New High Energy Electrochemical Couple for Automotive Application

ANL IC3P Research Focus on Diagnostic Studies at BNL

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BROOKHAVEN NATIONAL LABORATORY

Overview

Timeline

- ▣ Start: 10/01/2014
- ▣ Finish: 09/30/2016

Budget

- ▣ Funding received in FY14

  DOE: $350k

- ▣ Funding received in FY15

  DOE: $175k

Barriers addressed

- Li-ion batteries with high energy densities
- To reduce the production cost of a PHEV battery
- Li-ion batteries with long calendar and cycle life
- Li-ion batteries with superior abuse tolerance

Collaborators

- Argonne National Lab. (ANL)
- Johnson Control Inc.
- Hanyang University, Republic of Korea
- Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory

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 concentration gradient $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$ materials
- 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 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, such as soft x-ray absorption with both partial electron yield (PEY, for surface) and fluorescence yield (FY, for bulk) detection mode capability to improve the calendar and cycle life of Li-ion batteries.

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

Milestones

Month/Year	Milestones
Dec/14	Complete the thermal stability studies of bulk sample of $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$ materials using time-resolved x-ray diffraction (TR-XRD) and mass spectroscopy techniques in the temperature range of 25°C to 500°C ➥ *Completed.*
Mar/15	Complete the thermal stability studies of concentration gradient (CG) $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$ materials using time-resolved x-ray diffraction (TR-XRD) and mass spectroscopy techniques in the temperature range of 25°C to 500°C ➥ *Completed.*
Jun/15	Complete the thermal stability studies in comparison of concentration gradient (CG) $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$ with no concentration gradient (bulk) $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$ materials using soft x-ray absorption with both PEY and FY detection modes in the temperature range of 25°C to 500°C. ➥ *On schedule.*
Sep/15	Complete the preliminary studies of elemental distribution of Ni, Mn, and Co for concentration gradient (CG) $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$ cathode materials using transmission x-ray microscopy (TXM). ➥ *On schedule.*

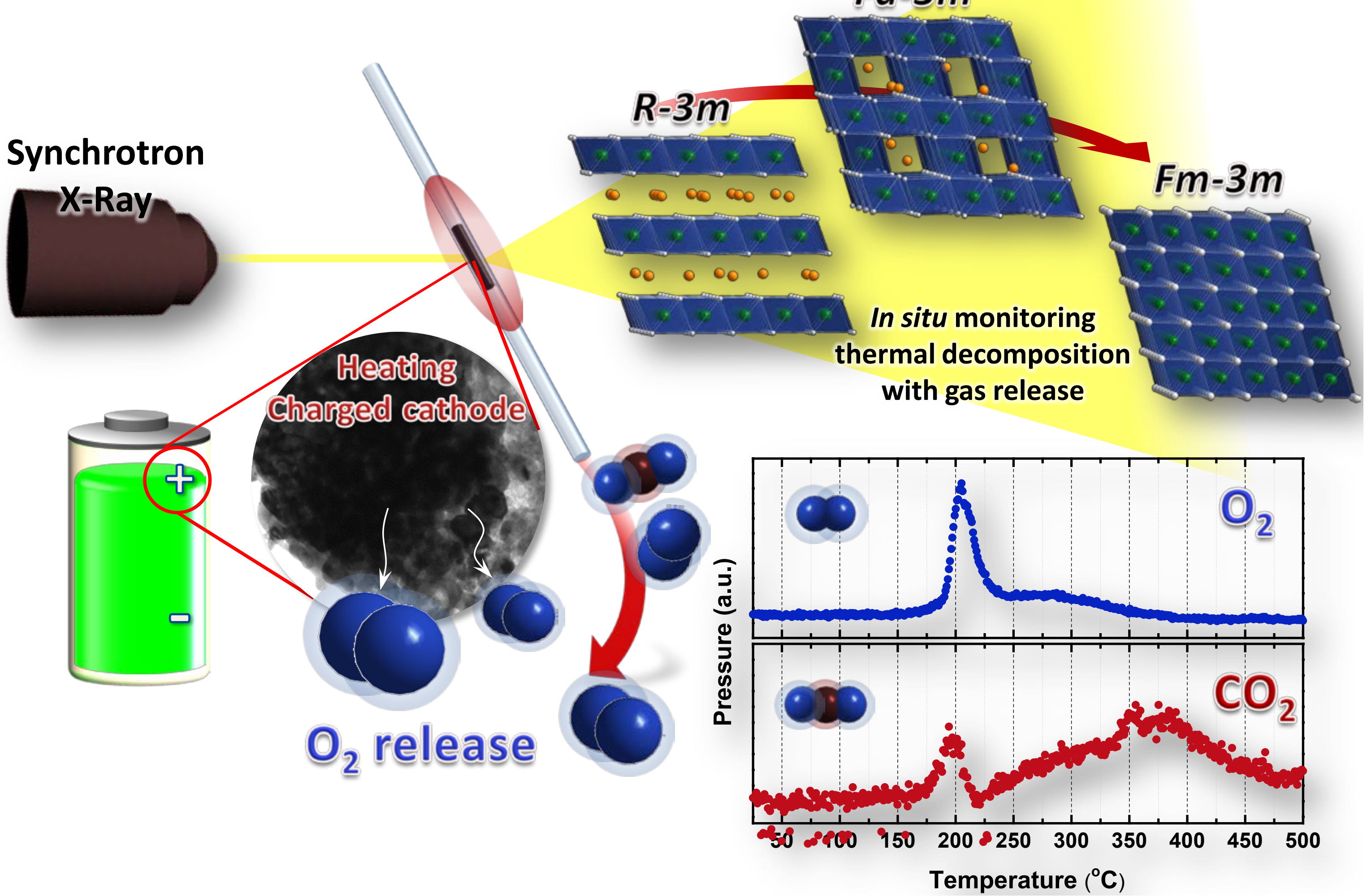
Approaches

- Using a combination of time resolved X-ray diffraction (TR-XRD) and mass spectroscopy (MS) to study the thermal stability of the new concentration gradient (CG) $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$ cathode materials developed by Argonne National Lab. (ANL), in comparison with the no concentration gradient (bulk) $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$ materials

- Using soft x-ray absorption spectroscopy (SXAS) to study the structural changes of the new concentration gradient layer structured cathode materials (developed by Argonne National Lab. ANL) during heating through the L-edges of transition metals and the K-edge of oxygen. Two different types of detection mode have been used: The partial electron yield (PEY) mode gives information about the surface properties (up to ~5 nm), whereas the fluorescence yield (FY) mode probes deeper in the bulk properties (up to ~300nm). The results will be very valuable to guide the further development of the concentration gradient materials with better thermal stability.

- Using transmission x-ray microscopy (TXM) to study the elemental distribution of Ni, Mn, and Co in concentration gradient (CG) $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$ cathode materials .

