Application of combined in situ XAS and XRD to the study of battery materials during electrochemical cycling or heating

To be presented at the short course in "In-situ Methods of X-ray Absorption Spectroscopy", October 24, 2013, BNL.

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a passion for discovery

Acknowledgments

- U. S. Department of Energy (DOE), Vehicle Technologies Program Office.
- NSLS and CFN: U.S. DOE, Basic Energy of Science.

Office of Science
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Outline

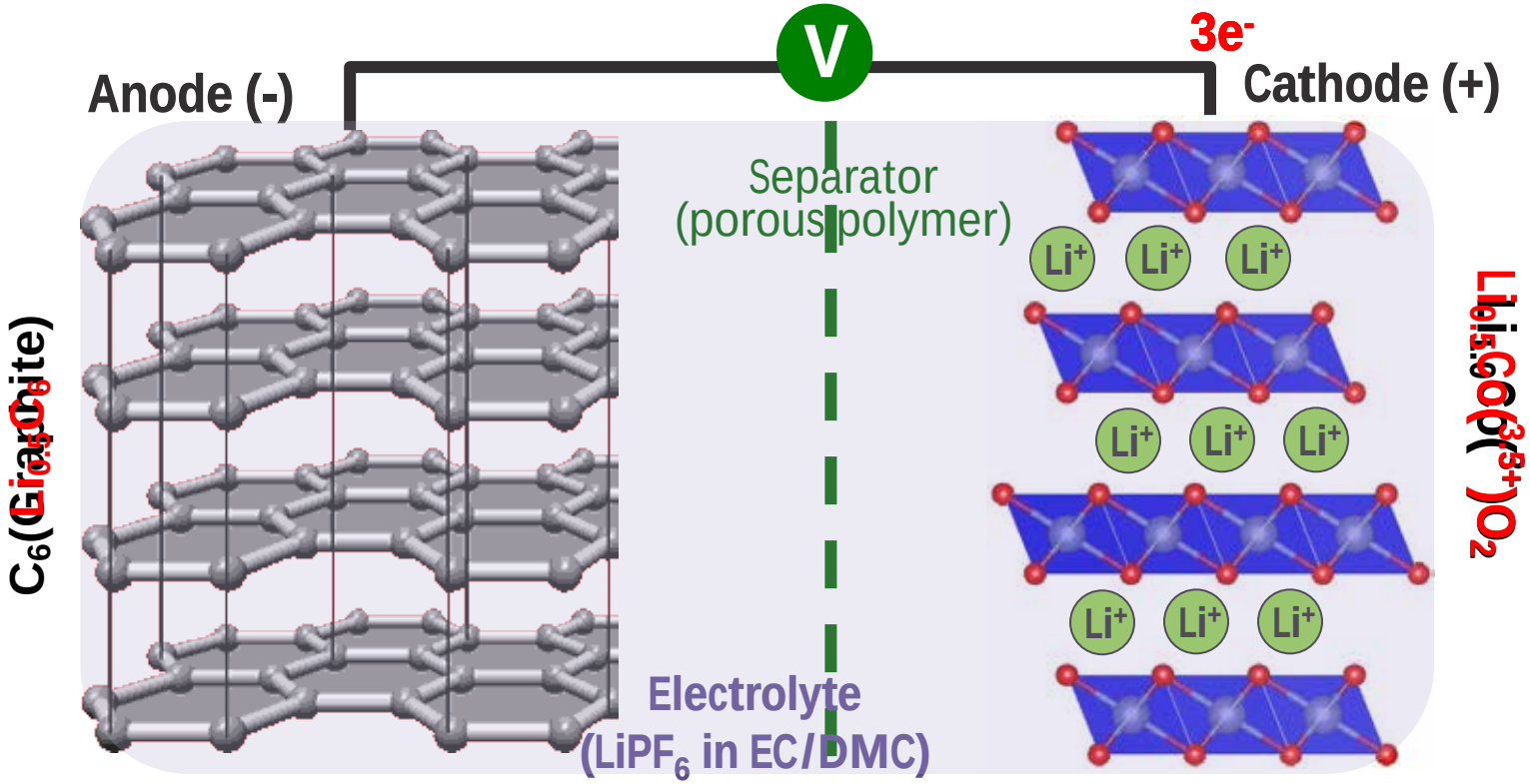
Part 1. Charge compensation and phase transition behavior of $LiFe_{0.5}Mn_{0.5}PO_4$ cathode materials studied by using combined in situ XAS and XRD study during electrochemical charging

Part 2. Thermal stability study of charged battery materials using combined XRD/mass spectroscopy, XAS and TEM study during heating (Safety related issue)

Working principle of Lithium-ion battery (LIB)

Discharged state when assembled (~3.5V)

Charging (~4.3V)



$$LiCoO_2 + C_6 \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Li_{1-x}CoO_2 + Li_xC_6$$

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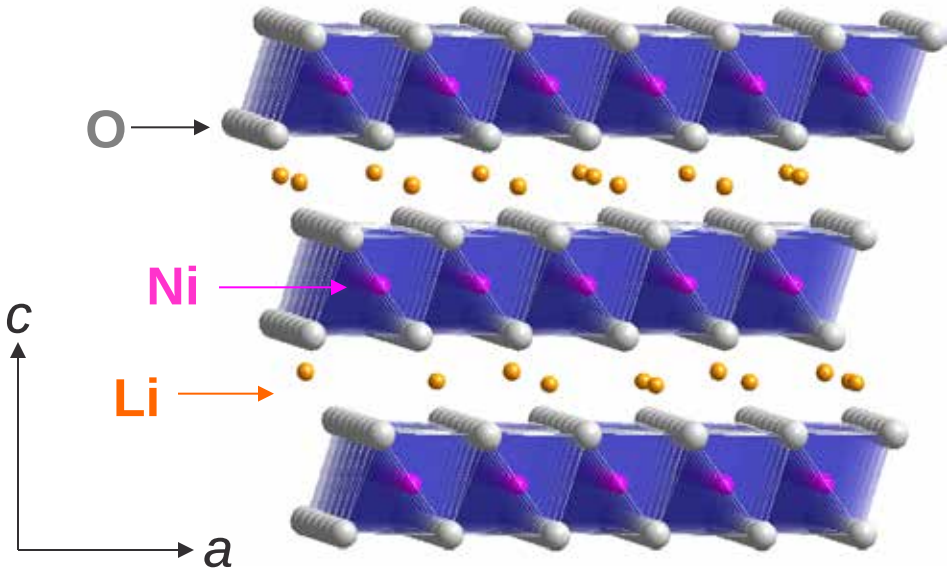
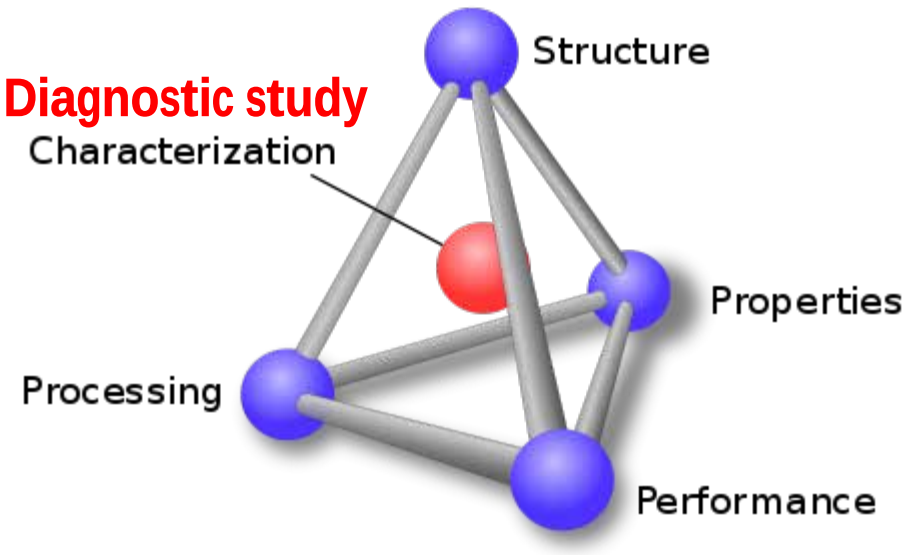
Need for advanced diagnostic study of LIB materials

Layer structured $LiNiO_2$ Cathode (positive) material





Need to identify key materials properties and materials interactions that limit battery lifetime, performance and safety.

▣ Approach

- *in situ X-ray diffraction (XRD) during charge-discharge* or heating.
- *in situ X-ray absorption spectroscopy (XAS) during charge-discharge* or heating.
- *ex situ Soft XAS of transition metal L- and oxygen K-edges*
  - XRD: Long range structure, Hard XAS: bulk local structure, Soft XAS: bulk vs. surface structure

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Part 1.

Charge compensation and phase transition behavior of $LiFe_{0.5}Mn_{0.5}PO_4$ cathode materials:

Combined in situ XAS and XRD study during charging

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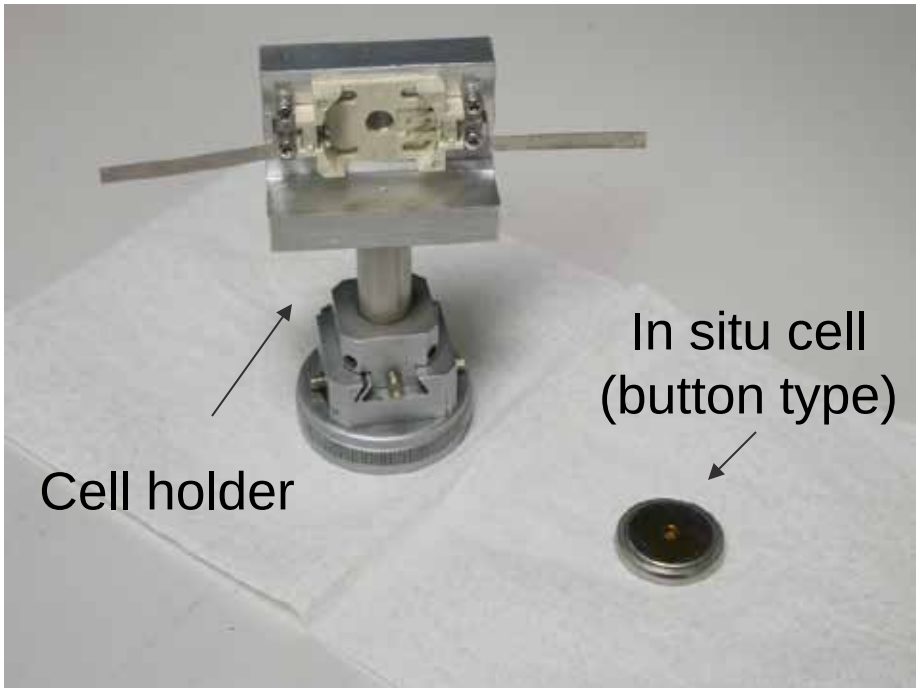
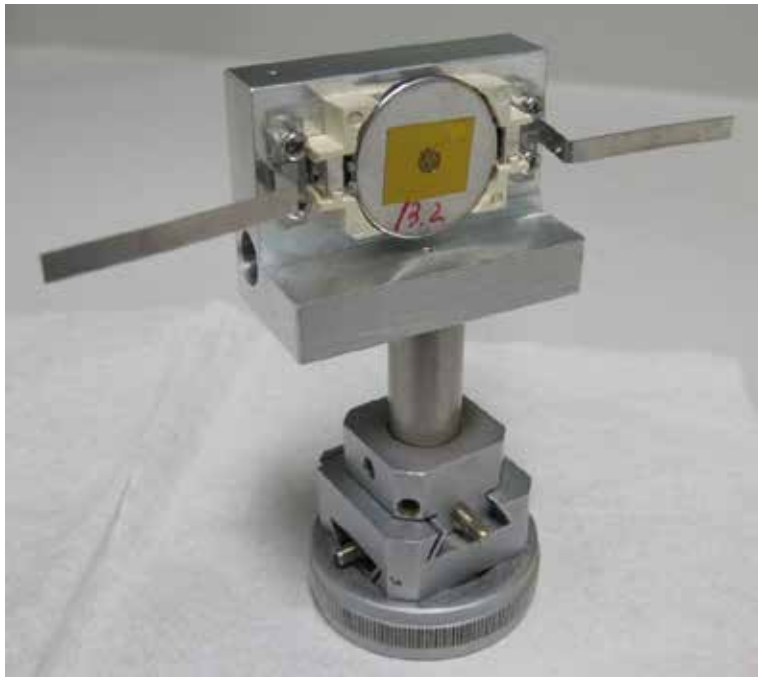
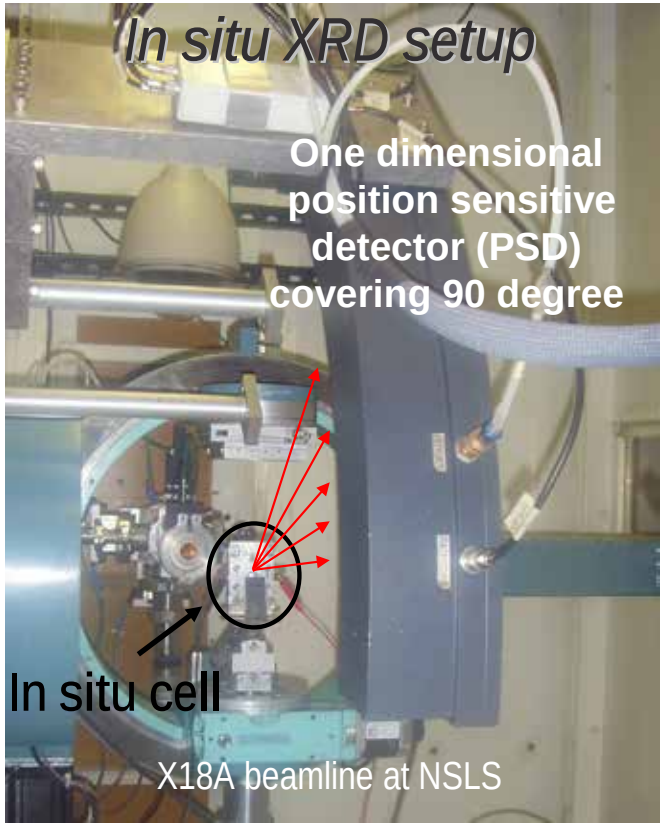
Li-ion battery cell for *in situ* X-ray study (diffraction & absorption)





In situ X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) during electrochemical cycling



In situ X-ray absorption spectroscopy (XAS) setup

Potable battery cycler

© ***In situ*** **high resolution X-ray diffraction (X14A, X18A) : Crystalline structure**

© ***In situ*** **X-ray absorption spectroscopy (X18A, X18B, X19A) :**
Local and electronic structure (e.g., valance state, coordination number, bond length and disorder)

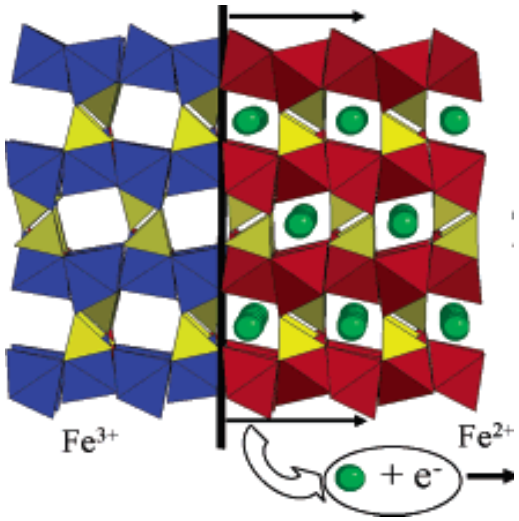
Ê ***Provide various combinations of in situ X-ray techniques to better understand the structure-property relationship of lithium battery materials.***

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

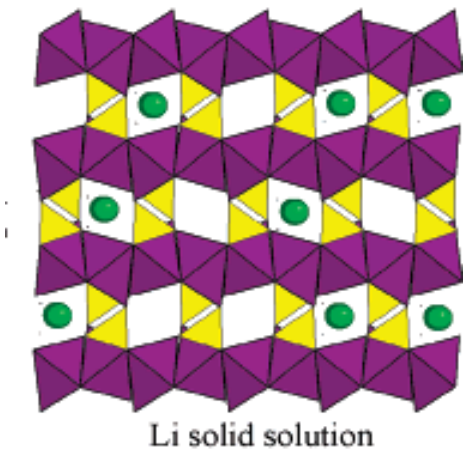
$FePO_4$ $LiFePO_4$



vs.

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

Li_xFePO_4



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

Ê *In situ* XAS and XRD to study the relationship between **phase transition behaviors** and **introduction of 3d transition metals** (Mn) into $LiFePO_4$, $LiFe_{0.5}Mn_{0.5}PO_4$.

