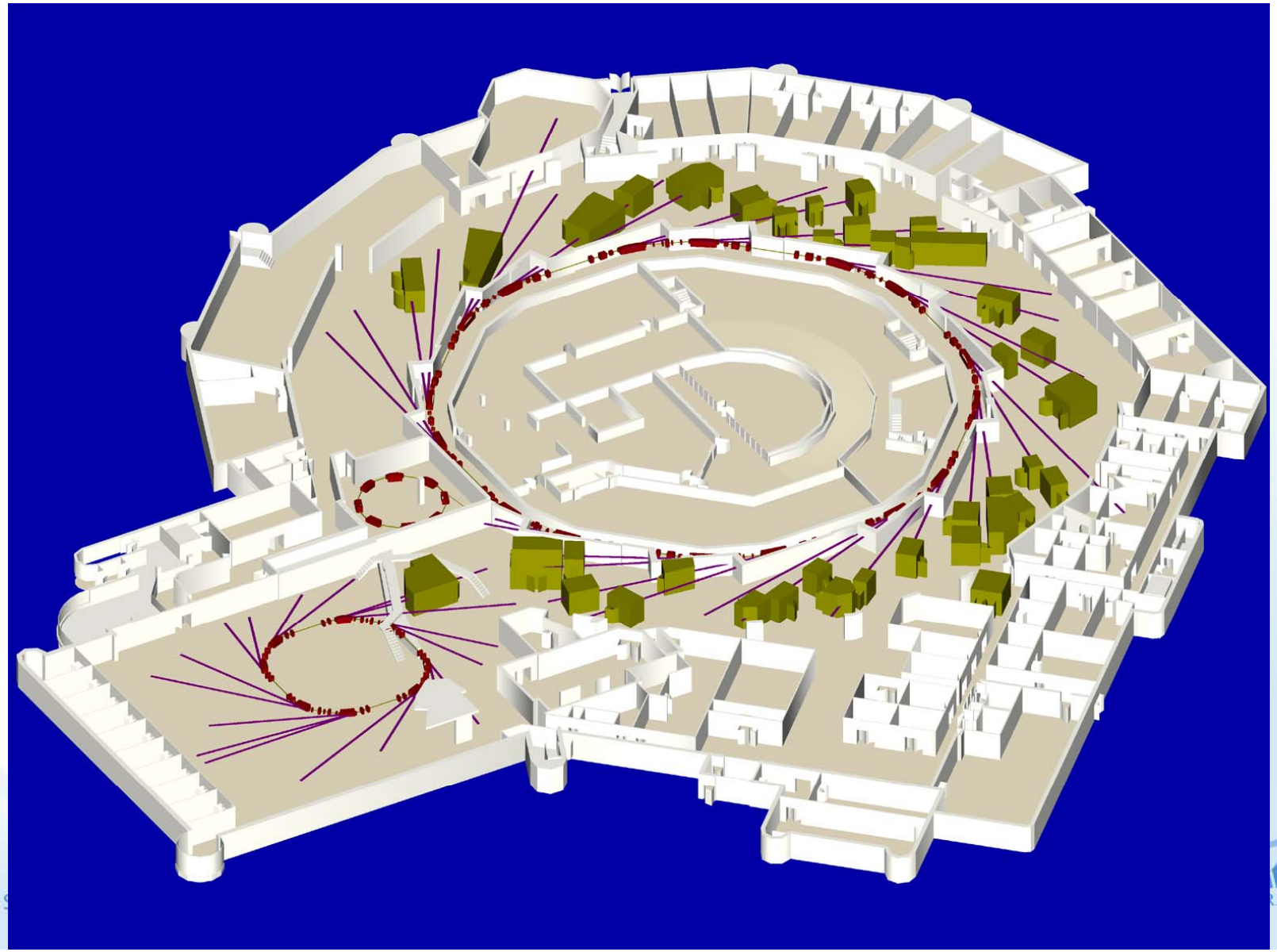
Application of synchrotron based in situ X-ray techniques to the study of lithium-ion batteries for HEV,PHEV, and EV

Xiao-Qing Yang
Chemistry department, Brookhaven National Laboratory, Upton, NY 11973

Presented at the U.S. – China Electric Vehicle and Battery Technology Workshop
Argonne National Lab.
August 30 to September 1st, 2010

NSLS experimental floor



Center for Functional Nano-materials at BNL

NSLS II (under construction)

Diagnostic studies of battery materials using synchrotron X-rays

- Objectives

  To identify key materials properties and materials interactions that limit battery lifetime, performance and thermal stability (related to safety issues) using synchrotron based X-ray techniques.

- Approach

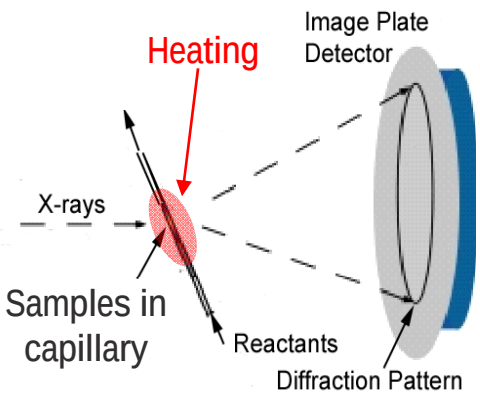
  ➥ *Combined in situ X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) studies about charge compensation mechanisms of electrode materials during charge-discharge.*

  ➥ *Combined time-resolved (TR) XRD and XAS studies about thermal decomposition mechanism of charged cathode materials during heating (safety related issue).*

  - XRD: Long range structural information.
  - Hard XAS: Local structural information.
  - Soft XAS: Structural information about bulk and surface.

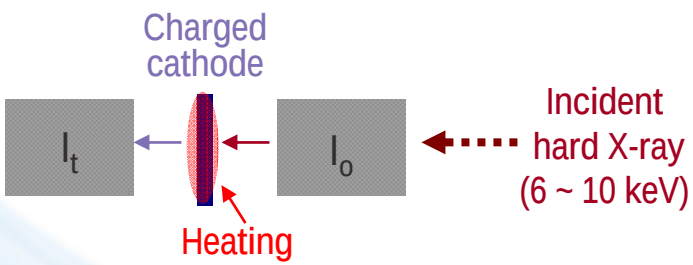
Our approach: In situ XRD & XAS during heating of charged cathode materials (thermal stability study)

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



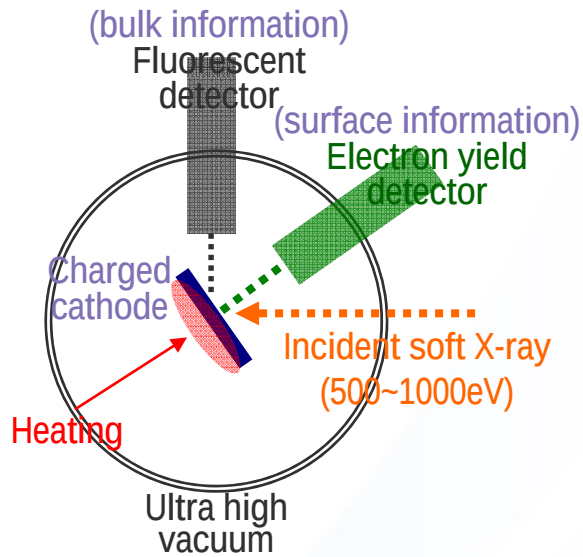
- Average structural information (long range order) during heating

2. *Hard X-ray absorption spectroscopy* of charged cathode materials



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

3. *Soft X-ray absorption spectroscopy* of charged cathode materials



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

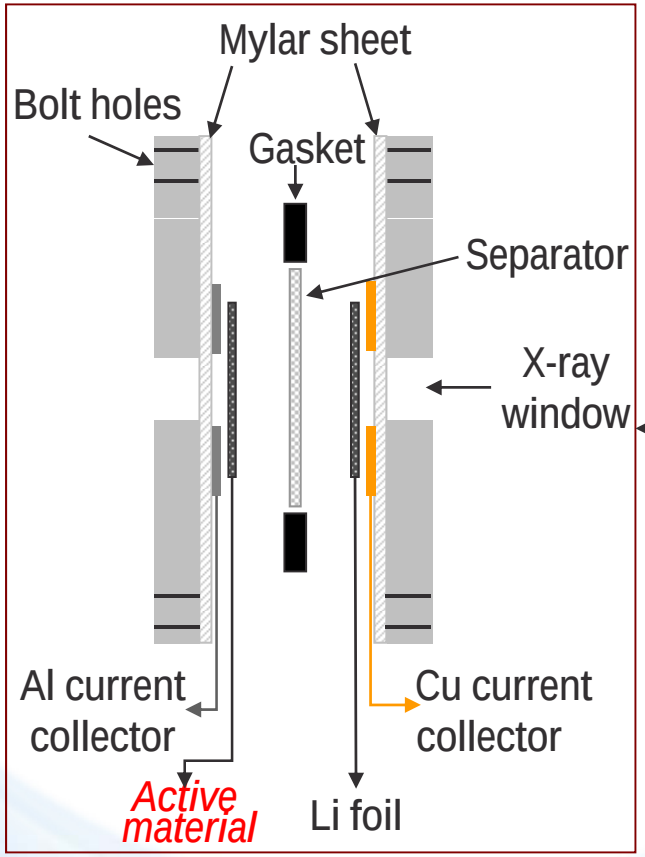
➥ Combination of these techniques will clearly provide valuable information about thermal stability of various types of cathodes materials and help designing thermally stable and safer cathode materials.

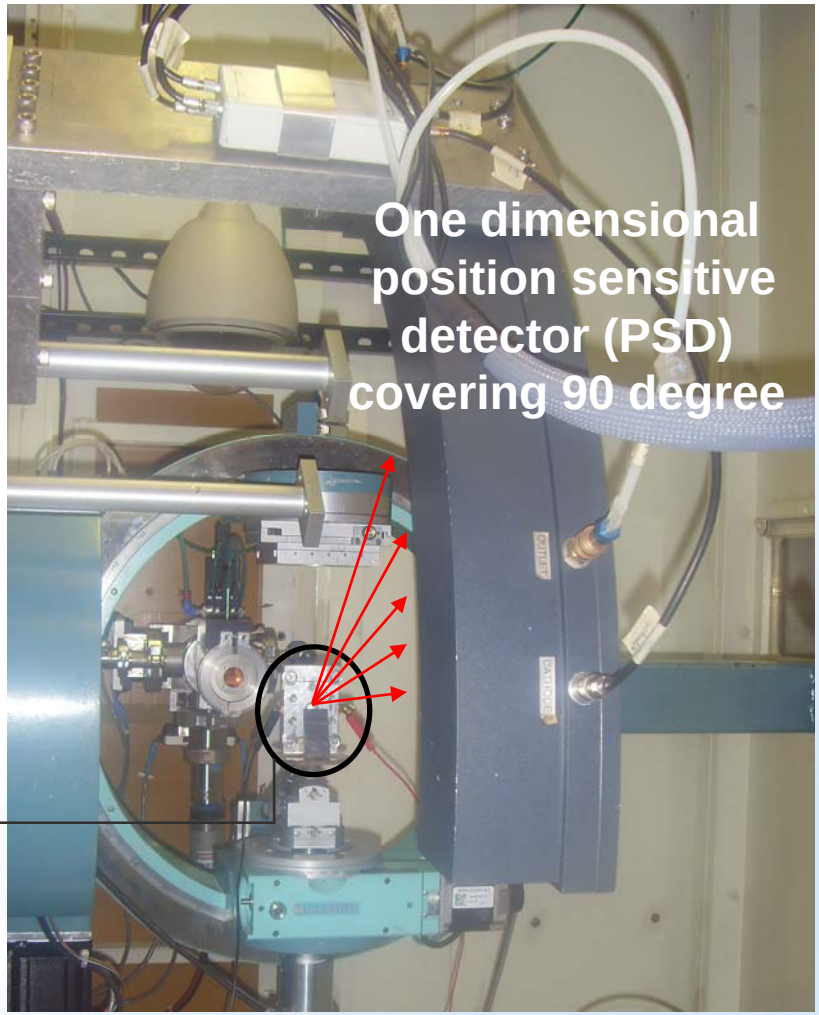
➥ Studied cathode materials: $Li_{0.33}NiO_2$, $Li_{0.33}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ & $Li_{0.33}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$

Experimental setup for *in situ* X-ray diffraction (XRD)

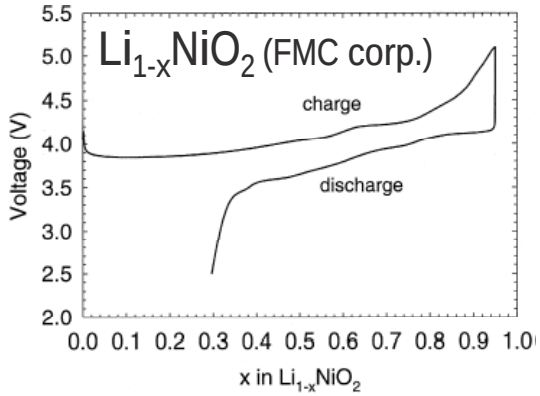
X18A beamline at National Synchrotron Light Source in BNL