In situ TR-XRD with MS

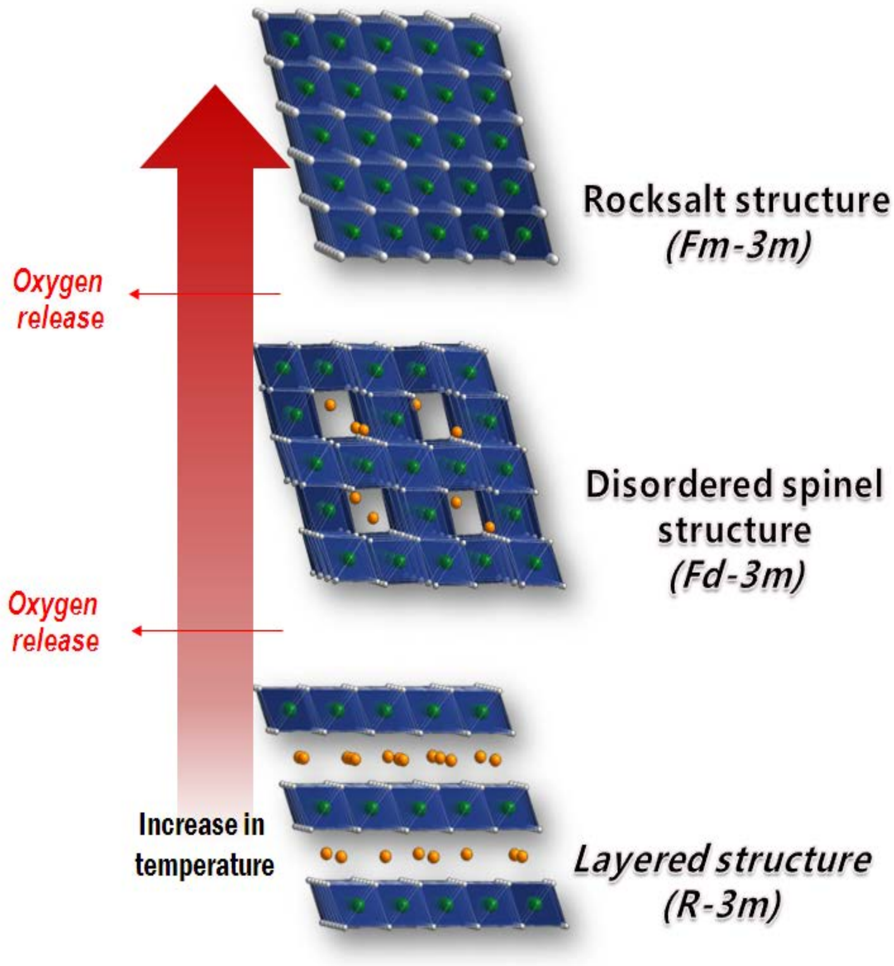


S.-M. Bak et al., *Chem. Mater.* 25, 337 (2013)
E. Hu et al., *Chem. Mater.* 26, 1108 (2014)
S.-M. Bak et al., *ACS Appl. Mater. Interfaces* 6, 22594 (2014)

Technical Accomplishments

- Using the combination of time-resolved x-ray diffraction (TR-XRD) and mass spectroscopy techniques in the temperature range of 25° C to 500° C , the structural changes and oxygen release properties of concentration gradient (CG) $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$ materials have been studied in comparison with bulk sample of $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$ materials. It was found that the structural changes and oxygen release of CG samples occurred at much higher temperatures than the reference bulk sample, showing the much better thermal stability of CG materials.
- Using soft x-ray absorption spectroscopy (SXAS), the structural changes of the new concentration gradient materials during heating have been studied through the L-edges of transition metals and the K-edge of oxygen . The better thermal stability of concentration gradient (CG) $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$ materials in comparison with bulk sample of $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$ was discovered. The results will be very valuable to guide the further development of the concentration gradient materials with better thermal stability.
- Using a new technique of transmission x-ray microscopy (TXM) the elemental distribution of Ni, Mn, and Co in concentration gradient (CG) $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$ cathode materials have been studied. The results show that the concentration gradient in the sample matched well with what was designed for.

Thermal instability of Ni-based layered transition metal oxide



Typical phase transition of Ni-based layered cathode materials during thermal decomposition by heating

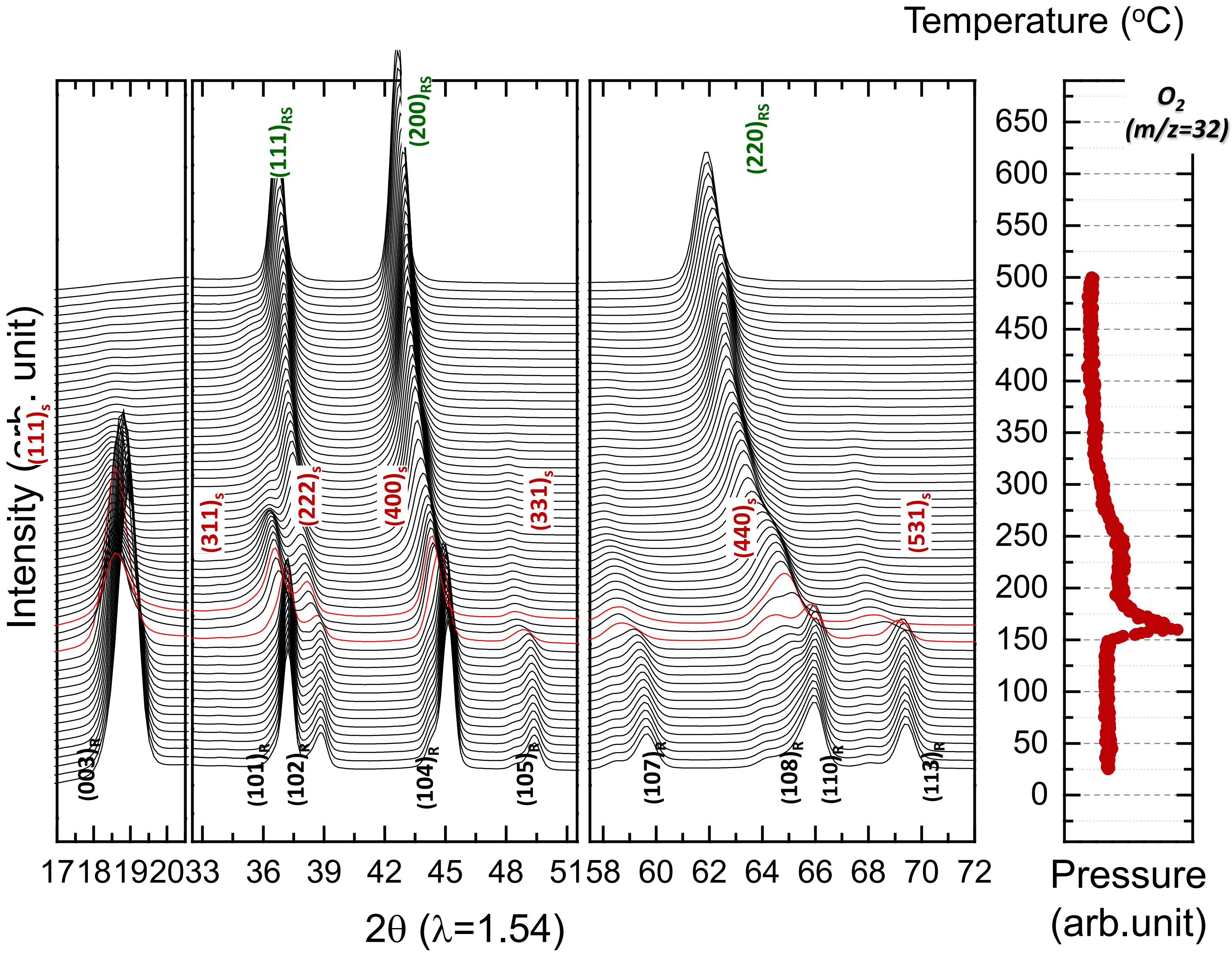
- At highly charged state (i.e., delithiate state), Li_xNiO_2 cathode materials become unstable due to the reduction of Ni^{4+} at high temperature and exothermically decomposed through phase transitions accompany with oxygen release.

- Released oxygen containing species (O_2^-, O_2^{2-}, O^- and O_2) are highly reactive thus can accelerate severe thermal runaway by reacting with flammable electrolyte.