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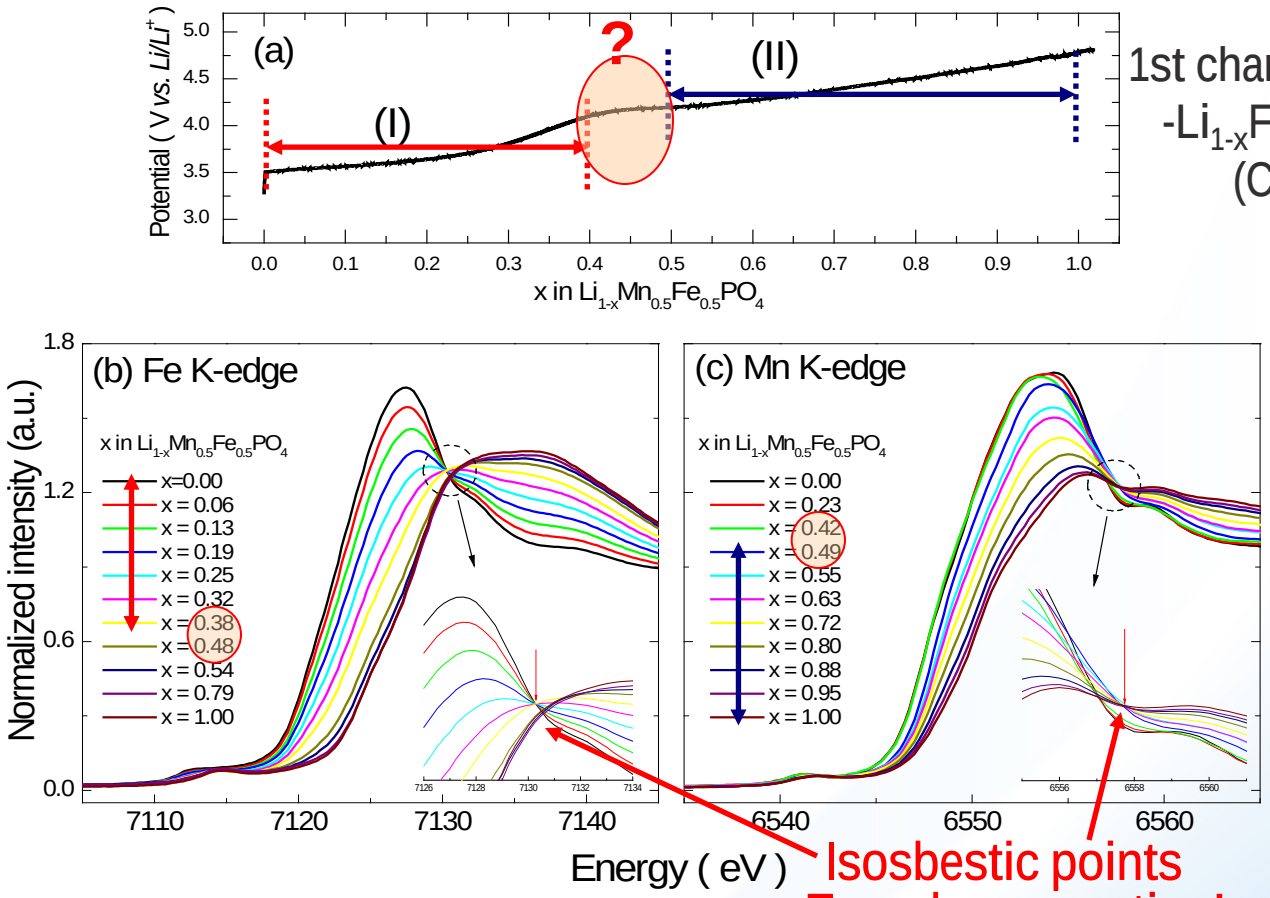
In situ Fe, Mn K-edge XANES spectra of C-$LiFe_{0.5}Mn_{0.5}PO_4$

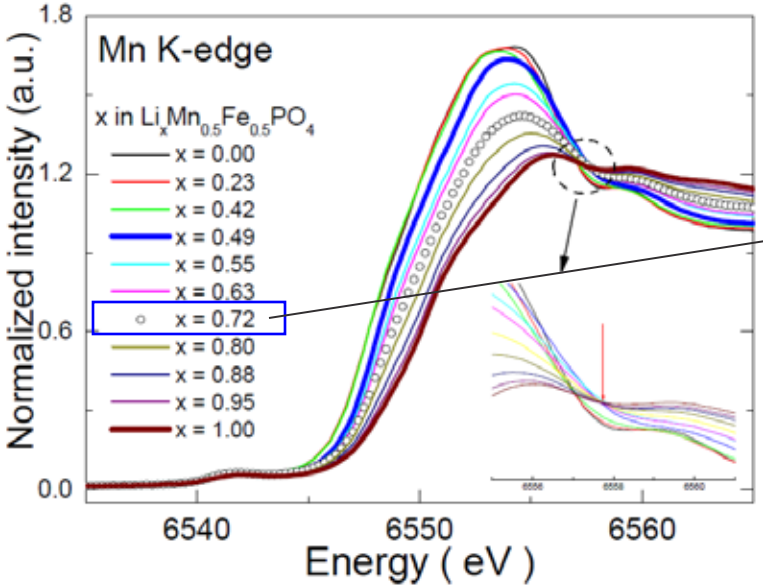


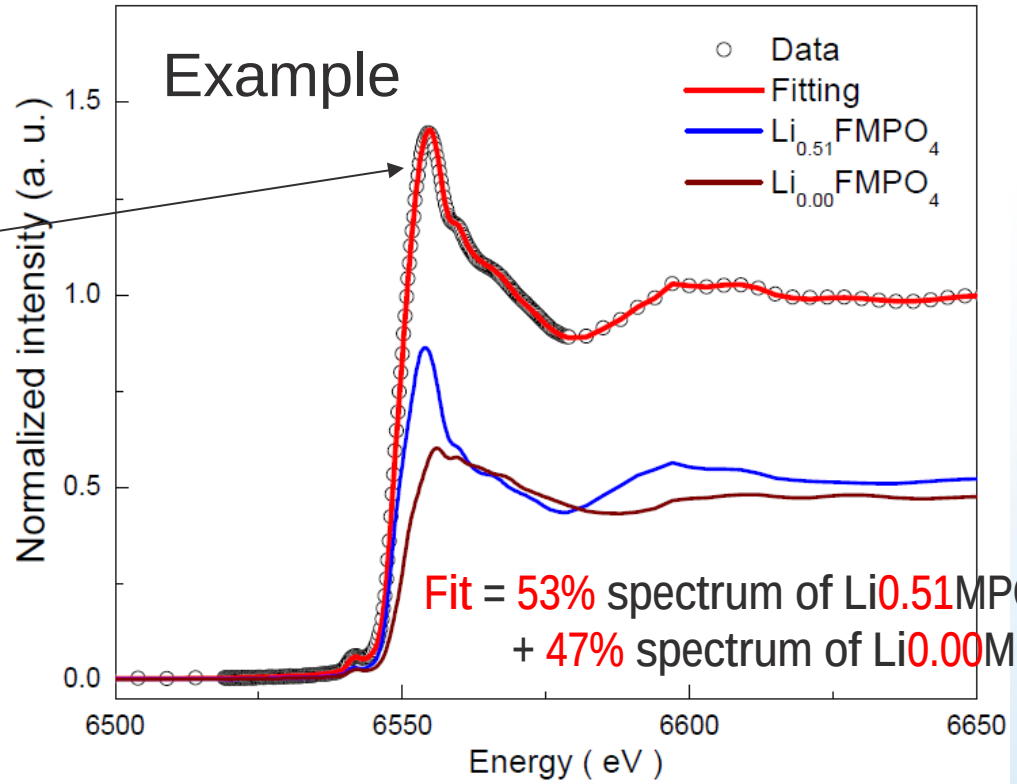
1st charge curve of C -$Li_{1-x}Fe_{0.5}Mn_{0.5}PO_4$ (C/20 rate)

- 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-$LiFe_{0.5}Mn_{0.5}PO_4$



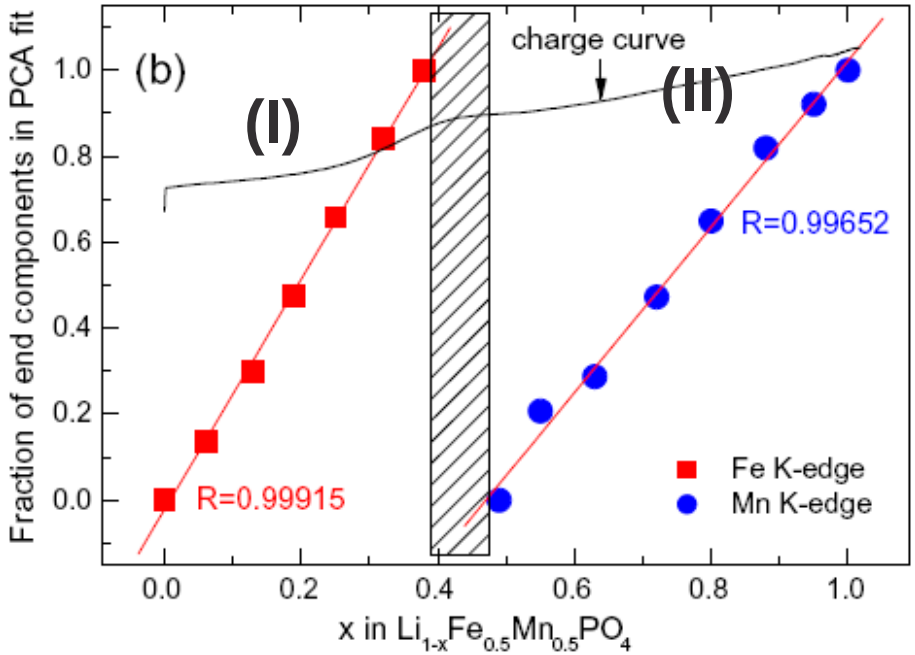


Two phase reaction

$Li_{0.51}Mn_{0.5}Fe_{0.5}PO_4$ **D** 0.53 $Li_{0.51}Mn_{0.5}Fe_{0.5}PO_4$ + 0.47 $Li_{0.00}Mn_{0.5}Fe_{0.5}PO_4$ + 0.47 Li^+ + 0.47e-

Electrochemistry Communication, 11 (2009) 2023 pp.

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 ≤ x ≤ ~0.4 in C-$Li_{1-x}Mn_{0.5}Fe_{0.5}PO_4$ (Fe^{2+}/Fe^{3+} redox reaction);

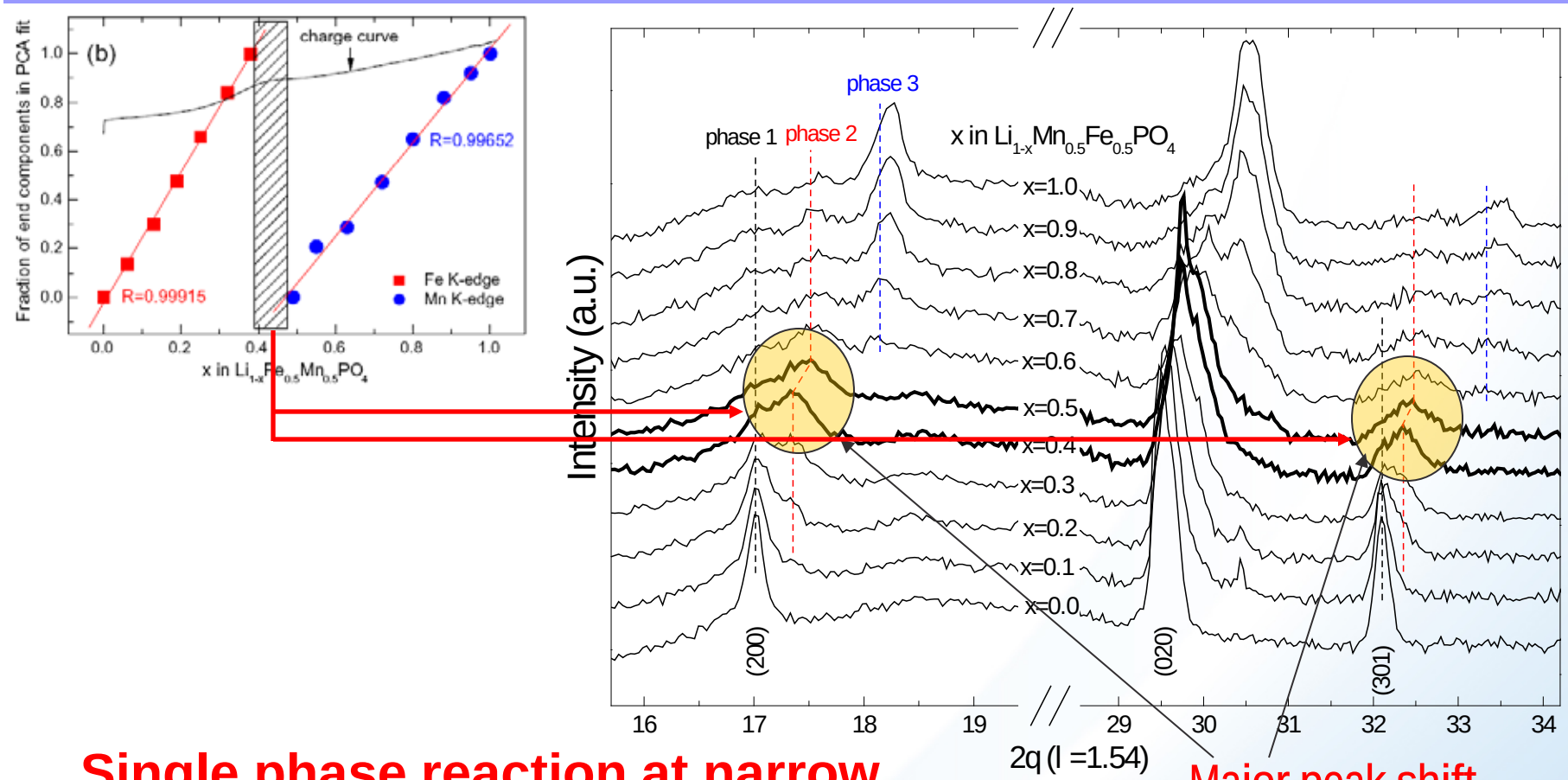
Ê $Li_{1.00}Mn_{0.5}Fe_{0.5}PO_4$ D $(1-z)Li_{1.00}Mn_{0.5}Fe_{0.5}PO_4 + zLi_{0.62}Mn_{0.5}Fe_{0.5}PO_4 + zLi^+ + ze-$ **(0≤z≤1)**

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

Ê $Li_{0.51}Mn_{0.5}Fe_{0.5}PO_4$ D $(1-y)Li_{0.51}Mn_{0.5}Fe_{0.5}PO_4 + yLi_{0.00}Mn_{0.5}Fe_{0.5}PO_4 + yLi^+ + ye-$ **(0≤y≤1)**

Electrochemistry Communication, 11 (2009) 2023 pp.

In situ XRD of C-$LiFe_{0.5}Mn_{0.5}PO_4$



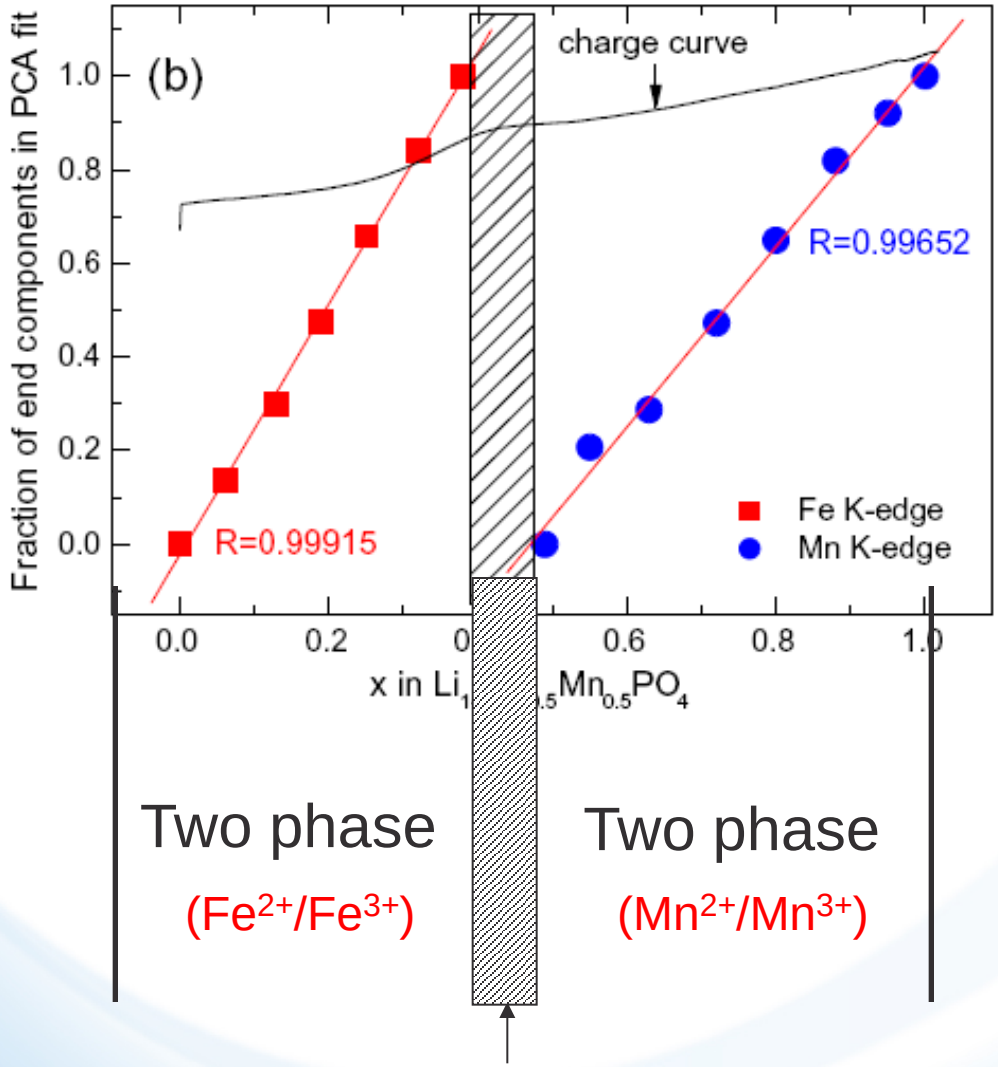
Single phase reaction at narrow intermediate region

Major peak shift
: Single phase reaction!