In situ cell

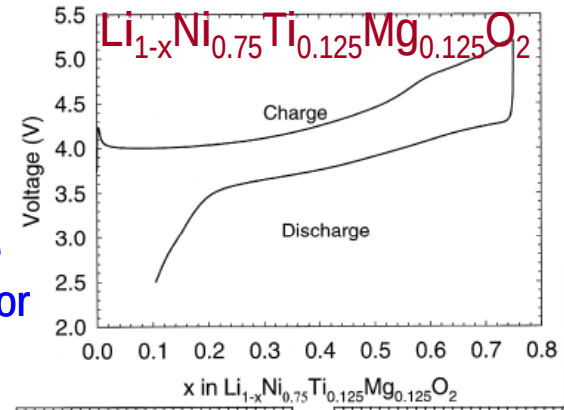


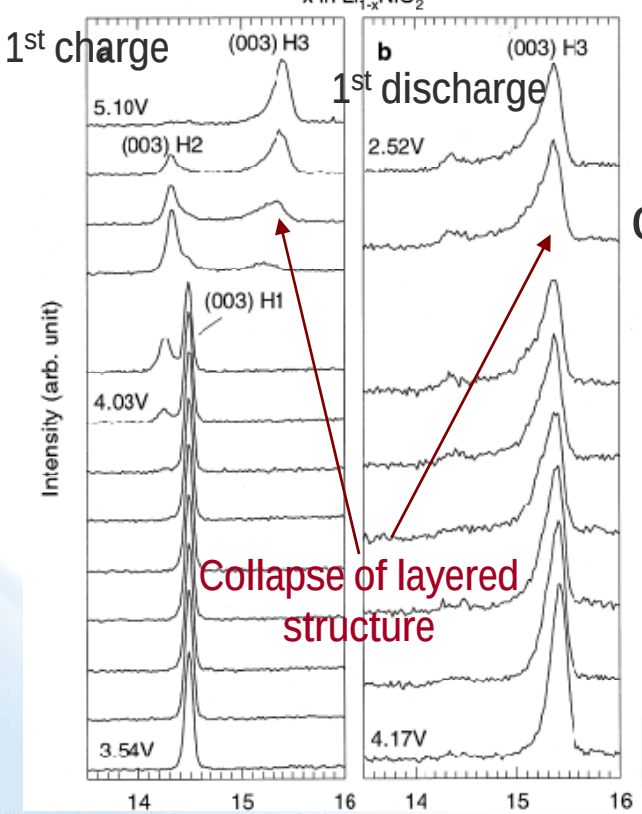


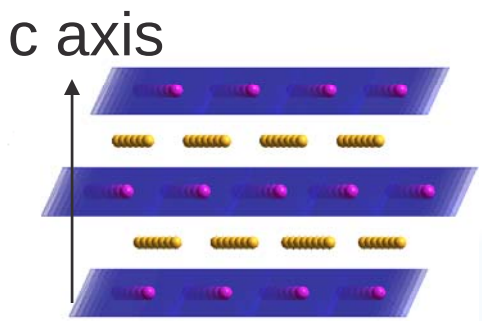
Examples of using *in situ* XRD to study the relationship between the structural changes and electrochemical performance

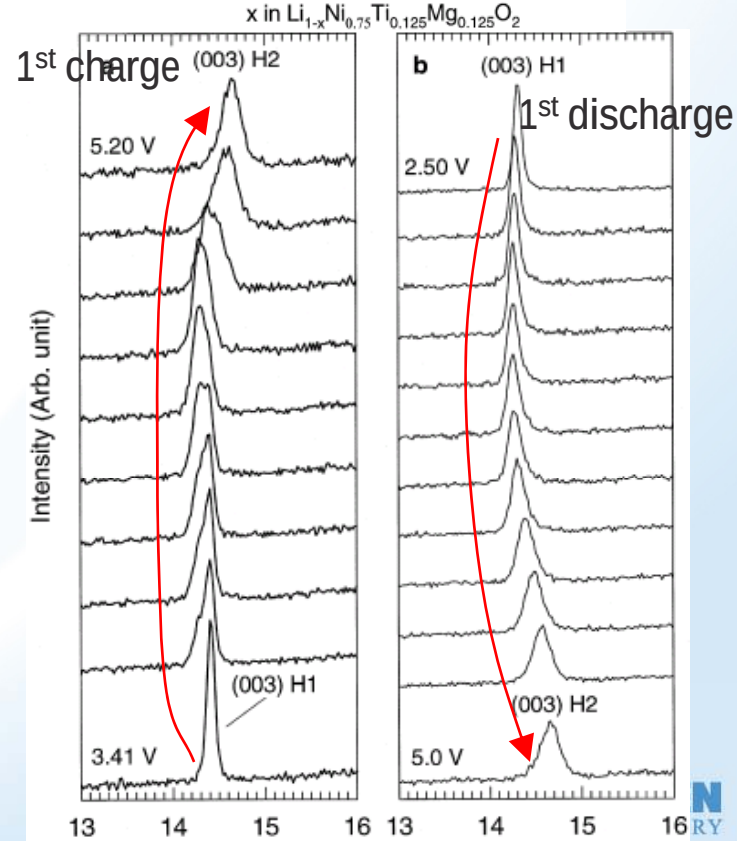


Overcharge to 5.0V the structure clasped for $LiNiO_2$ but preserved for $LiNi_{0.75}Ti_{0.125}Mg_{0.125}O_2$!

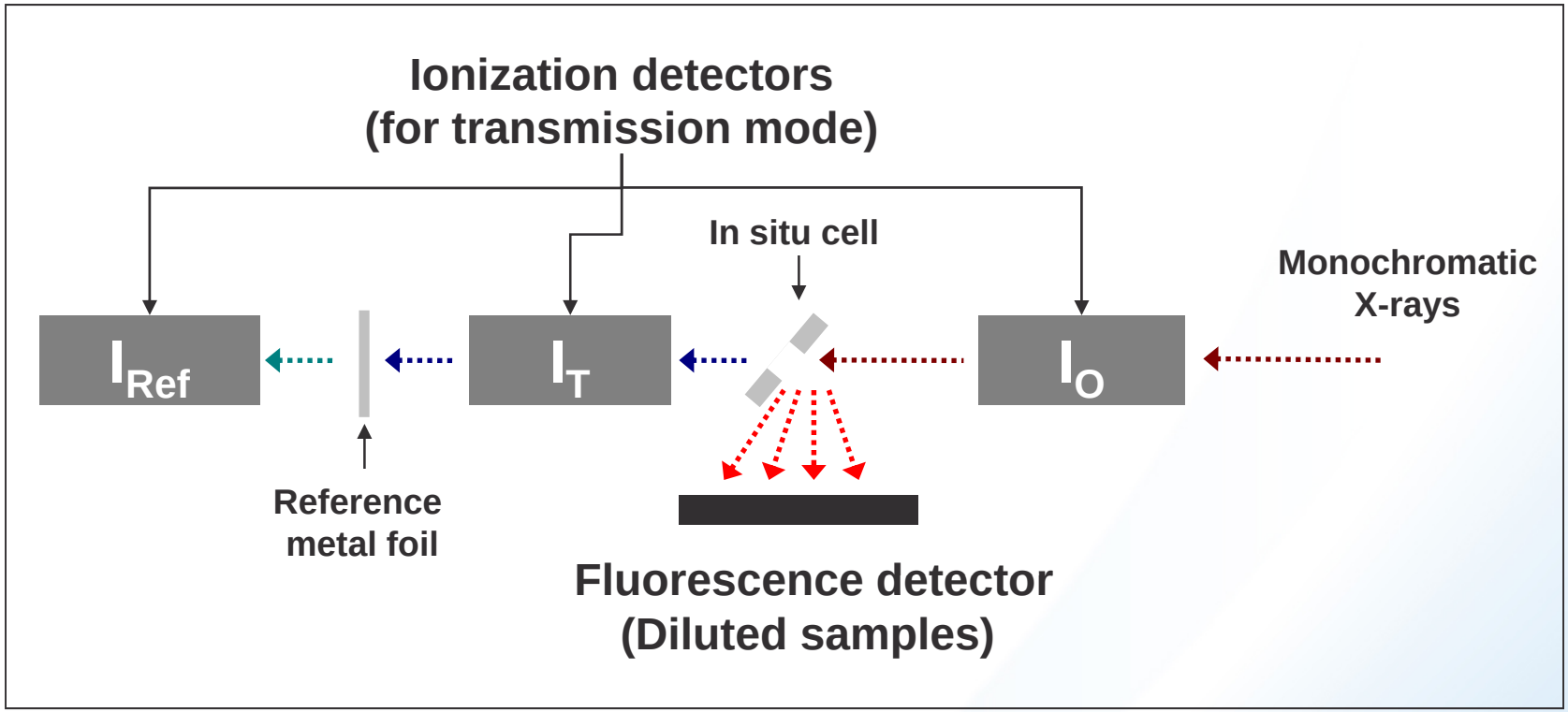


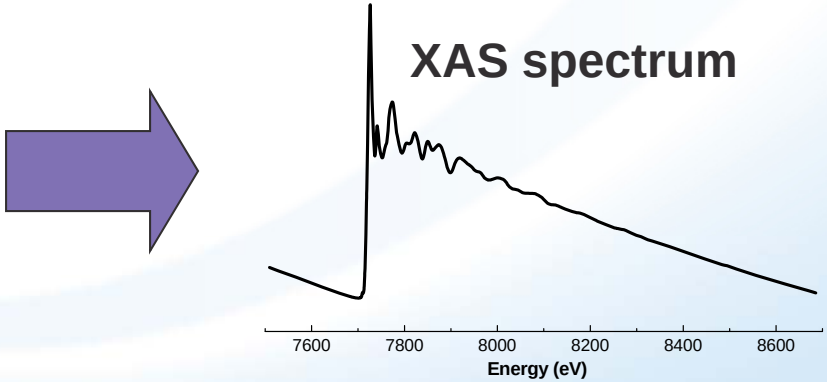




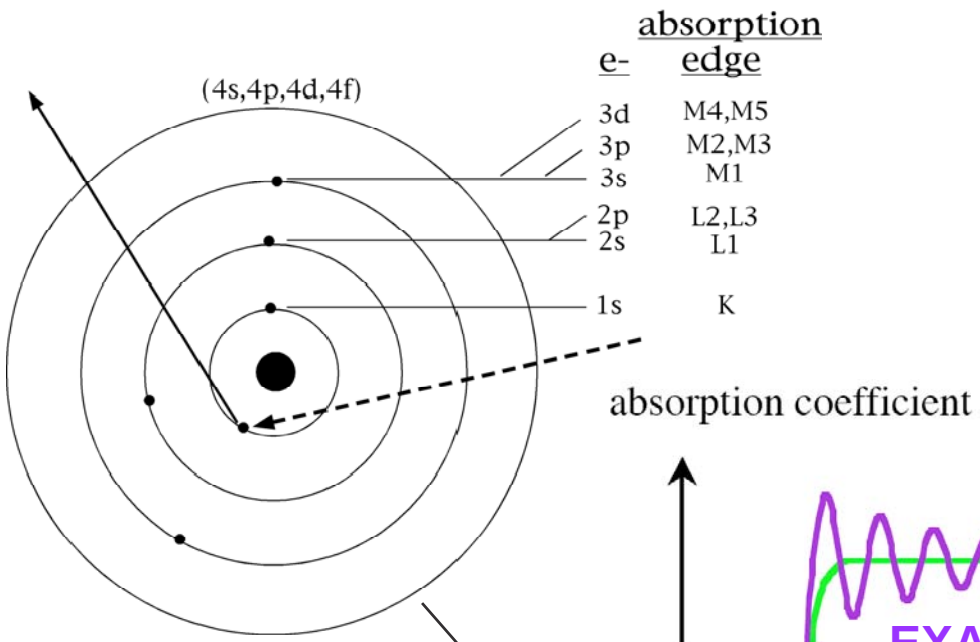


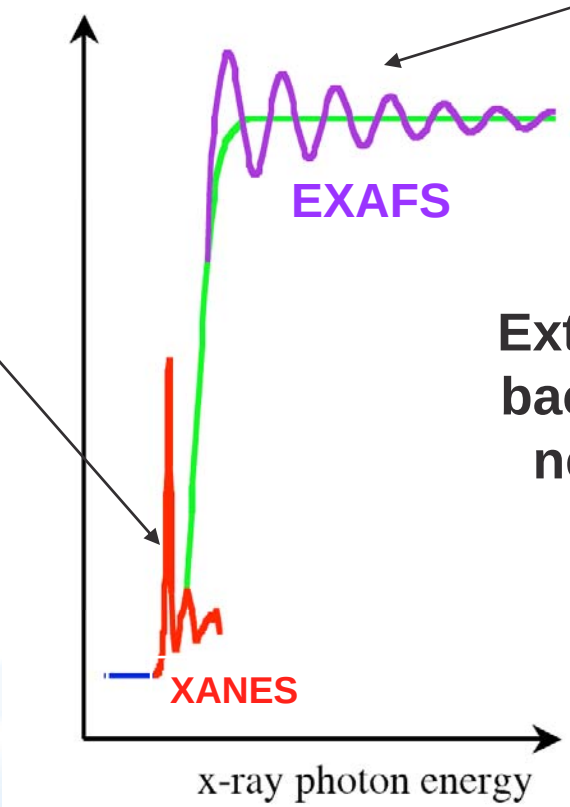
Experimental setup for *in situ* X-ray absorption spectroscopy (XAS)

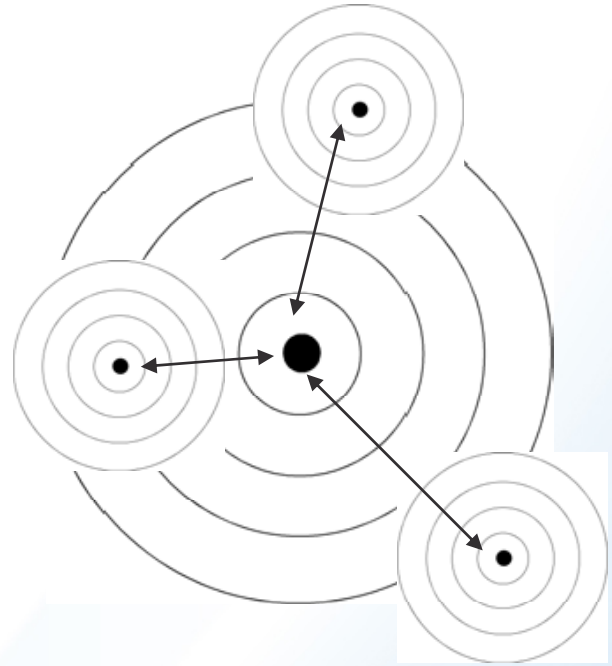




X-ray absorption spectroscopy





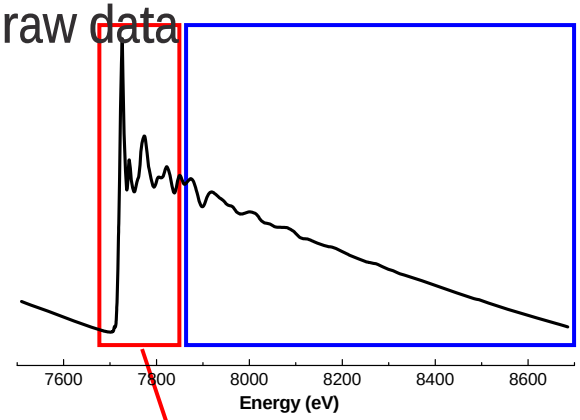


Absorption occurs when the energy of the incident photon is sufficient to eject the electron.

