Advanced *in situ* Diagnostic Techniques for Battery Materials

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BAT059

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Overview

Timeline

- Start:　10/01/2017
- 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 FY17

  DOE:　$600k

- Funding received in FY18

  DOE:　$500k

Collaborators

- University of Wisconsin at Milwaukee
- University of Maryland at College Park
- Oak Ridge National Laboratory (ORNL)
- Argonne National Lab. (ANL)
- Pacific Northwest National Lab. (PNNL)
- Johnson Control Inc.

Relevance and Project Objectives

✓*Diagnostic studies to understand the structural changes of cathode materials during high rate charge-discharge cycles (to improve the rate capability of electrode materials for Li-ion batteries).*

➡ to investigate the structural changes of various cathode materials, especially the   NMC materials cycled at different rates, especially at high rate cycling.

➡ to search new approaches to improve the high rate capability of cathode materials including optimize the content of transition metal elements, as well as doping and surface modification techniques.

➡ to provide valuable information about how to design cathode materials with better rate capability for xEV applications.

➡ to develop new *in situ* diagnostic techniques to study the high rate capability cathode materials.

✓ *Diagnostics study to understand the voltage and capacity fading mechanism during multiple cycling for high energy density materials (to increase the energy density and cycling life of Li-ion 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.

➡ to develop multi scale imaging diagnostic techniques such as TEM , nano-probe, as well as TXM imaging, and combining them together with spectroscopy (x-ray absorption) to improve calendar and cycle life of batteries by studying the mechanism of capacity, voltage, and power fading of Li-ion battery.

✓ *Diagnostics study aimed to improve the safety characteristics of batteries.*

➡ to develop in situ diagnostic techniques with surface and bulk sensitivity to study the thermal stability of cathode materials at different charged states and cycling conditions and history aimed to improve the thermal stability and safety characteristics of Li-ion batteries.

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

Milestones

| Month/Year	Milestones
Dec/2017	Complete the in situ TXM studies of $LiCoO_2$ cathode materials during charge-discharge cycling to evaluate the inhomogeneity of the charged (discharged) states among large number of material particles and using data mining technique to detect the under (over) reacted minority regions . ↬ *Completed.*
Mar/2018	Complete the neutron diffraction studies of $LiCoO_2$ as high energy density cathode material at high voltage charge in comparison with the pristine state ↬ *Completed.*
Jun/2018	Complete the pair distribution function (PDF) studies of $LiCoO_2$ using both x-ray (x-PDF) and neutron (n-PDF) probes to study the mechanism of anionic redox reaction (ARR) in such widely used commercial cathode materials for Li-ion batteries and explore the potential of using this material for high energy density cell applications. ↬*On schedule.*
Sep/2018	Complete the experimental design, data collection and analysis of three dimensional (3D) STEM tomography studies of high energy density $Li_{1.2}Ni_{0.15}Co_{0.1}Mn_{0.55}O_2$ cathode materials at pristine state and after multiple cycling. ↬ *On schedule.*

Approaches

- Using nano-probe beamline at NSLSII to study the elemental distribution of new solid electrolyte materials for Li-ion batteries
- Using pair distribution function (PDF) to study $LiCoO_2$ materials. Using both x-ray (x-PDF) and neutron (n-PDF) probes to study the mechanism of anionic redox reaction (ARR) in such widely used commercial cathode materials for Li-ion batteries and explore the potential of using this material for high energy density battery applications.
- Using high resolution transmission electron microscopy (TEM) to obtain multiple dimensional (3D + elemental, valence state, and time) mapping of new cathode materials for advanced Li-ion batteries.
- Using transmission x-ray microscopy (TXM) for the studies $LiCoO_2$ cathode materials during charge-discharge cycling to evaluate the inhomogeneity of the charged (discharged) states among large number of material particles and using data mining technique to detect the under (over) reacted minority regions.
- Using 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 to study the thermal stability of the electrode materials
- Using *in situ* XRD and XAS, to study the new concentration gradient cathode materials to improve the cycle life of Li-ion batteries

Approach: Using Neutron Diffraction and Neutron PDF (with Jue Liu at ORNL) to study Cathode Materials for Li-ion batteries
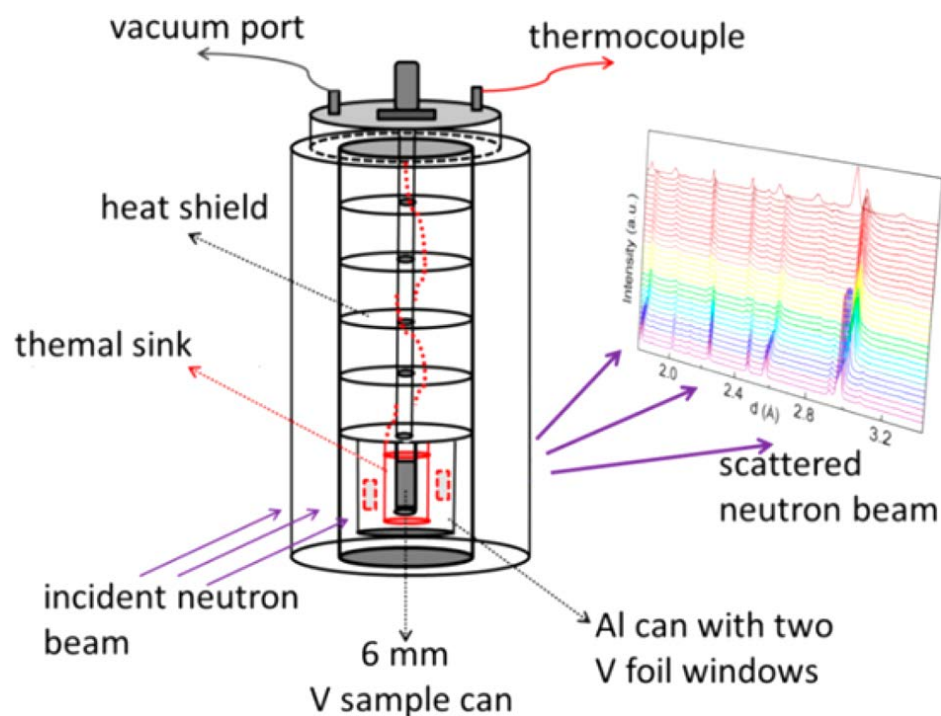

