Advanced *in situ* Diagnostic Techniques for Battery Materials

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DOE Vehicle Technologies Office

ES059

BROOKHAVEN NATIONAL LABORATORY

Overview

Timeline

- Start: 10/01/2015
- Finish: 09/30/2018

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

Budget

- Funding received in FY15

  DOE: $500k

- Funding received in FY16

  DOE: $600k

Collaborators

- University of Wisconsin at Milwaukee
- Drexel University
- Massachusetts Institute of Technology (MIT)
- University of Maryland at College Park
- Lawrence Berkeley National Laboratory (LBNL)
- Oak Ridge National Lab. (ORNL)
- Argonne National Lab. (ANL)
- Pacific Northwest National Lab. (PNNL)
- Johnson Control Inc.

- Beijing Institute of Physics
- Beijing Institute of Technology

Relevance and Project Objectives

✓ ***Diagnostics study of thermal abuse tolerance (to improve the safety characteristics of electrode materials).***

- ➥ to establish and investigate the structural origin of thermal instability of various cathode materials, especially the high voltage $LiNi_{0.5}Mn_{1.5}O_4$ materials
- ➥ to search new approaches on how to improve the thermal stability of cathode materials including doping and surface modification techniques.
- ➥ 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 aimed to improve the calendar and cycle life of batteries.***

- ➥ to develop in situ diagnostic techniques with surface and bulk sensitivity to improve the calendar and cycle life of batteries by studying the mechanism of capacity, voltage, and power fading of Li-ion battery.

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

Milestones

Month/Year	Milestones
Dec/15	Complete the thermal stability studies of Fe substituted high voltage spinel cathode materials $LiNi_{1/3}Mn_{4/3}Fe_{1/3}O_4$ in comparison with un-substituted $LiNi_{0.5}Mn_{1.5}O_4$ using in situ time-resolved x-ray diffraction (XRD) and mass spectroscopy techniques. ➥ *Completed.*
Mar/16	Complete the energy resolved transmission X-ray microscopic (TXM) investigation on new concentration gradient NCM cathode sample particles in a noninvasive manner with 3D reconstructed by images through tomography scans to study the 3D Ni, Co, and Mn elemental distribution from surface to the bulk. ➥ *Completed.*
Jun/16	Complete the In situ TR-XRD studies of the structural changes of $Li_{1-x}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ from x=0 to x=0.7 during high rate charge process at different C rates at 10C, 30C, and 60C. ➥*On schedule.*
Sep/16	Complete the in situ time resolved TR- XAS of $Li_{1-x}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode material at Ni, Co and Mn K-edge during 30C high rate charge. ➥ *On schedule.*

Approaches

- 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) during heating and transmission electron microscopy (TEM) to study the thermal stability of the electrode materials, especially the high voltage spinel $LiNi_{1/3}Mn_{4/3}Fe_{1/3}O_4$ with Fe substitution

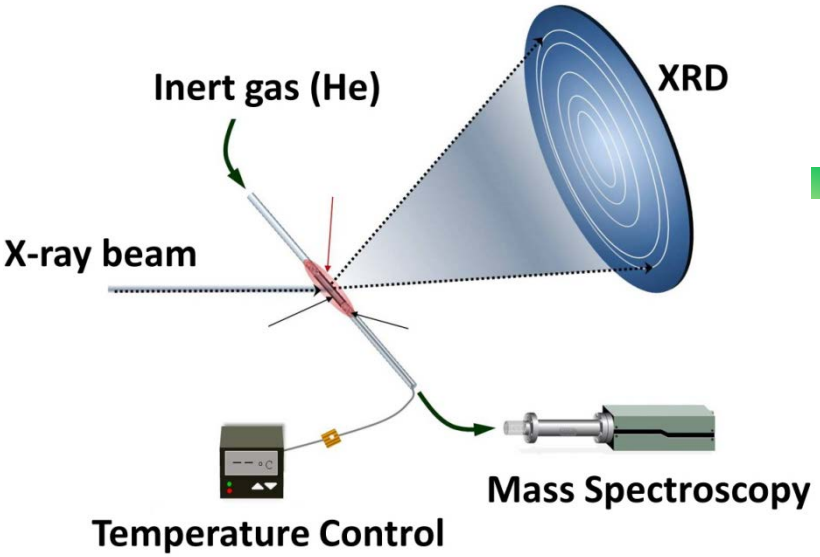
- Using *in situ* XRD and XAS, as well as TEM to study the new concentration gradient cathode materials to improve the cycle life of Li-ion batteries

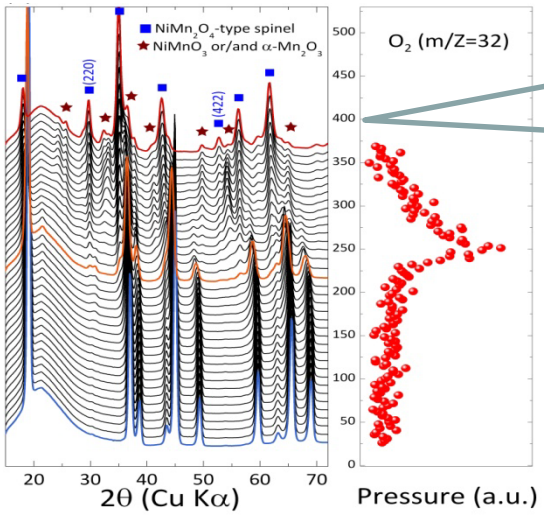
- Using quick x-ray absorption spectroscopy and time resolved x-ray diffraction techniques to study the kinetic properties and the structural changes of $Li_{1-x}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode material from x=0 to x=0.7 during high rate charge process for high rate capability of Li-ion batteries.

- Extended collaboration with other US and international academic institutions and US industrial partners.