Extended oscillations due to backscatter of electron from neighboring atoms giving information on

X-ray absorption spectroscopy : *XANES* and *EXAFS*

raw data

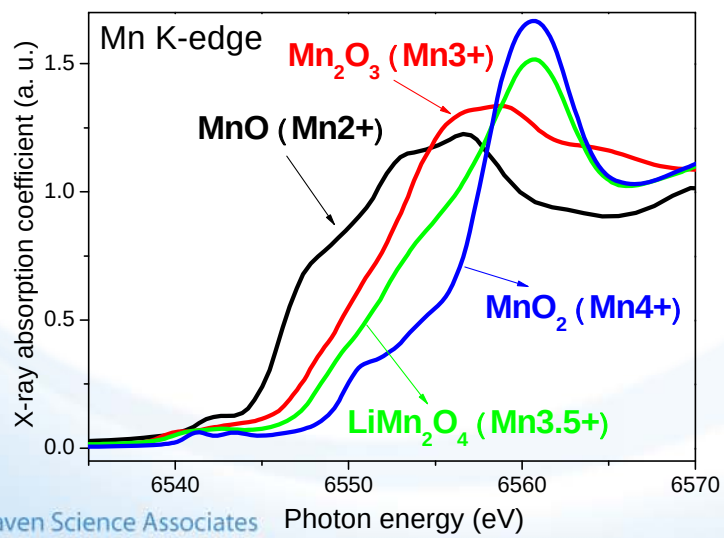


Extended X-ray Absorption Fine Structure (EXAFS)

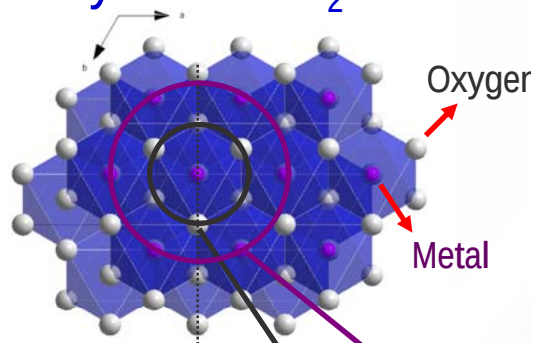
; Local structural information like bond distance, coordination number, degree of disorder

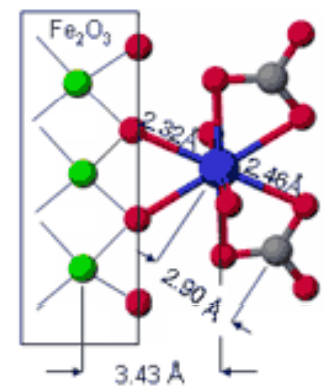
X-ray Absorption Near Edge Structure (XANES)

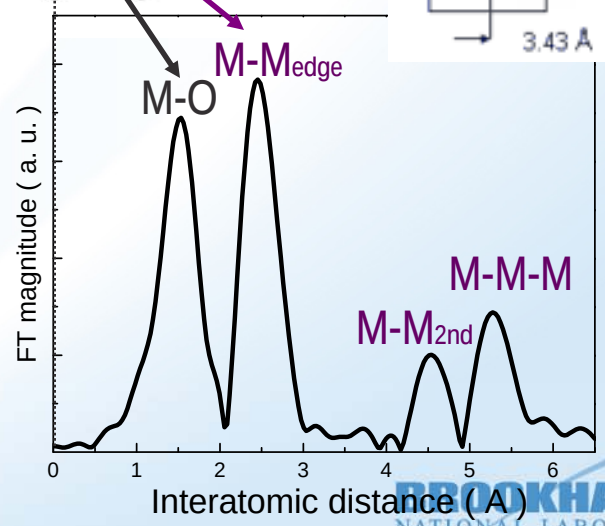
; Oxidation state, site symmetry, covalent bond strength



Layered $LiMO_2$ structure







Olivine $LiMPO_4$ (M=Fe, Mn, Co, Ni) cathode materials

- $LiFePO_4$ as a cathode material for Li ion battery
  - Olivine structure with orthorhombic unit cell (space group : Pmnb or Pnma).
  - Best chemistry in terms of safety characteristics.
  - Excellent power capability due to nanosize.
  - However, energy is low because of low cathode voltage (3.4 V vs. 3.8 V for nickel-based layered oxide system)

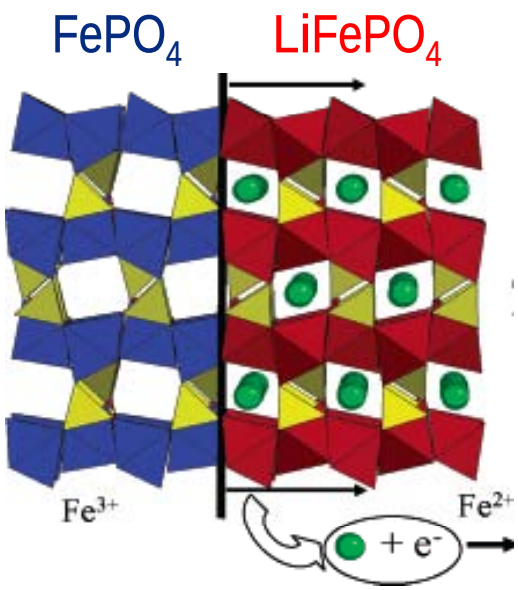
- Other olivine structured compounds : $LiMPO_4$ (M=Mn, Co, and Ni)
  - High operating voltages of 4.1V for Mn, 4.8V for Co, and 5.07 V for Ni.
    - ➥ Poor electrochemical properties (capacity and rate capability) compared to $LiFePO_4$.

- Olivine structured mixed transition metal phosphates
  - e.g.) $LiFe_yMn_{1-y}PO_4$, $LiFe_yCo_{1-y}PO_4$, $Li(Fe_{1/3}Mn_{1/3}Co_{1/3})PO_4$, etc.
  - Better electrochemical utilization of Mn, Co than those in $LiMnPO_4$ & $LiCoPO_4$.

Phase transition behaviors of olivine $LiMPO_4$ cathode materials

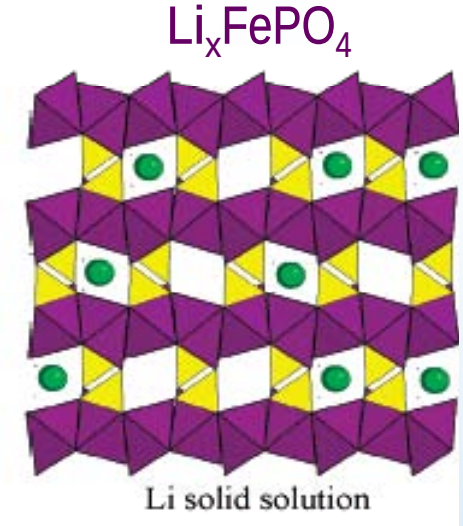
- Ongoing debates about the phase transition behaviors of olivine structured $LiMPO_4$ materials during lithium extraction/insertion.

Two phase reaction



vs.

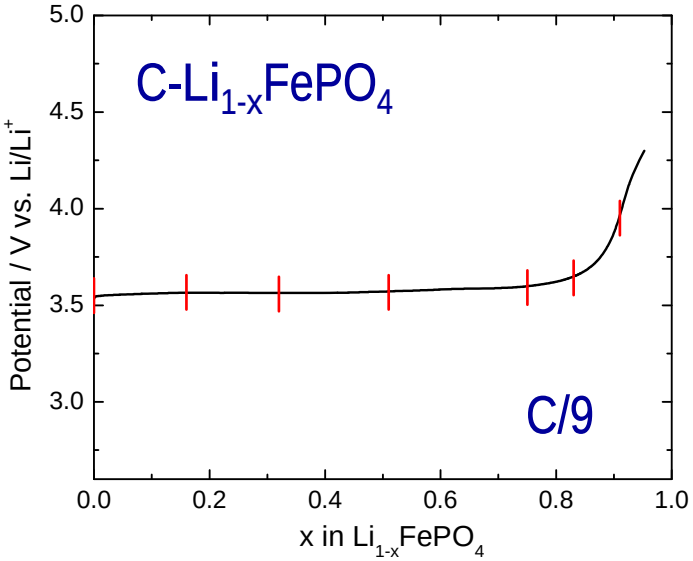
Single phase reaction (i.e. solid solution reaction)



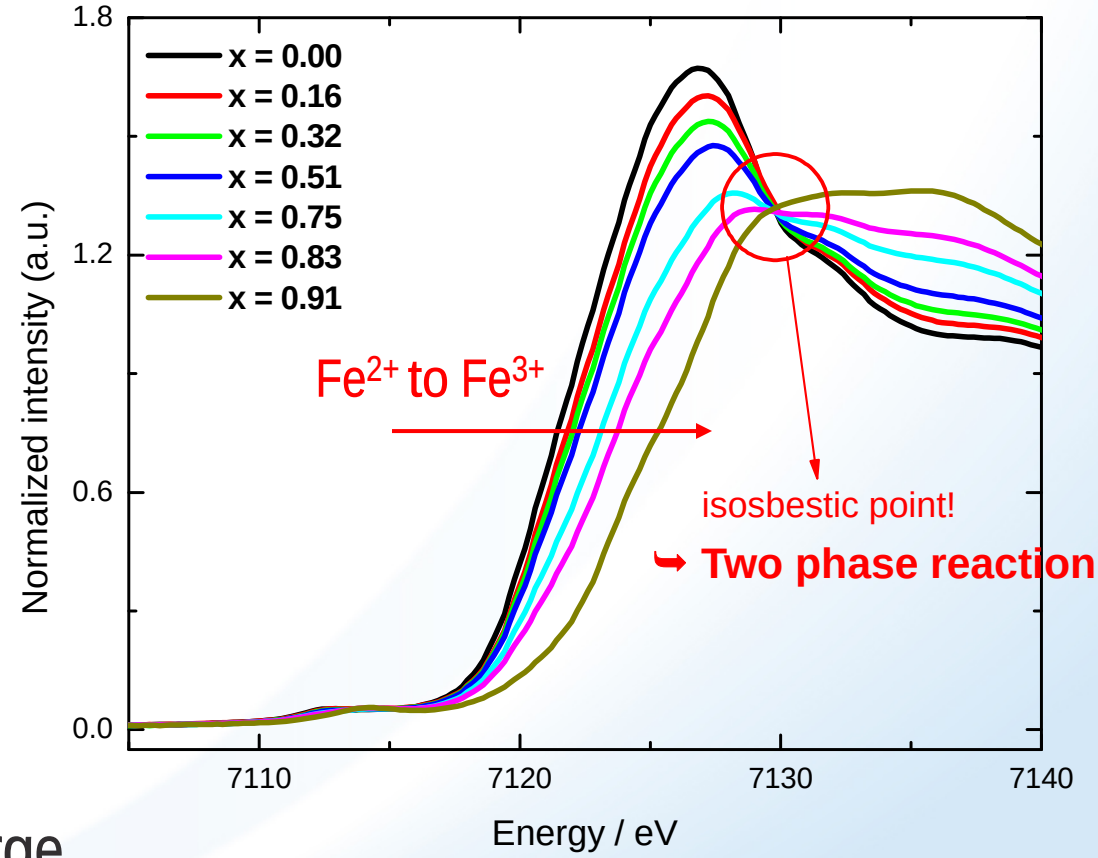
Images From B. Ellis et al., JACS, Vol. 128 (2006) 11416 p.