Intermediate region: ***0.40≤x≤~0.50 in C-$Li_{1-x}Mn_{0.5}Fe_{0.5}PO_4$*** ($Fe^{2+}/Fe^{3+}$ & Mn^{2+}/Mn^{3+} redox reactions);

Ê $Li_{0.60}Mn_{0.5}Fe_{0.5}PO_4$ D $Li_{0.60-a}Mn_{0.5}Fe_{0.5}PO_4$ + aLi + ae^- **(0.0≤ a≤ 0.1)**

Phase transition behavior of C-$LiFe_{0.5}Mn_{0.5}PO_4$



Single phase (Fe^{2+}/Fe^{3+} & Mn^{2+}/Mn^{3+})

First principle calculation

By Prof. Ceder at MIT

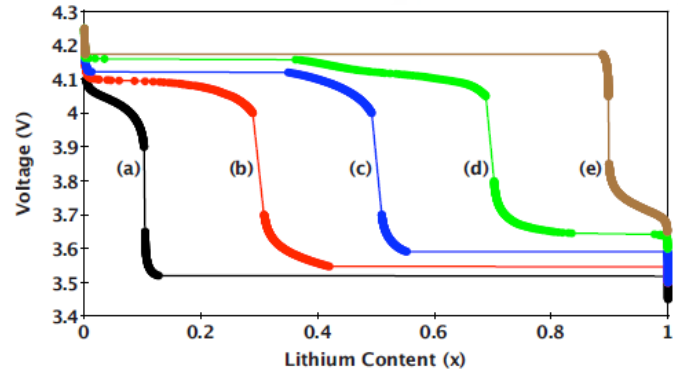
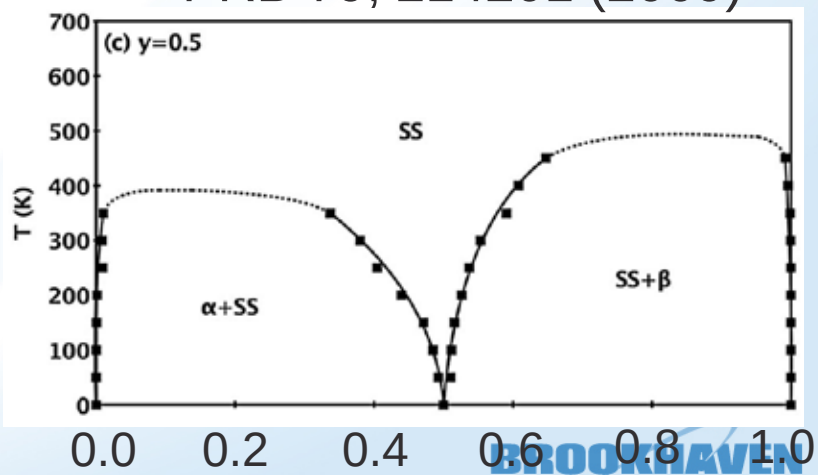


FIG. 2. (Color online) Equilibrium voltage curves of $Li_x(Fe_{1-y}Mn_y)PO_4$ at 300 K for (a) $y=0.1$, (b) $y=0.3$, (c) $y=0.5$, (d) $y=0.7$, and (e) $y=0.9$ as determined by Monte Carlo free-energy integration.

PRB 79, 214201 (2009)



Part 2.

Thermal stability of charged battery materials:

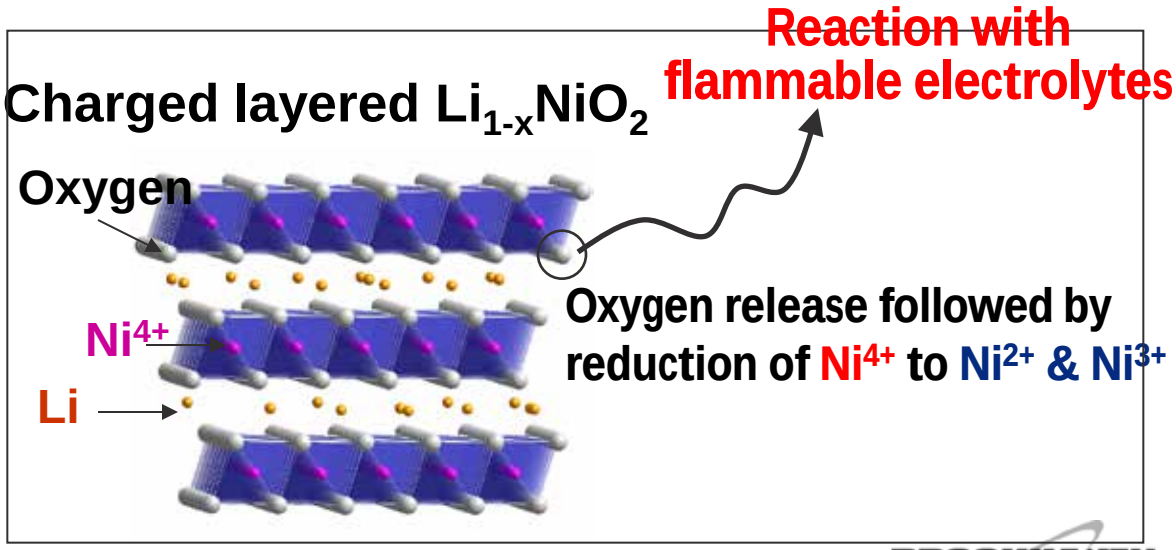
Combined XRD/mass spectroscopy, XAS and TEM study during heating (Safety related issue)

Safety issue of Li-ion battery

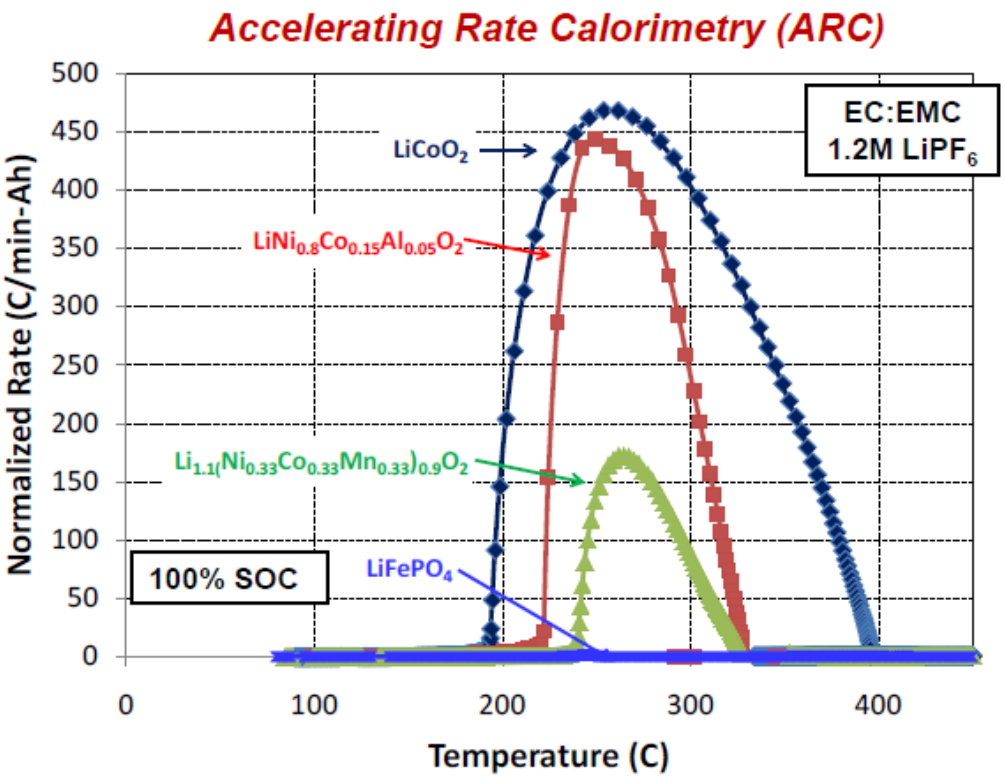
- Lithium-ion batteries are safe under normal operating conditions.
- However, if the battery is ***overcharged,*** or if there is ***a short circuit***, then the battery temperature can increase.

Thermal runaway

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



Cathode is critical to the LIB safety



SNL Built 18650 cell.

Dr. Christopher J. Orendorff (Sandia National Lab.)

- There is little information about why particular cathode materials have good thermal stability and some others do not.

- How do we design thermally stable cathode materials?
  - **need better understanding of origin of thermal instability of the charged cathode materials.** ***(may co-related to the materials stability during electrochemical cycling, battery life)***

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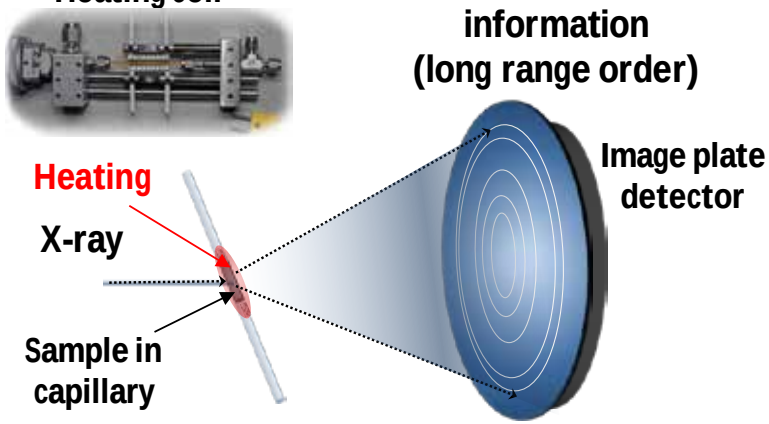
In situ Diagnostic Studies during heating

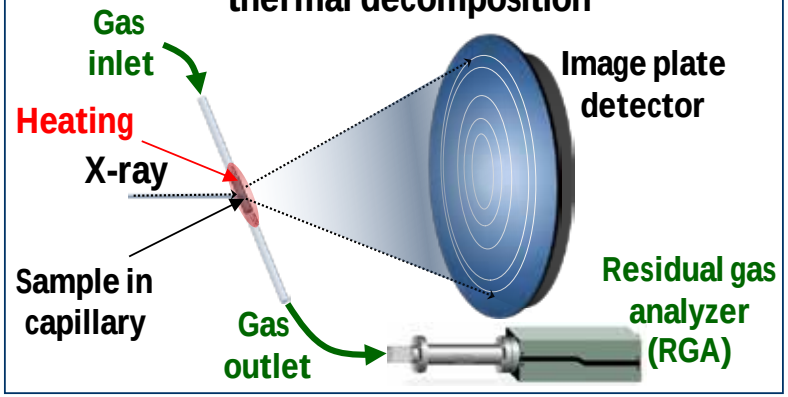
(a) *In situ* Time-Resolved (TR) XRD

Ÿ **Average structural information (long range order)**

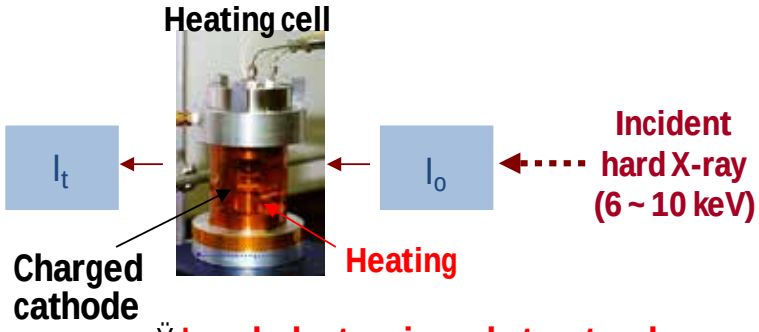


(b) *In situ* TR-XRD with mass spectroscopy

Ÿ **Oxygen releasing behavior during thermal decomposition**



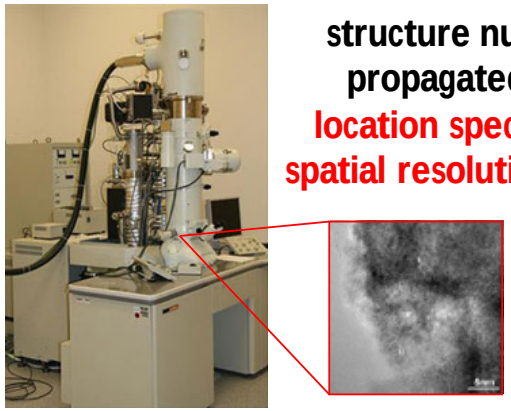
(c) *In situ* X-ray absorption spectroscopy



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

(d) *In situ* transmission electron microscopy

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



***Chem. Mater.* 23 (17), pp 3953–3960 (2011); *Adv. Func. Mater. 23 (8), 1047-1063* (2013); *Chem. Mater.* 25 (3), pp 337–351 (2013).**

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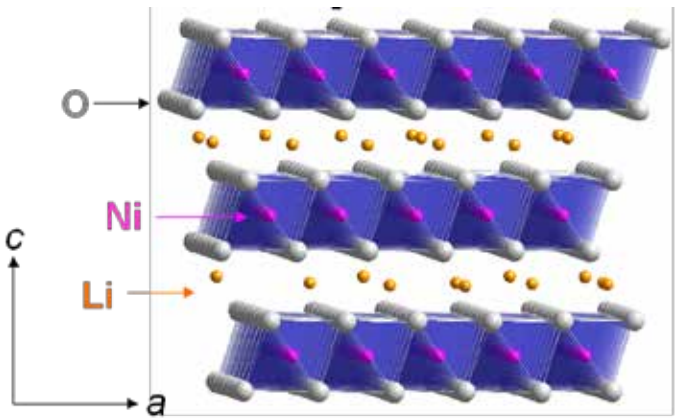
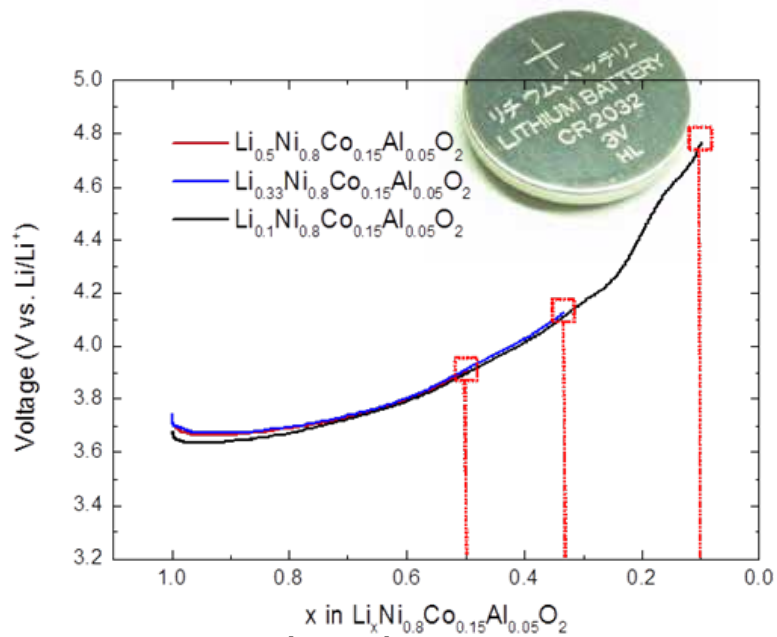
Cathode Materials Studied

Ni-based layer structured cathode materials

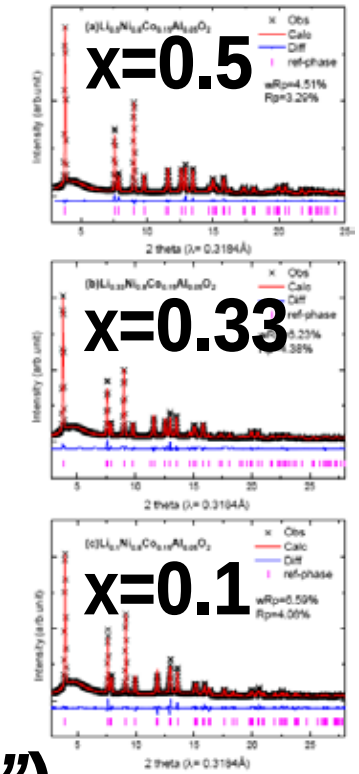
1. *Charged* $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (so called "*NCA*")
; different states of charge, x= 0.5, 0.33, and 0.1.