Key factor for considering thermal stability of Ni-based layered cathode material

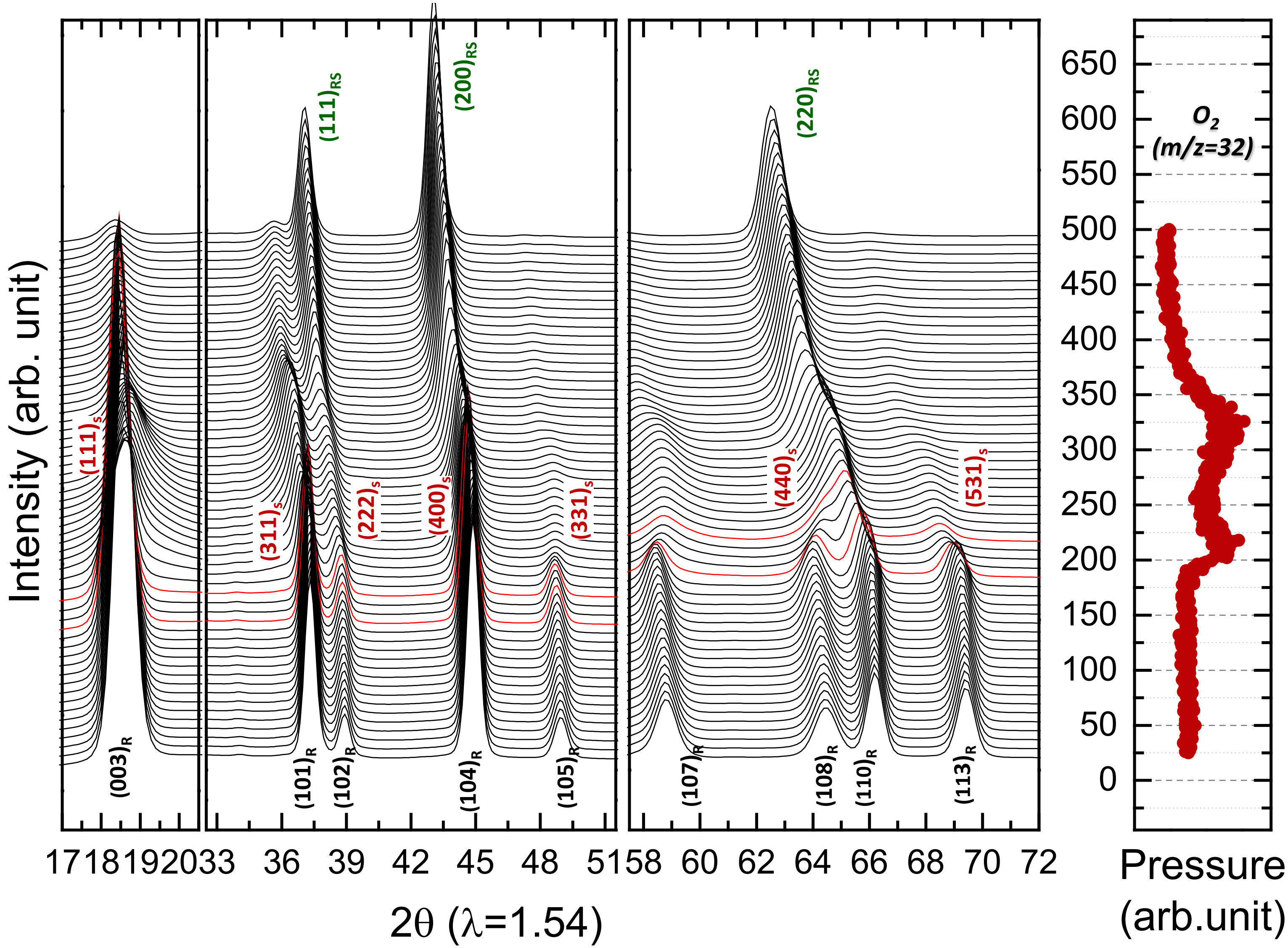
1. Structural change during thermal decomposition
2. Oxygen release during structural changes

TR-XRD/MS of bulk sample (no concentration gradient of $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$ (bulk 622 NMC)



- Sharp O_2 gas release (at *ca.* 150 °C) during phase transition from layered to disordered spinel phase

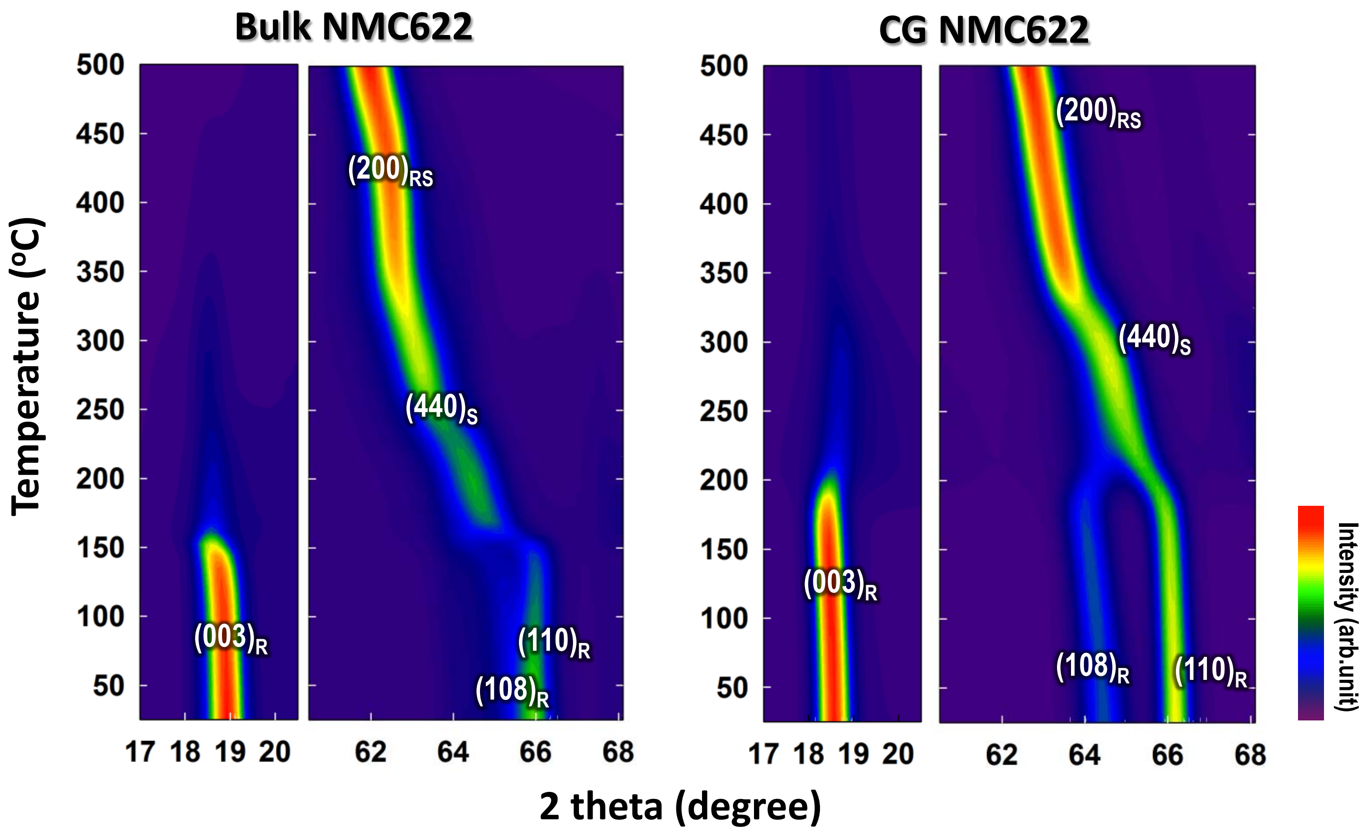
TR-XRD/MS of concentration gradient of $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$ (CG 622 NMC)

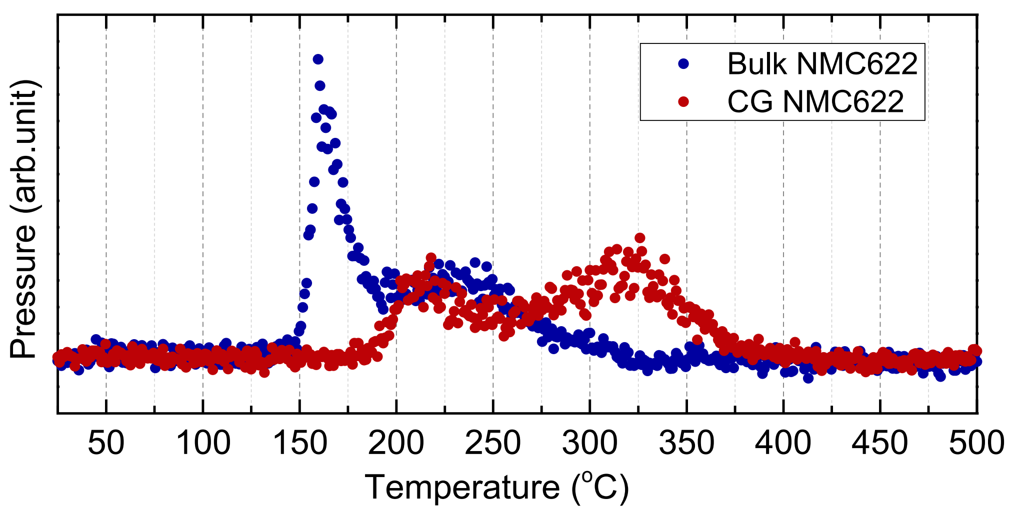


-Concentration gradient sample shows much better thermal stability than bulk NMC 622