➥ ***In situ*** **XAS and XRD to study the relationship between phase transition behaviors and introduction of 3d transition metals (Mn, Co, Ni) in $LiFePO_4$.**

In situ Fe K-edge XANES spectra of C-LiFePO$_4$



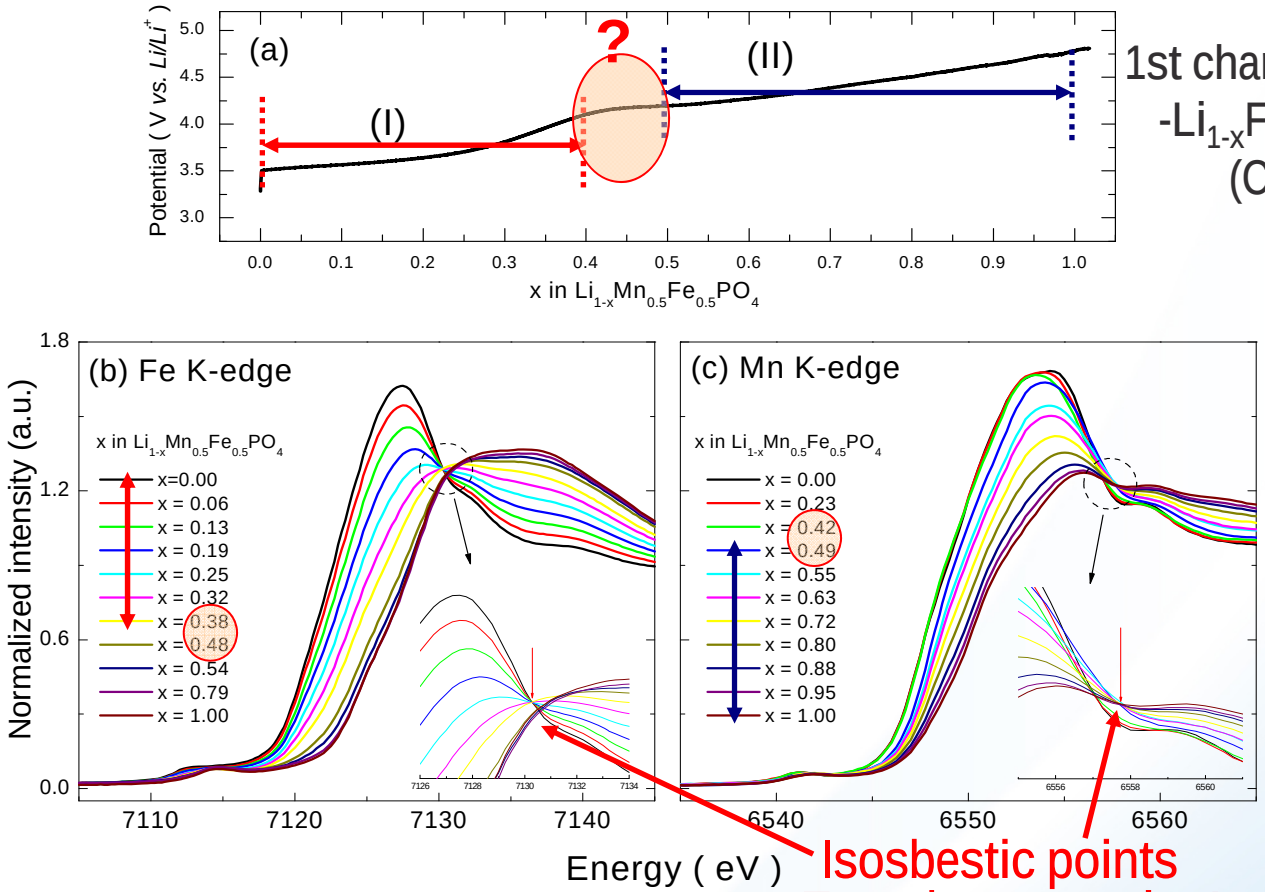
XANES (X-ray Absorption Near Edge Structure)
: Shift of K-edge position toward higher energy
⇨ *Increase in oxidation state*



Li extraction during charge

: LiFe(II)PO$_4$ - xLi$^+$ - xe$^-$ ⇆ xFe(III)PO$_4$ + (1-x)LiFe(II)PO$_4$

In situ Fe, Mn K-edge XANES spectra of C-$LiFe_{0.5}Mn_{0.5}PO_4$



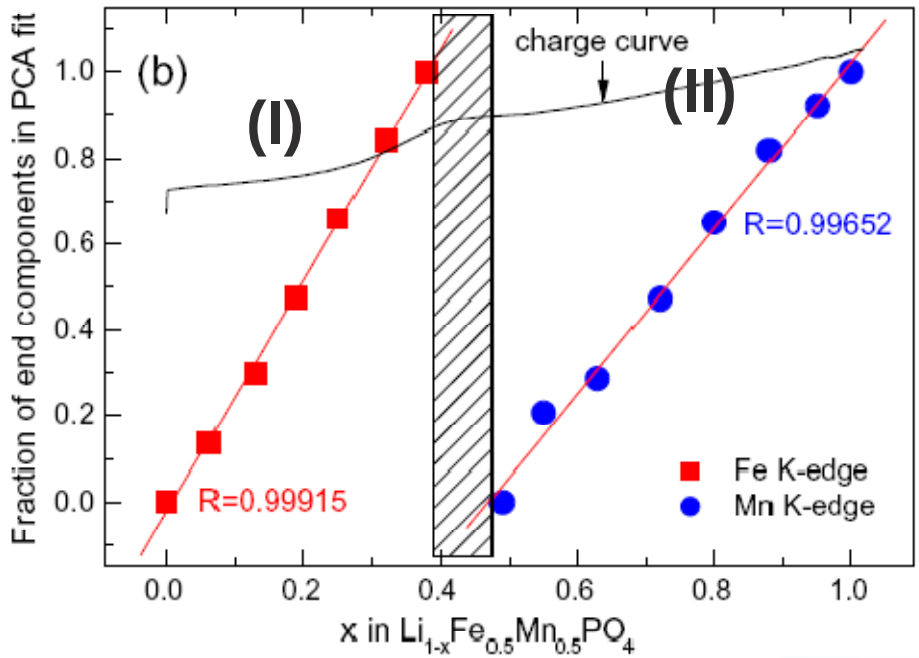
1st charge curve of C -$Li_{1-x}Fe_{0.5}Mn_{0.5}PO_4$ (C/20 rate)

Isosbestic points : Two phase reaction!

- ➥ Two voltage plateaus of 3.6 (Fe^{2+}/Fe^{3+}) and 4.2 V (Mn^{2+}/Mn^{3+}) : two phase reactions.
- ➥ Narrow intermediate region ($0.4 \leq x \leq 0.5$ in $Li_{1-x}Fe_{0.5}Mn_{0.5}PO_4$) : single phase reaction? & simultaneous Fe^{2+}/Fe^{3+} and Mn^{2+}/Mn^{3+} redox reactions.

Electrochemistry Communication, 11 (2009) 2023 p.

Linear combination analysis *of in situ* XANES spectra of C-$LiFe_{0.5}Mn_{0.5}PO_4$



Supporting Two phase reaction at plateaus (I)&(II)

Plateau (I) : $0.0 \leq x \leq \sim 0.4$ in C-$Li_{1-x}Mn_{0.5}Fe_{0.5}PO_4$ (Fe^{2+}/Fe^{3+} redox reaction);

➥ $Li_{1.00}Mn_{0.5}Fe_{0.5}PO_4 \leftrightarrows (1-z)Li_{1.00}Mn_{0.5}Fe_{0.5}PO_4 + zLi_{0.62}Mn_{0.5}Fe_{0.5}PO_4 + zLi^+ + ze^-$ $(0 \leq z \leq 1)$

Plateau (II) : $\sim 0.5 \leq x \leq 1.0$ in C-$Li_{1-x}Mn_{0.5}Fe_{0.5}PO_4$ (Mn^{2+}/Mn^{3+} redox reaction);

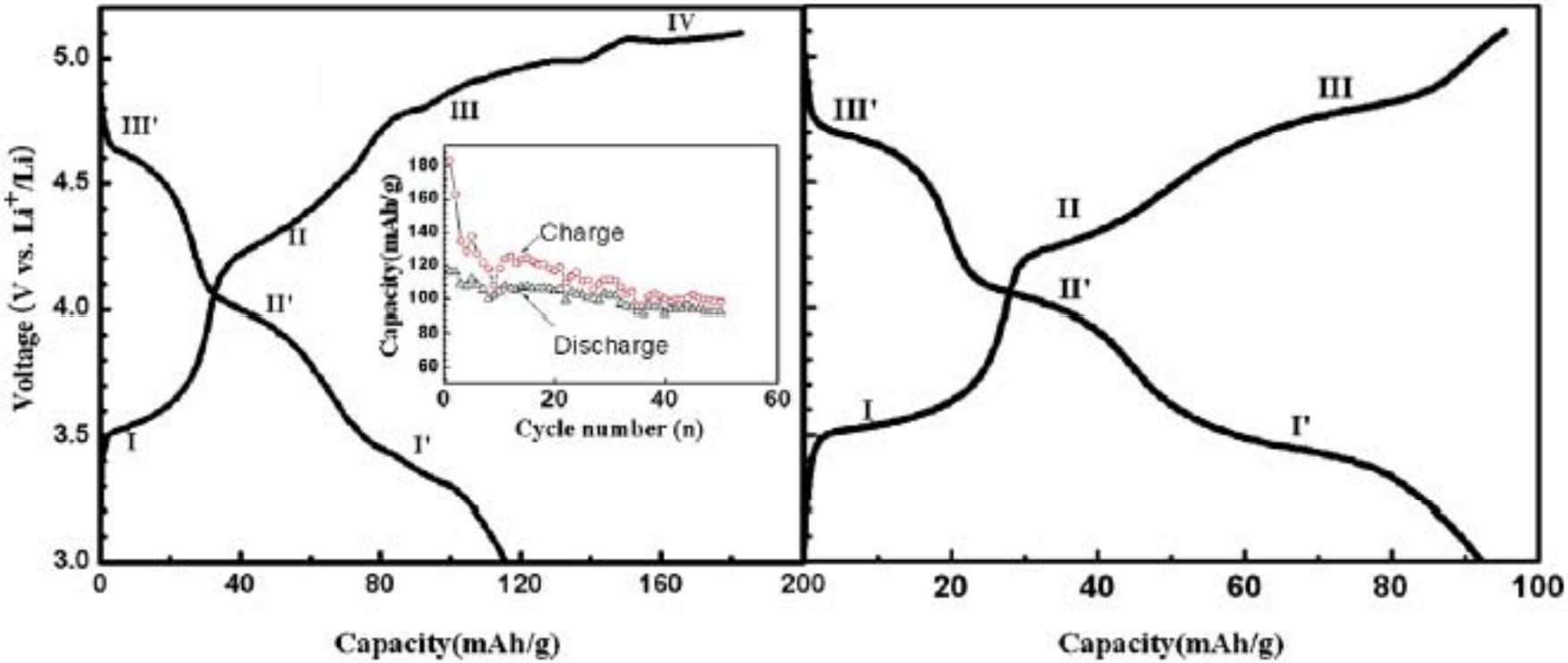
➥ $Li_{0.51}Mn_{0.5}Fe_{0.5}PO_4 \leftrightarrows (1-y)Li_{0.51}Mn_{0.5}Fe_{0.5}PO_4 + yLi_{0.00}Mn_{0.5}Fe_{0.5}PO_4 + yLi^+ + ye^-$ $(0 \leq y \leq 1)$

Electrochemistry Communication, 11 (2009) 2023 pp.

Electrochemical properties of C-Li$Fe_{1/4}Mn_{1/4}Co_{1/4}Ni_{1/4}PO_4$

1st charge/discharge

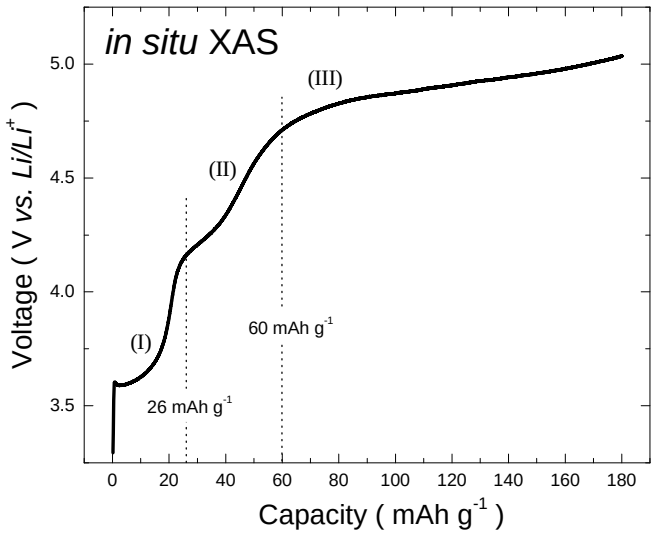
36th charge/discharge



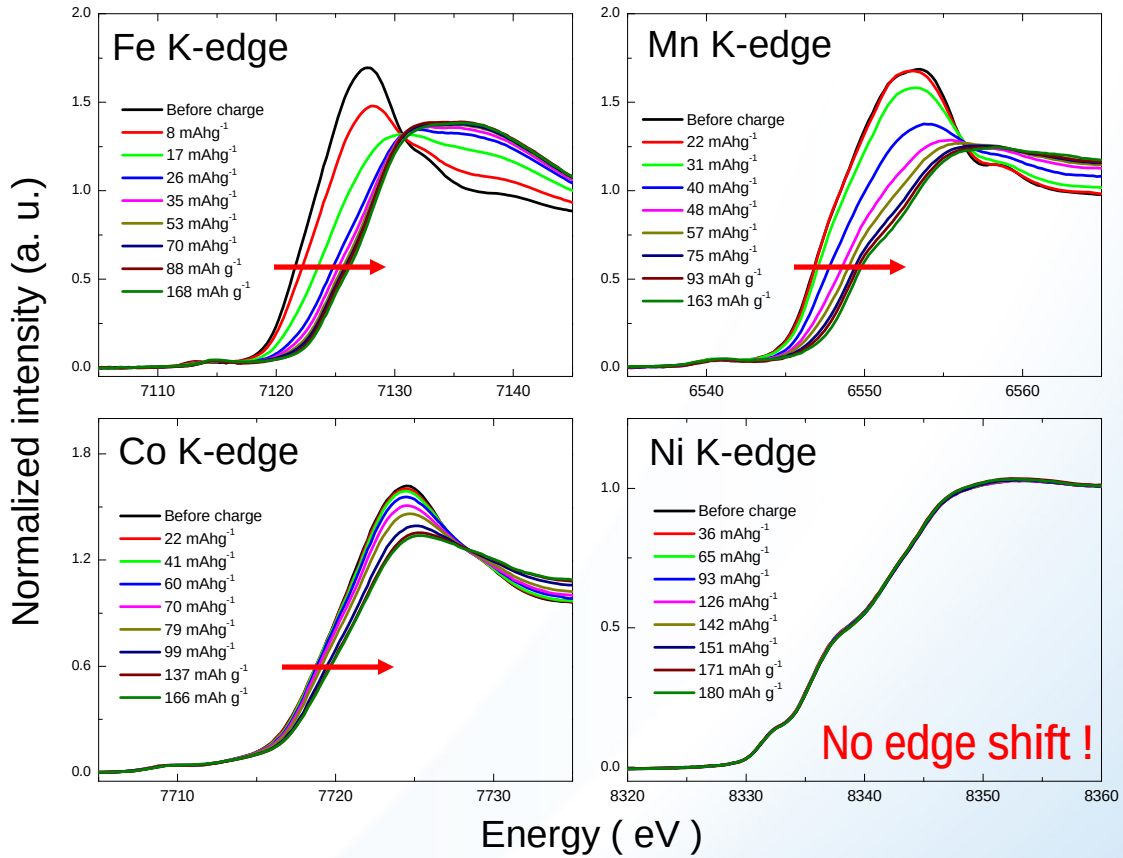
- C-Li$Mn_{1/4}Fe_{1/4}Co_{1/4}Ni_{1/4}PO_4$ solid solution with olivine structure.
- Three distinct voltage plateaus during charge-discharge.