Schematic of in situ neutron diffraction experiments
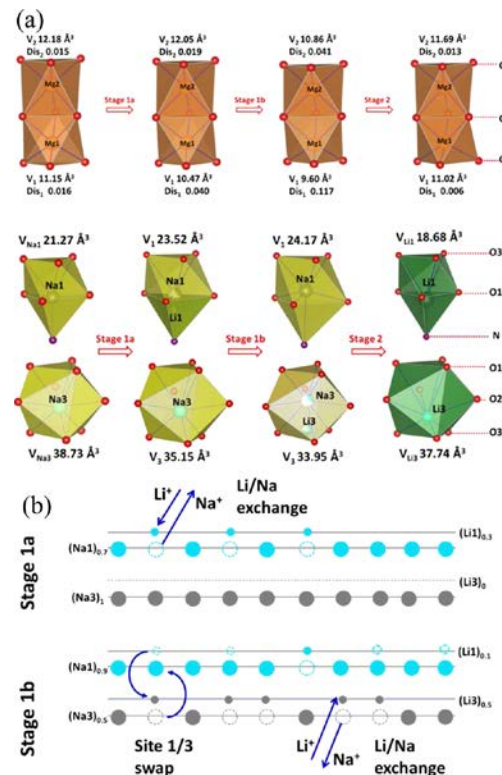
(a) Representation (to scale) of the evolution of cation coordination polyhedral volume that occurs during ion exchange based on the structures obtained from in situ neutron diffraction studies for the initial phase (Na2Mg2P3O9N) and the phases at the end of stage 1a (Li0.4Na1.6Mg2P3O9N), stage 1b (Li0.7Na1.3Mg2P3O9N), and stage 2 (Li2Mg2P3O9N). Polyhedral volumes (Å3) are indicated, as is the distortion index of the MgO6 octahedra. (b) Different patterns for changes in site occupancies that occur during stage 1a (top) and site 1b (bottom).

Jue Liu et al, JACS 2017.