: 1st phase transition occurred at ca. 190 ° C and broadening of O2 gas release in much wider temperature range

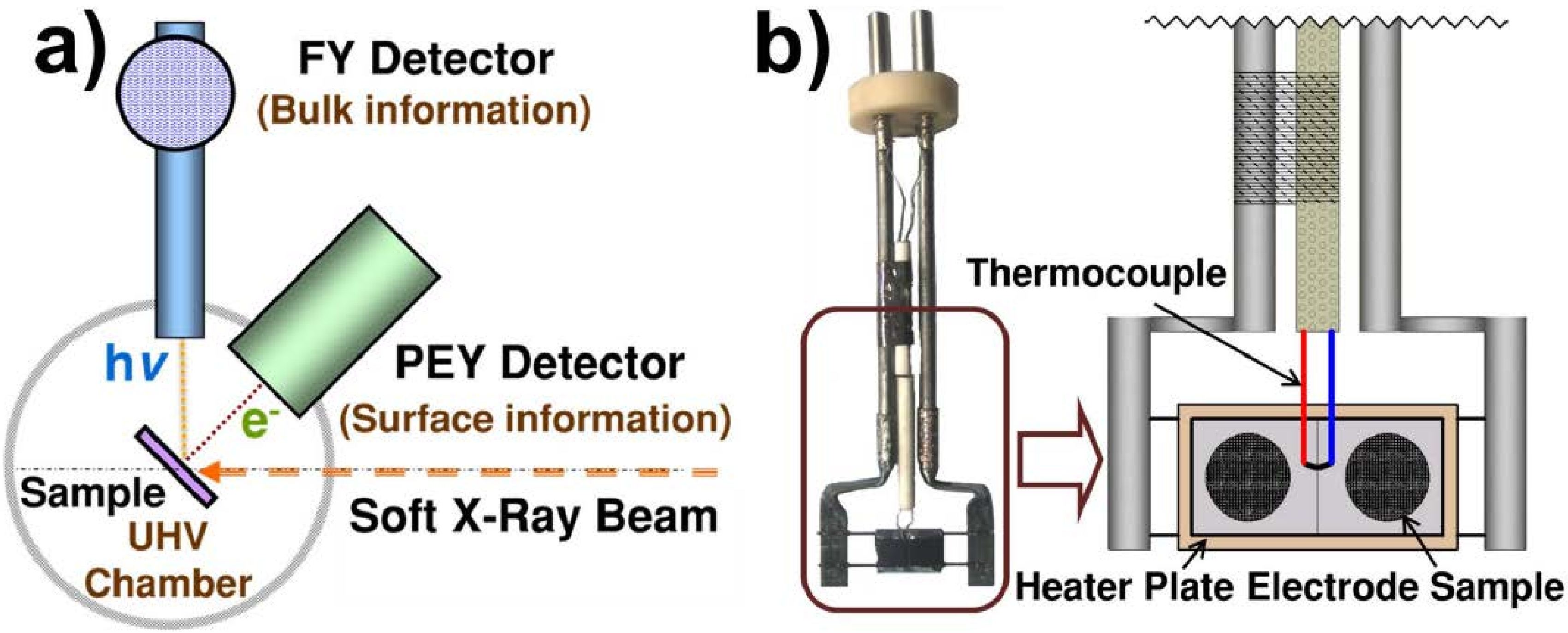
Contour plot





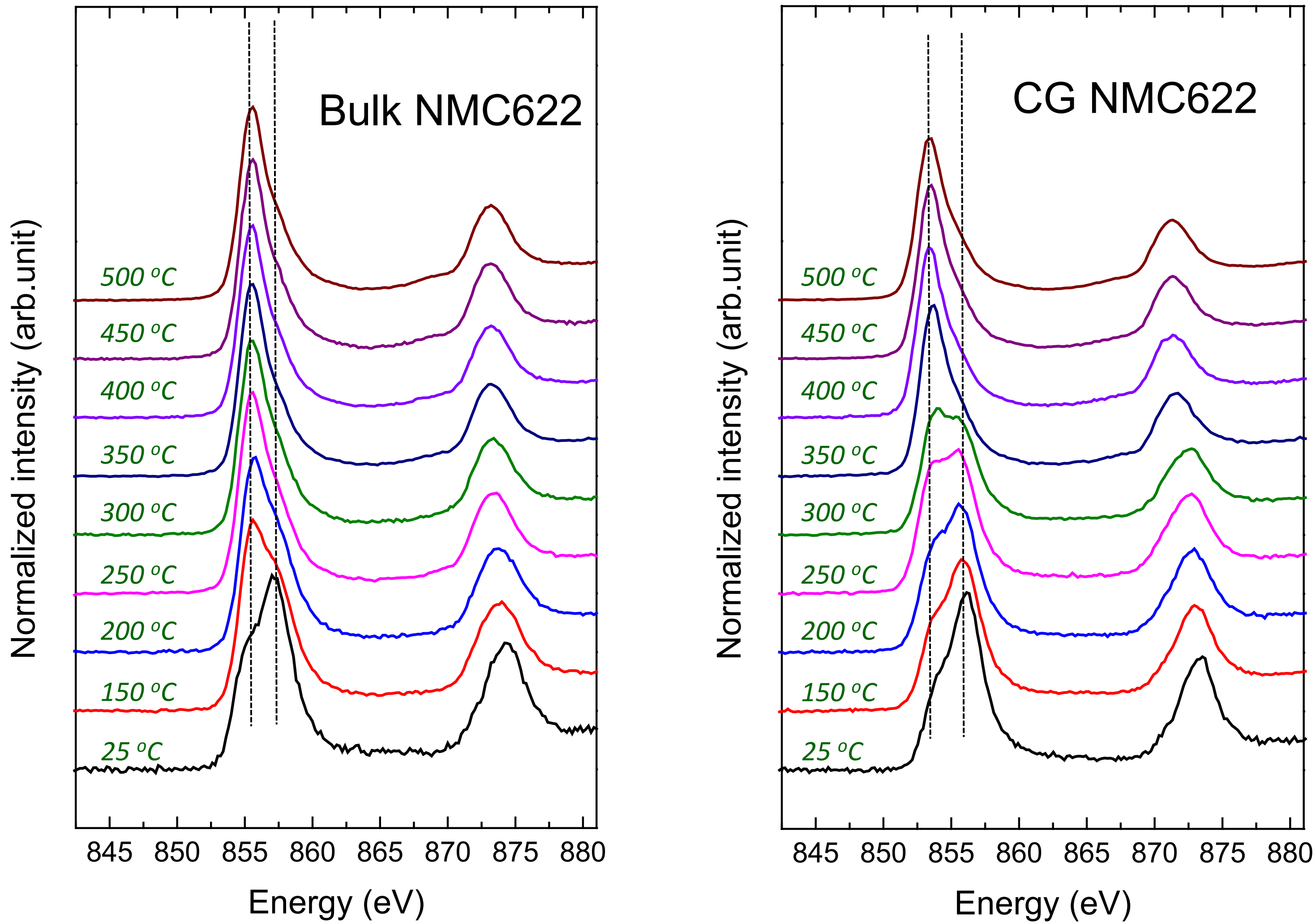
- The on-set temperature of 1st phase transition pushed to higher temperature. And also O_2 gas releasing started at higher temperature for CG NMC622.
- Broadened O_2 release is much safer than sharp O_2 gas release

Schematic diagram of (a) in situ soft XAS experimental setup and (b) sample heater with heating stage for in situ soft XAS experiment.
W.-S. Yoon et al., Scientific Reports 4, 6827 (2014)