Crystal structure of $LiMO_2$
(space group: *R*-3*m*)



Charging curve



2. *Charged* $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (so called "*NCM*")
; different states of charge, x= 0.33, and 0.1

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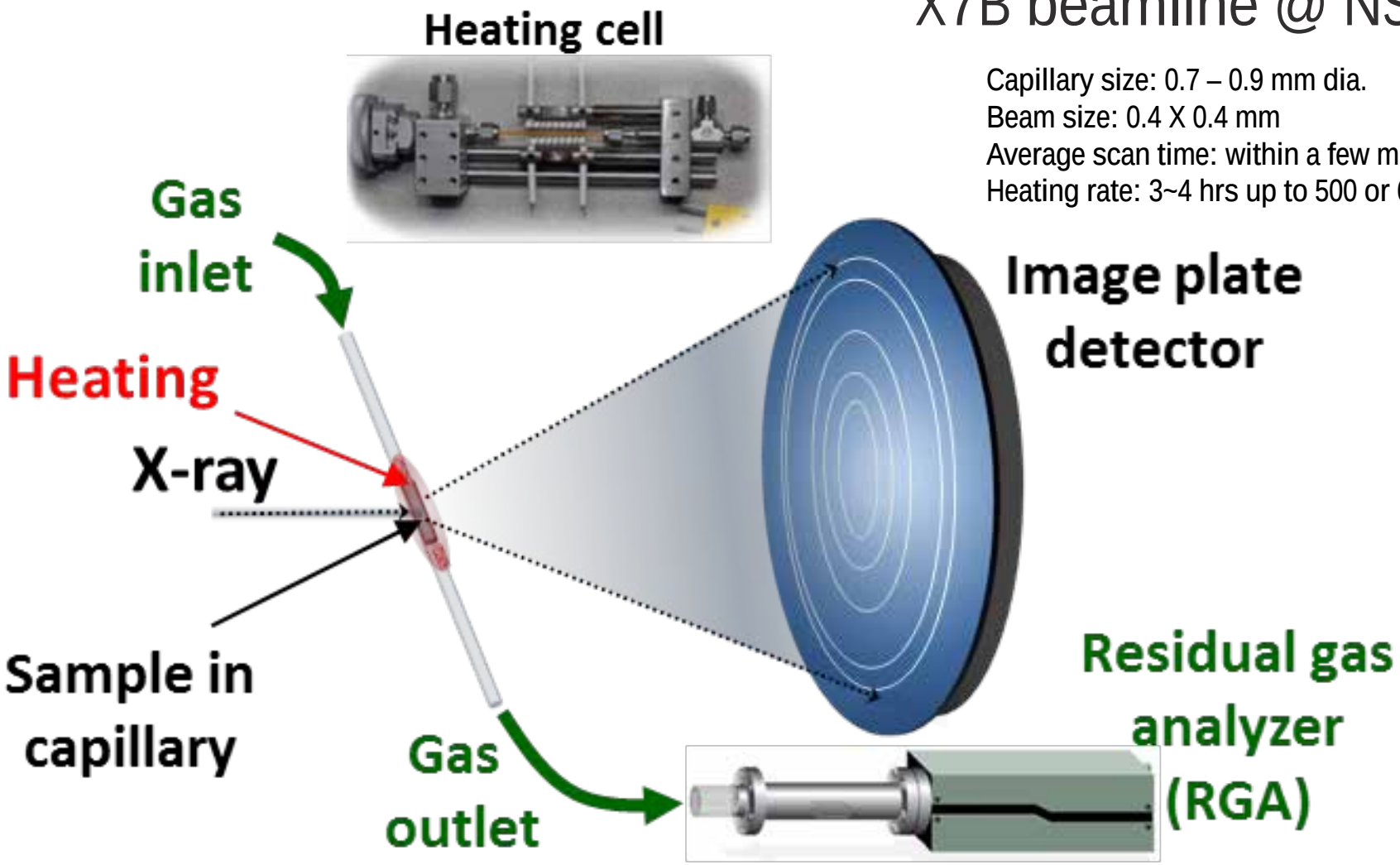
1. In situ TR-XRD with mass spectroscopy

X7B beamline @ NSLS

Capillary size: 0.7 – 0.9 mm dia.
Beam size: 0.4 X 0.4 mm
Average scan time: within a few minute
Heating rate: 3~4 hrs up to 500 or 600 °C



S.M. Bak et al., Chem. Mater. 25 (3), pp 337–351 (2013).

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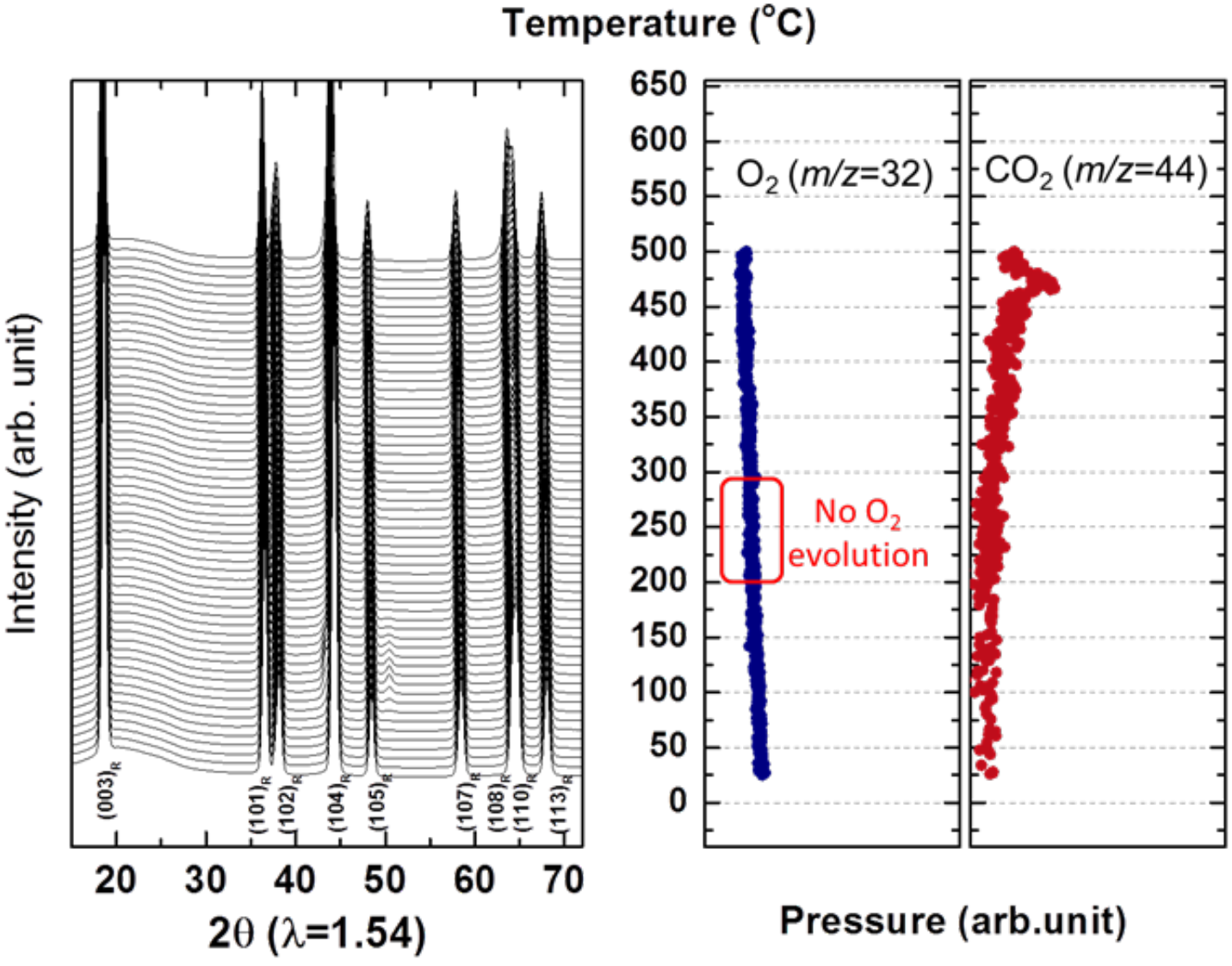
Uncharged $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ is very stable



- No thermal degradation (maintain layered structure).
- No oxygen release.

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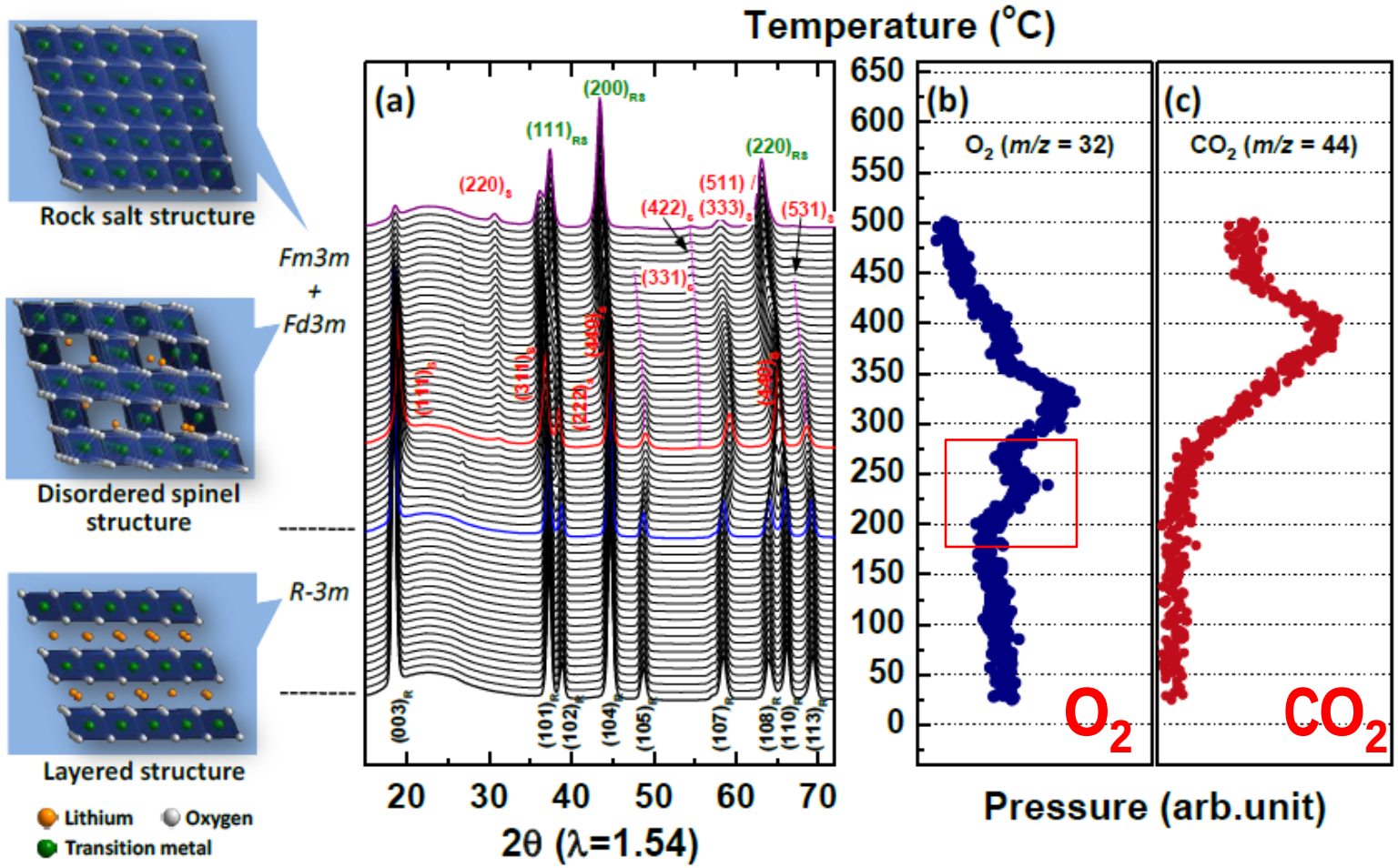
Charged $Li_{0.5}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ (3.9V *vs. Li/Li*$^+$)



Theory

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

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

- But oxygen release !! at 200^{0}C (1st phase transition region, layered ð disordered spinel)

- Why? Due to the non-uniform Li delithiation during charging process. (TEM)

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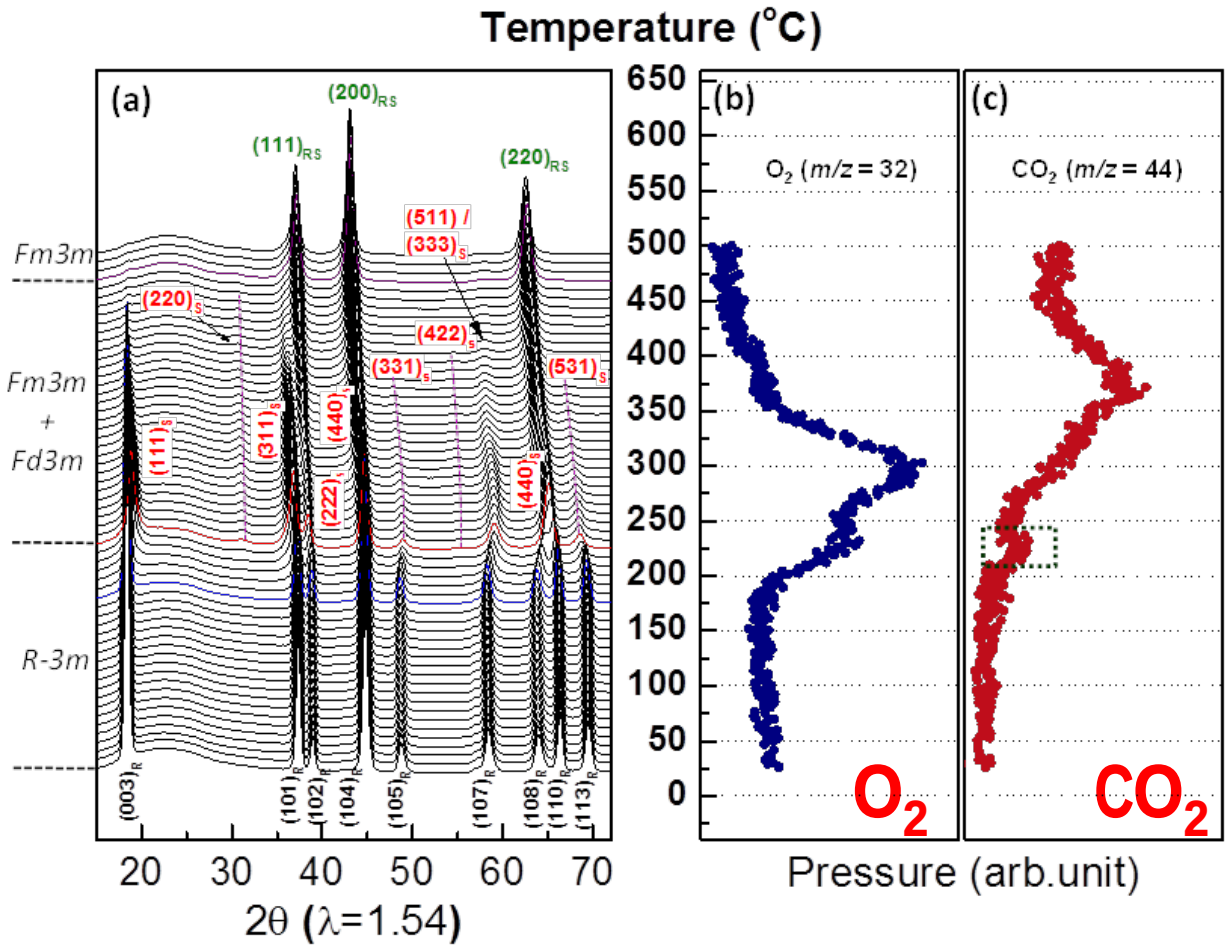
Charged $Li_{0.33}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ (4.1V *vs. Li/Li*$^+$)



When x= 0.33 (67% of SOC) in $Li_{1-x}MO_2$

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

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

-More O_2 gas released during 2nd phase transition than those of during 1st phase transition => well coincident with theoretical estimated result.