Approach: Using TXM (with Yijin Liu at SLAC) to do multiple dimensional (3D + elemental, valence state, time) mapping and spectroscopy (XAS) for electrode materials of Li-ion batteries
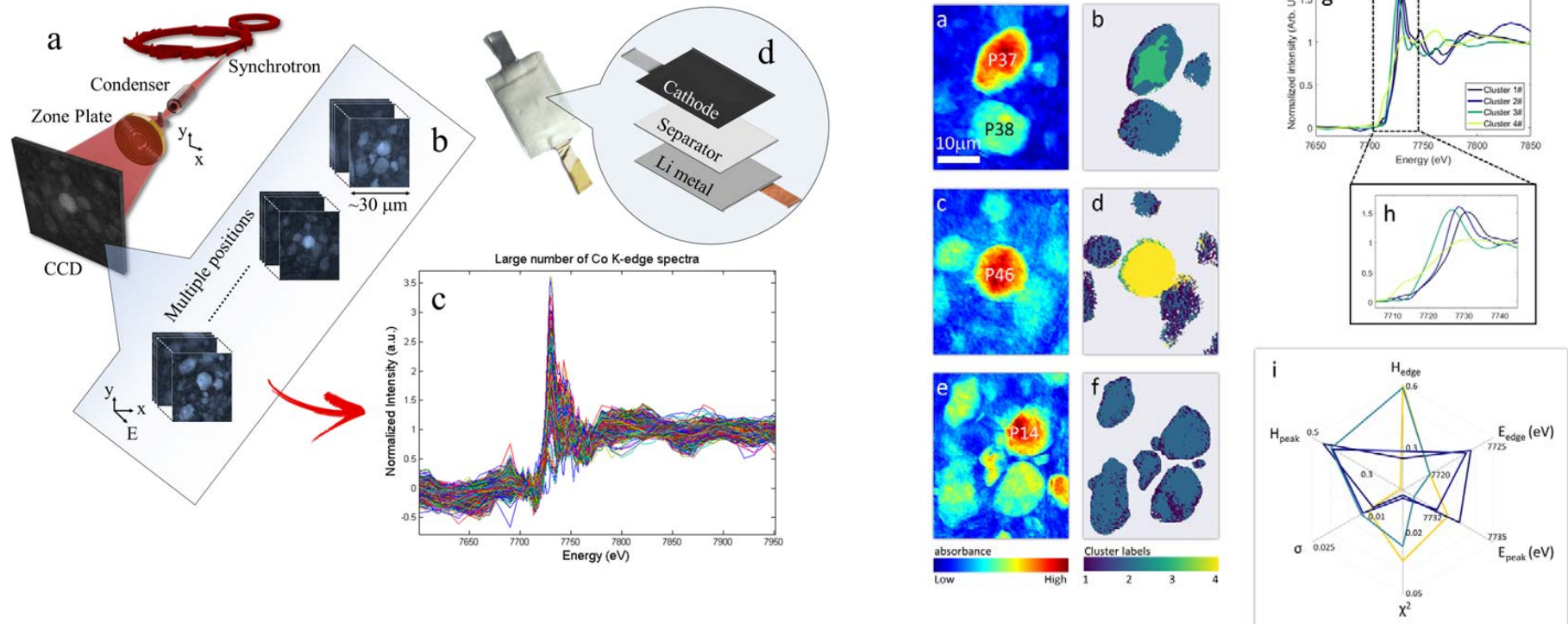
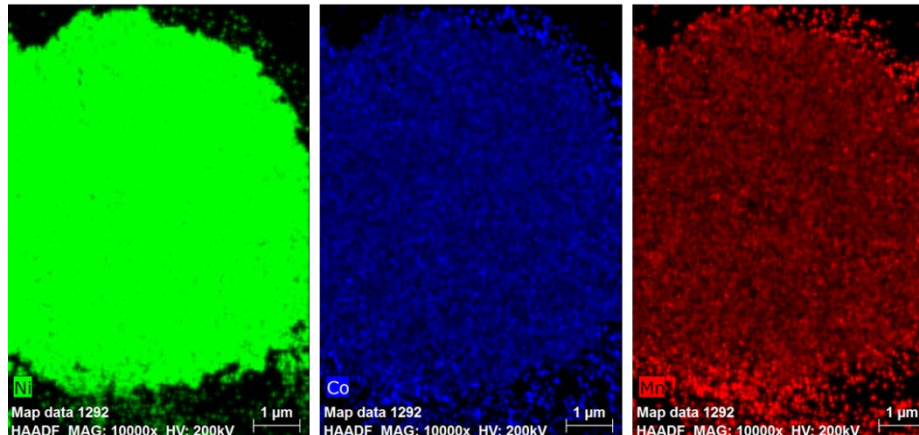
Kai Zhang et al, Nano Letter 2017.

Approach: Using TEM and EELS (with Huolin Xin at BNL) to do multiple dimensional (3D + elemental, valence state, time) mapping
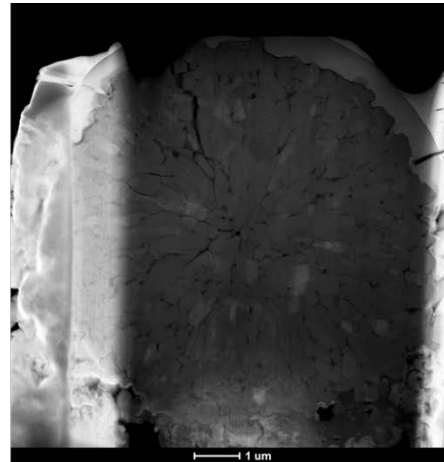
STEM-EDX quantification map

Element	Atomic %
Ni	78.13699593
Mn	10.63291739
Co	11.23008668

Chemical distribution is uniform.

Example of using TEM to study the concentration gradient NMC 811

Technical Accomplishments and Progress

- Through collaboration with Prof. Xiqian Yu at Institute of Physics, Chinese Academy of Sciences, and Dr. Yijin Liu at Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, the studies of $LiCoO_2$, a widely used cathode material have been carried out using TXM. The results were published on *ACS Energy Lett*

- Through collaboration with Dr. Jue Liu at ORNL, and Prof. at Stony Brook University, studies of ion exchange synthesis mechanism of $Li_2Mg_2P_3O_9N$ have been carried out and the results were published on *JACS*

- Through collaboration with Prof. Xiqian Yu at Institute of Physics, Chinese Academy of Sciences and Dr. Khal Amine at Argonne National Lab., correlations between transition metal chemistry and structure in $Li_2Ru_{0.5}Mn_{0.5}O_3$ has been investigated in a wide voltage window. The results were published on *Chem. Mater.*

- The complexities of structural changes in layered oxide cathode materials for Li-ion batteries during fast charge–discharge cycling and heating were investigated using synchrotron based XRD and XAS, as well as TEM. The results were published on *Account of Chemical Research.*