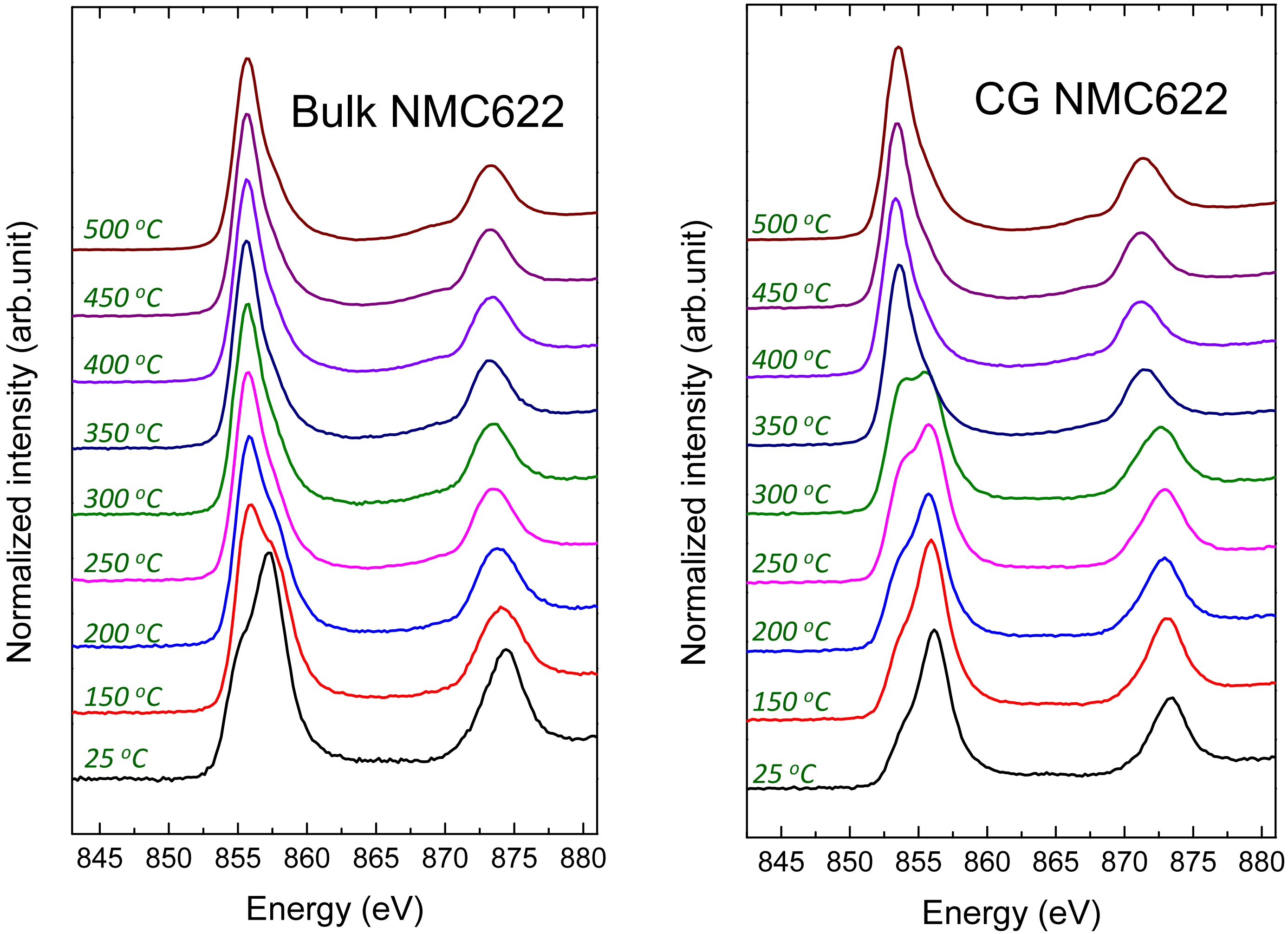
The partial electron yield (PEY) measurement in soft XAS gives information about surface properties (up to ~5 nm), while the fluorescence yield (FY) measurements probes bulk properties (up to ~300nm).

Ni L-edge soft XAS for bulk NMC622 (left) and CG NMC622 (right) Using Fluorescence detection (FY, bulk probing)



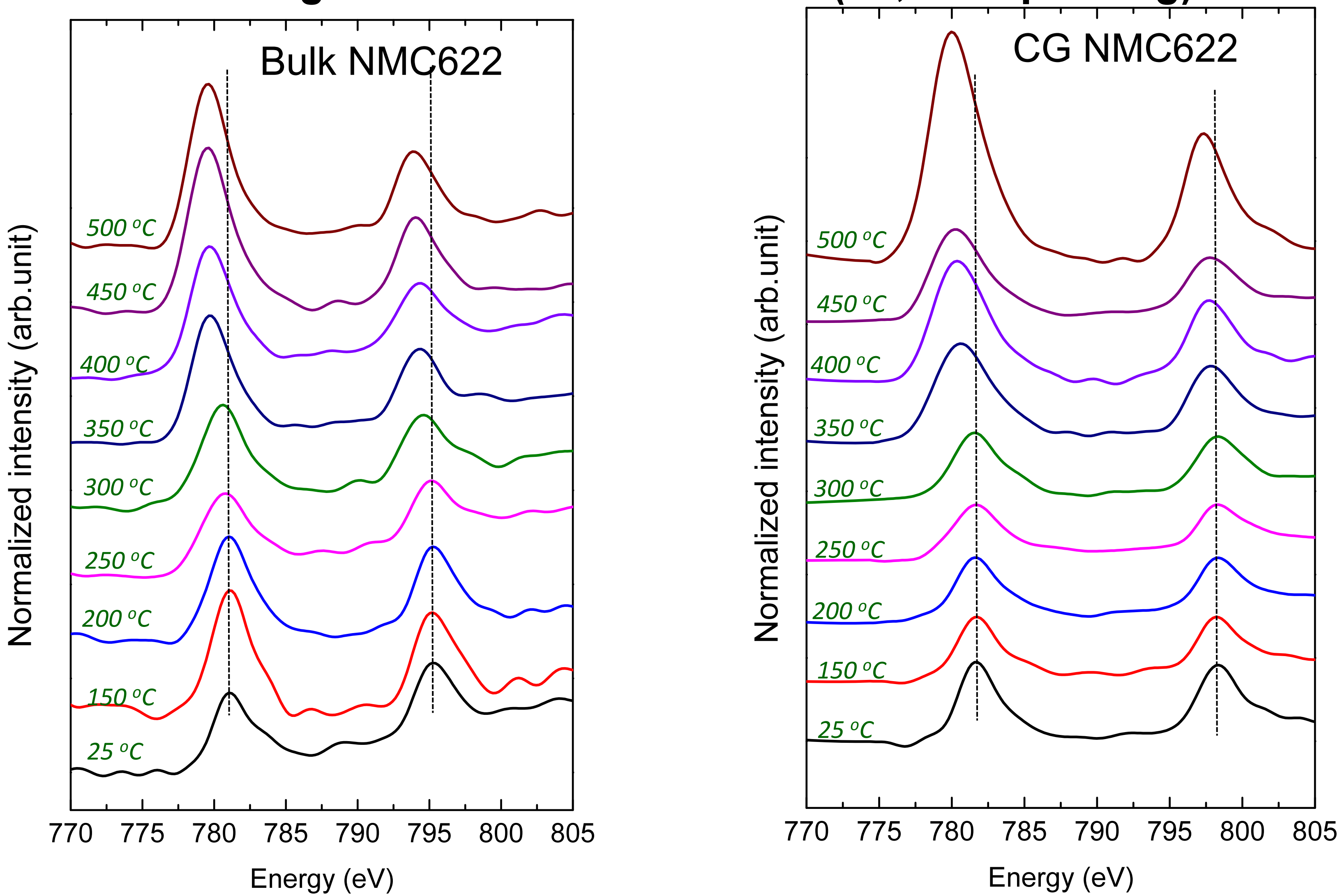
Ni reduction reflected as the lower energy peak occurred quickly at low temperature (~150 °C) in bulk NMC622. In contrast, CG NMC622 is more stable and Ni is stable up to 250 °C and gradually reduced, and completed at 350 °C

Ni L-edge soft XAS for bulk NMC622 (left) and CG NMC622 (right) Using partial electron yield detection (PEY, Surface probing)



