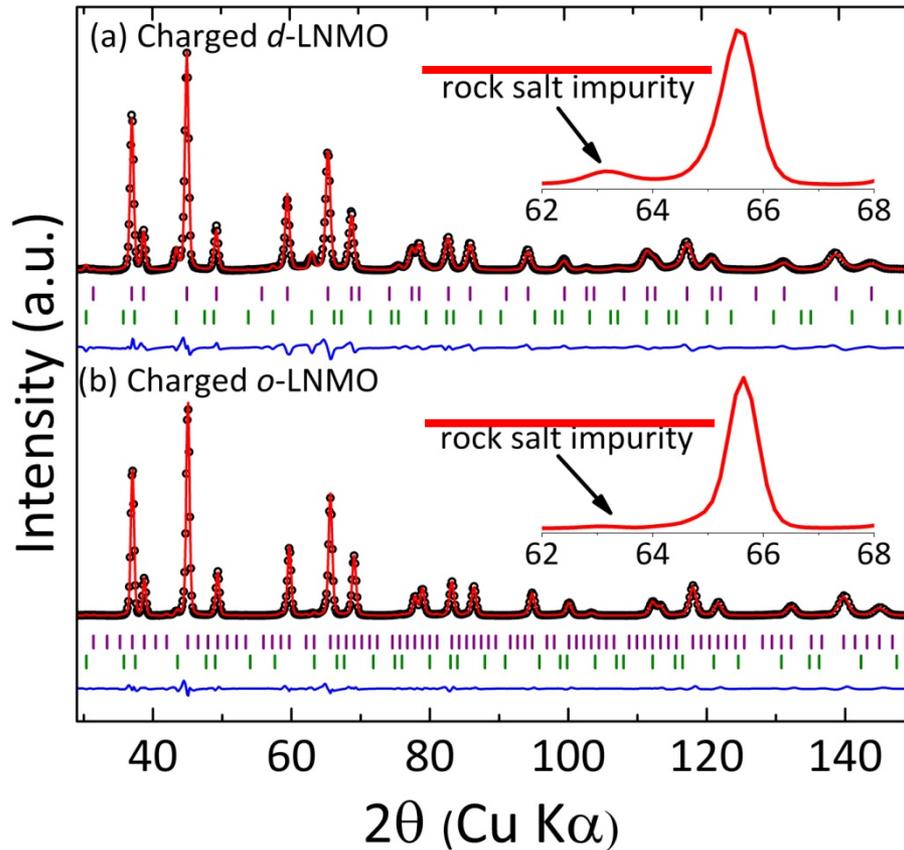


## Path 2 (ordered)

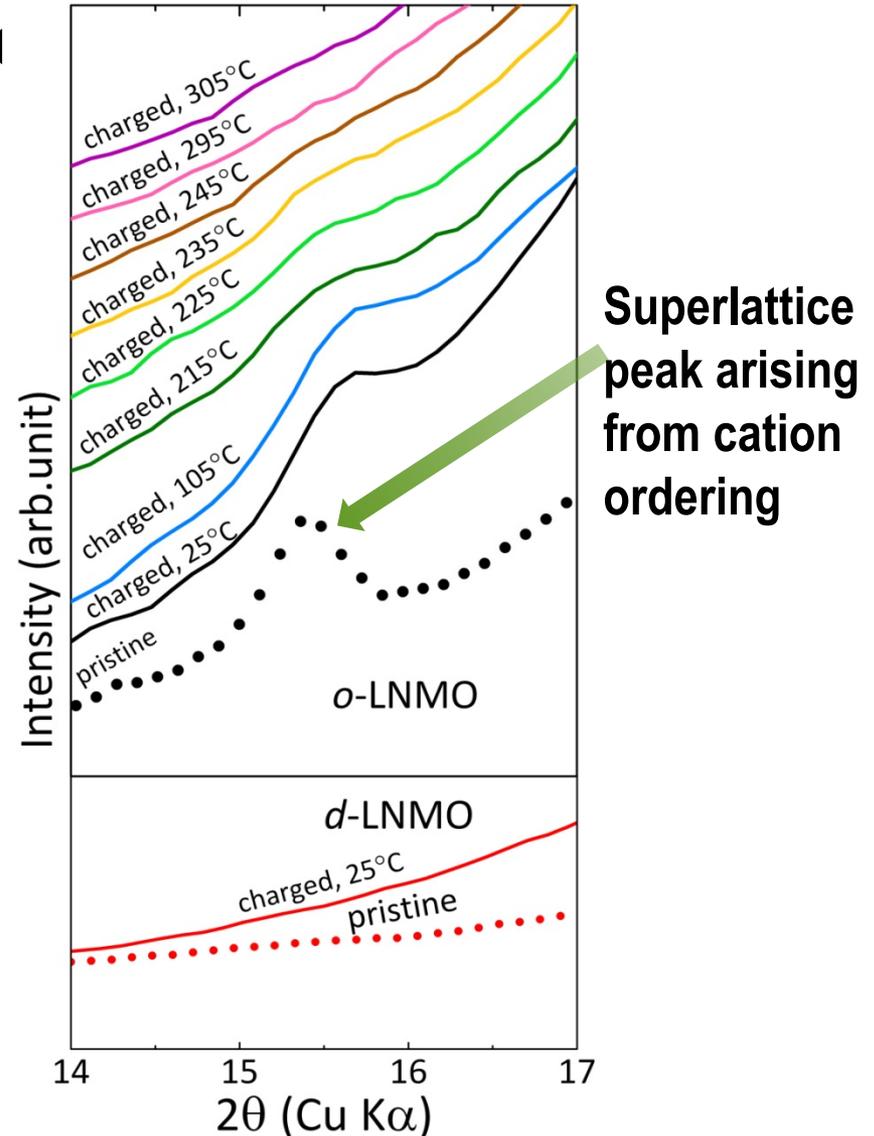


# The effects of NiO impurity

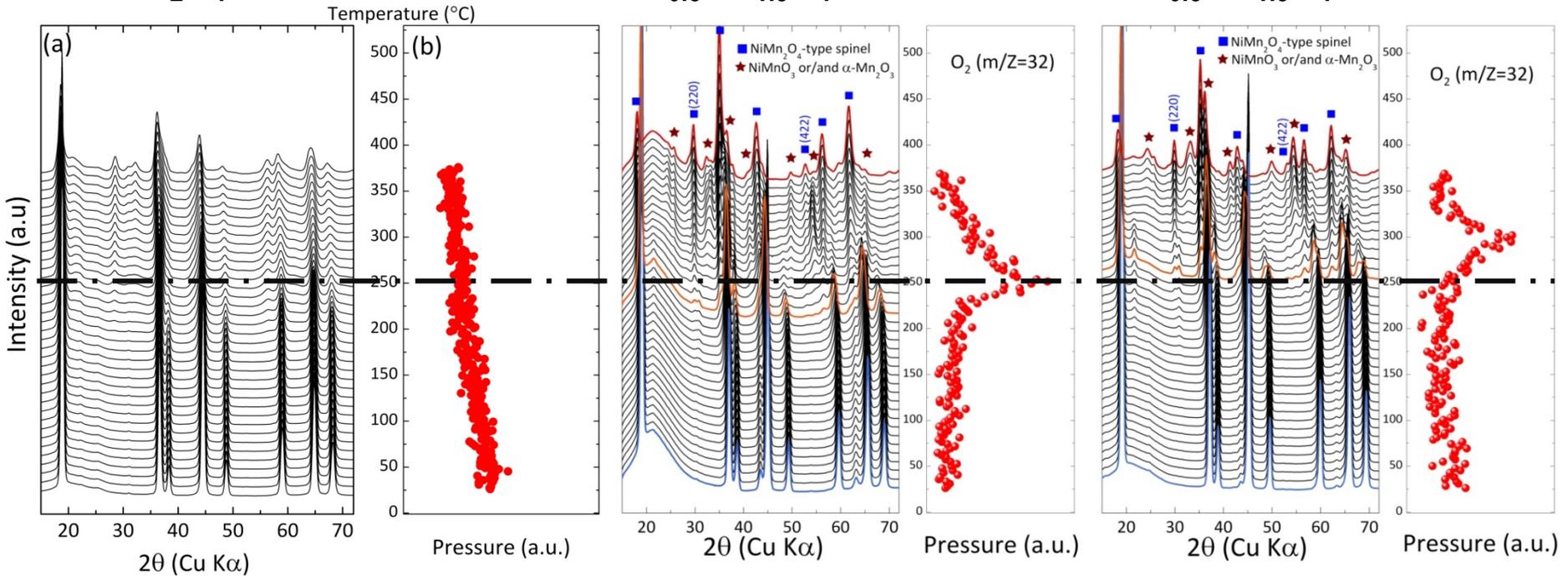
## 1. Impurity (availability of $\text{Ni}^{2+}$ in the rock salt facilitates the $\text{Ni}^{2+}\text{Mn}^{4+}\text{O}_3$ formation)