Unexpected minority structure identified by TXM and data mining method in a large number of selected LiCoO$_2$ particles during cycling.
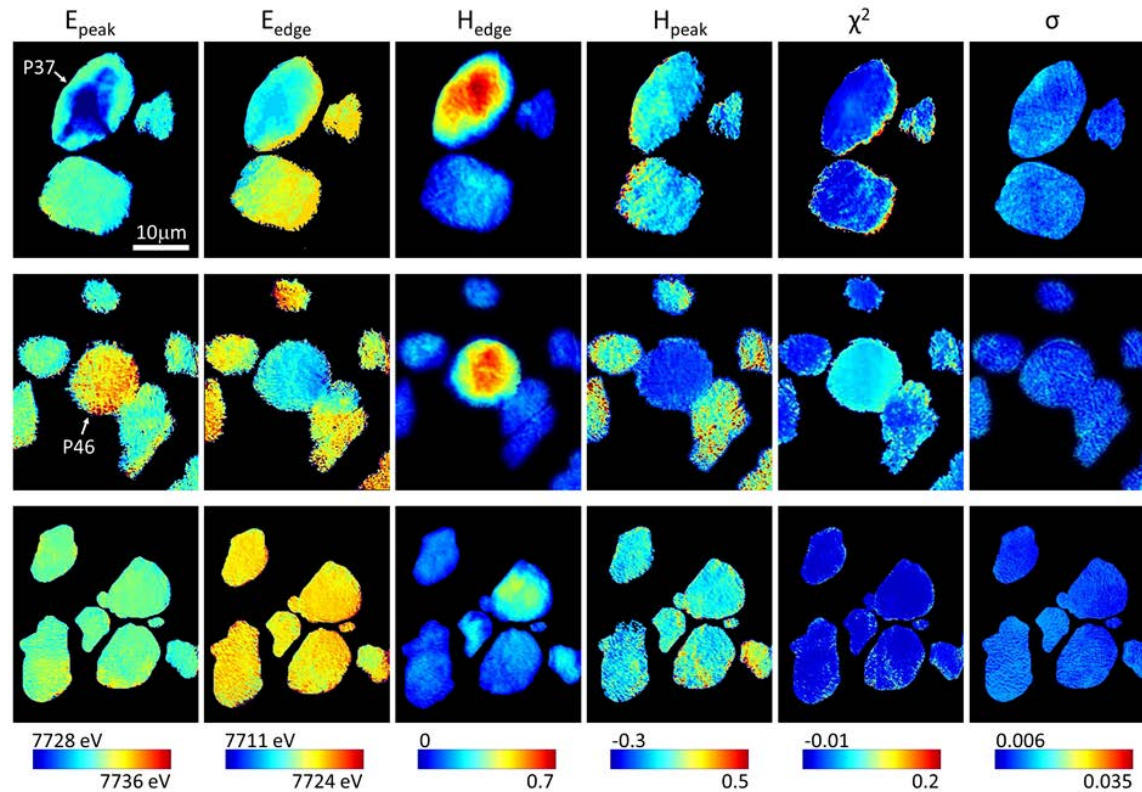

The spatial distribution of the extracted data attributes over selected regions of interest. The top and the middle rows contain the unanticipated minority phases (P37 and P46 as labeled in the first column and identified by our data mining method. The bottom row is a typical field of view that contains normal LiCoO$_2$ particles.

The minority structures identified by TXM and data-mining approach for $LiCoO_2$
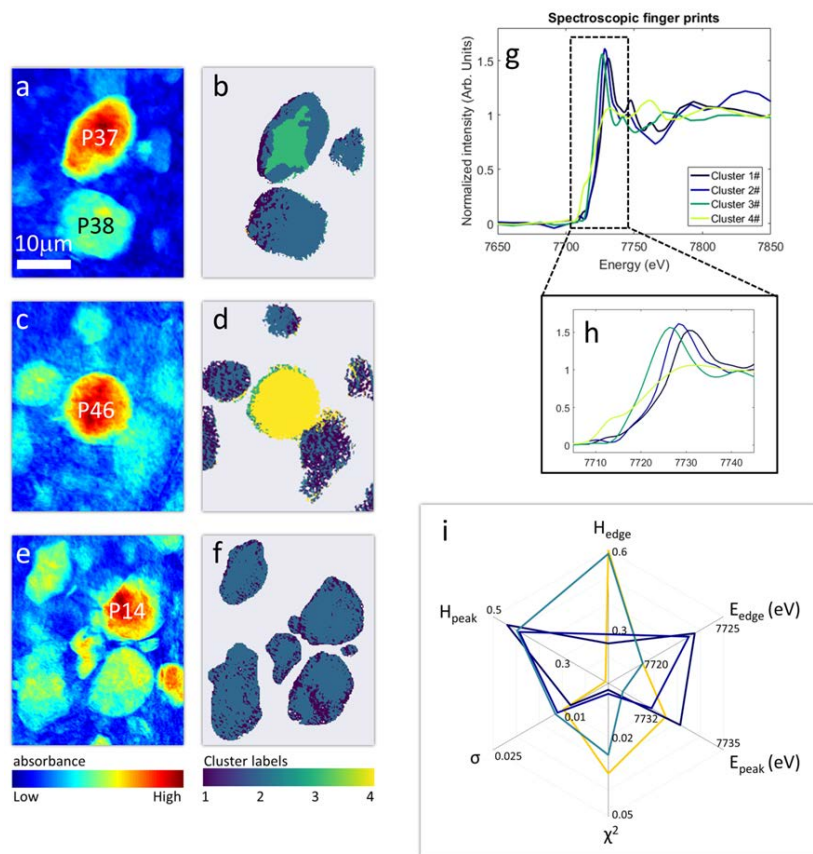