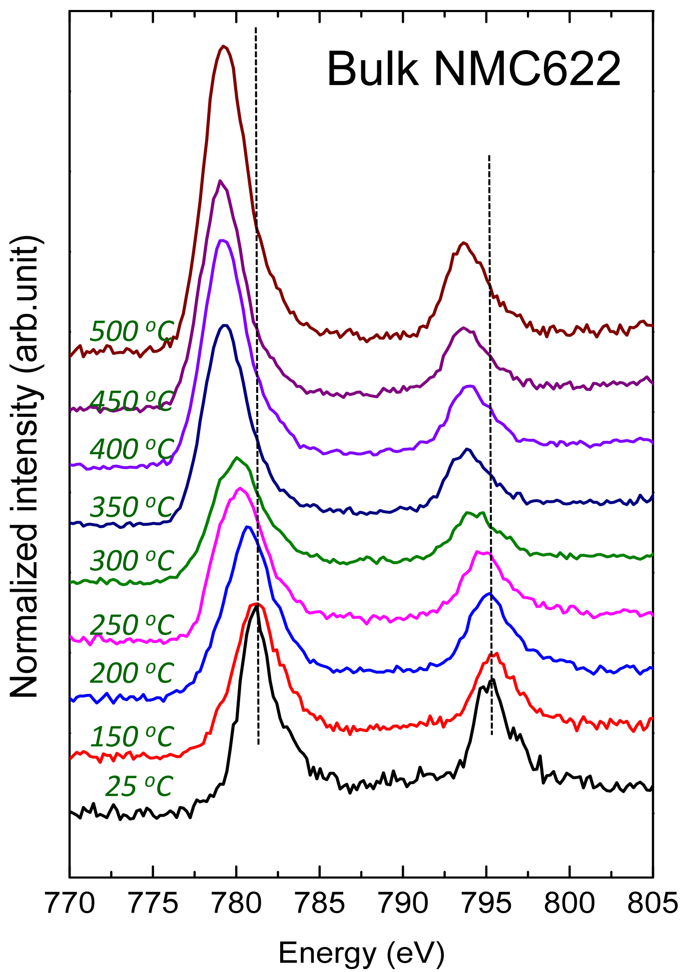
- The structural change at near surface also shows same trend with bulk structure.
- Ni reduction temperature is well coincident with the temperature of the phase transition and O2 release in TR-XRD/MS data

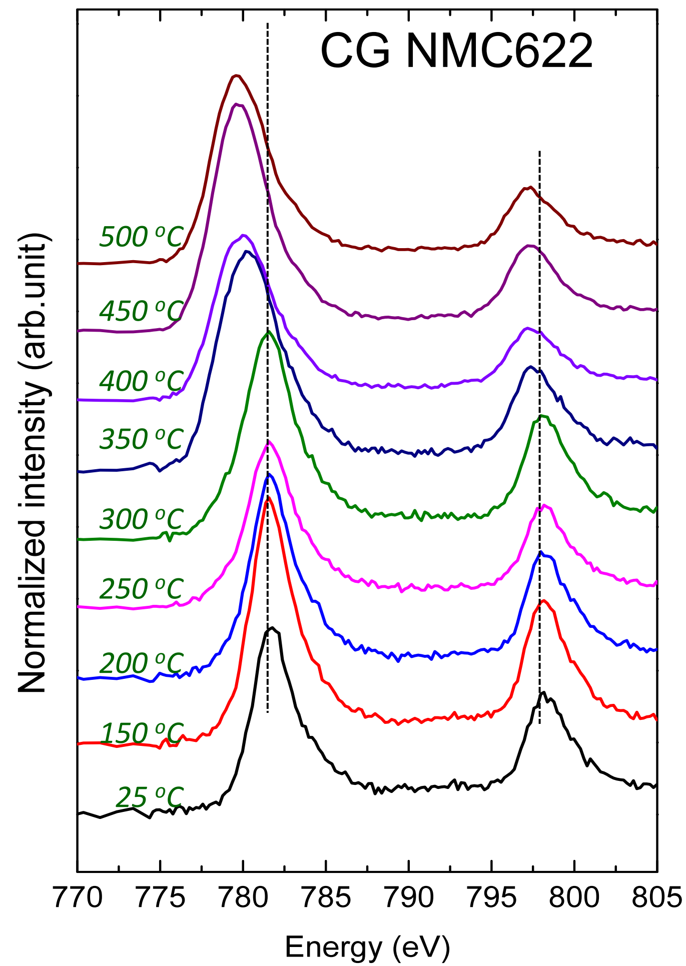
Co L-edge soft XAS for bulk NMC622 (left) and CG NMC622 (right) Using Fluorescence detection (FY, bulk probing)



- Co does not show significant change compare with Ni. (Co is stable element)
- Co reduction started at *ca.* 300 °C in bulk NMC622, whereas it begins at *ca.* 350 °C in CG NMC622.

Co L-edge soft XAS for bulk NMC622 (left) and CG NMC622 (right) Using partial electron yield detection (PEY, Surface probing)

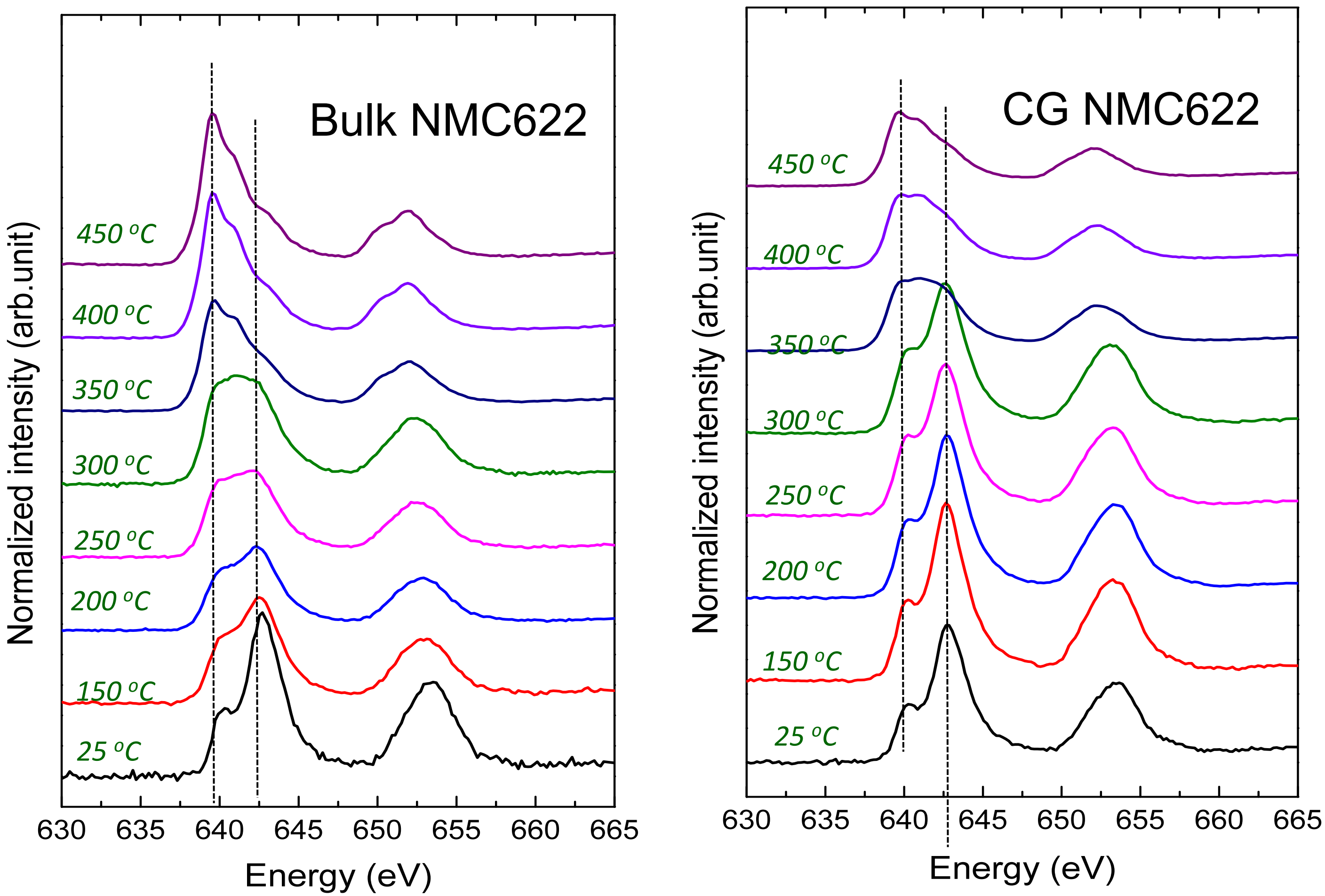




- The structural change at near surface is more significant than bulk structure.