X. J. Wang et al, Electrochemistry Communication, 10 (2008) pp.1347.

In situ Fe, Mn, Co, Ni K-edge XANES spectra of C-Li$Fe_{1/4}Mn_{1/4}Co_{1/4}Ni_{1/4}PO_4$



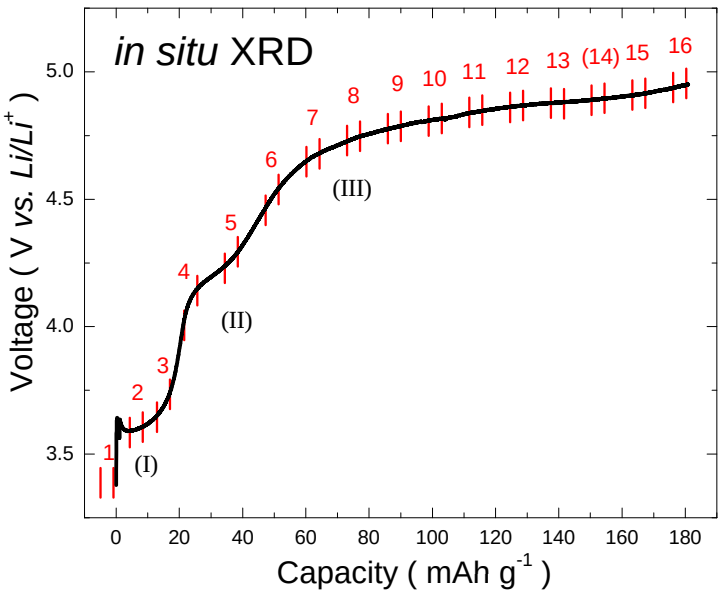
Cut-off voltage: ~ 5.0 V, C/7 rate



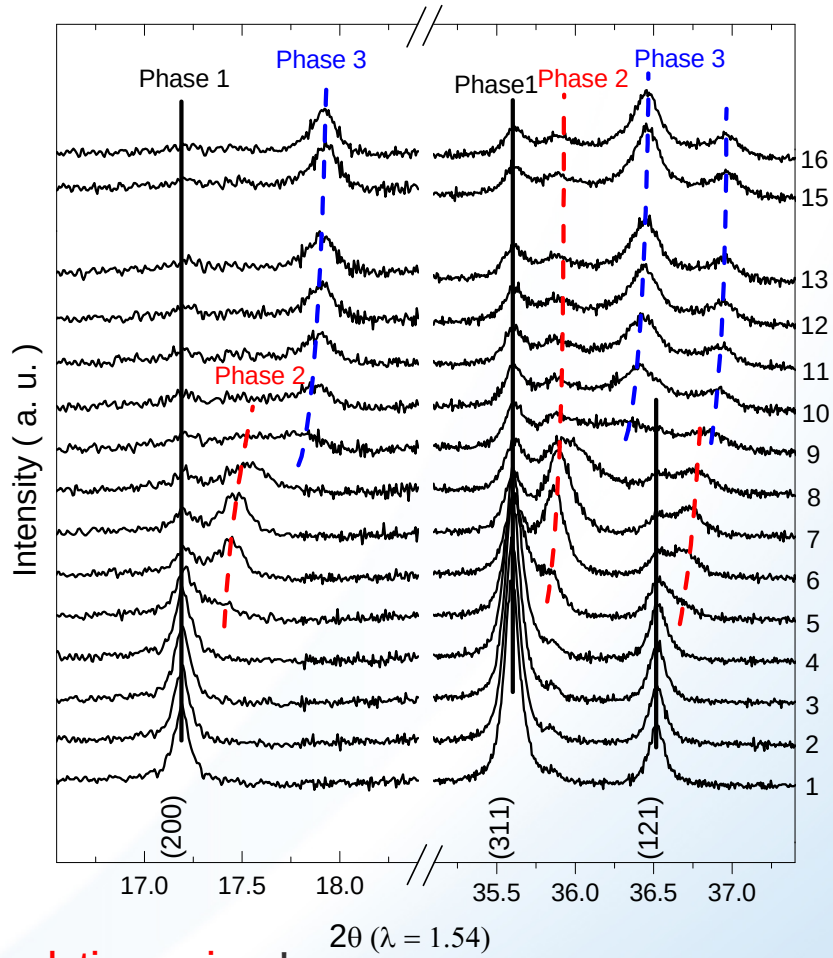
- ➥ Three voltage plateaus at ~ 3.6, 4.2 and 4.7 V ⇨ Redox reactions of Fe^{2+}/Fe^{3+}, Mn^{2+}/Mn^{3+} and Co^{2+}/Co^{3+}.
- ➥ Voltage plateau over ~ 4.9V ⇨ Mostly electrolyte decomposition.
- ➥ Electronic structural changes following the lithium extraction quite well to balance the electrical neutrality.

Electrochemistry Communication, 11 (2009) 913 p.

In situ XRD of C-$LiFe_{1/4}Mn_{1/4}Co_{1/4}Ni_{1/4}PO_4$



Cut-off voltage: ~ 5.0 V, C/7 rate



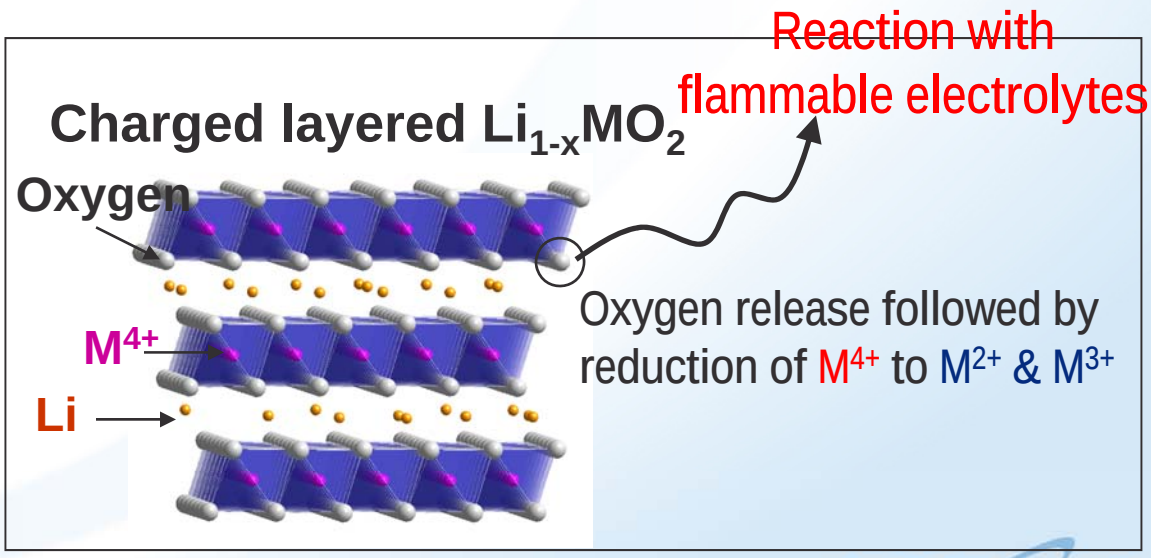
- Appearance of intermediate phase (phase 2) and solid-solution regions!
- From scan 2 to 4 (1st plateau region), small changes in the XRD patterns (slow crystal structural change).
- Fast electronic structural changes (from *in situ* XAS) and slow bulk crystal structural changes in this system!

Electrochemistry Communication, 11 (2009) 913 p.

Thermal runaway in Li-ion cells

- Lithium-ion batteries are safe under normal operating conditions.
- However, if overcharge protection circuitry fails, or if there is a short circuit, then the battery temperature can increase.

- *Stage 1*: Room Temperature to 125°C ⇨ Onset of thermal runaway
  ; Anode passive films/Electrolyte reactions occur (film decomposes) - Exothermic
- *Stage 2*: 125 °C to 180 °C ⇨ Venting and accelerated heating (smoke)
  ; Oxygen release from the cathode – Highly Exothermic
- *Stage 3*: 180 °C and above ⇨ Explosive decomposition (flame)



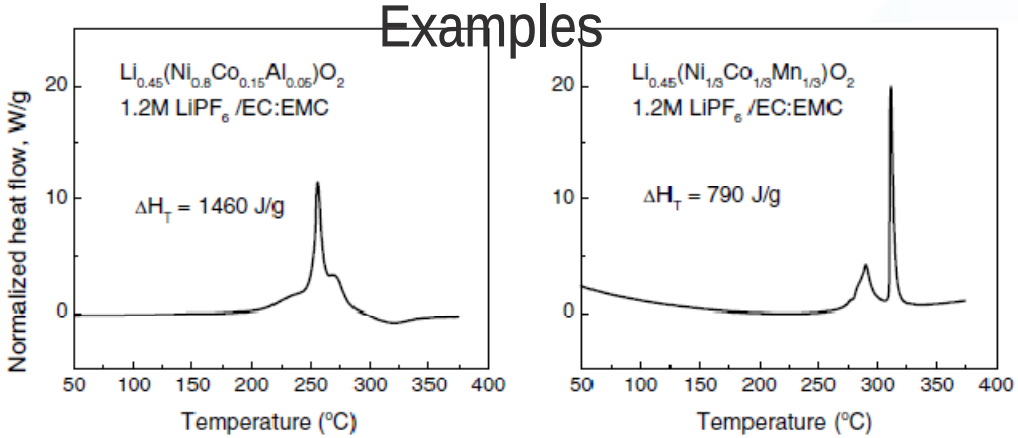
Thermal stability study of charged cathode materials (Safety related issue)

- Improving the thermal stability of the electrode materials
  - ⇨ many approaches: doping, surface coating, cathode chemistry, and so on.

- How do we improve thermal stability of cathode materials?
  - ⇨ need better understanding of thermal behavior of the charged electrode !

General method to evaluate thermal stability of charged cathode materials : TG/DSC

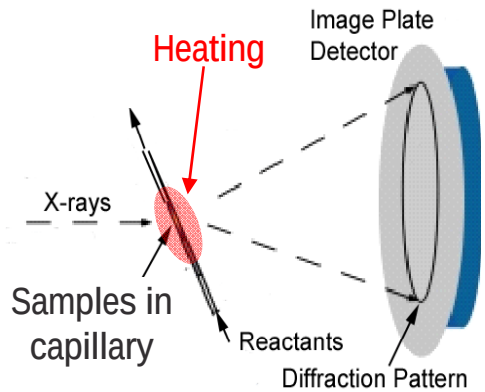
Examples



I. Belharouak et al, Electrochemistry Communication, 8 (2006) 329 p.

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

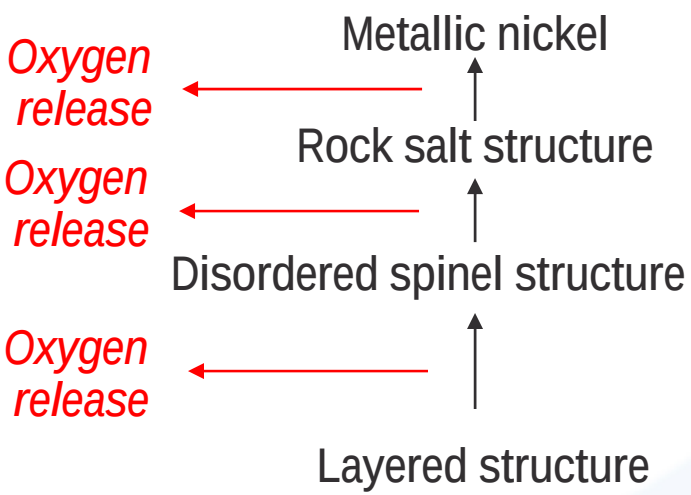
In situ time-resolved (TR) XRD of charged cathode materials during heating