Approach: *In Situ* Techniques to Address the Mechanism

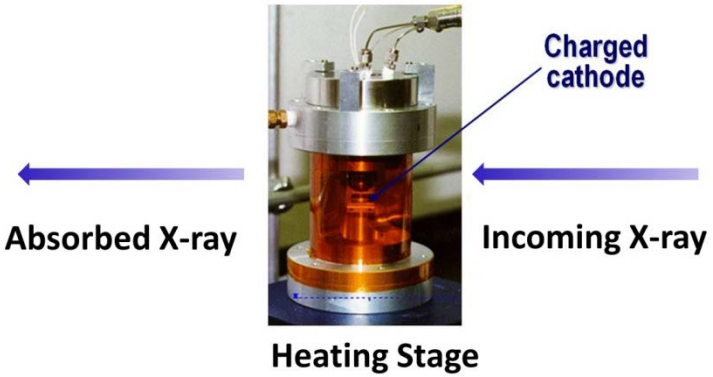
In situ XRD

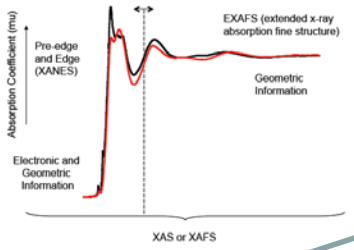


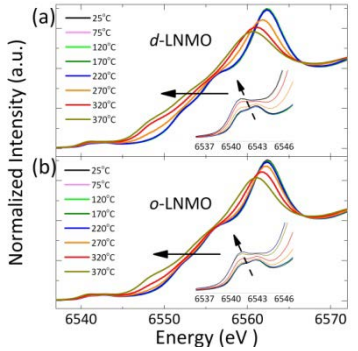


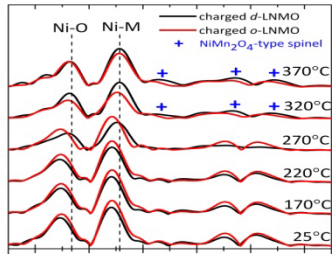
Crystal Structure and Gas Evolution

In situ XAS









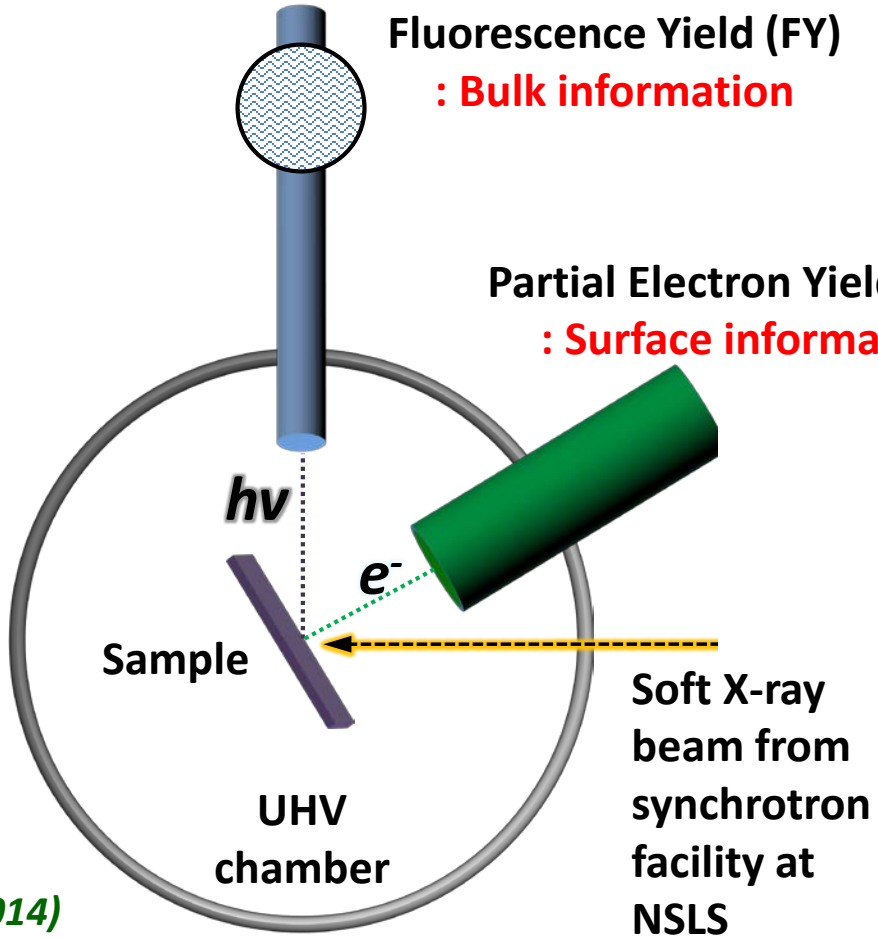
Electronic Structure and Local Environment

S.Bak et al, Chem. Mater. 2013
K.Nam et al, Adv. Funct. Mater. 2013

Approach: Thermal stability study using in situ soft X-ray

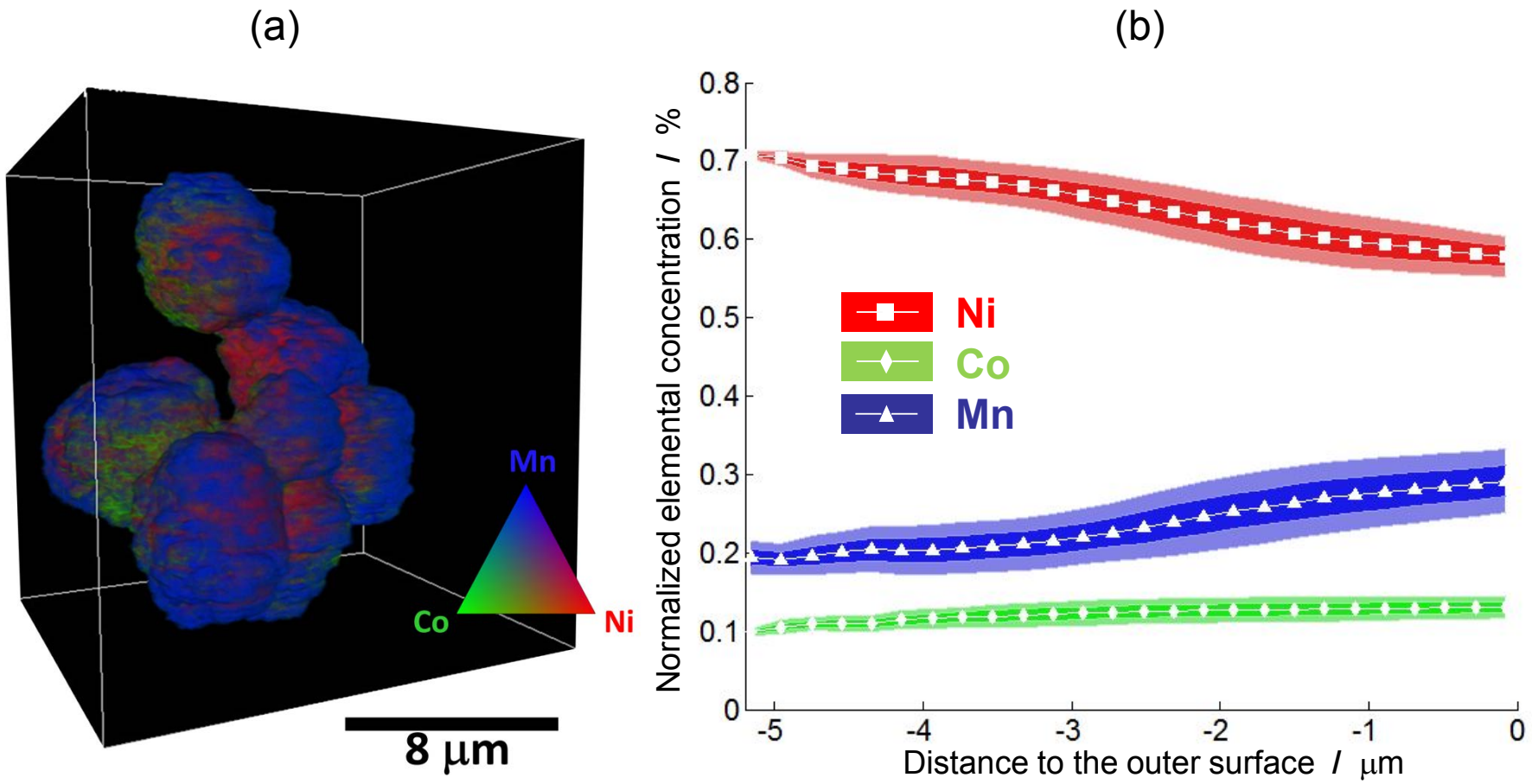
In situ soft XAS sample holder with heating stage

W.-S. Yoon et al., Scientific Reports 4, 6827 (2014)



The partial electron yield (PEY) measurement in soft XAS give information about surface properties (up to ~5 nm), whereas the fluorescence yield (FY) measurements identify more or less bulk properties (up to ~300nm) similar to XRD measurement.