The minority structures identified by TXM and data-mining approach. Panels (a) and (c) show the transmission images of the field-of-views covering particles (P37 and P46), which are identified as minority structures. Panel (e) is the transmission image of another typical field-of-view that contains several normal $LiCoO_2$ particles. Panels (b), (d), and (f) show the clustering results, with the four different clusters color coded to the corresponding inset. We compare the spectroscopic fingerprints of all the four clusters in panels (g) and (h). It is interesting to note that clusters 1# and 2# are both similar to $LiCoO_2$. The radar chart in panel (i) shows the differences in the spectroscopic fingerprints of all the 4 clusters The scale bar in panel (a) is 10 microns.

The schematic illustration of LiCoO$_2$ particle degradation mechanism during cycling
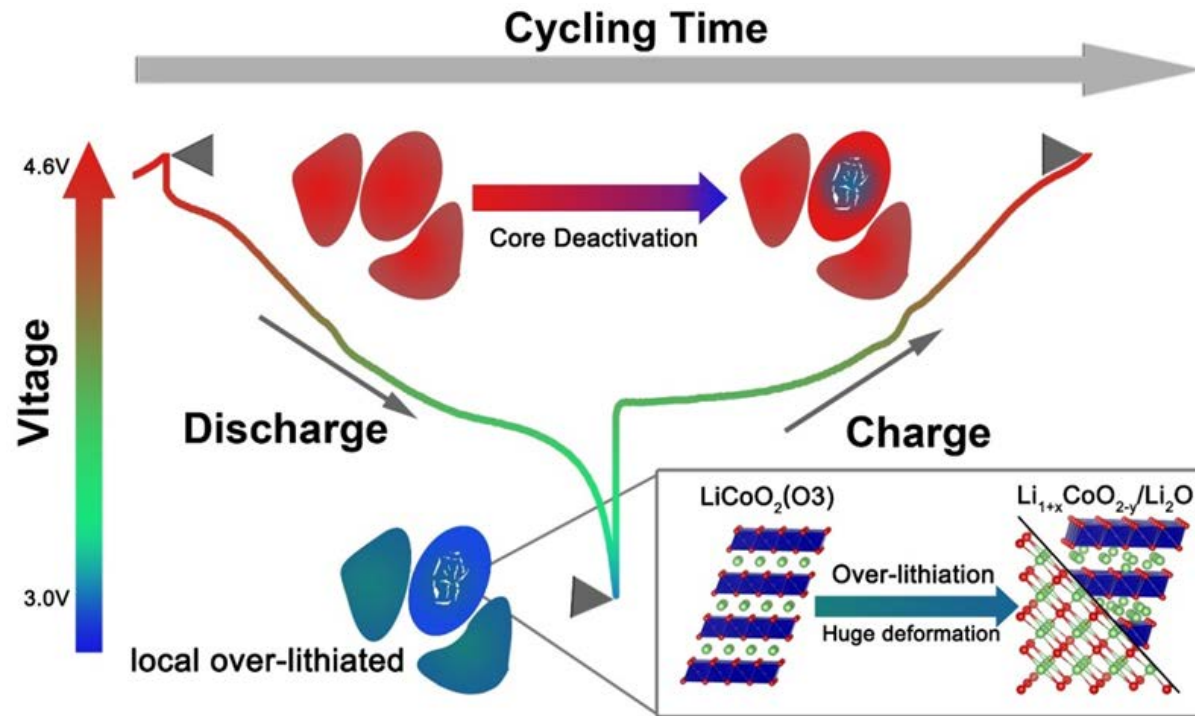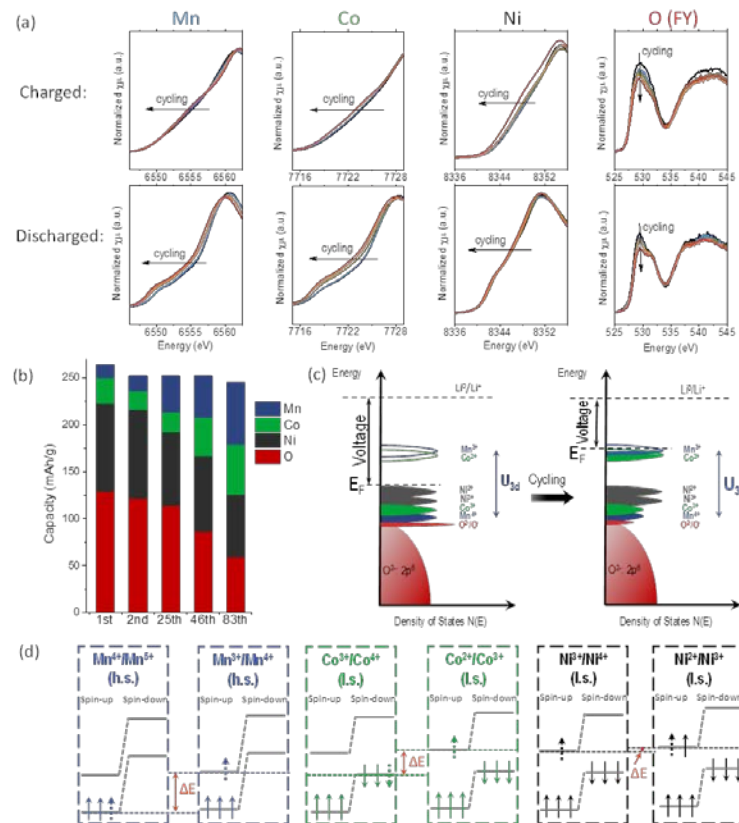