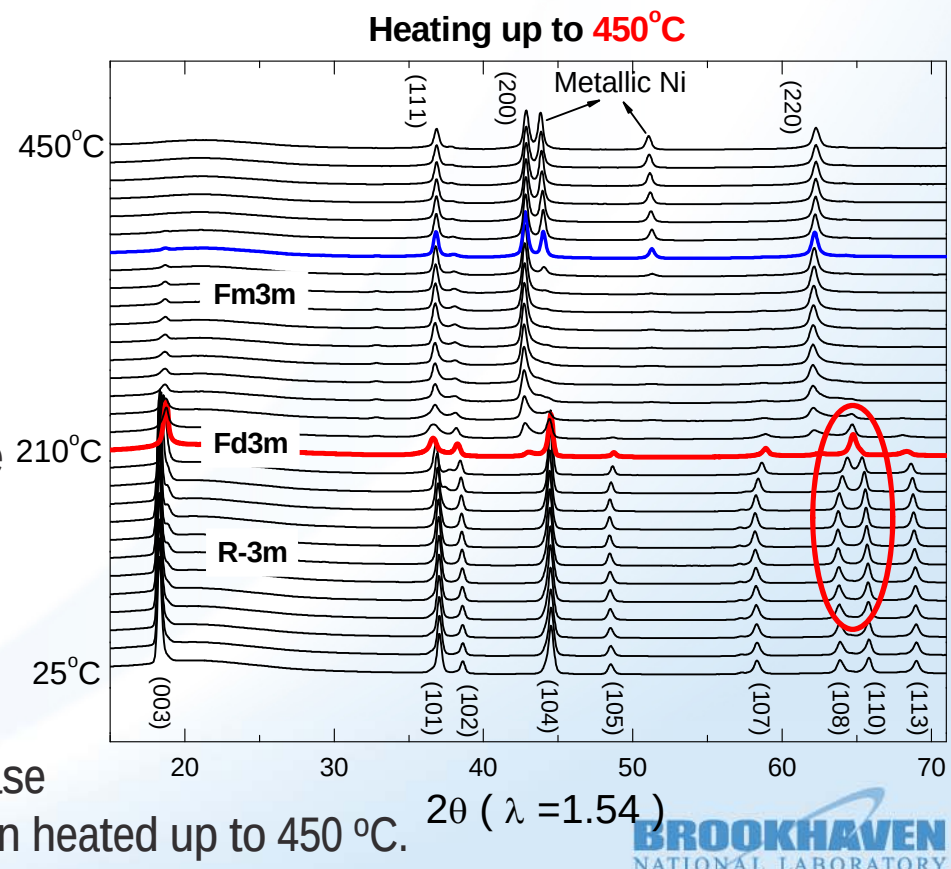


- Average structural information (long range order) during heating

- $Li_{0.33}NiO_2$

➥ A good road map for the structural changes of nickel-based cathode materials during heating.

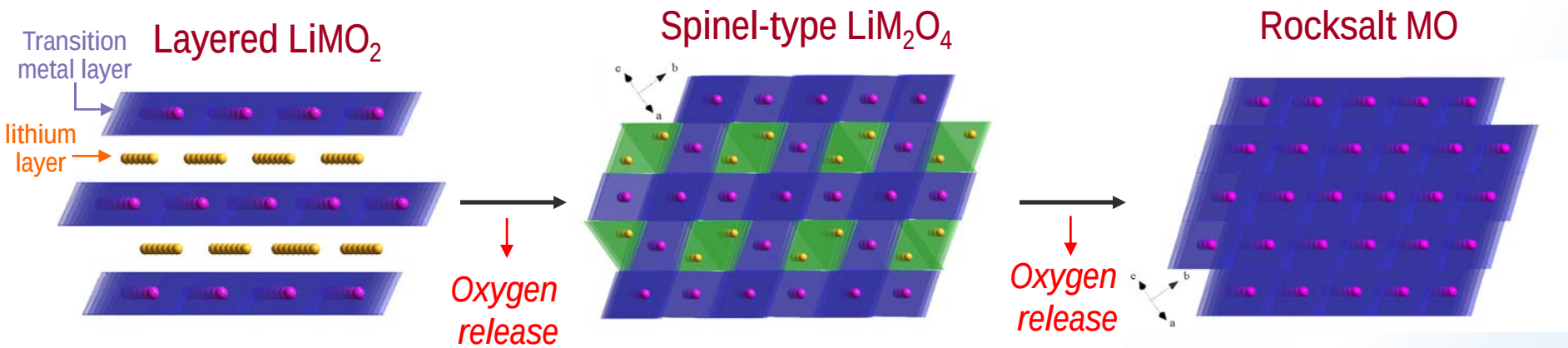




➥ $Li_{0.33}NiO_2$ goes through a whole series of phase transitions (i.e., thermal decomposition) when heated up to 450 °C.

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!!*

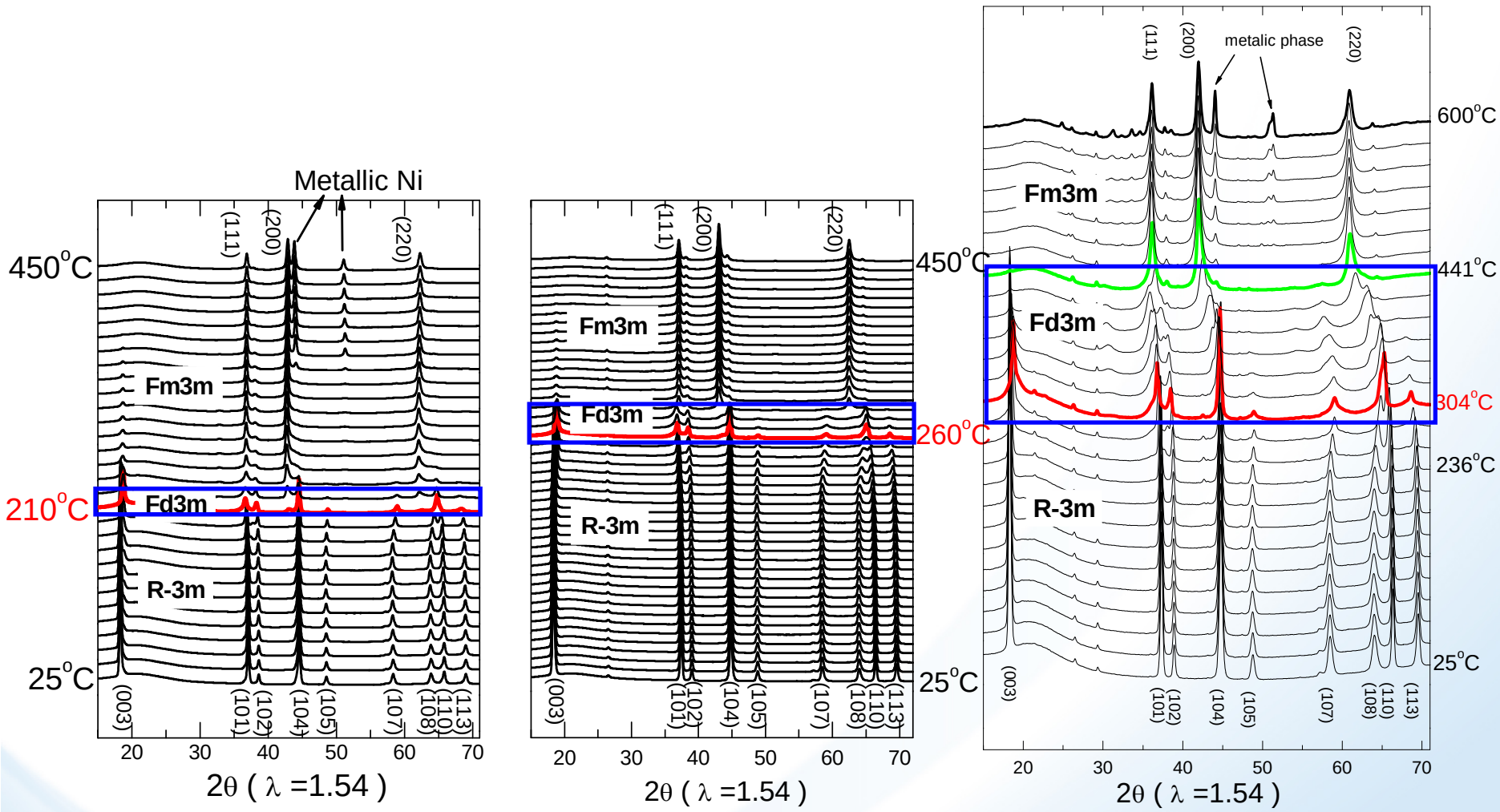
When x= 0.33 (67% of SOC) in Li_xMO_2

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

Comparison of thermal stability of charged layered cathodes *with* electrolyte



$Li_{0.33}NiO_2$ $Li_{0.33}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ $Li_{0.33}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$

➥ NCM cathode shows the best thermal stability due to the large spinel stabilized temperature region.

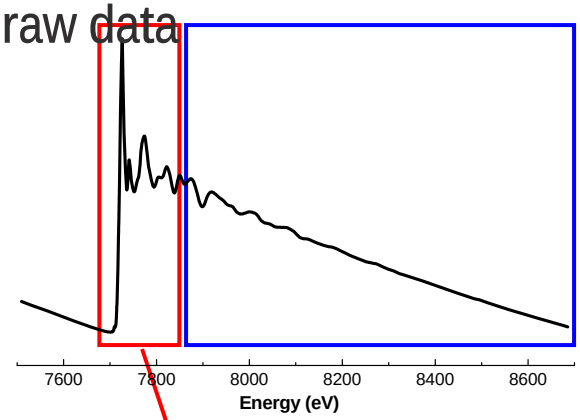
why? ⇨ Need better understanding of role of each elements during thermal decomposition.

Solution: Soft & Hard X-ray absorption spectroscopy !!

BROOKHAVEN NATIONAL LABORATORY

X-ray absorption spectroscopy : *XANES* and *EXAFS*

raw data

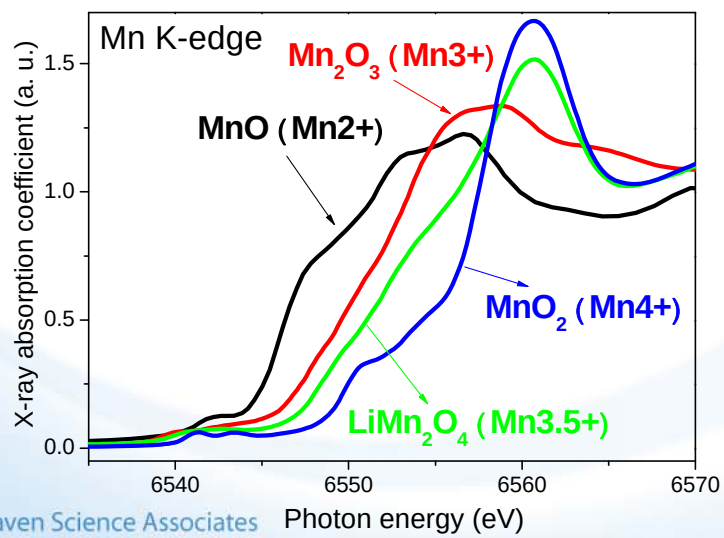


Extended X-ray Absorption Fine Structure (EXAFS)

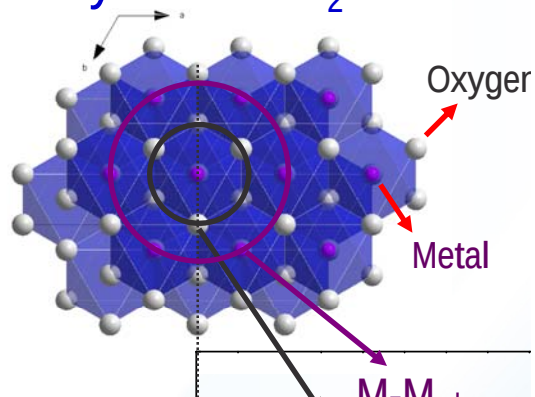
; Local structural information like bond distance, coordination number, degree of disorder

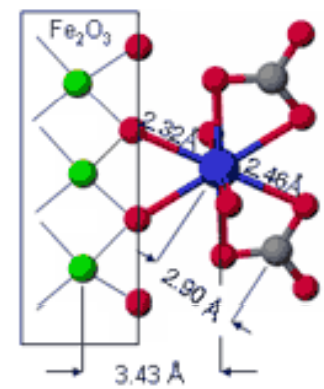
X-ray Absorption Near Edge Structure (XANES)

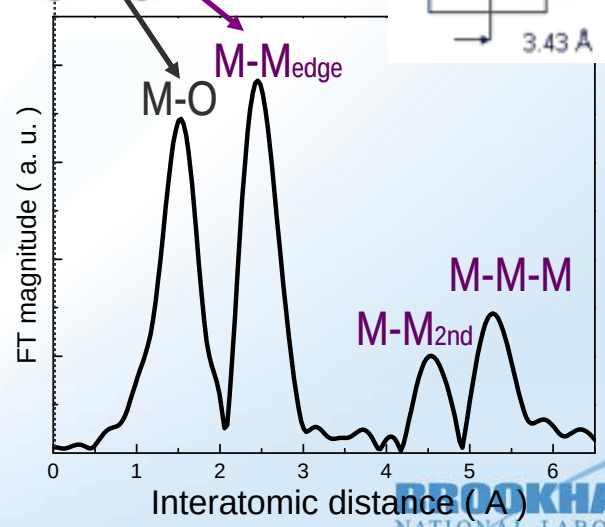
; Oxidation state, site symmetry, covalent bond strength