Approach: Using TXM to study 3-D Ni, Mn, and Co distribution

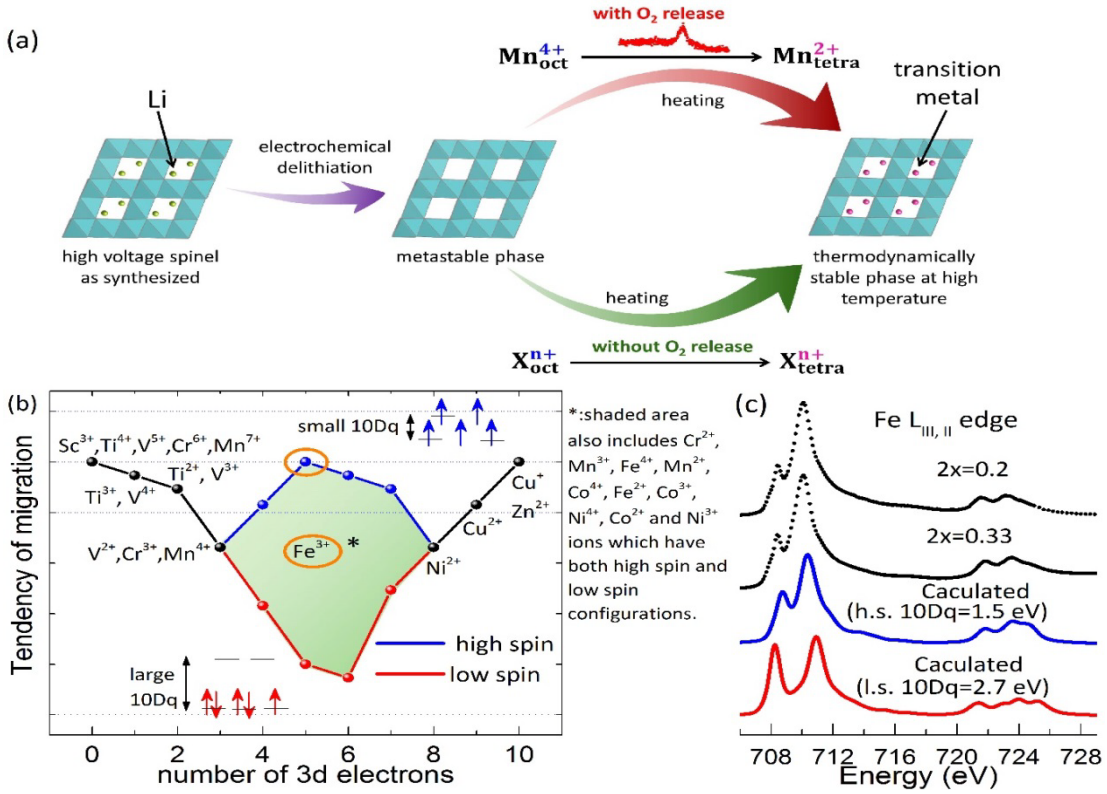


The Ni, Mn, and Co concentration changes from the surface to the center of a $LiNi_{0.6}Co_{0.2}Mn_{0.2}$ particle follow the designed concentration gradient very well.

Technical Accomplishments and Progress

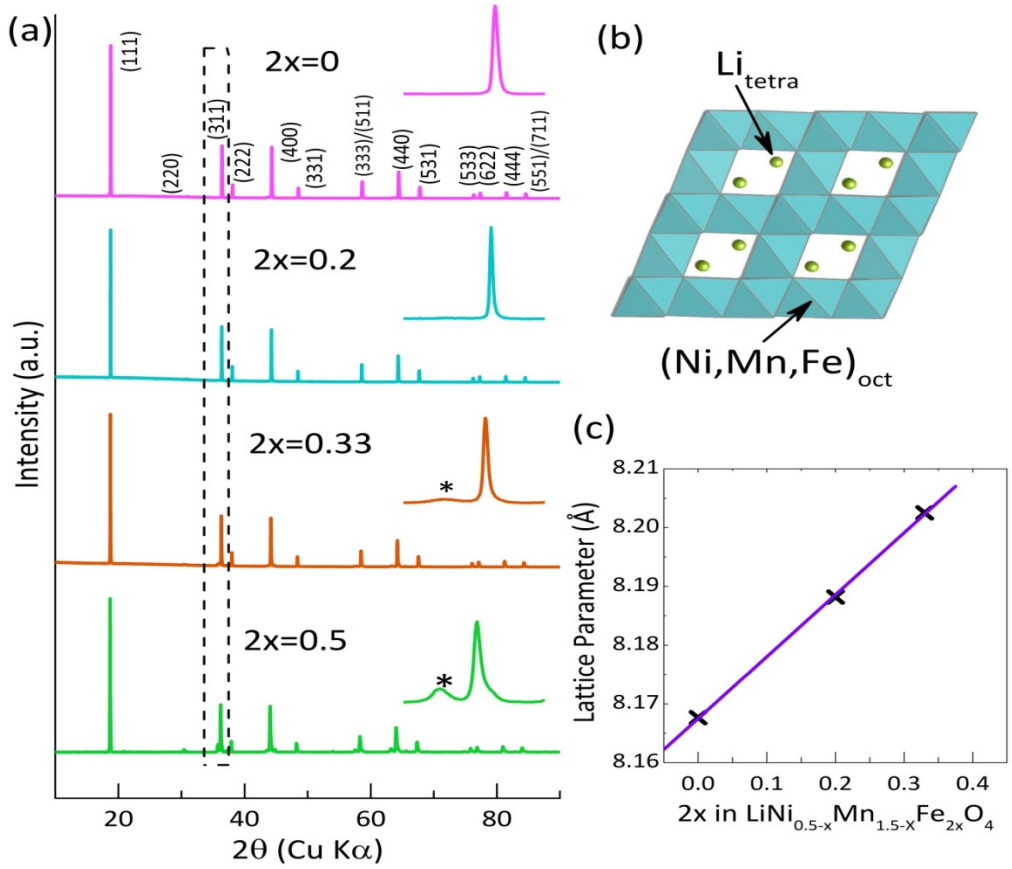
- By collaborating with Dr. Yijin Liu at Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory and other collaborators, designed, synthesized Fe substituted high voltage spinel $LiNi_{0.5-x}Mn_{1.5-x}Fe_{2x}O_4$ (LNMFO) cathode materials and carried out thermal stability studies these materials. The optimized $LiNi_{1/3}Mn_{4/3}Fe_{1/3}O_4$ materials showed outstanding thermal stability.
- By collaborating with Prof. Lin Gu at Institute of Physics, Chinese Academy of Sciences, through a systematic study of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) cathode materials cycling at different charge-discharge rates, using *in situ* synchrotron based XRD and XAS, as well as using atomic resolution *ex situ* STEM after high rate cycling, intermediate phase formation at high rate cycling was discovered. The results of these studies would provide important guidance for designing new cathode materials for high power usage of lithium-ion batteries, such as for HEV and PHEV.
- By collaborating with beamline scientists at X-ray powder diffraction (XPD) and Hard x-ray nano-probe (HXN) beamlines at NSLSII, new *in situ* and *ex situ* studies of battery materials using the unique capability of these two beamlines have been designed and carried out. The preliminary results are promising and further studies are planned.