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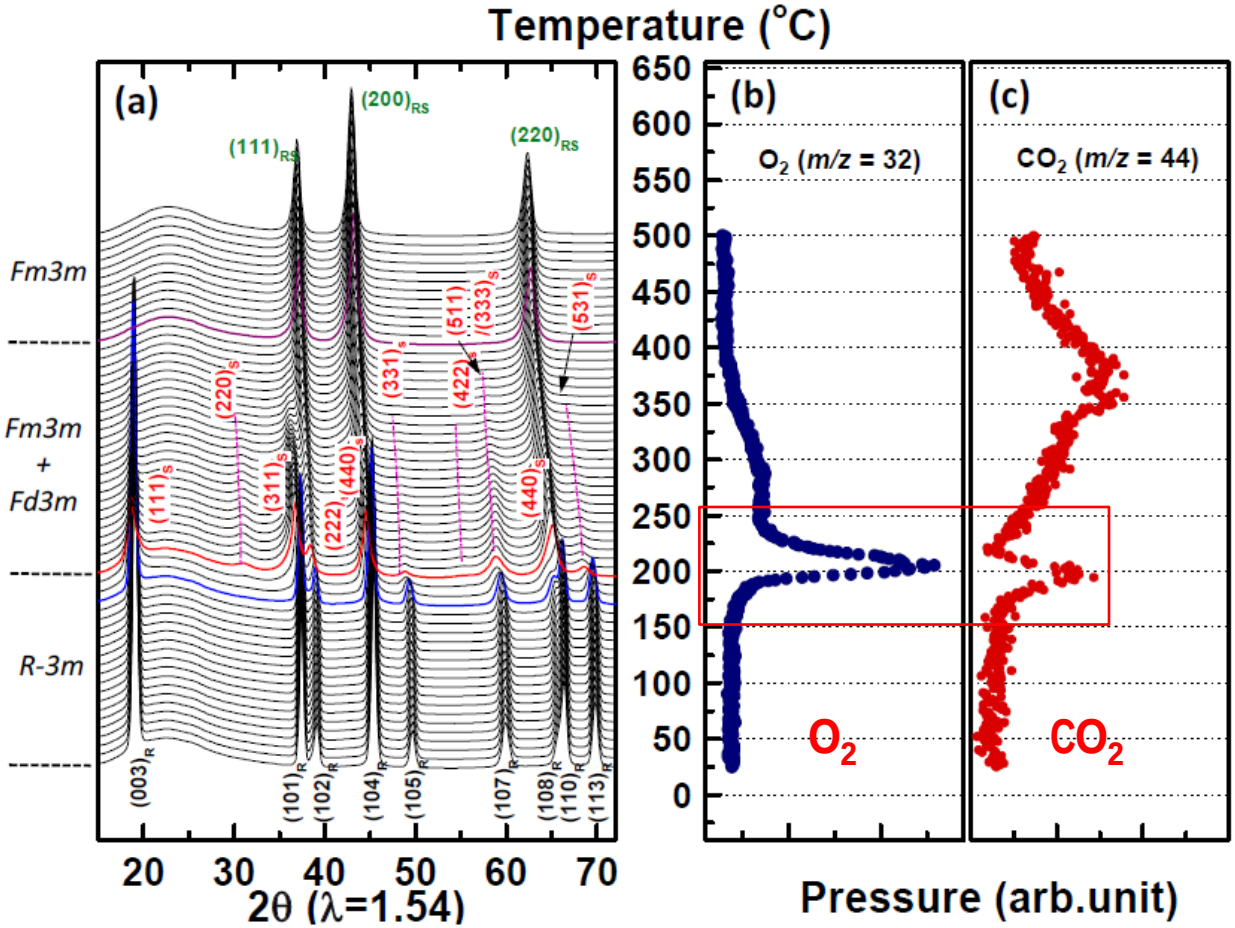
Overcharged $Li_{0.1}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ (4.8V *vs. Li/Li*$^+$)



- *Rapid & massive O_2 gas evolution during phase transition from layered to disordered spinel.*
- Deeper charging leads to materials that are more thermally unstable, and which release more substantial amounts of oxygen and CO_2 at ever lower temperatures.
- Volatile oxygen species are likely to be highly reactive
- Could accelerate severe thermal runaway by reacting with the flammable electrolyte.

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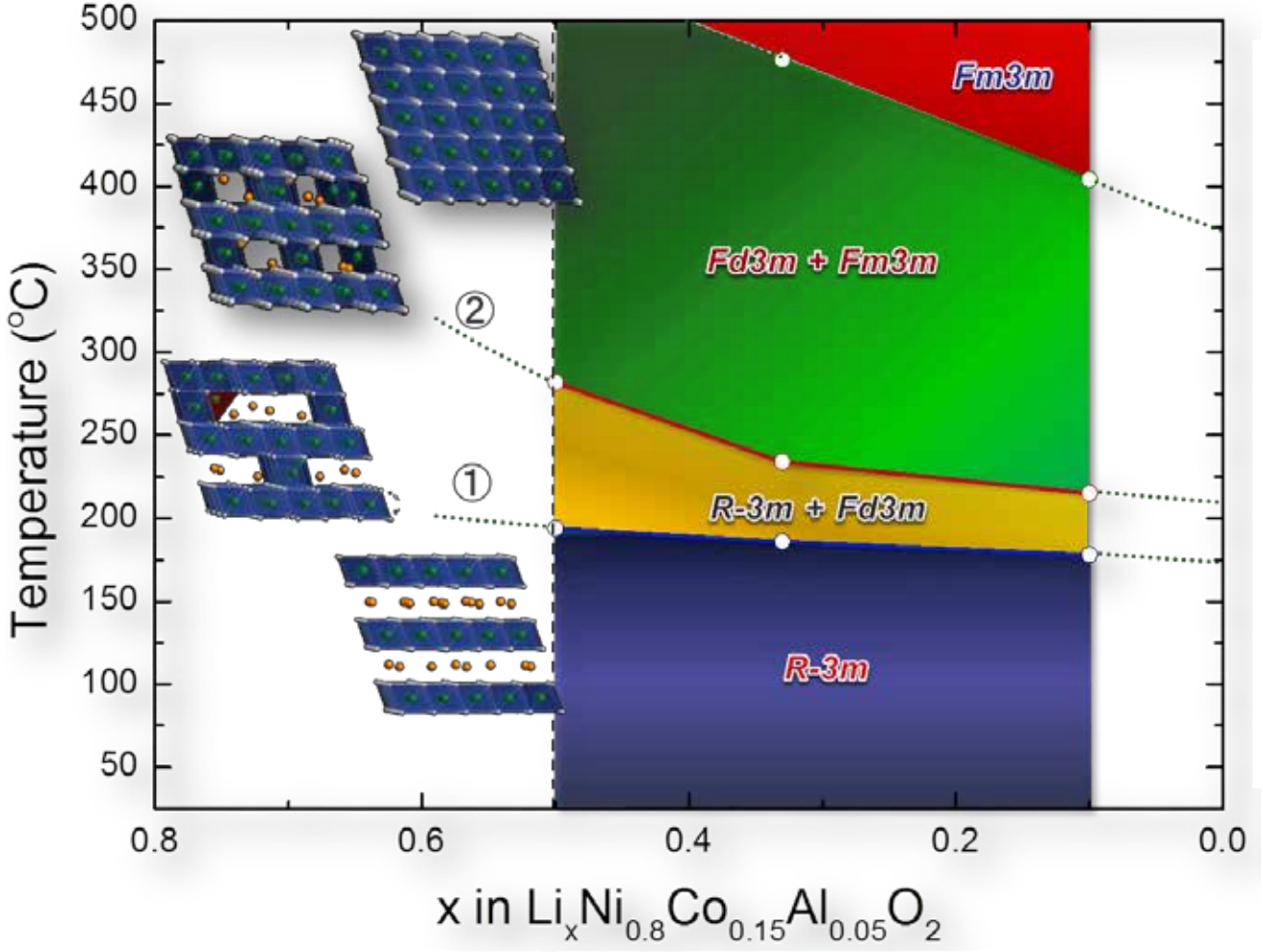
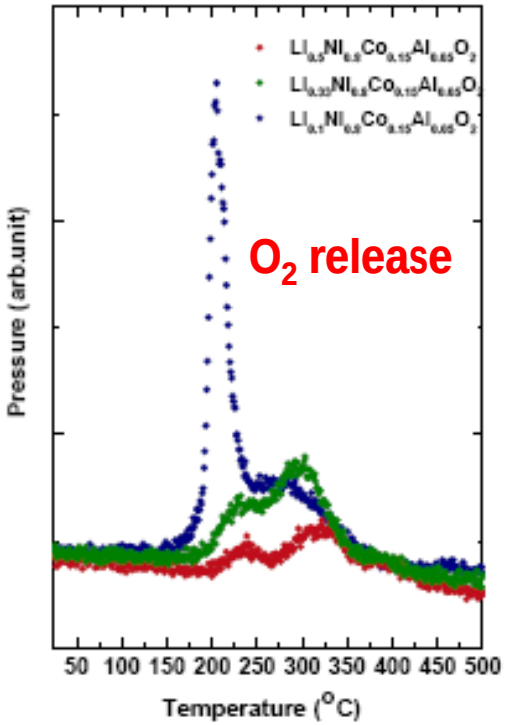
Phase transition of Li_xNCA with state of charge

Less-charged ⟷ Over-charged





Deeper charging leads to materials that are more thermally unstable (e.g., narrow phase transition temperature range).

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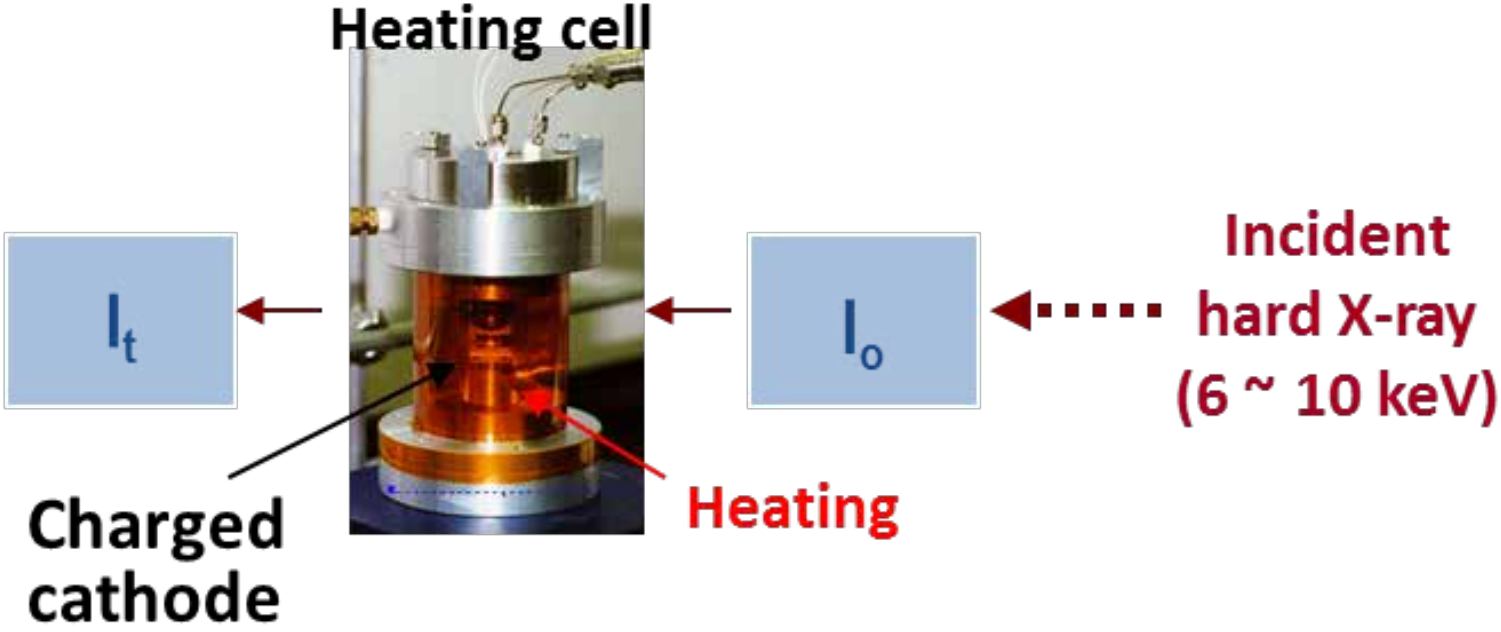
2. *In situ* X-ray absorption spectroscopy

X18A & X19A beamlines @ NSLS



Ê **Local electronic and structural information (bulk) in elemental-selective way ; Mn, Co, and Ni.**

- **XANES (X-ray near edge absorption structure): oxidation state, symmetry.**
- **EXAFS (Extended X-ray absorption fine structure): bond length, coordination number, degree of disorder.**

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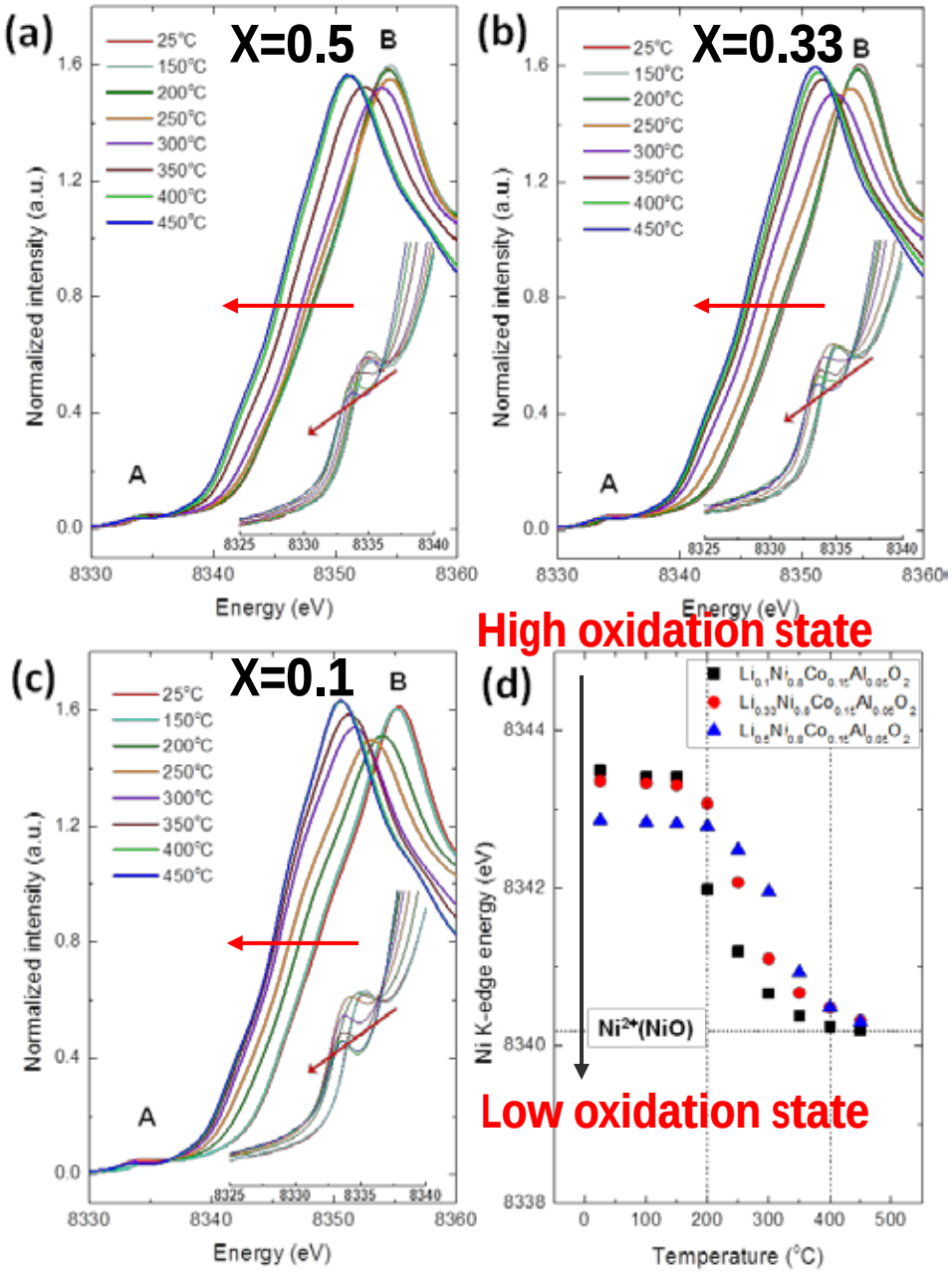
Ni K-edge XANES upon heating of Li_xNCA



- Edge shift consistent with a reduction of average oxidation state with heating for all samples ($Ni^{3+/4+}$ to Ni^{2+}).

- This valence change drives oxygen release to maintain charge neutrality.

- Again, over-charged sample shows lowest onset temp. and most narrow temperature window.

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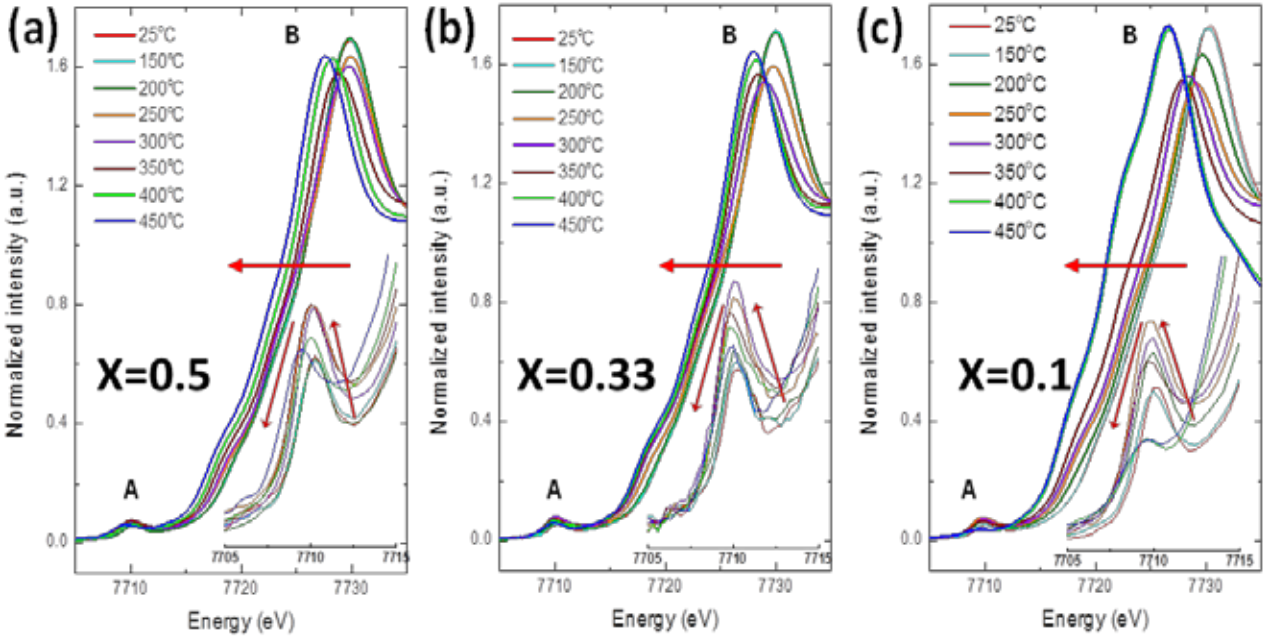
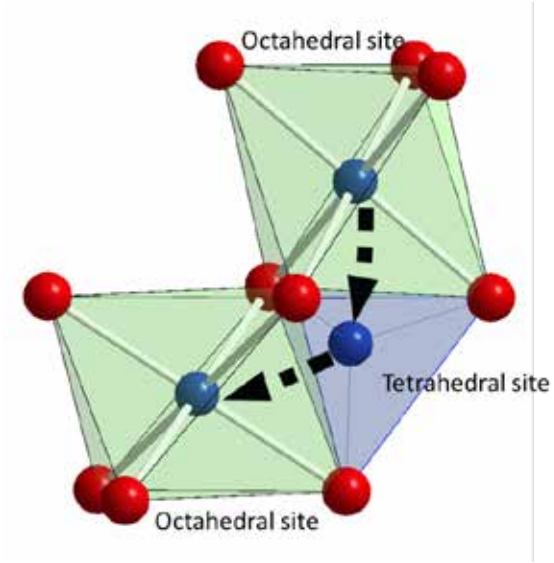
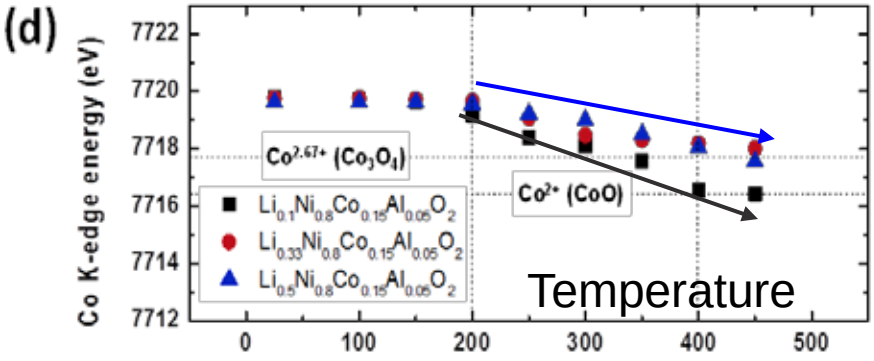
Co K-edge XANES upon heating of Li_xNCA







- General trends are the same as for Ni .
- But at slightly higher temperatures and the extent of reduction is less.