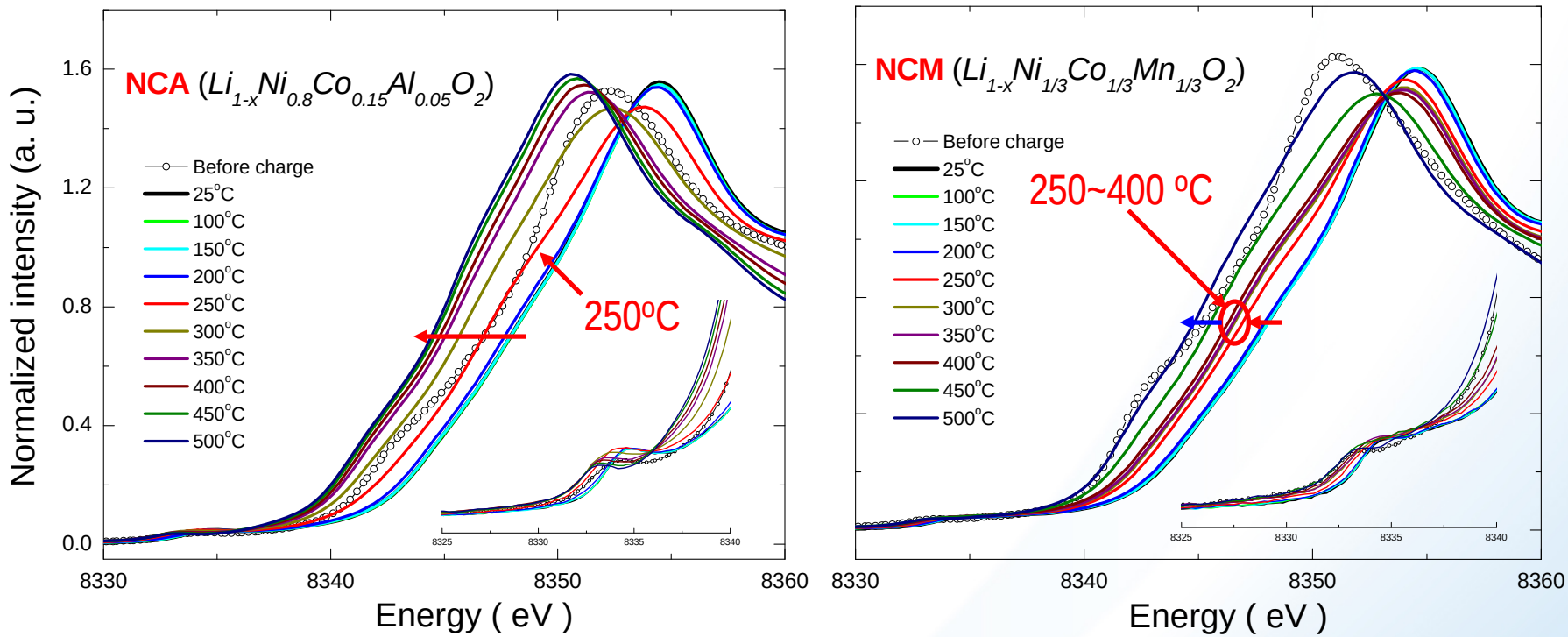
Layered $LiMO_2$ structure





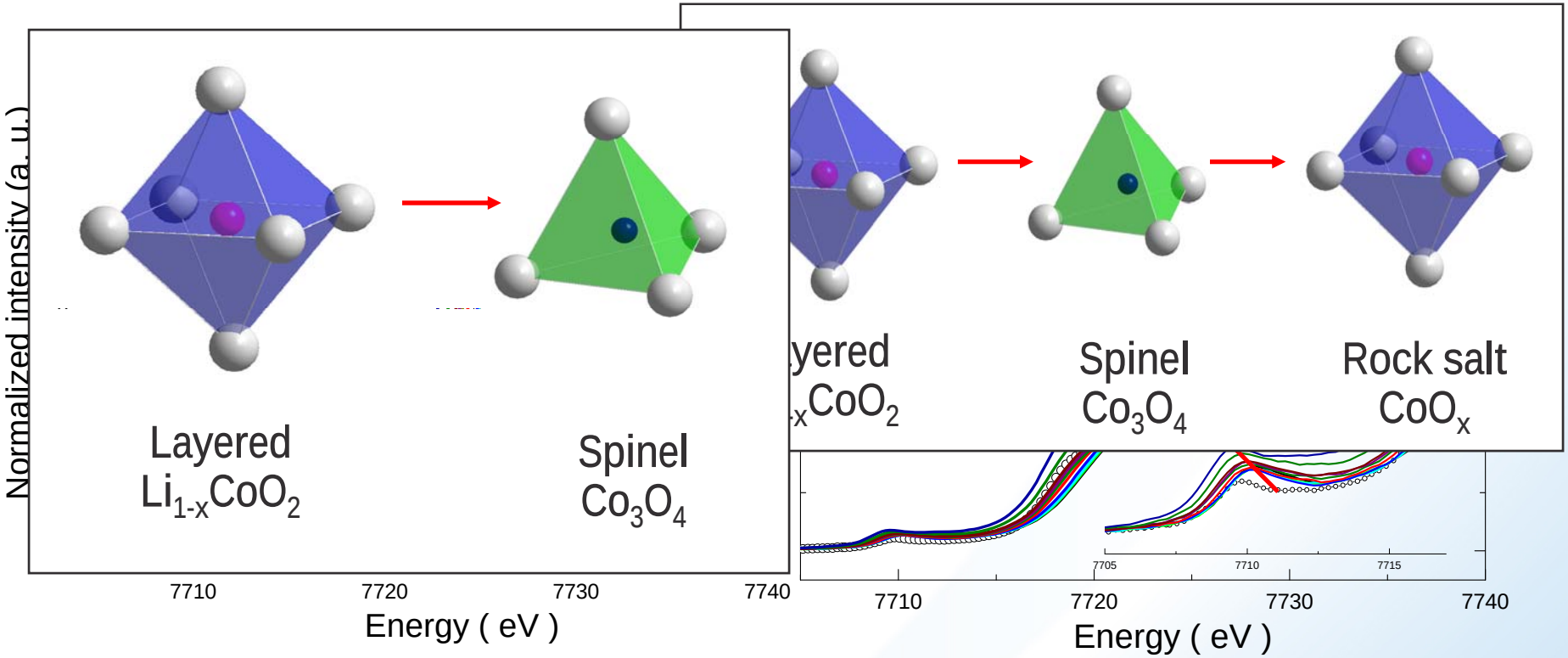


Ni K-edge XANES of charged $Li_{0.33}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) and $Li_{0.33}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) during heating



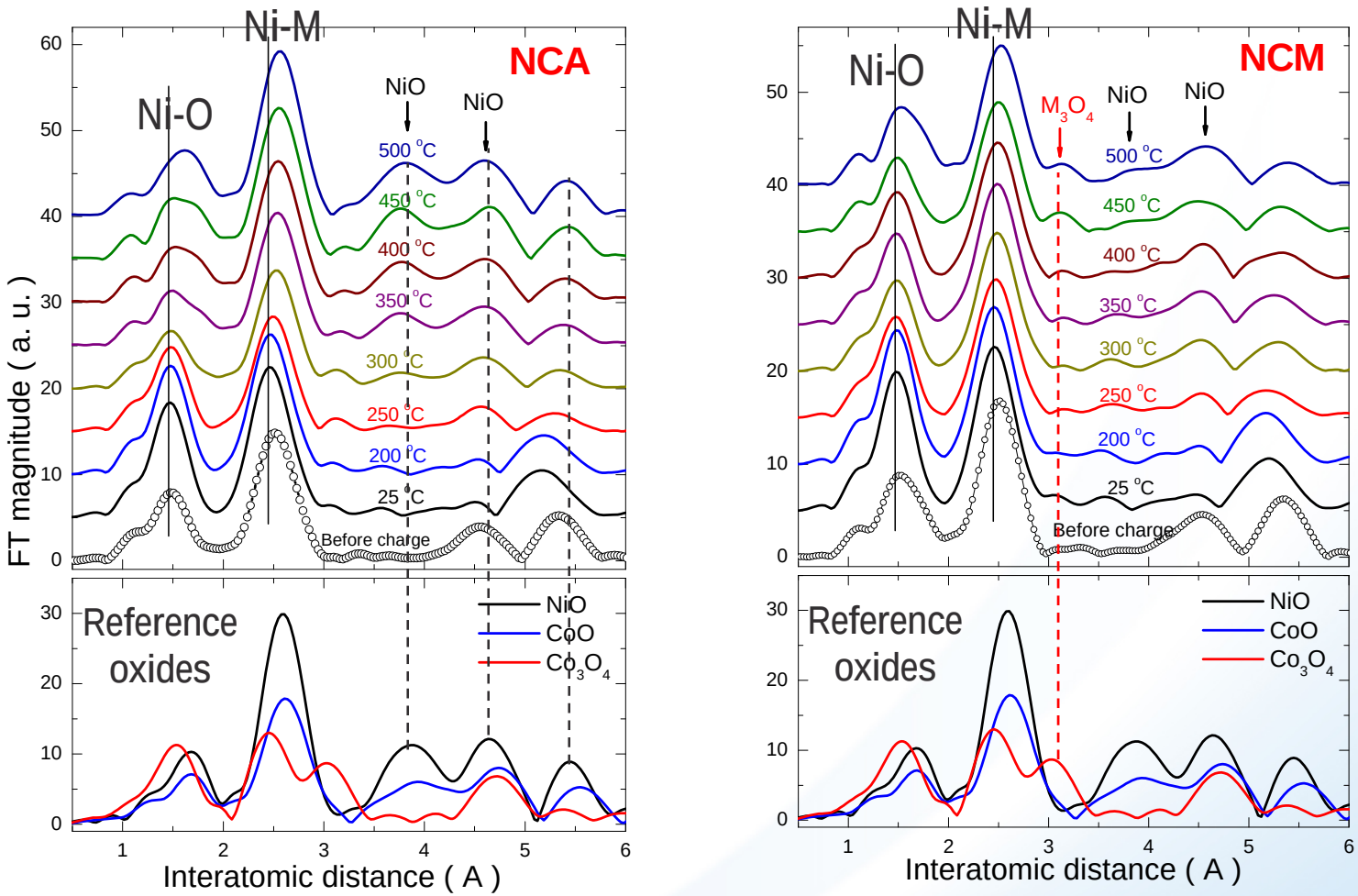
- Much slower reduction in oxidation state of Ni ions in NCM than NCA during heating.
- Better thermal stability of Ni ions in NCM is likely due to the combined effects of the stabilization of spinel type-phase and good thermal stability of Mn ions near Ni ions.

Co K-edge XANES of charged $Li_{0.33}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) and $Li_{0.33}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) during heating



- Much slower reduction in oxidation state of Co ions in NCM than NCA during heating.
- Better thermal stability of Co ions in NCM is likely due to the stabilization of Co_3O_4 type-spinel phase prevent further thermal degradation to CoO type-rock salt phase.
- New observation of the Co_3O_4 type-spinel phase formation (tetrahedral coordination) in local atomic arrangement in NCA which was not detected in TR-XRD during heating. (Pre-edge region in NCA)

Ni K-edge EXAFS of charged $Li_{0.33}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) and $Li_{0.33}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) during heating

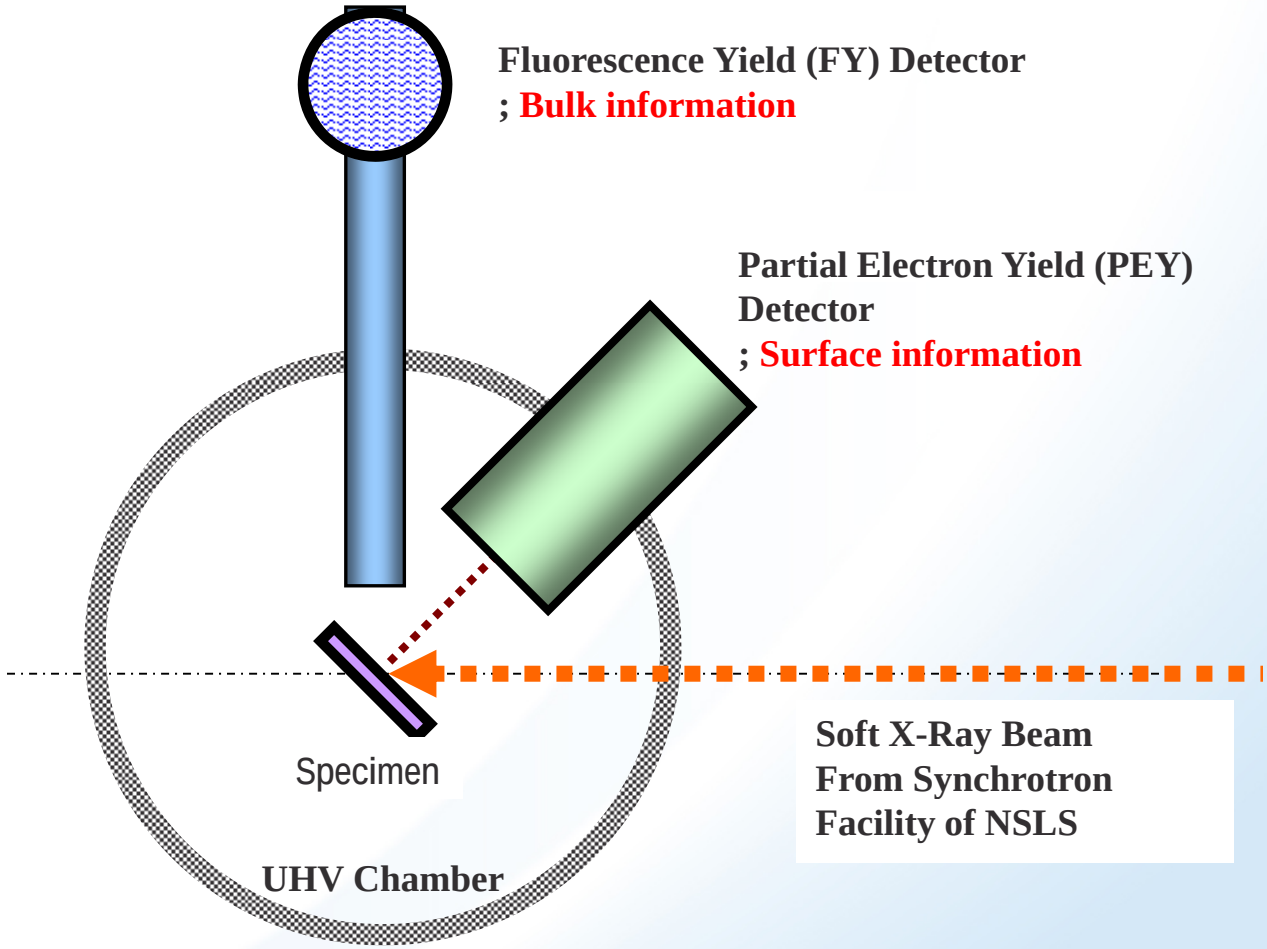


- NCM shows much slower thermal decomposition to MO type-rock salt phase in local structure around Ni compared to NCA.
- Ni K-edge EXAFS clearly supports the better thermal stability of NCM than NCA due to the combined effects of the stabilization of spinel-type phase (likely Co_3O_4) and excellent thermal stability of Mn in NCM.