## 2. Ordering/Segregation



# Comparison of the thermal stability for conventional and high voltage spinels



When 25% of **Mn** is substitution by **Ni**, the thermal stability is significantly changed

# Collaborations with other institutions and companies

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## ▣ Argonne National Lab. (ANL)

↳ *In situ* XRD and XAS study of high energy density  $\text{Li}_2\text{MnO}_3\text{-LiMO}_2$  composite (LMR-NCM). (LMR-NCM sample preparation and distribution by the “post-testing facility” at ANL).

## ▣ Pacific Northwest National Lab. (PNNL)

↳ HR-TEM study of high voltage  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  spinel cathode materials.

## ▣ Beijing Institute of Physics

↳ ALD surface coated cathode materials and new electrolyte additives.

## ▣ GM R&D Center

↳ *In situ* XRD and XAS study for high energy density  $\text{Li}_2\text{MnO}_3\text{-LiMO}_2$  composite.

# Planned work for *FY 2014* and *FY2015*

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- ▣ Design, synthesis, and test the high voltage  $\text{LiNi}_{0.5-x}\text{Mn}_{1.5-x}\text{M}_{2x}\text{O}_4$  (M is transition metal other than Ni and Mn) type cathode materials with spinel structure to further study the novel strategy of improving the thermal stability of cathode material through redesigning their structures.
- ▣ Using time resolved XRD combined with MS to study the thermal stability of the high voltage  $\text{LiNi}_{0.5-x}\text{Mn}_{1.5-x}\text{M}_{2x}\text{O}_4$  (M is transition metal other than Ni and Mn) type cathode materials with spinel structure
- ▣ Using in situ XRD and XAS to study the capacity fading mechanism of cathode materials during high voltage charging limit cycling.
- ▣ Expand the collaborative research with US and international academic research institutions and US industrial partners.

# Summary

- By collaborating with Dr. Huiming Wu and Dr. Khal Amine, the elementally related delithiation kinetic behaviors studied by time-resolved XAS technique during 5V constant voltage charging show that the lithium extraction with a concomitant oxidation of  $\text{Ni}^{2+}$  to  $\text{Ni}^{4+}$  has fast reaction kinetic which is not much negatively affected by the irreversible structure change of the  $\text{Li}_2\text{MnO}_3$  component after initial delithiation process. In contrast much poorer delithiation kinetic was revealed in Mn region during and after the activation process. These results show that Mn sites have a much poorer reaction kinetics both before and after initial "activation" of  $\text{Li}_2\text{MnO}_3$ , comparing with Ni and Co, providing valuable guidance in designing various Li-rich layered materials with desired balance of energy densities and rate capabilities for different applications.
- New findings on the thermal-stability are discovered for the high-voltage spinel  $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$  (LNMO) with ordered (*o*-) and disordered (*d*-) structures at fully delithiated state using a combination of in situ time-resolved x-ray diffraction (TR-XRD) coupled with mass spectroscopy (MS) and x-ray absorption spectroscopy (XAS) during heating: Both *o*- and *d*- $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$  at their fully charged states start oxygen-releasing structural changes at temperatures below 300 °C, which is in sharp contrast to the good thermal stability of the 4V-spinel  $\text{Li}_x\text{Mn}_2\text{O}_4$ . In addition, charged *o*-LNMO shows better thermal stability than the *d*-LNMO counterpart.