- Pre-edge intensities are consistent with migration of Co to tetrahedral sites.

- Highly disordered and non-stoichiometric "Co_3O_4 type spinel" near Co atom positions, with substantial defects (oxygen vacancies and incorporation of Li, Ni and Al ions).

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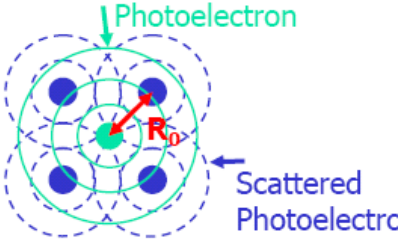
EXAFS analysis

The EXAFS Equation



$$\chi(k) = \Sigma_i \chi_i(k)$$

with

$$\chi_i(k) = \left(\frac{(N_i S_0^2) F_i(k)}{k R_i^2} \sin(2kR_i + \varphi_i(k)) \exp(-2\sigma_i^2 k^2) \exp(-2R_i/\lambda(k)) \right)$$

$$R_i = R_0 + \Delta R$$

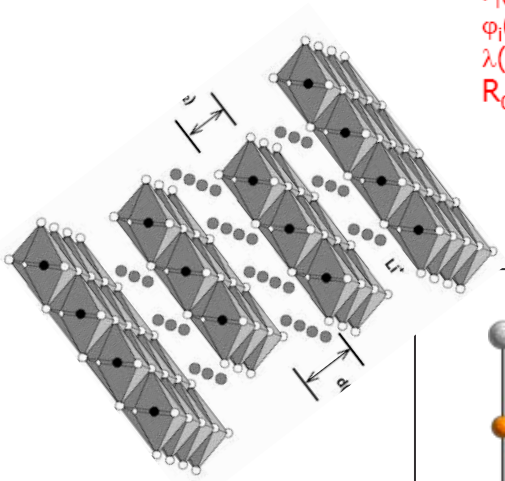
$$k^2 = 2\, m_e (E - E_0)/\hbar$$

Theoretically calculated values

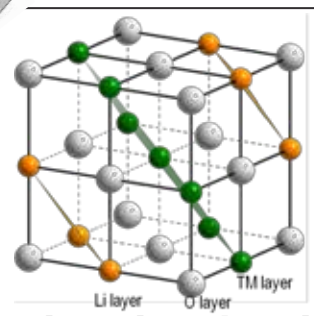
- $F_i(k)$ effective scattering amplitude
- $\varphi_i(k)$ effective scattering phase shift
- $\lambda(k)$ mean free path
- R_0 initial path length

Parameters often determined from a fit to data

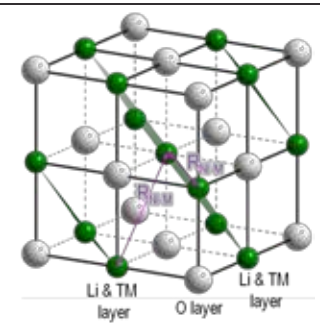
- N_i degeneracy of path
- S_0^2 passive electron reduction factor
- σ_i^2 mean squared displacement
- E_0 energy shift
- ΔR change in half-path length



Cubic rock-salt model structure



Ordered rock-salt (i.e., layered $LiMO_2$) : Ni-M CN = 6)



Disordered rock-salt :Ni-M CN = 12

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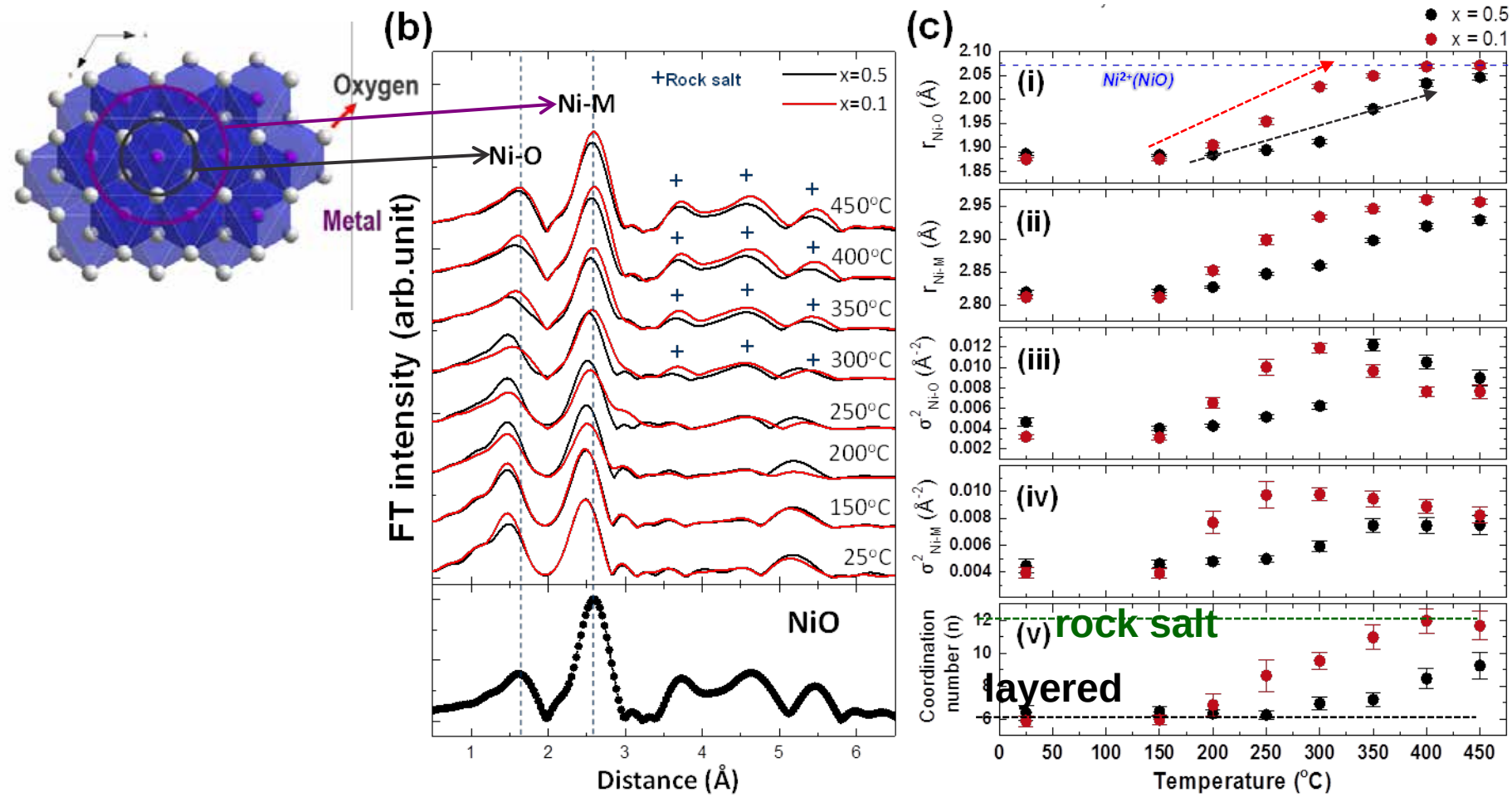
Ni K-edge EXAFS upon heating of Li_xNCA (x=0.5 &0.1)



- Variation in second Ni-M shell coordination #: indicator of cation mixing.
- Bond length expansion around Ni with increasing temperature (reduction of $Ni^{3+/4+}$ to Ni^{2+}): consistent trends with state of charge.
- Loss of oxygen leads to substantial local disorder around Ni sites.

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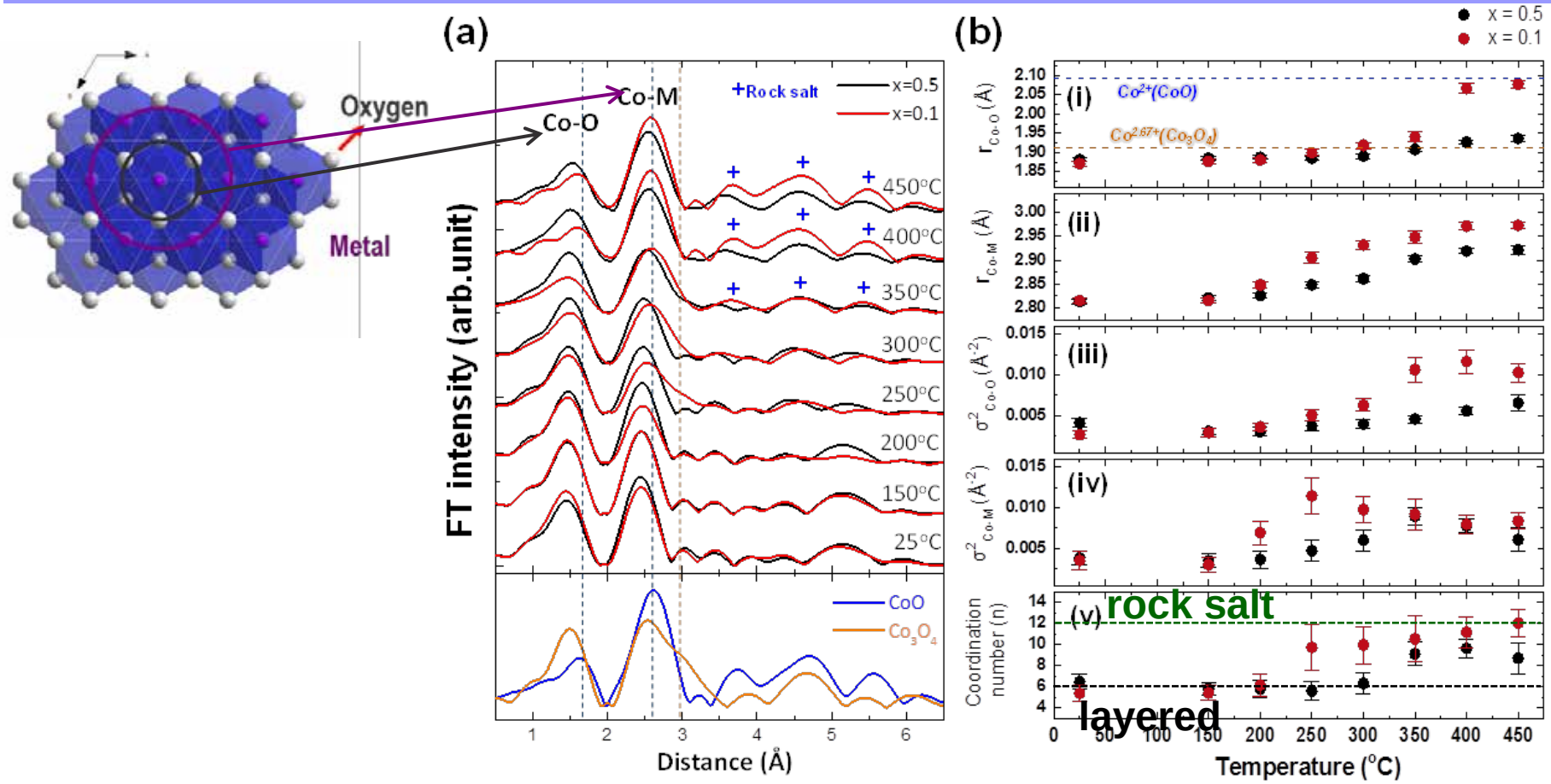
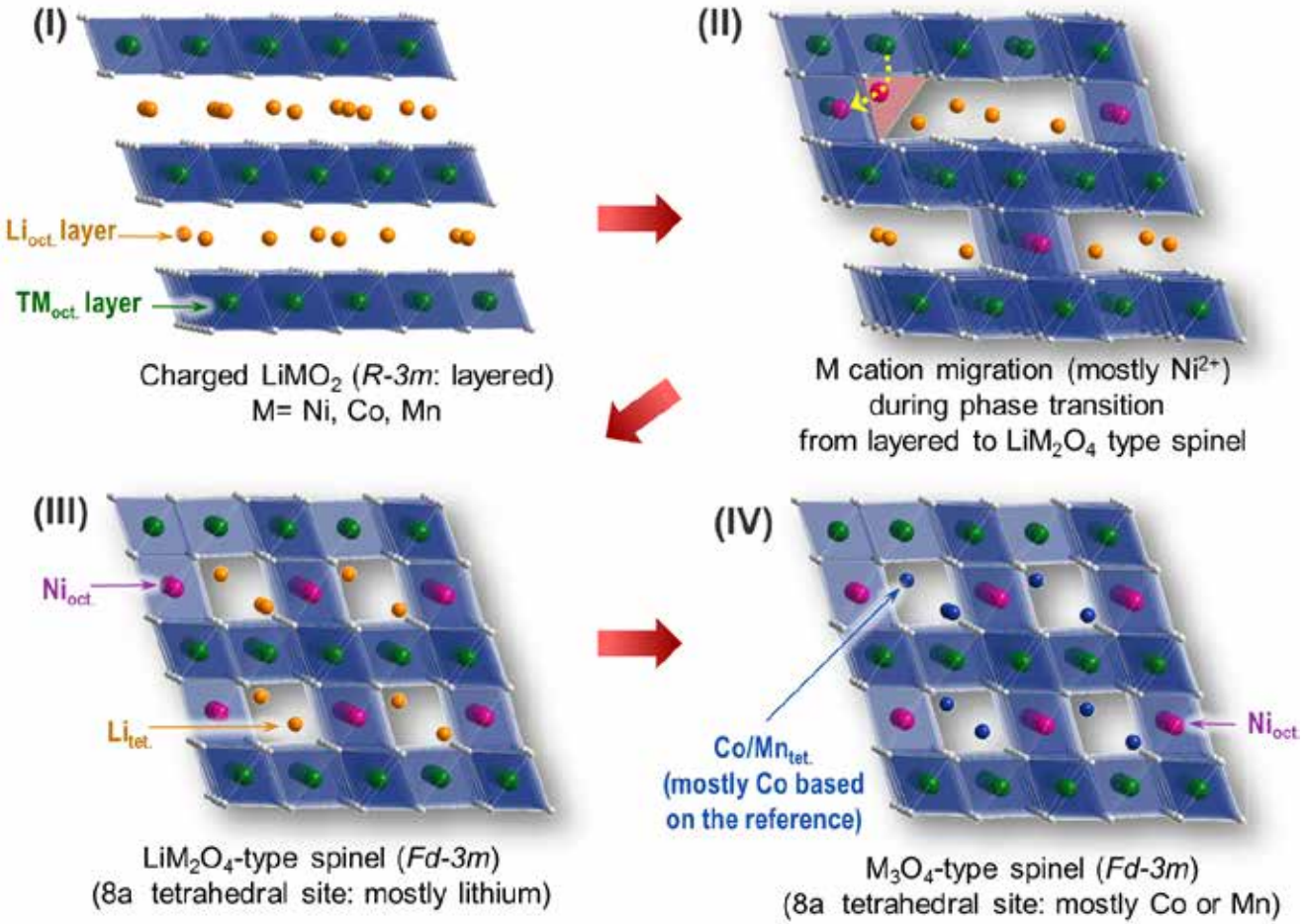
Co K-edge EXAFS upon heating of Li_xNCA (x=0.5 &0.1)



- Similar trends as for Ni EXAFS, but changes occurs at slightly higher temperatures and the extent of reduction is less (consistent with Co XANES).
- Co ions are more thermally stable than Ni.
- By comparing fits with CoO and Co_3O_4 spinel, the environment around Co first transforms to disordered Co_3O_4 spinel, and then to CoO rock salt upon heating.
- Ni content > 5 times Co content: this drives the phase transformation behavior.