The schematic illustration of particle P37 degradation mechanism. The red and blue figures refer to the LiCoO$_2$ particle at charged and discharged state. The electrochemical curve is posed to show the certain set where critical deformation occurred. The inset picture shows the comparison of standard and over-lithiated LiCoO$_2$. The red and green spheres represent oxygen and lithium ions and the dark blue octahedron stands for CoO$_6$ unit.

Neutron diffraction results of pristine and 4.6 V charged samples of LiCoO$_2$
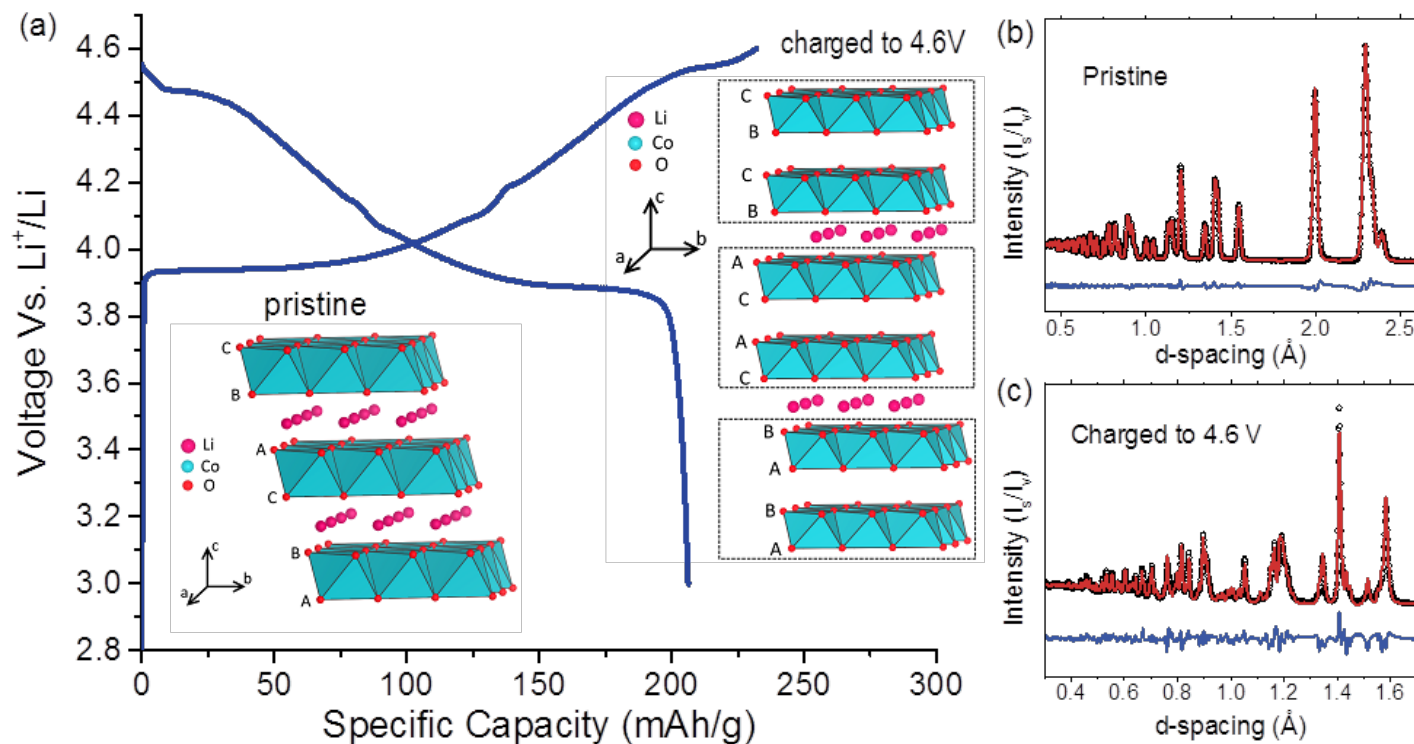

(a) Electrochemical profile of LiCoO$_2$ charged to 4.6 V followed by a discharge to 3 V. The lower-left and the right insert show the structures of the pristine sample and the charged sample respectively. (b) Rietveld refinement of the NPD pattern of pristine sample and (c) Rietveld refinement of the NPD pattern of charged sample.

(a) Transition metal K-edge XAS spectra for Mn, Co and Ni, and FY mode O K-edge XAS of samples at the 1st, 2nd, 25th, 46th, and 83th cycle (b) Redox couple evolution for $Li_{1.2}Ni_{0.15}Co_{0.1}Mn_{0.55}O_2$ upon cycling (c) Illustration of how voltage is influenced by the electronic structure change during cycling. (d) Illustration of how the characteristic electronic structures of Mn, Co and Ni lead to voltage difference between their respective successive redox couples. These results show that during cycling, the capacity contributions from Co and Mn are increased in the expense of reduced contribution from Ni, causing the voltage fading.