Illustration of the design strategy by using high spin Fe^{3+} to improve thermal stability of $LiNi_{0.5-x}Mn_{1.5-x}Fe_{2x}O_4$



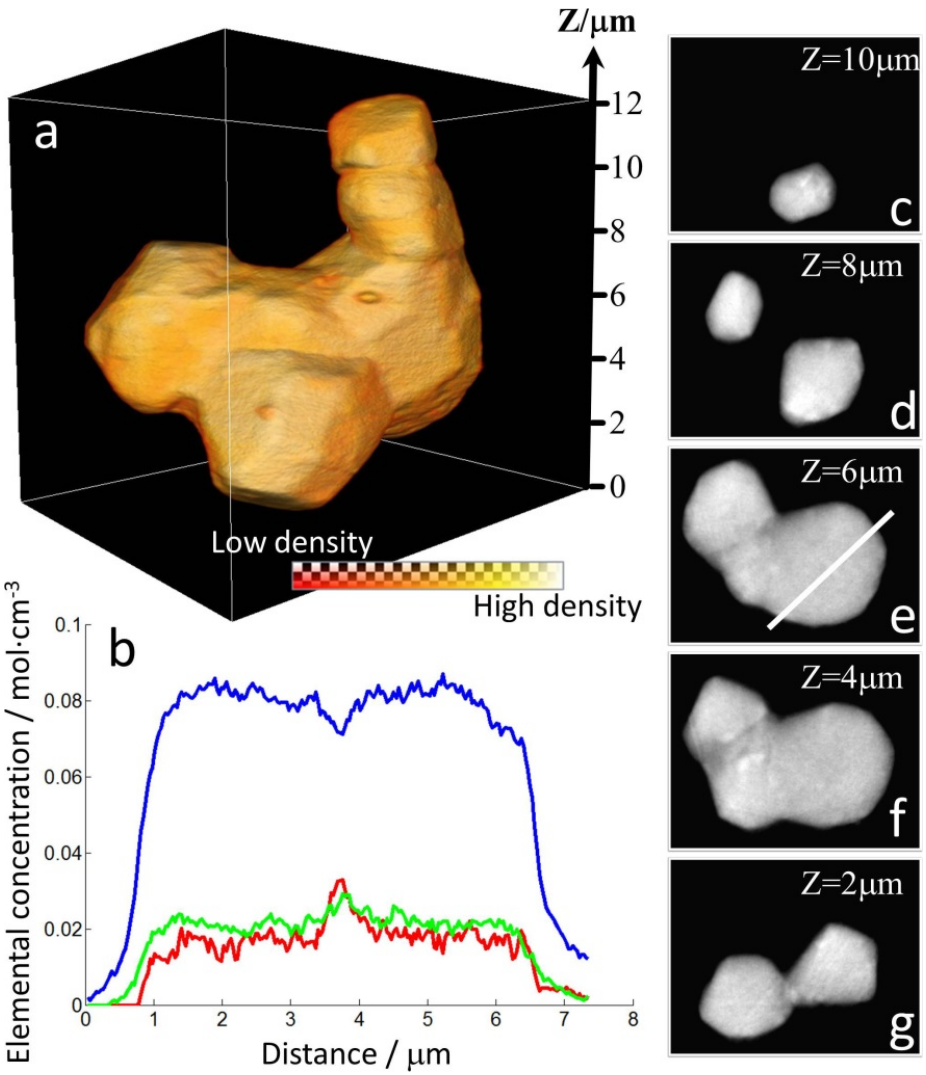
(a) Illustration of the design strategy. X^{n+} denotes a certain transition metal cation that readily migrates to tetrahedral site without reduction. (b) Tendency of migration (based on Octahedral Site Stabilization Energy) as a function of the electronic structure of 3d transition metal cations. Exchange energy is not considered in calculating the OSSE. (c) Experimental data of Fe L-edge x-ray absorption spectra for $LiNi_{0.5-x}Mn_{1.5-x}Fe_{2x}O_4$ (2x = 0.2, 0.33) compared with calculated spectra assuming high spin and low spin configurations.

Structural characterization of $LiNi_{0.5-x}Mn_{1.5-x}Fe_{2x}O_4$



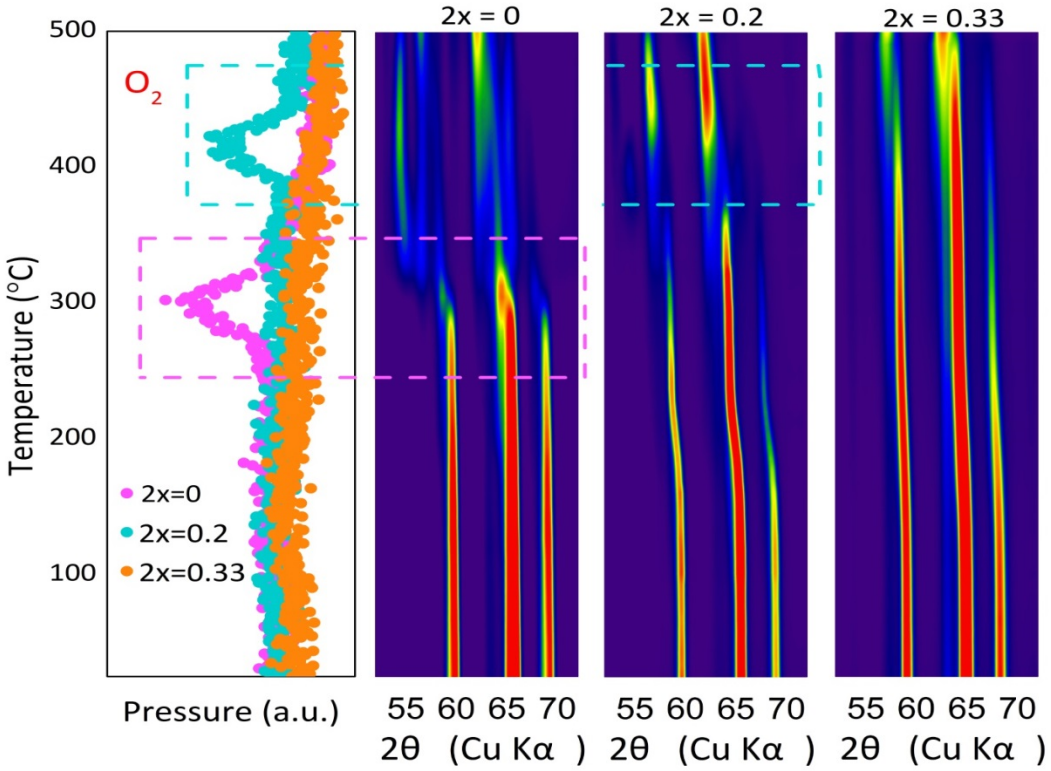
Structural characterization of $LiNi_{0.5-x}Mn_{1.5-x}Fe_{2x}O_4$. (a) XRD patterns for $LiNi_{0.5-x}Mn_{1.5-x}Fe_{2x}O_4$ (2x = 0, 0.2, 0.33, 0.5) with the inset graphs showing the emergence of impurity phase as 2x exceeds a certain limit. A pure phase can be indexed by the $Fd\bar{3}m$ space group. (b) Illustration of the crystal structure of $LiNi_{0.5-x}Mn_{1.5-x}Fe_{2x}O_4$. (c) Variation of the lattice parameter as a function of the concentration of Fe. The linear relationship indicates that solid solution is formed in the $LiNi_{0.5-x}Mn_{1.5-x}Fe_{2x}O_4$ (2x = 0, 0.2, 0.33) series.