Cation migration paths of charged $Li_xNi_{0.8}Co_{0.15}Co_{0.05}O_2$ during phase transitions (i.e., thermal degradation)



(i) layered structure

(ii) cation migration during the phase transition from layered to LiM_2O_4 type spinel structure

(iii) LiM_2O_4 type spinel structure

(iv) M_3O_4 type spinel structure.

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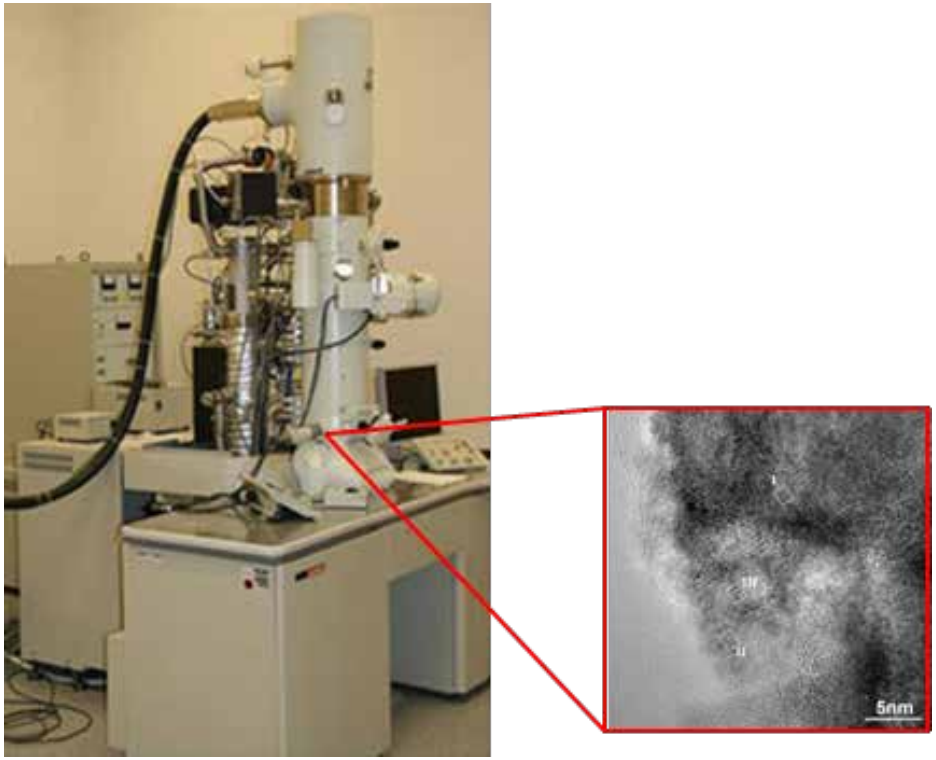
3. In situ Transmission electron microscopy (TEM) upon heating of charged particle



Ê **Where and how the new structure nucleated and propagated with high location specification and spatial resolution (nm range).**

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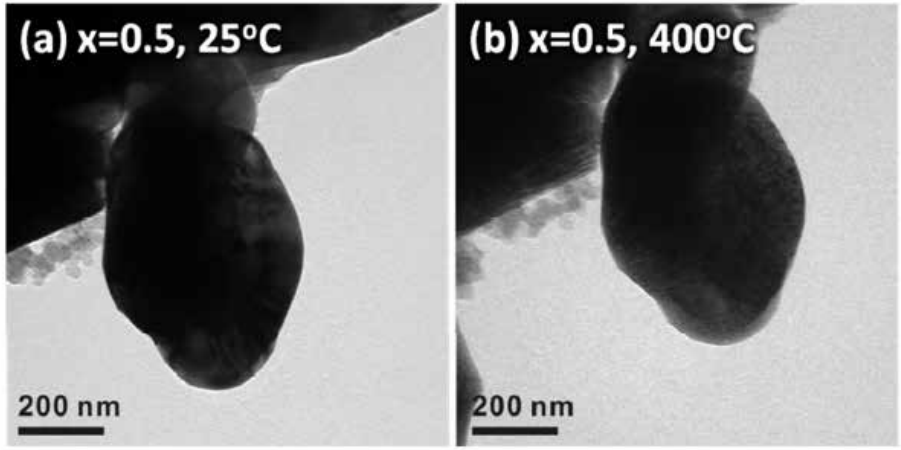
In situ TEM of charged $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (3.9V vs. 4.8V)

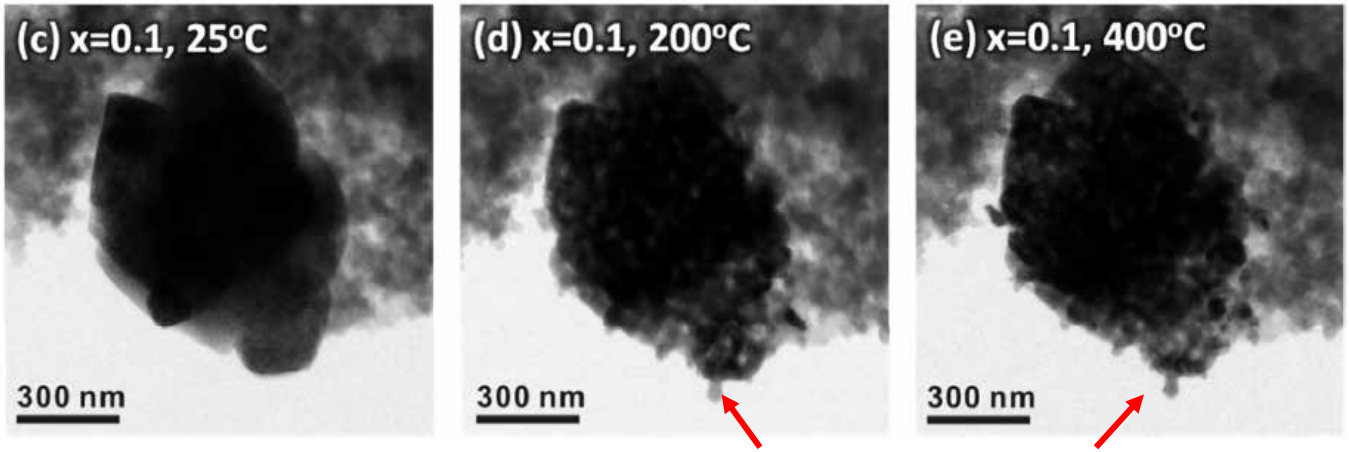
Courtesy of Dr. E. Stach (BNL-CFN)

Charged to 3.9V (x=0.5)



Heating

Overcharged to 4.8V (x=0.1)



Formation of highly porous microstructure due to massive O_2 release which agrees well with TR-XRD/MS result.

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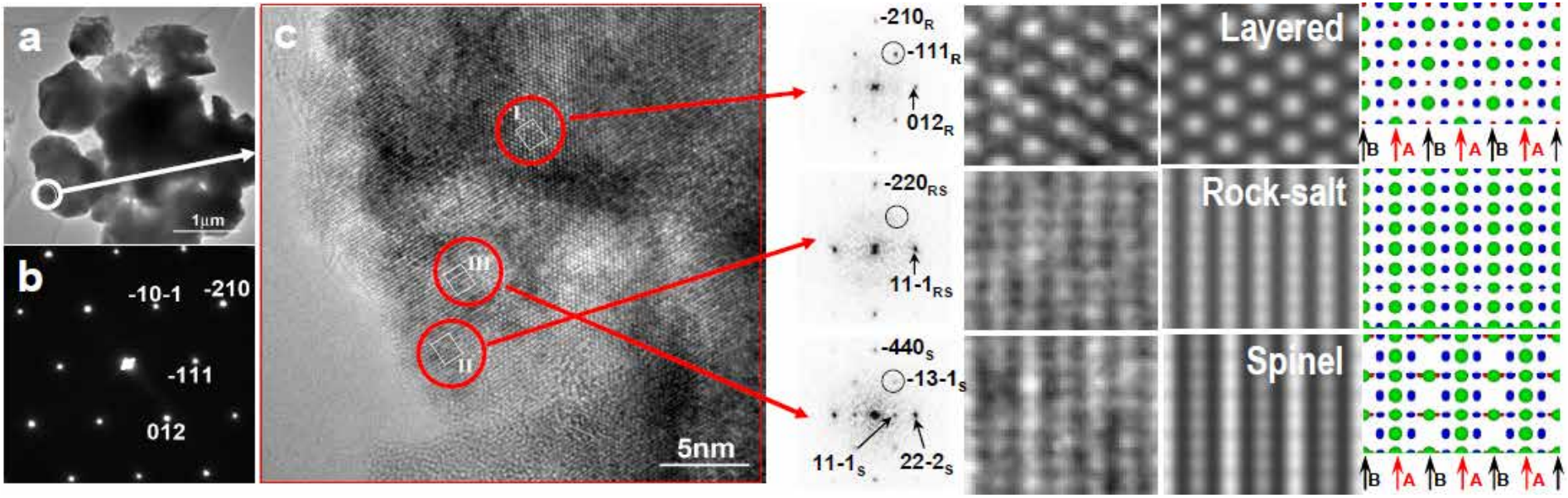
TEM of overcharged $Li_{\sim 0.1}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ (4.8V)

Courtesy of Drs. L. Wu and Y. Zhu (BNL)



Diffractograms

Magnified images

Simulated images

(a) Bright-field image from overcharged $Li_{0.1}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ 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.**

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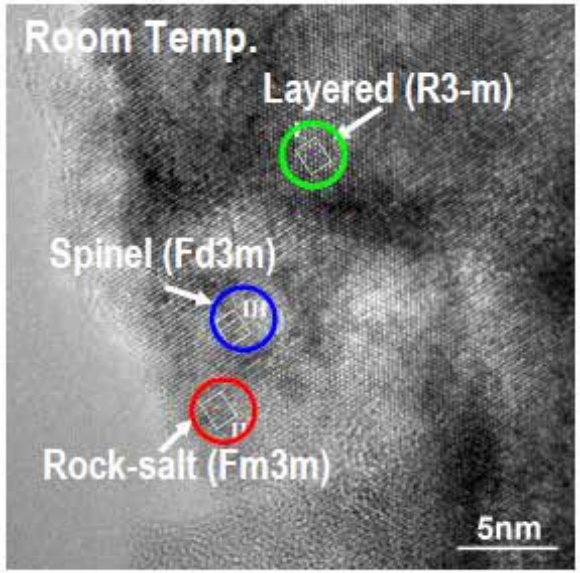
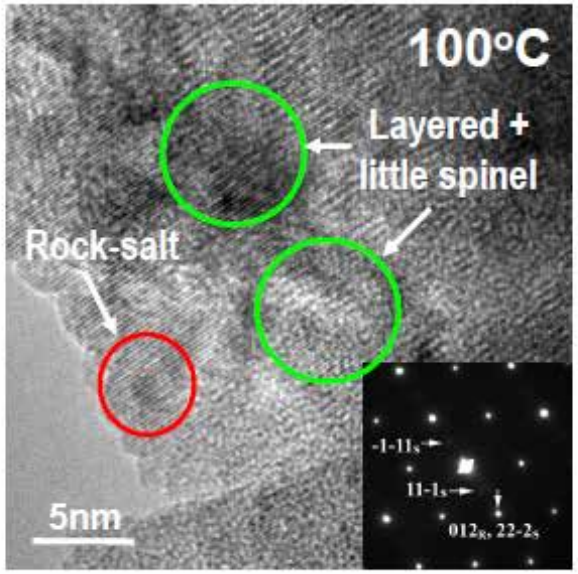
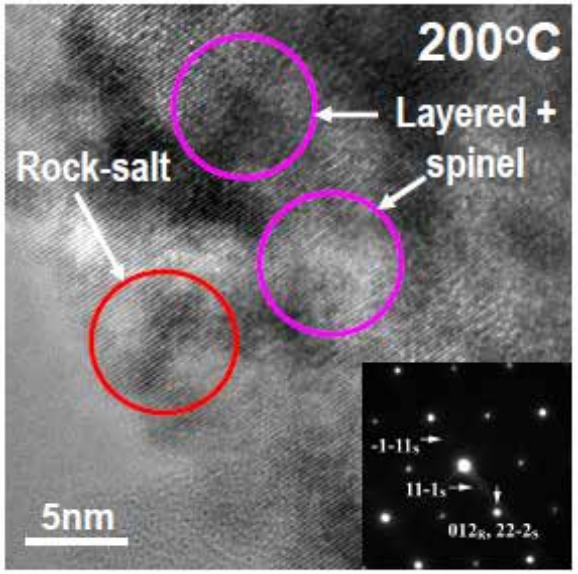
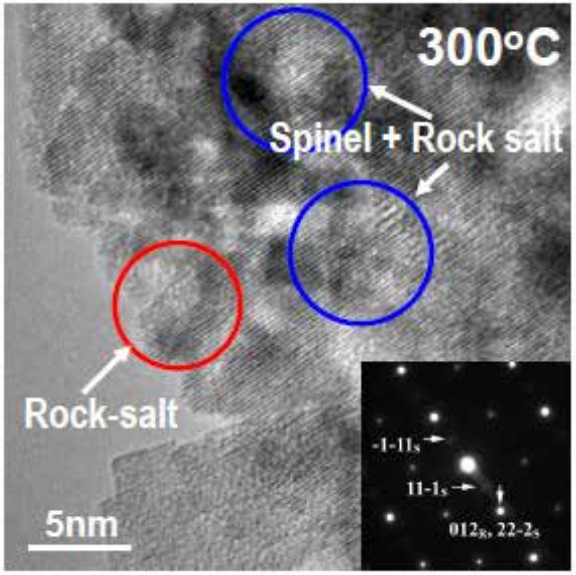
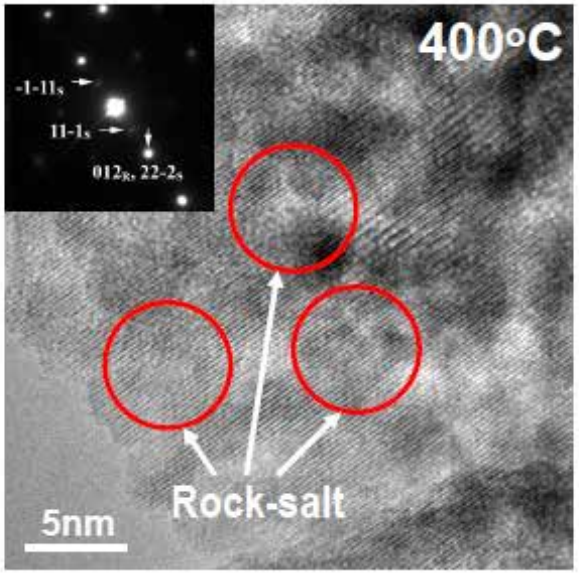
In situ TEM of overcharged $Li_{0.1}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ during heating





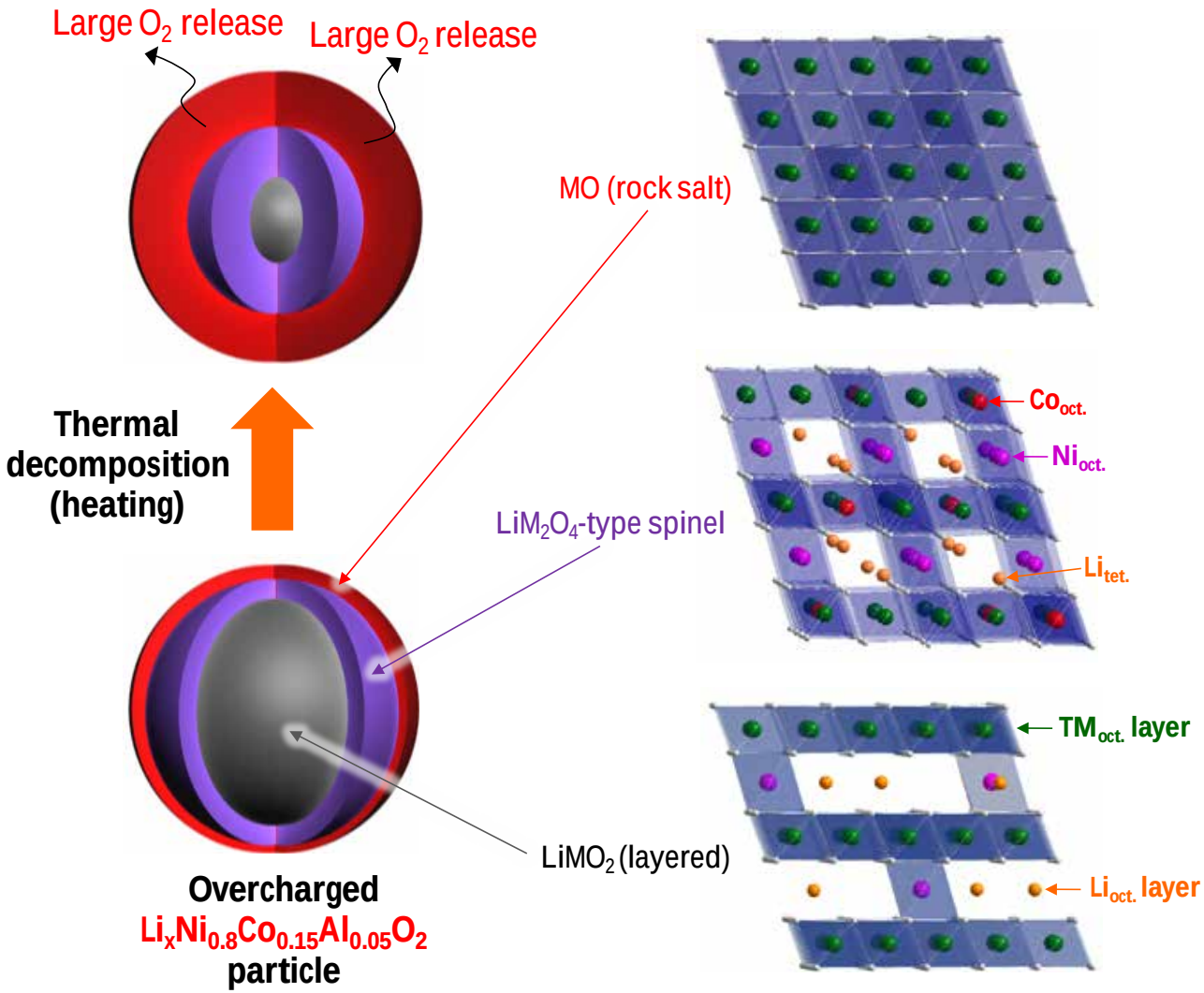






- During heating, the layered structure transformed to the spinel and the spinel further transformed to rock-salt structure.
- *The rock-salt structure continues to grow from the surface and edge into the core parts of the sample* and becomes the dominating phase at 400°C.