Three-dimensional electron tomography reconstructions of pristine and after 15 charge-discharge cycles of $Li_{1.2}Ni_{0.15}Co_{0.1}Mn_{0.55}O_2$ samples
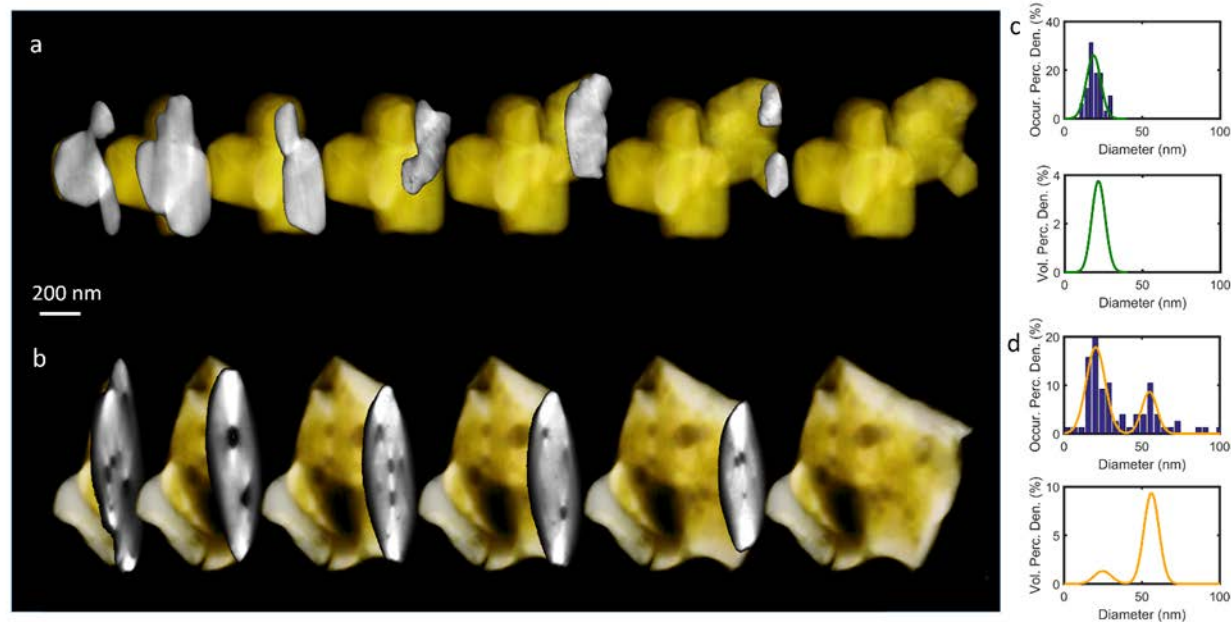
Three-dimensional electron tomography reconstructions of (a) pristine, (b) after 15 charge-discharge cycles of $Li_{1.2}Ni_{0.15}Co_{0.1}Mn_{0.55}O_2$ material. The internal pore size distribution weighted by occurrence (upper) and by volume (lower) of (c) the pristine materials and (d) the sample after 15 cycles. These results show that the number and size of pores are both increased during cycling.

Spatially resolved EELS mapping of concealed pore of $Li_{1.2}Ni_{0.15}Co_{0.1}Mn_{0.55}O_2$ samples
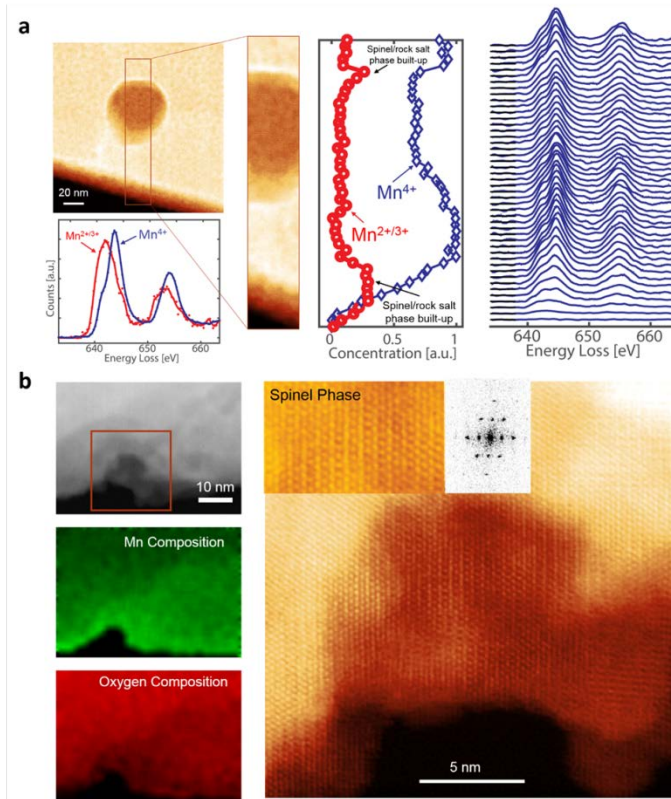
Spatially resolved EELS mapping of concealed pore and exposed pore. (a) STEM-EELS mapping of a concealed pore. (b) STEM-EELS mapping and atomic-resolution imaging of an exposed pore. These results show that large number of pores are not completely concealed or exposed, but partially exposed internal pores with oxygen pathways nearby in the form of microstructural defects such as dislocation, grain boundaries, and micro cracks.