$LiNi_{1/3}Fe_{1/3}Mn_{4/3}O_4$—TXM



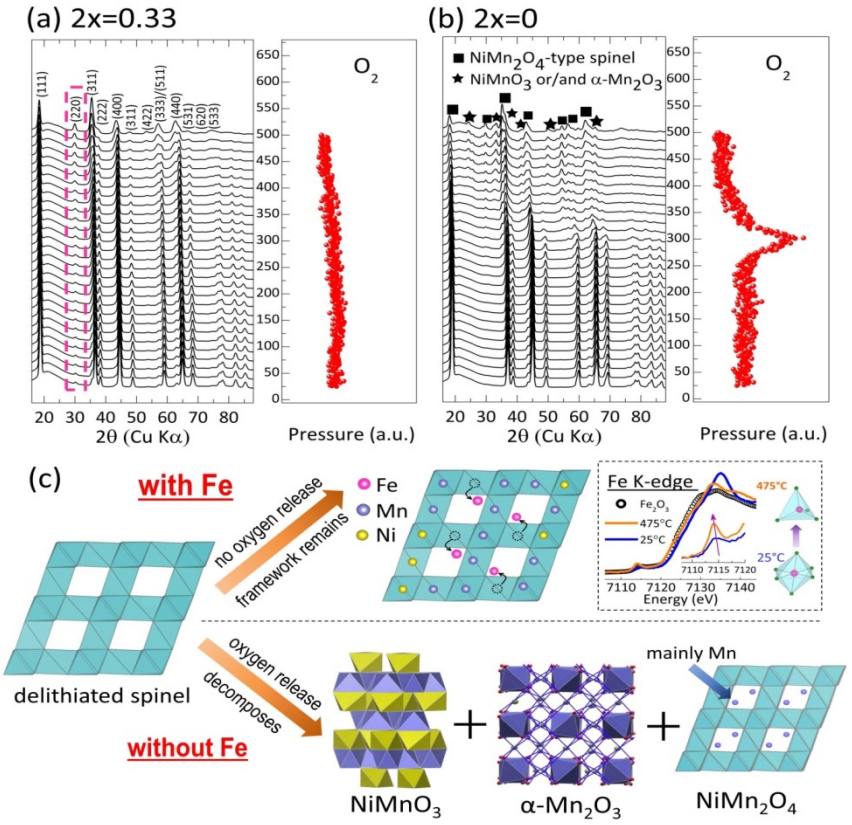
3D structure of a selected $LiNi_{0.33}Mn_{1.34}Fe_{0.33}O_4$ particle is shown in panel (a) with the scale indicated in the axis and the color legend shown in the inset. Panels (c) through (g) are slices at different depth of the particle showing that it is a solid piece with no internal pores and the density distribution is relatively homogeneous. The elemental concentration over the line path indicated in panel (e) is plotted in panel (b) (the blue, green, and red curves represent the concentration of Mn, Ni, and Fe respectively), which is in good agreement with the elemental composition of the material. Panels (a) and (c) through (g) are reconstructed from nano-tomography data collected at 8380 eV (above the absorption k edges of all the three transition metal elements), while the data plotted in panel (b) is retrieved from the evaluation of the energy dependency of the absorption coefficient using a method known as Absorption Correlation Tomography

Effect of Fe substitution on the structural evolution and oxygen release during heating for charged samples of $LiNi_{0.5-x}Mn_{1.5-x}Fe_{2x}O_4$ (2x=0, 0.2, 0.33)



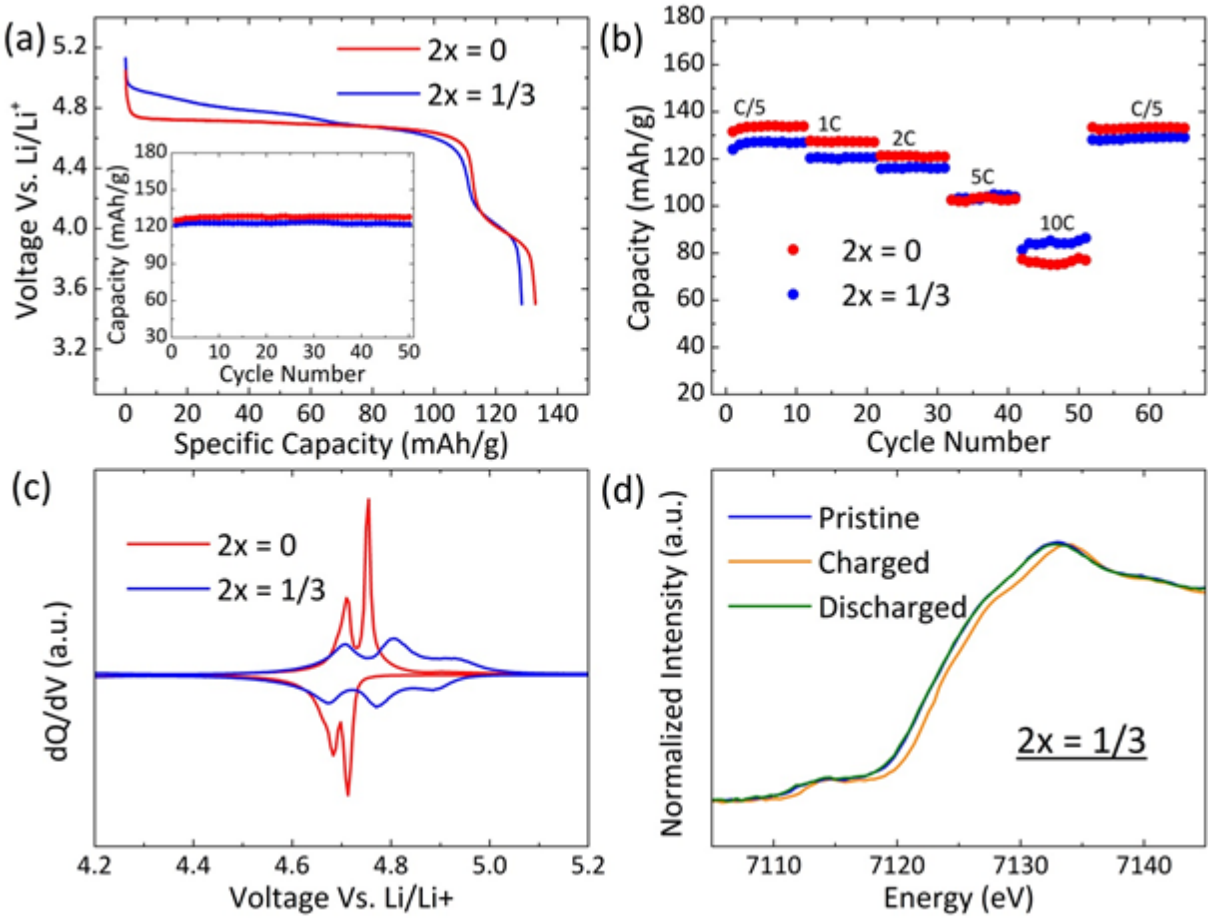
Effect of Fe substitution on the structural evolution and oxygen release during heating the charged samples of $LiNi_{0.5-x}Mn_{1.5-x}Fe_{2x}O_4$ (2x=0, 0.2, 0.33). The left panel is the *in situ* MS data for oxygen and the right three panels are the *in situ* XRD data for $LiNi_{0.5-x}Mn_{1.5-x}Fe_{2x}O_4$ (2x=0, 0.2, 0.33). .