Thermal Abuse: Newly developed *in situ* soft XAS

Experimental setup: in situ heating stage and detectors in UHV chamber

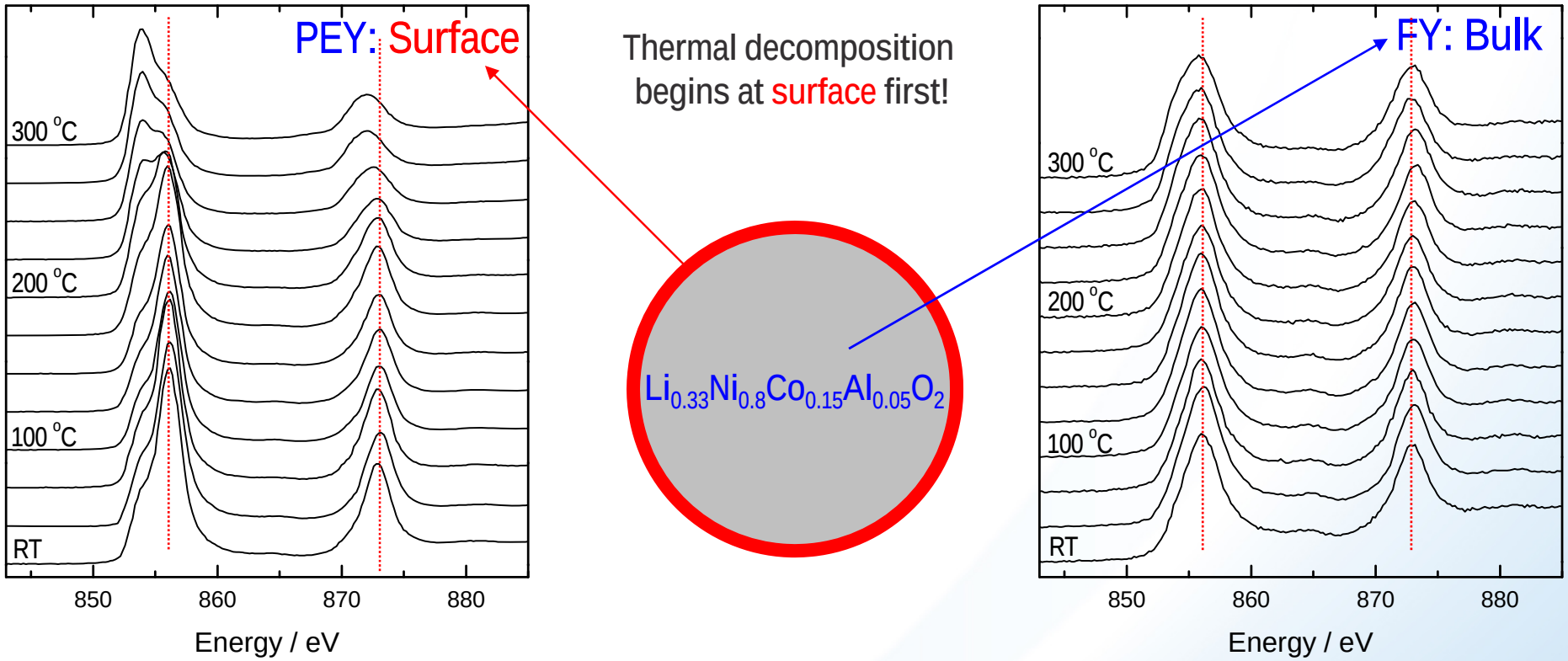
In situ soft X-ray XAS sample holder with heating stage



➥ In situ soft X-ray absorption technique: we are able to monitor structural changes at the surface and in the bulk at the same time during heating.

Thermal Abuse: Preliminary results of *in situ* soft XAS

Ni L-edge XAS for NCA cathode ($Li_{0.33}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$) during heating

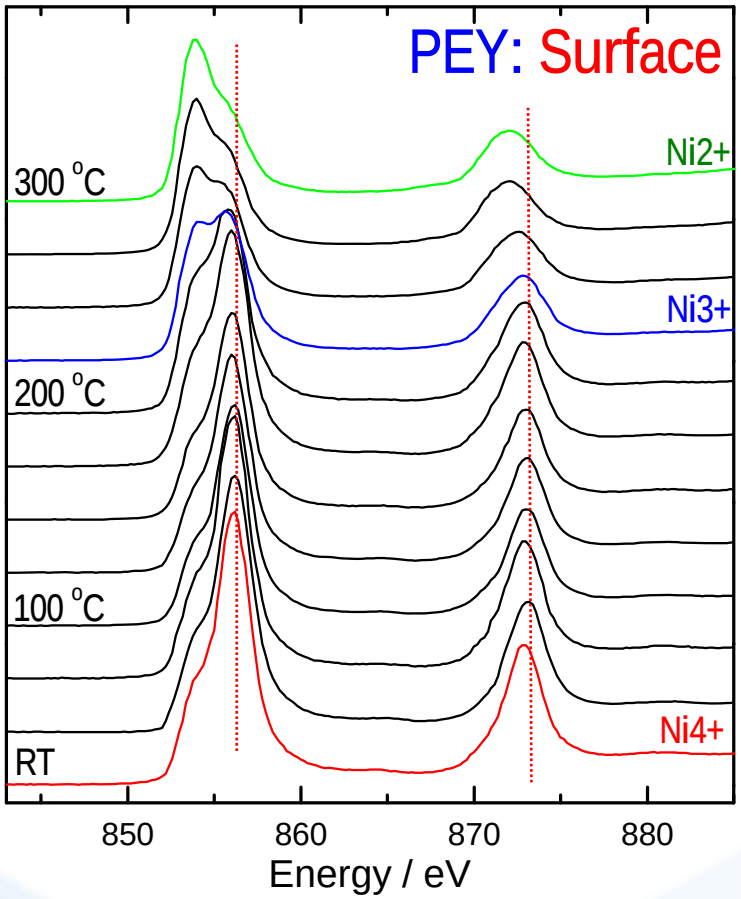


- ➥ Clear observation of the reduction of Ni^{4+} ions at the surface during heating.
- ➥ The surface of the electrode is decomposed at much earlier temperature than the bulk.
- ➥ Surface coating with thermally stable material will improve the thermal stability.

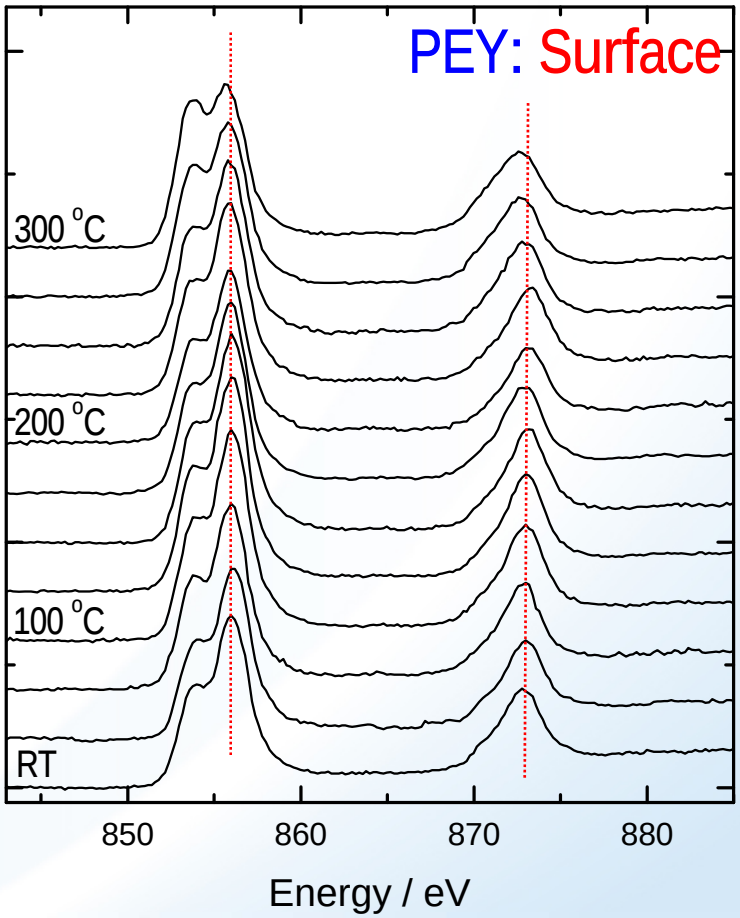
Thermal Abuse: Preliminary results of *in situ* soft XAS

Comparison of NCA and NCM cathodes at Ni L-edge

$Li_{0.33}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA)



$Li_{0.33}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$ (NCM)

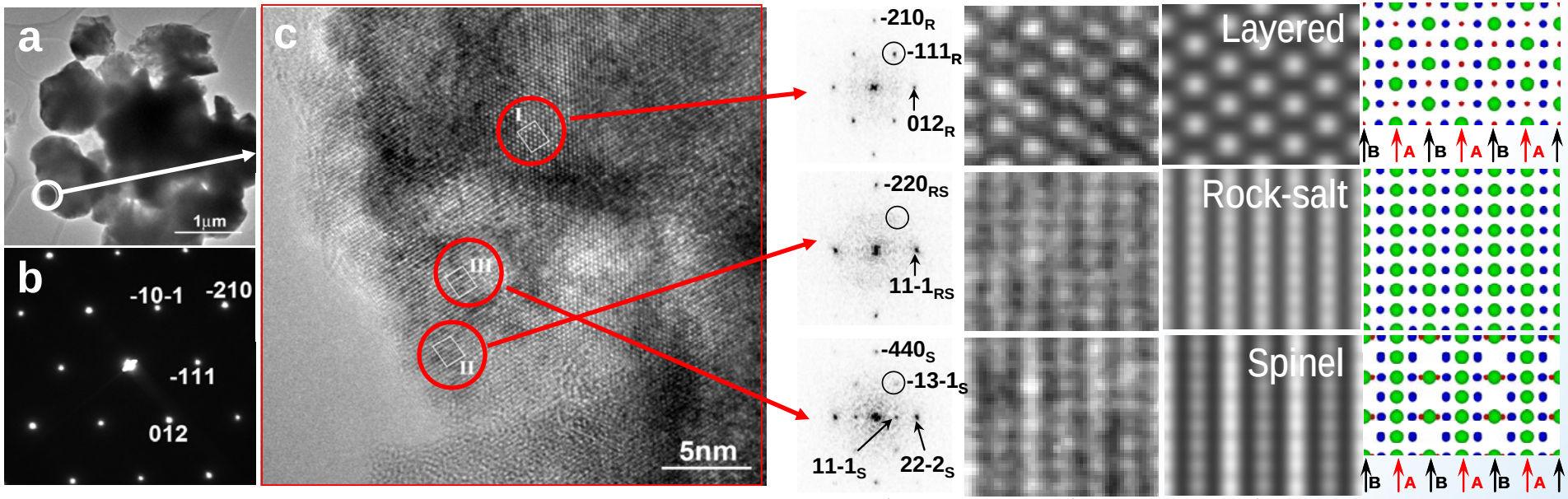


➥This result is well agreed with our previous results and confirming the better thermal stability of NCM cathode material.

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)

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



Diffractograms

Magnified images

Simulated images

(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.

Concluding remarks

- Synchrotron based X-ray techniques are very promising tools to study electrode materials for Li-ion batteries and supercapacitors.
  - ➥ *In situ* X-ray diffraction (XRD) studies during charge-discharge and heating.
    : comprehensive average bulk structural information.
  - ➥ *In situ* X-ray absorption (XAS) studies during charge-discharge and heating.
    : local structural and electronic information.

⇨ *Combination of above techniques will give a new insight on identifying key factors that limit battery safety, performance and lifetime !*

⇨ *The results will contribute to the development of safe, stable, and high electro-chemical performance electrode materials.*

Acknowledgement

▣U. S. Department of Energy (DOE), Vehicle Technologies Office
U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences through the Northeastern Center for Chemical Energy Storage, an Energy Frontier Research Center under Contract Number DE-SC0001294

▣ Co-workers
- Dr. *Kyung-Wan Nam*
- Dr. *H. S. Lee*
- Dr. *O. Haas*
- Dr. *X. J. Wang*
- Dr. *Y. N. Zhou*
- Dr. *L. Wu*
- Dr. *Y. Zhu*

▣ NSLS
- X7B : Dr. *J. Hanson*
- X14A : Dr. *J. Bai*
- X18A : Dr. S. *Ehrlich*
- X18B & X19A : Dr. *S. Khalid & N. Marinkovic*
- U7A : Dr. *C. Jaye, Z. Fu & D. Fischer*

▣ Collaborators
- Prof. *H. Li & X. Huang* (Institute of Physics (IOP), Chinese Academy of Sciences, China)
- Dr. *S. Kang & Dr. M. Thackeray*, and Dr. K. Amine (Argonne National Lab)
- Dr. *S. Choi* (LG Chem. LTD)