Thermal degradation mechanism of overcharged $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$



K.W. Nam et al., Adv. Func. Mater. 23 (8), 1047-1063 (2013).

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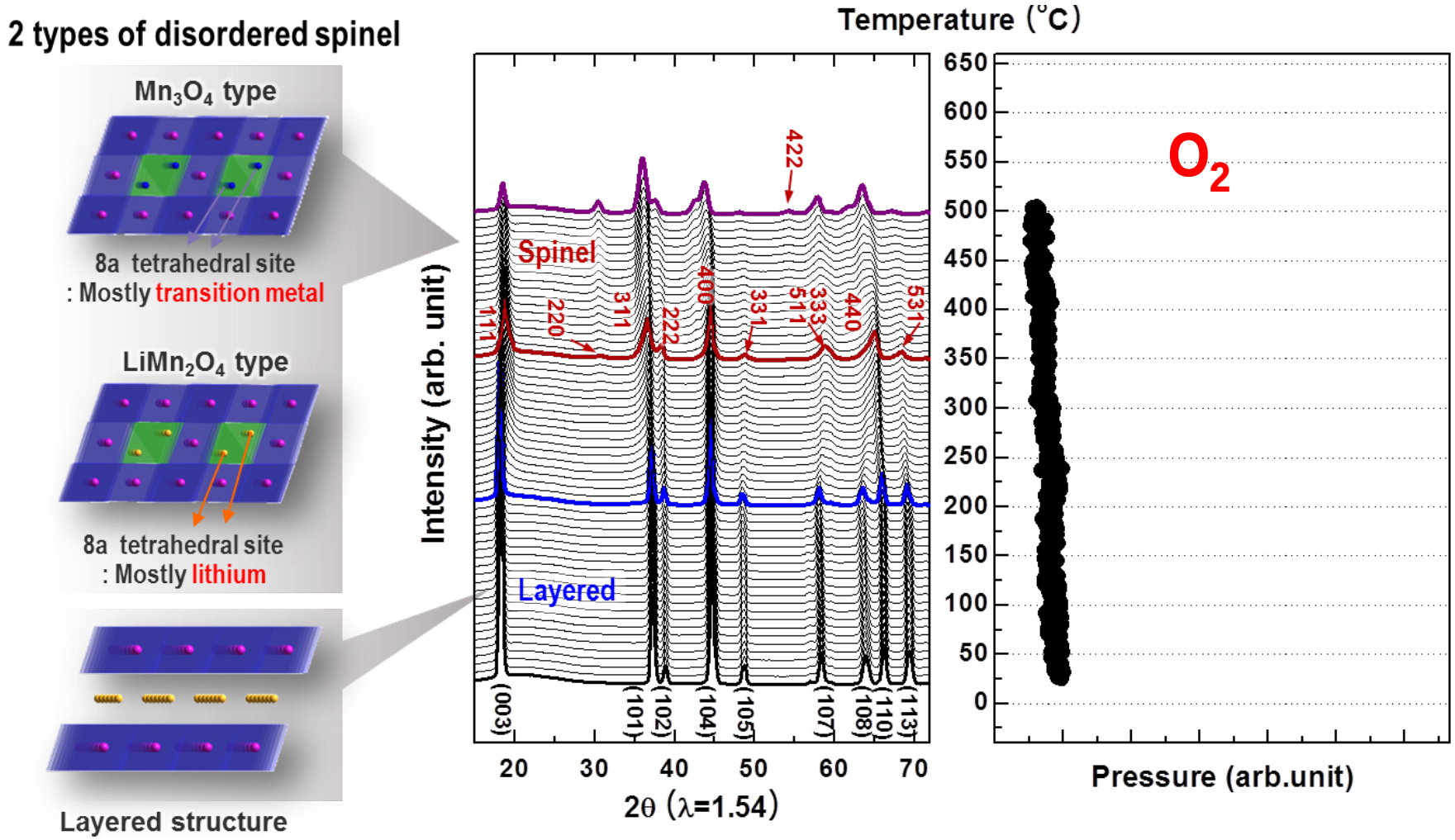
In situ TR-XRD/MS of charged $Li_{0.33}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$



- Much wider temperature range for the disordered spinel region due to the stabilization of two different spinel type structures (e.g., LiM_2O_4 and M_3O_4).

- Much better thermal stability than NCA cathode material!!

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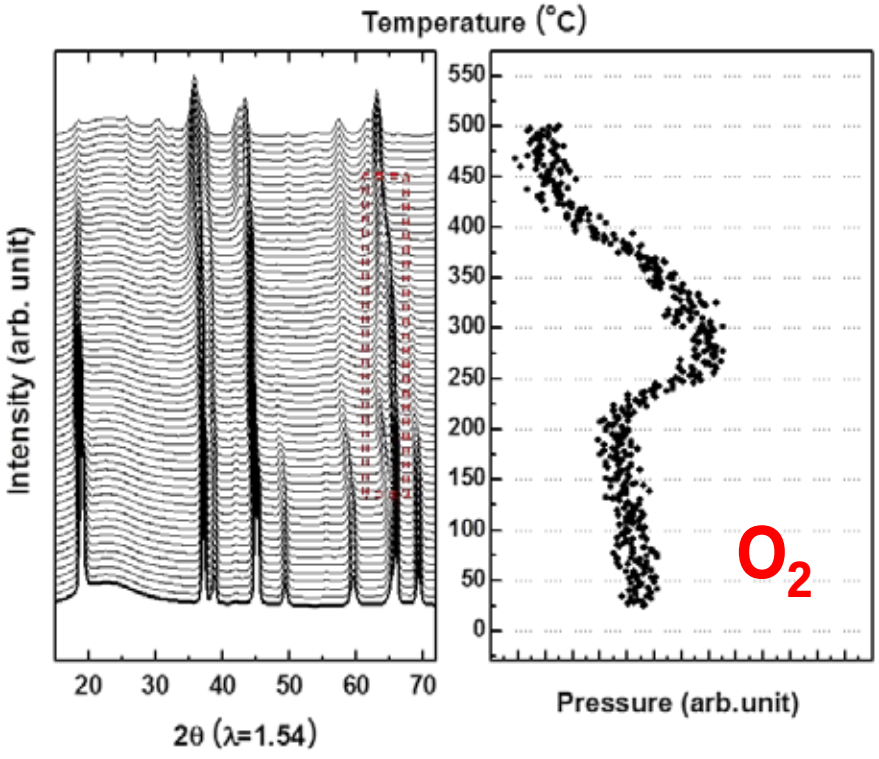
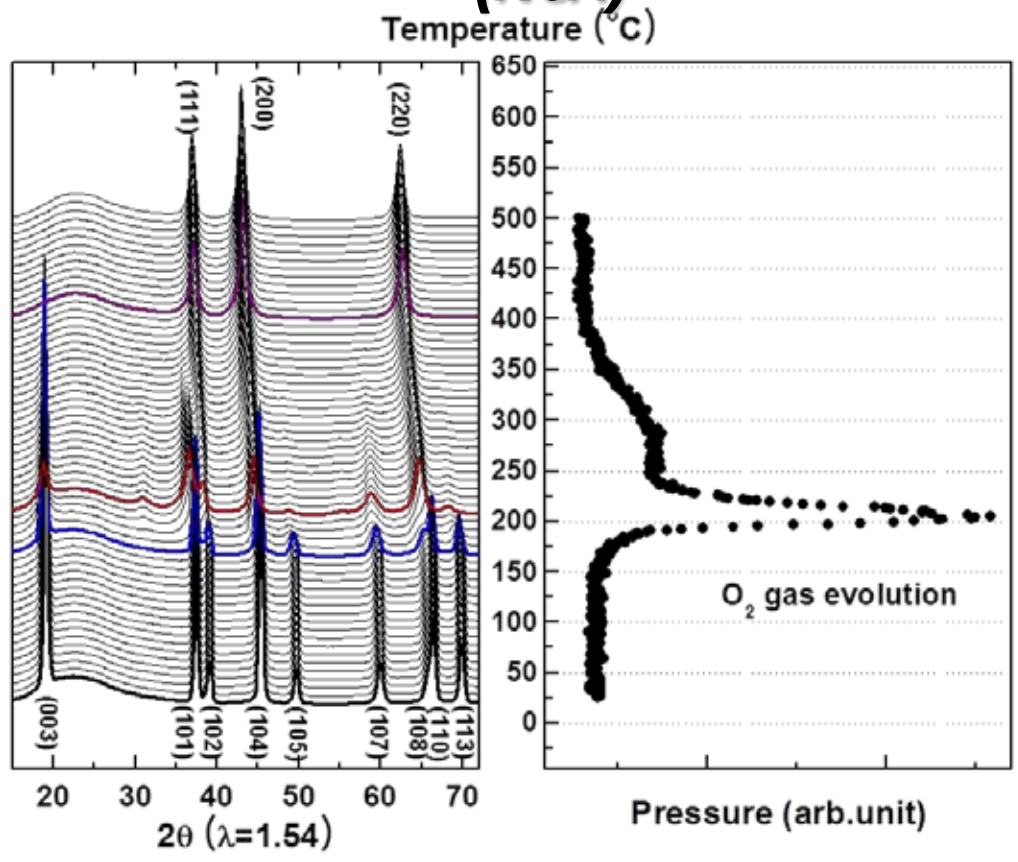
In situ TR-XRD/MS of overcharged $Li_{0.1}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$

$Li_{0.1}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$
(NCM333)



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



- *Broad oxygen evolution during heating (200~ 450 °C) for NMC333.*
- *Much better thermal stability (better safety property) of NMC333 than NCA.*

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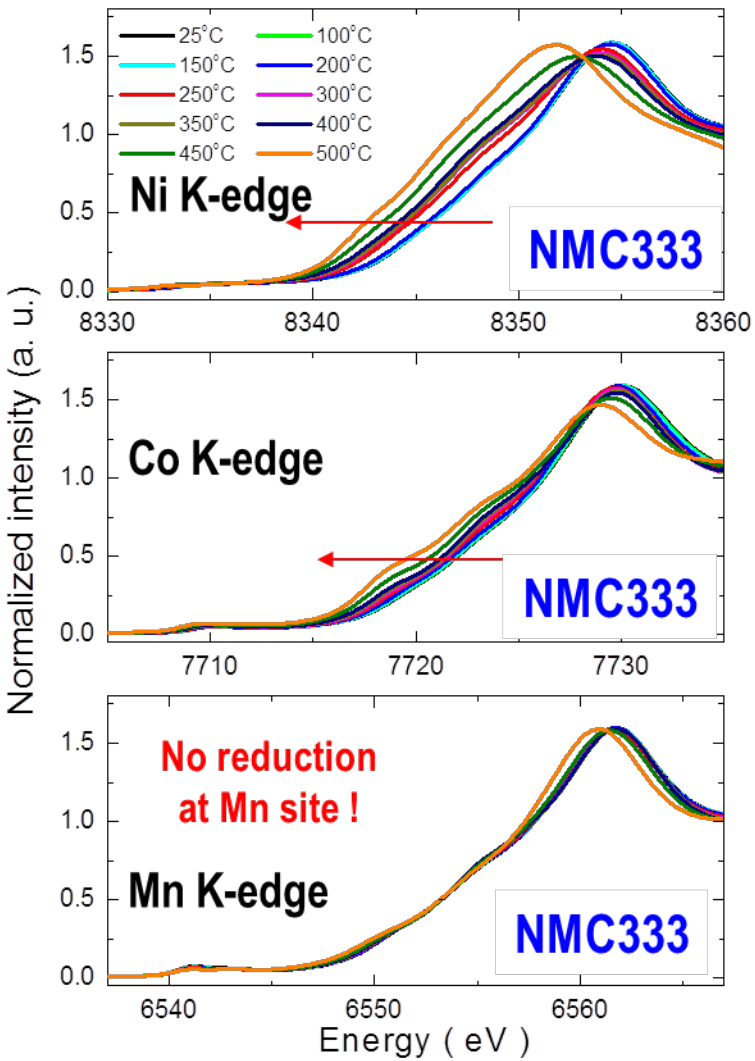
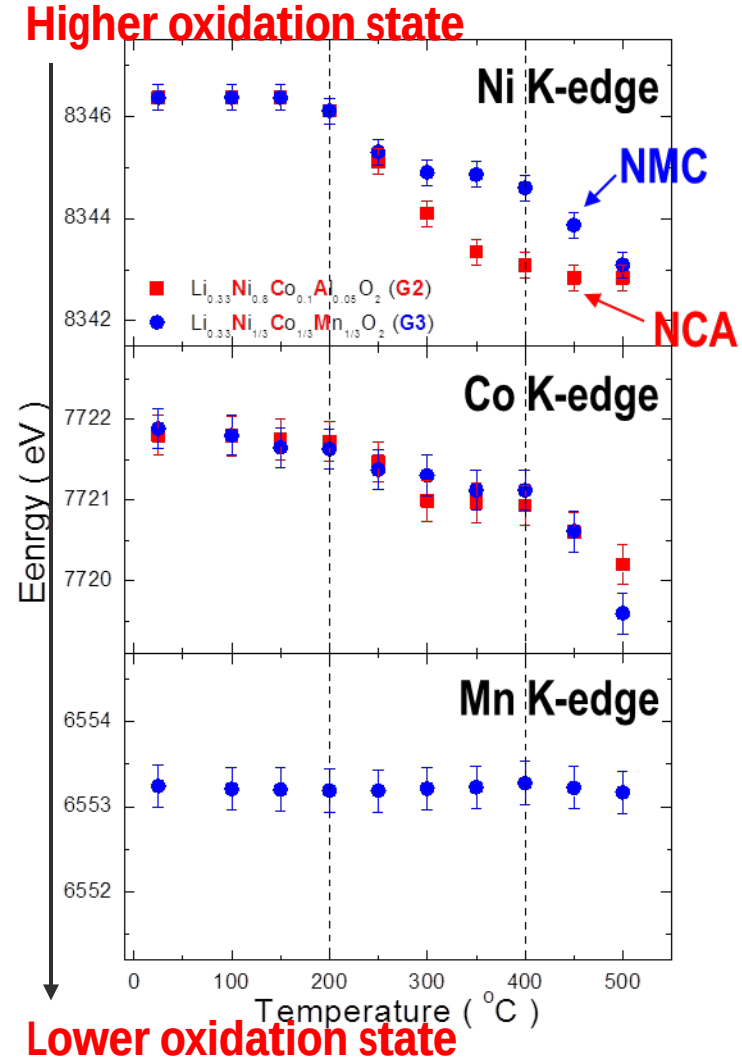
XANES upon heating of $Li_{0.33}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$





- Ni and Co reduce upon heating, but less extent compared with NCA .
- Mn shows almost no reduction: excellent thermally stability

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Summary

- By combining multiple in-situ approaches, it is possible to elucidate - in great detail -the mechanisms by which phase transitions occur in Li-cathode materials during electrochemical cycling or heating.

- In layer structured materials, phase transformation from layered (*R*-3*m*) to disordered spinel (*Fd*-3*m*), finally to rock salt (*Fm*-3*m*) occurs in charged cathodes accompanying with oxygen release during each transition.

- Overcharged materials are less thermally stable.

- Phase transitions accompanied with morphology change at the surface takes place at lower temperature than bulk.
  - **XRD/MS**: Correlation of phase transitions with O_2 & CO_2 release.
  - **XAS**: Ni reduction and migration occurs at lower temperatures than for Co (and Mn). This reduction drives the oxygen release to maintain charge neutrality.
  - **TEM/SAED**: Phase transitions initiate at the surface and propagate inwards, with substantial porosity.

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- Dr. *X. Yu*
- *Dr. Y. Zhou*
- *Dr. S.M. Bak*
- *E. Hu (Ph.D. Student)*

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- X18A : Drs. *S. Ehrlich & Q. Wang*
- X18B & X19A : Drs. *S. Khalid, N. Marinkovic*
- U7A : Drs. *C. Jaye, Z. Fu & D. Fischer*

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