Comparison of In situ XRD-MS results of fully charged $LiNi_{0.5-x}Mn_{1.5-x}Fe_{2x}O_4$ of 2x = 0.33 and x=0 and illustration of effect of Fe substitution on structural stability during heating



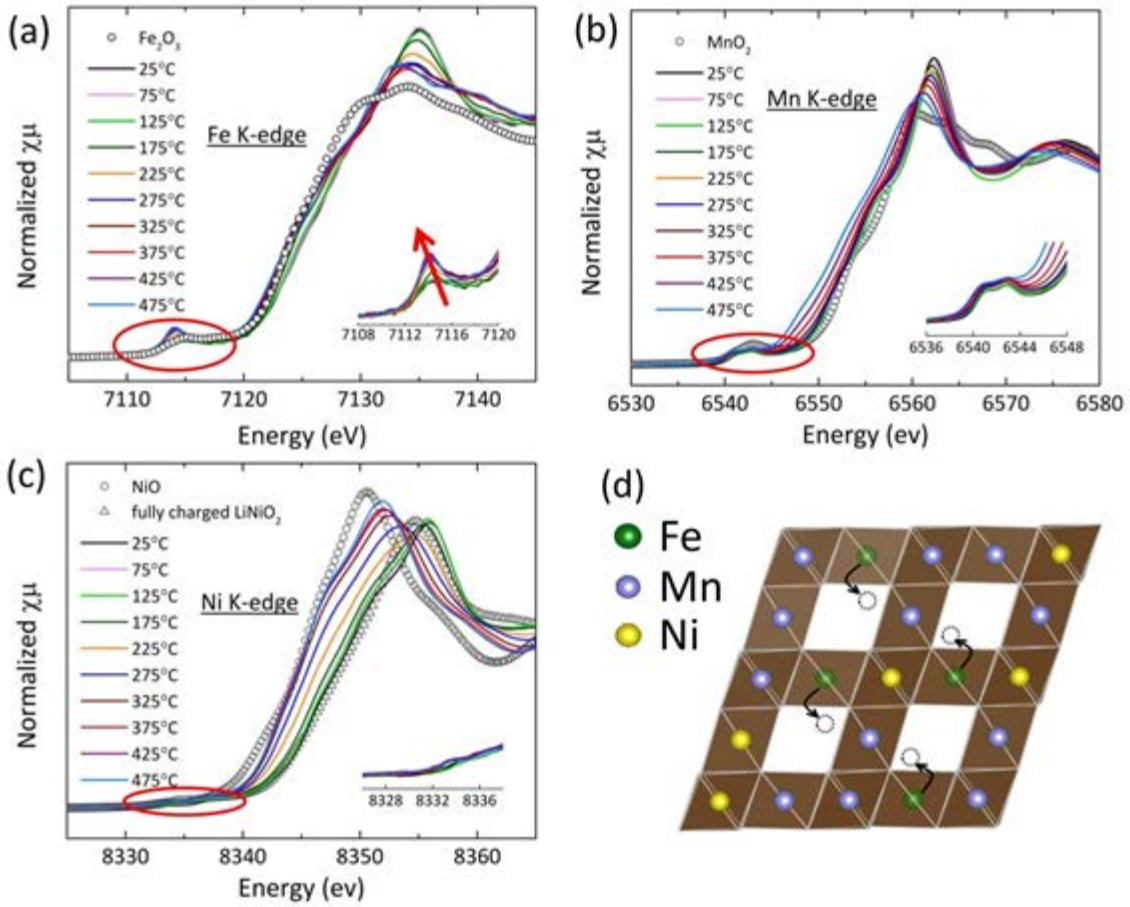
(a) *In situ* XRD-MS data of fully charged $LiNi_{0.5-x}Mn_{1.5-x}Fe_{2x}O_4$ (2x = 0.33) and (b) *In situ* XRD-MS data of fully charged $LiNi_{0.5-x}Mn_{1.5-x}Fe_{2x}O_4$ (2x = 0). (c) Illustration of effect of Fe substitution on structural evolution and oxygen release and Fe K-edge x-ray absorption spectroscopy results.

Electrochemical performance and XANES spectra of Un-substituted and Fe substituted LNMO



Electrochemical performance and XANES spectra. (a) Discharge profiles together with capacity retention (lower left inset) of LNMO and $LiNi_{1/3}Mn_{4/3}Fe_{1/3}O_4$. Cells were cycled at C/5. (b) Rate capability of LNMO and $LiNi_{1/3}Mn_{4/3}Fe_{1/3}O_4$. (c) dQ/dV plot of LNMO and $LiNi_{1/3}Mn_{4/3}Fe_{1/3}O_4$. (d) Fe K-edge XANES spectra of pristine charged and discharged samples of $LiNi_{1/3}Mn_{4/3}Fe_{1/3}O_4$.

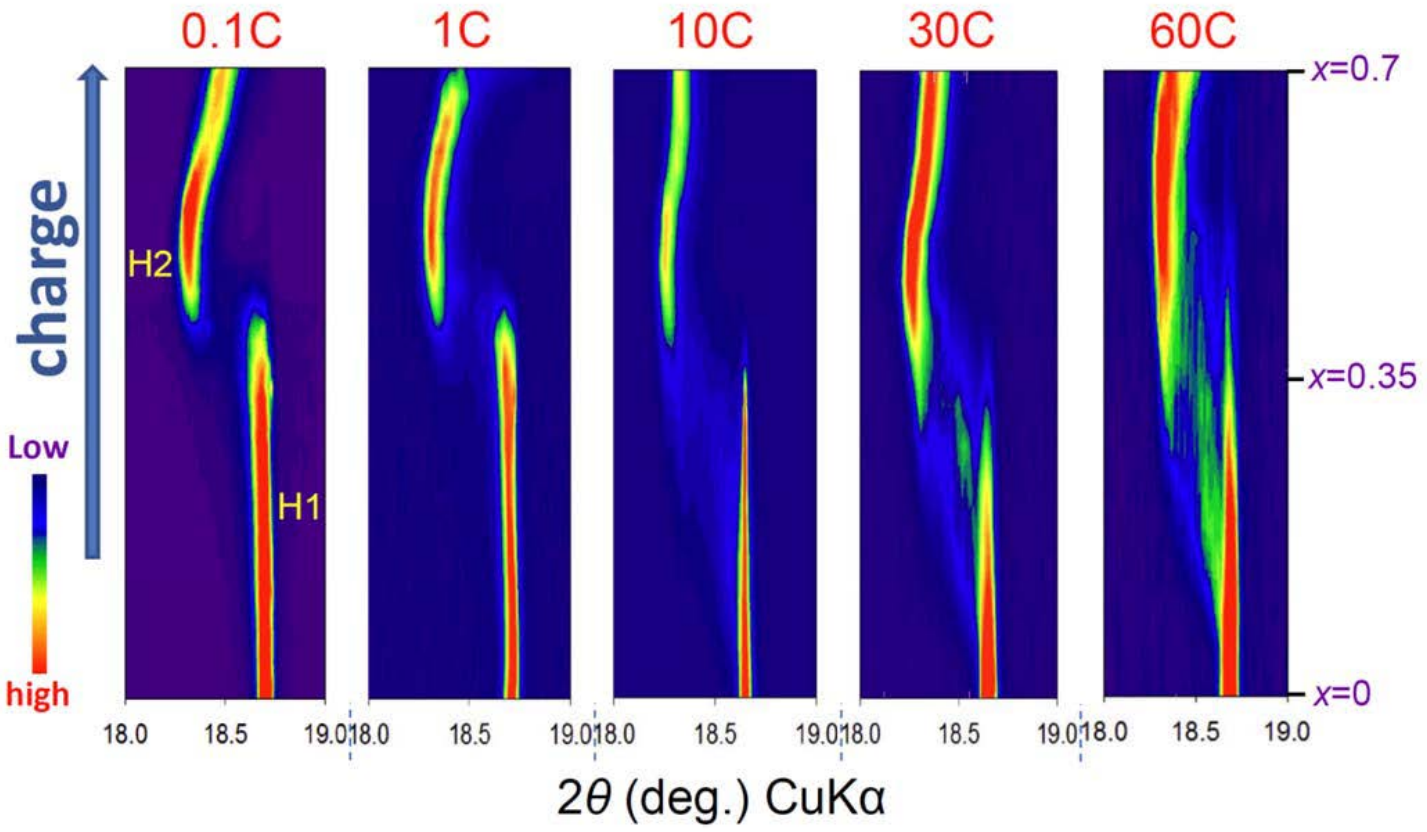
The migration of Fe in Fe substituted LNMO during heating evidenced by in situ XANES