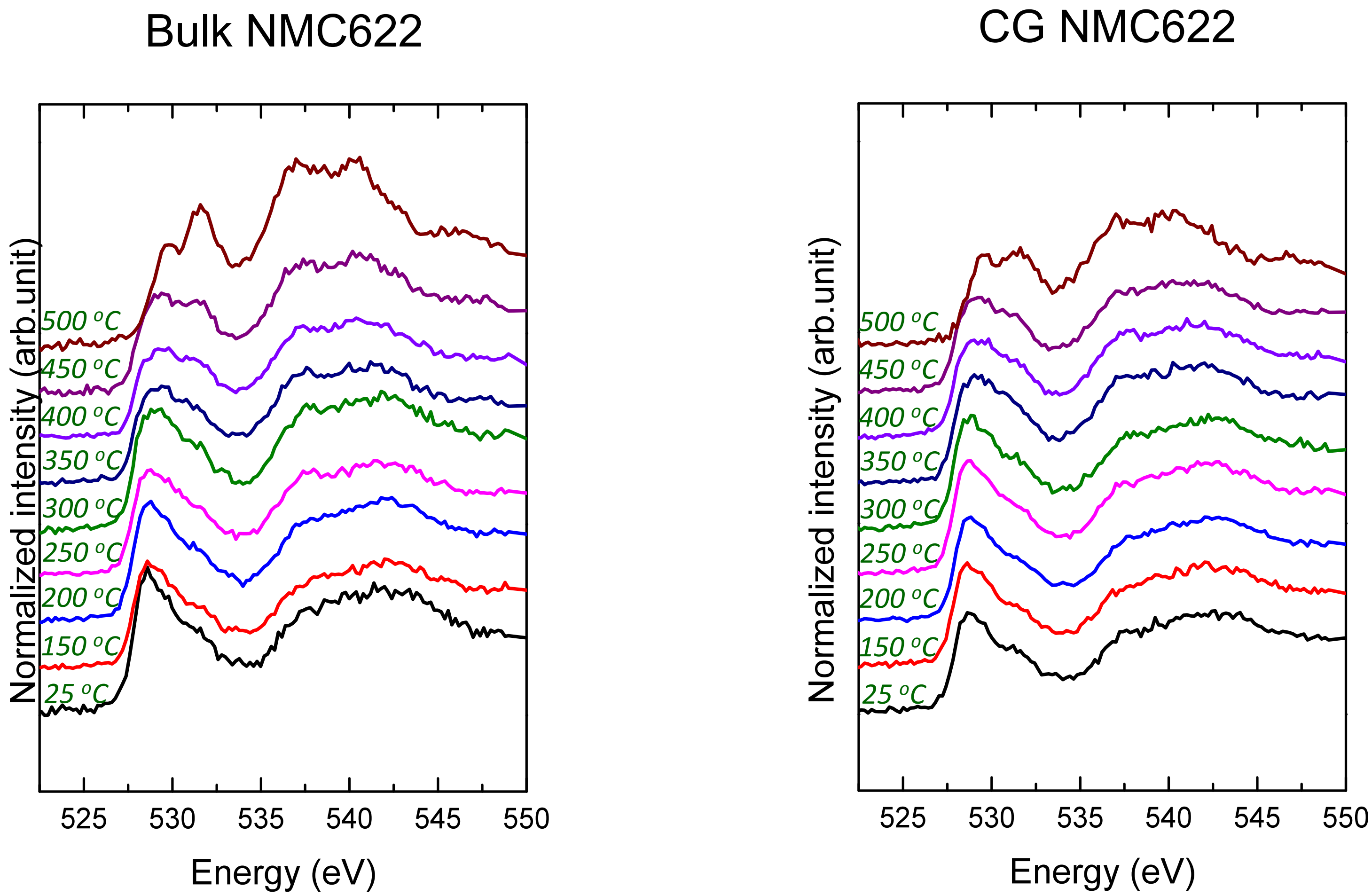
: Co reduction started at lower temperature ~200 °C in Bulk NMC622, but the CG NMC 622 does not change up to 300 °C.

Mn L-edge soft XAS for bulk NMC622 (left) and CG NMC622 (right) Using partial electron yield detection (PEY, Surface probing)



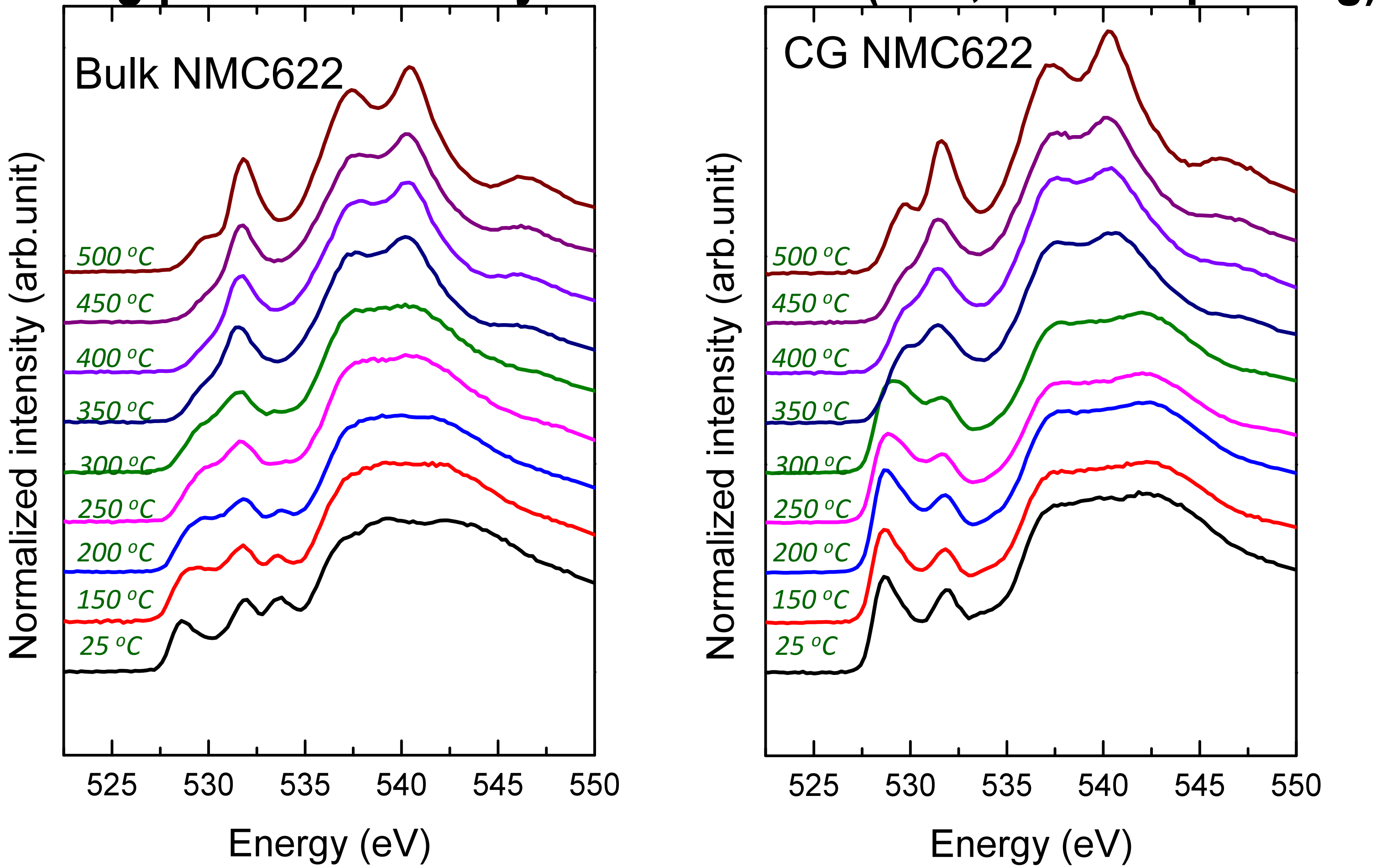
- Mn is known as thermally stable element, but at surface the Mn was reduced during heating.
- Mn in bulk NMC622 reduction started at 200 °C , In contrast, CG NMC622 maintained until 300 °C and started reduction at about 350 °C.