Response to 2017 reviewer's comments

This project was presented as an oral presentation in the 2017 AMR review as ES059

Comments from 2017AMR

- ▣ One reviewer pointed out that " the great collaboration with several laboratories and institutions to obtain necessary knowledge to perform certain experiments, especially those working with X-rays. However, it is advisable to also get collaborators in the industry in order to have different points of view to make the project progress more significant yet."
- ▣ One reviewer noted that "it is important to continue to develop the TXM work, including STEM studies to further understanding of reaction paths of cathode materials. Also, the XFM method development will give further structural detail to the reactions in the cathode."

Response

- ▣ Thanks to the positive comments of the reviewer on this project for the collaborations with other research institutions. The collaboration with industrial partners was somewhat improved in FY2018. Unfortunately, there are not many Li-ion battery industrial partners in the US we can find.

- ▣ The development of TXM, STEM, XFM techniques for battery material studies has been continued and strengthened through BAT059 project in FY2018.

Collaborations with other institutions and companies

- ◙ Yale University
  Li-S batteries
- ◙ University of Maryland at College Park
  High energy density cathode materials for Li-ion batteries
- ◙ Argonne National Lab. (ANL)
  In situ XRD and XAS study of high energy density Li_2MnO_3-$LiMO_2$ composite (LMR-NCM).
- ◙ Oak Ridge National Lab. (ORNL)
  In situ and *ex situ* neutron diffraction and n-PDF studies of cathode materials
- ◙ Pacific Northwest National Lab. (PNNL)
  Effects of structural defects on the electrochemical activation of Li_2MnO_3.
- ◙ Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory,
  TXM studies of Li-rich materials as high energy density cathode materials for Li-ion batteries
- ◙ Johnson Control Inc.
  In situ XRD and XAS study of high Ni content 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

- 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. High energy density anode and cathode materials will be studied using these new diagnostic tools and the combination of them to obtain the multi-length scale imaging and spectroscopy to provide valuable guidance for the new material developments.

- The In situ and ex situ diagnostic tools developed up today have been demonstrating their importance in understand the governing mechanism of performance and degradation of electrode materials for batteries. However, most of these studies are limited on the material level and the in situ techniques are mostly not under the real operating conditions. The diagnostic tools at operando conditions need to be developed and applied to the component (electrode) and cell and pack level.

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

◉ FY2018 Q3 Milestone:

Complete the pair distribution function (PDF) studies of $LiCoO_2$ using both x-ray (x-PDF) and neutron (n-PDF) probes to study the mechanism of anionic redox reaction (ARR) in such widely used commercial cathode materials for Li-ion batteries and explore the potential of using this material for high energy density cell applications.

◉ FY2018 Q4 Milestone:

Complete the experimental design, data collection and analysis of three dimensional (3D) STEM tomography studies of high energy density $Li_{1.2}Ni_{0.15}Co_{0.1}Mn_{0.55}O_2$ cathode materials at pristine state and after multiple cycling

FY2018 work proposed:

◉ The x-ray pair distribution function (PDF) and neutron pair distribution function (N-PDF) will be developed and applied for Li-ion and Li-metal battery research. These techniques will be combined with STEM to have a multi-length scale Imaging and spectroscopy tool for battery material studies.

◉ The x-ray fluorescence microscopy (XFM) technique 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 aimed to improve the rate capability of batteries.*
  - ✓ *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**
  - *Using nano-probe beamline at NSLSII to study the elemental distribution of new solid electrolyte materials for Li-ion batteries*
  - *Using pair distribution function (PDF) to study $LiCoO_2$ materials. Using both x-ray (x-PDF) and neutron (n-PDF) probes to study the mechanism of anionic redox reaction (ARR) in such widely used commercial cathode materials for Li-ion batteries and explore the potential of using this material for high energy density battery applications.*
  - *Using high resolution transmission electron microscopy (TEM) to obtain multiple dimensional (3D + elemental, valence state, and time) mapping of new cathode materials for advanced Li-ion batteries.*

- **Technical Accomplishments**
  - *Studies of $LiCoO_2$, a widely used cathode material have been carried out using TXM technique*
  - *Studies of ion exchange synthesis mechanism of $Li_2Mg_2P_3O_9N$ have been carried out*
  - *The correlations between transition metal chemistry and structure in Li2Ru0.5Mn0.5O3 has been investigated in a wide voltage window.*
  - *The complexities of structural changes in layered oxide cathode materials for Li-ion batteries during fast charge–discharge cycling and heating were investigated using synchrotron based XRD and XAS, as well as TEM*

- **Proposed Future work**
  - *Continue and complete the PDF and STEM studies of $LiCoO_2$*
  - *Continue and complete the TXM studies of $LiCoO_2$*
  - *Develop and apply the XFM techniques as well as neutron pair distribution function techniques for battery material studies*