In situ XANES spectra at the K-edge of (a) Fe (b) Mn and (c) Ni for fully charged $LiNi_{1/3}Mn_{4/3}Fe_{1/3}O_4$ during heating up to 475 ºC. (d) Schematic of Fe migration to spinel tetrahedral site.

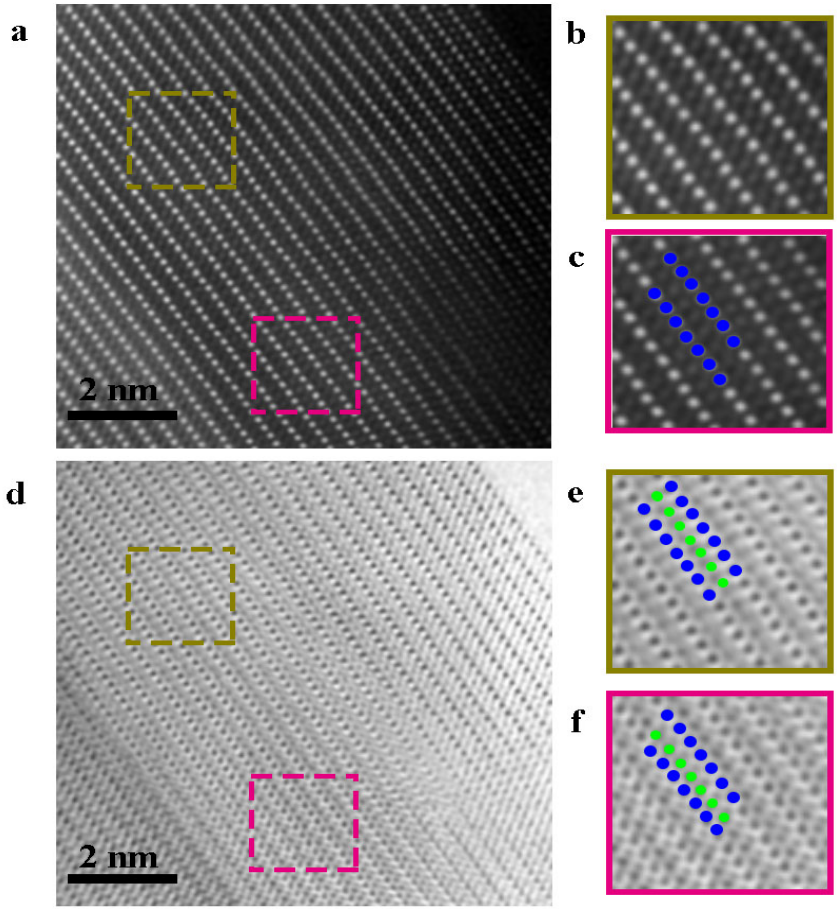
Xiao-Qing Yang *et. al*., ***Adv. Energy Mater.***, (December 2015), DOI: 10.1002/aenm.201501662

In situ XRD of $Li_{1-x}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NMC) during the first charge: the contour plot of the (003) diffraction peak show intermediate phase at 10 C, 30C and 60C high rates



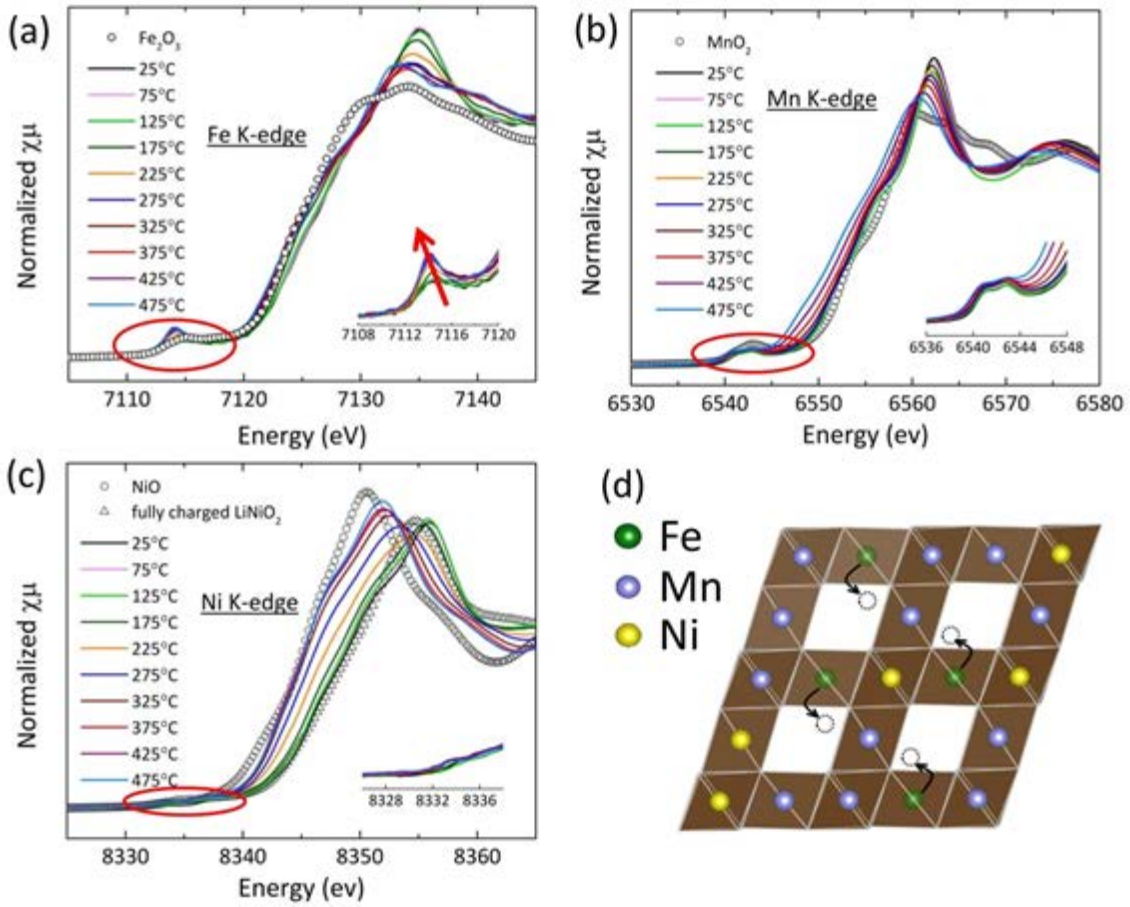
***In situ* XRD of NMC during the first charge.** Contour plot of the (003) diffraction peak of $Li_{1-x}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ with increasing x between x=0 and x=0.7 during the first charge process at different C rates (0.1C, 1C, 10C, 30C, 60C).