Oxygen K-edge soft XAS for bulk NMC622 (left) and CG NMC622 (right) Using Fluorescence detection (FY, bulk probing)



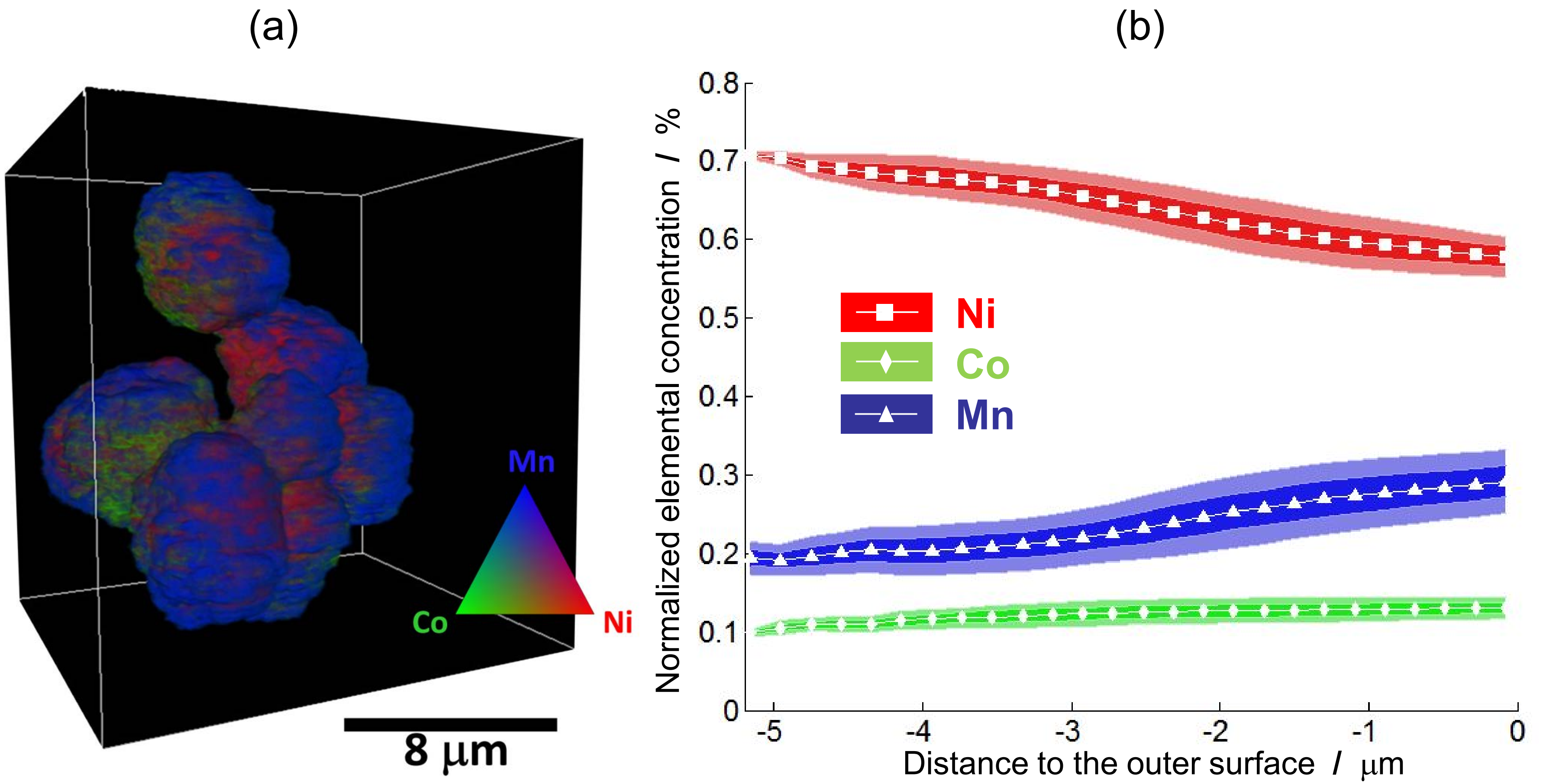
- In bulk structure, no significant changes were observed in oxygen K-edge results, even there are substantial oxygen release during thermal decomposition of both cathode.

Mn L-edge soft XAS for bulk NMC622 (left) and CG NMC622 (right)
Using partial electron yield detection (PEY, Surface probing)



- The spectral changes in oxygen K-edge results probed by PEY at surface is show clear evidence for the oxygen release comparing with data collected by FY in the bulk.
- The temperature region started change in O K-edge peaks are very well coincident with those of Ni L-edge. This imply the oxygen release behavior is mostly related to the reduction of Ni.

Three dimensional Ni, Mn, and Co distribution obtained by TXM



- The Ni, Mn, and Co concentration changes from the surface to the center of a CGNMC622 particle follow the designed concentration gradient very well.

Response to last year reviewer's comments

This project is a new start and
no comments from 2014 AMR is available

Collaborations with other institutions and companies

- **Argonne National Lab. (ANL)**
  Studies of thermal stability on concentration gradient (CG) $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$ materials using time-resolved x-ray diffraction (TR-XRD) and mass spectroscopy (MS) techniques in the temperature range of 25° C to 500° C .
- **Pacific Northwest National Lab. (PNNL)**
  High resolution transmission electron microscopy (HR-TEM) study of on concentration gradient (CG) $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$ materials .
- **Johnson Control Inc.**
  In situ XRD and XAS study of high energy density cathode materials
- **Hanyang University, Republic of Korea (South Korea)**
  SEM and electrochemical performance studies on concentration gradient (CG)
- **Stanford Synchrotron Radiation Lightsource, SLAC, National Accelerator Laboratory**
  Transmission x-ray microscopy (TXM) on concentration gradient (CG)

Proposed Future Work for *FY 2015* and *FY2016*

▣ **FY2015 Q3 Milestone:**

Continue the thermal stability studies in comparison of concentration gradient (CG) $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$ with no concentration gradient (bulk) $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$ materials using soft x-ray absorption with both PEY and FY detection modes in the temperature range of 25° C to 500° C.

▣ **FY2015 Q4 Milestone:**

continue the studies of elemental distribution of Ni, Mn, and Co for concentration gradient (CG) $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$ cathode materials using transmission x-ray microscopy (TXM).

▣ **FY2016 work proposed:**

In collaboration with Hanyang University, Republic of Korea (South Korea) and Argonne National Lab., carry out electrochemical performance studies and in situ XRD and XAS studies on concentration gradient (CG) $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$ cathode materials

▣ Expand the collaborative research with US academic research institutions and industrial partners.

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 and ex situ soft x-ray absorption spectroscopy with both partial electron yield (PEY) and fluorescence yield (FY) detection modes*
  - *High resolution transmission electron microscopy (HR-TEM) and transmission x-ray microscopy (TXM)*
- **Technical Accomplishments**
  - *Demonstrated the superior thermal stability of concentration gradient (CG) $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$ materials over bulk sample of $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$ materials using TR-XRD, MS and soft x-ray absorption studies.*
  - *Carried out elemental distribution of Ni, Mn, and Co in concentration gradient (CG) LiNi0.6Mn0.2Co0.2O4 materials using transmission x-ray microscopy (TXM)*
- **Proposed Future work**
  - *Continue the thermal stability studies of concentration gradient (CG) LiNi0.6Mn0.2Co0.2O4 using soft x-ray absorption.*
  - *continue the studies of elemental distribution of Ni, Mn, and Co for concentration gradient (CG) $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$ cathode materials transmission x-ray microscopy (TXM)*
  - *Carry out electrochemical performance studies and in situ XRD and XAS studies on concentration gradient (CG) $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$ cathode materials.*