Structure of half charged NMC at 30C rate studied by TEM: HAADF images



Structure of half charged NMC at 30C rate. (a) Typical atomic resolution high-angle annular dark-field HAADF image taken along the [110] zone axis of the NMC electrode after 55s charging at the current rate of 30C. (b,c) The zoom-in image of the areas marked with orange and pink squares, respectively. (d) Corresponding ABF images of NMC electrode after 55s charging. (e,f) The zoom-in image of the areas marked with orange and pink squares, respectively. The blue and green dots indicate the TM ions and Li ions, respectively showing the intermediate phase with Li ions located at tetrahedral sites.

The migration of Fe in Fe substituted LNMO during heating evidenced by in situ XANES



In situ XANES spectra at the K-edge of (a) Fe (b) Mn and (c) Ni for fully charged $LiNi_{1/3}Mn_{4/3}Fe_{1/3}O_4$ during heating up to 475 ºC. (d) Schematic of Fe migration to spinel tetrahedral site.

Xiao-Qing Yang *et. al*., submitted to ***Adv. Energy Mater.***

Response to last year reviewer's comments

Comments from 2015 AMR	Response
▣ Blended $LiMn_2O_4$ (LMO)-$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) cathode materials with different stoichiometric ratios have been studied. The discovered specific physicochemical processes in the LMO and NCM should be described clearly in the annual report, the reviewer urged.	▣ The results of Blended $LiMn_2O_4$ (LMO)-$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) cathode materials with different stoichiometric ratios had been published. The discovered specific physicochemical processes in the LMO and NCM have been clearly described in details in the annual report
▣ The loss of key equipment at Brookhaven has led to a number of fruitful collaborations with laboratories and partners around the country, the reviewer observed, and the work has also engaged industry partners, which is key to transitioning diagnostic techniques out of the lab. Active engagement of the broader battery community is a key strong point of this work.	▣ The collaborations with scientists at other synchrotron facilities such as APS at Argonne National Lab and SSRL at Stanford University and ALS at Berkeley National Lab. had been further strengthened. High quality data had been collected and scientific papers have been prepared or published. More industry partners have been contacted and broader collaboration with battery community are being developed
▣ The reviewer recommended much more collaboration with other national laboratories, universities and battery companies working on novel materials or cells that meet DOE electric vehicle (EV) or plug-in hybrid electric (PHEV) goals..	▣ More collaborations with other national laboratories, universities and battery companies working on novel materials to meet DOE electric vehicle (EV) goals have been developed. These institutions including ANL, PNNL, LBNL, ORNL, MIT, Drexel University, and Johnson Control

Collaborations with other institutions and companies

- Lawrence Berkeley National Laboratory
  Transitions from Near-Surface to Interior Redox upon Lithiation using high resolution TEM
- University of Maryland at College Park
  Transitions from Near-Surface to Interior Redox upon Lithiation using high resolution TEM
- Drexel University
  Probing the mechanism of high capacitance in 2D titanium carbides
- Argonne National Lab. (ANL)
  In situ XRD and XAS study of high energy density Li_2MnO_3-$LiMO_2$ composite (LMR-NCM).
- Pacific Northwest National Lab. (PNNL)
  Effects of structural defects on the electrochemical activation of Li_2MnO_3.
- Johnson Control Inc.
  In situ XRD and XAS study of high energy density cathode materials

- Beijing Institute of Physics, Chinese Academy of Sciences
  High energy density cathode material diagnostic studies using atomic level resolution STEM and in situ XRD and XAS
- Beijing Institute of Technology, Beijing, China.
  High-Rate and Cycling-Stable Li-Ion Batteries

Remaining Challenges and Barriers

- The relationships between the high-rate capabilities and nanometer-size effects have been extensively studied. However, the fundamental understanding about the structural changes of the electrode materials during high rate cycling in real time is quite limited, partly due to experimental difficulties in ultrafast data collection requirement under operando conditions. Time resolved XRD and XAS will be good tools for such studies
- Morphology and elemental mapping of anode and cathode materials are needed as diagnostic tools for Li-ion battery research. The full field transmission x-ray microscopy (TXM) technique as well as micro- and nano- probe scanning TXM will be developed for battery research based on the high penetration power of x-ray beam at beamline at SLAC and APS, as well as new nano-probe beamline at NSLSII. Silicon based anode and high voltage spinel cathode materials will be studied using these new diagnostic tools.

Proposed Future Work for *FY 2016* and *FY2017*

▣ **FY2016 Q3 Milestone:**

Complete the In situ TR-XRD studies of the structural changes at different C rates at 10C, 30C, and 60C, for $Li_{1-x}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ from x=0 to x=0.7 during high rate charge process.

▣ **FY2016 Q4 Milestone:**

Complete the in situ time resolved TR- XAS of $Li_{1-x}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode material at Ni, Co and Mn K-edge during 30C high rate charge.

FY2017 work proposed:

- ▣ **The synchrotron based ex situ and in situ x-ray pair distribution function (PDF) technique will be developed and applied for battery material research, especially on the high energy density cathode materials.**
- ▣ **The full field transmission x-ray microscopy (TXM) technique as well as micro- and nano- probe scanning TXM techniques will be developed and applied for Li-ion battery research.**
- ▣ **The collaborative research with US academic research institutions and industrial partners will be further expanded and strengthened.**

Summary

Relevance

- ✓ *Diagnostics study of thermal abuse tolerance (to improve the safety characteristics).*
- ✓ *Diagnostics study aimed to improve the calendar and cycle life of batteries.*
- ✓ *Diagnostics study of electrode materials with lower cost potential.*

Approaches

- *Time resolved X-ray diffraction (TR-XRD) and mass spectroscopy (MS)*
- *In situ x-ray diffraction and absorption spectroscopy*
- *Quick x-ray absorption spectroscopy*
- *Full field as well as micro- and nano- probe scanning TXM*
- *High resolution transmission electron microscopy (HR-TEM)*

Technical Accomplishments

- *Completed the energy resolved transmission X-ray microscopic (TXM) investigation on new concentration gradient NCM cathode sample particles in a noninvasive manner with 3D reconstructed by images through tomography scans to study the 3D Ni, Co, and Mn elemental distribution.*
- *Completed the thermal stability studies of Fe substituted high voltage spinel cathode materials $LiNi_{1/3}Mn_{4/3}Fe_{1/3}O_4$ in comparison with un-substituted $LiNi_{0.5}Mn_{1.5}O_4$ using in situ time-resolved x-ray diffraction (XRD) and mass spectroscopy techniques.*

Proposed Future work

- *Continue and complete the XAS studies of $LiNi_{1/3}Mn_{4/3}Fe_{1/3}O_4$*
- *Develop synchrotron based PDF technique and apply it to the high energy density cathode material studies*
- *Develop and apply the full field transmission x-ray microscopy (TXM) as well as micro- and nano- probe scanning TXM techniques for battery materials to study the silicon based anode materials*