Develop & evaluate materials &additives that enhance thermal & overcharge abuse

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Overview

Timeline

- Start: 10/01/2008
- End: 09/30/2014
- 60% completed

Budget

- Total project funding
  - DOE - $1850K
  - Contractor - $ 0
- Funding received in FY10
  - $470K
- Funding for FY12
  - DOE - $500K

Barriers

- Barriers addressed
  - Safety

Partners

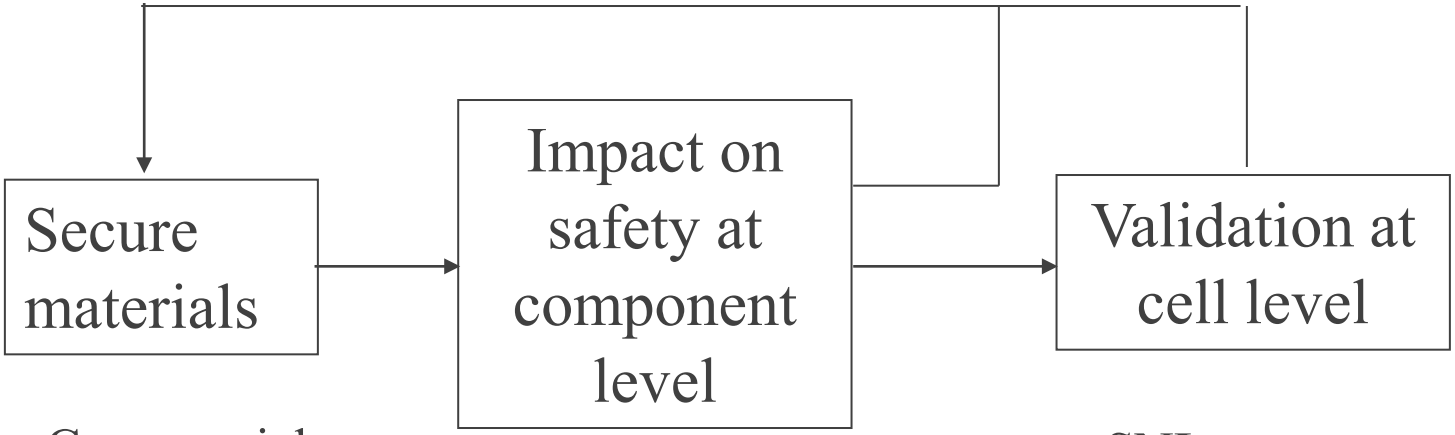
- Sandia National Laboratory
- Superior Graphite Inc.
- Hanyang University, Korea (YK Sun).
- Yang Ren (APS)

Objectives of the work

- Identify the role of each cell material/components in the abuse characteristics of different cell chemistries.
- Identify and develop more stable cell materials that will lead to more inherently abuse tolerant cell chemistries.
- Secure sufficient quantities of these advanced materials (and electrodes) & supply them to SNL for validation of safety benefits in 18650 cells.

Approach

Current targets: a) Safer electrode materials – cathode and anode
b) Impact of surface chemistry on graphite
c) Redox shuttles for overcharge protection



- Commercial source
- Partners
- In-house synthesis

- Thermal analysis
- Electrochemical analysis

- SNL
- Industrial partners

Recent Accomplishments and Progress

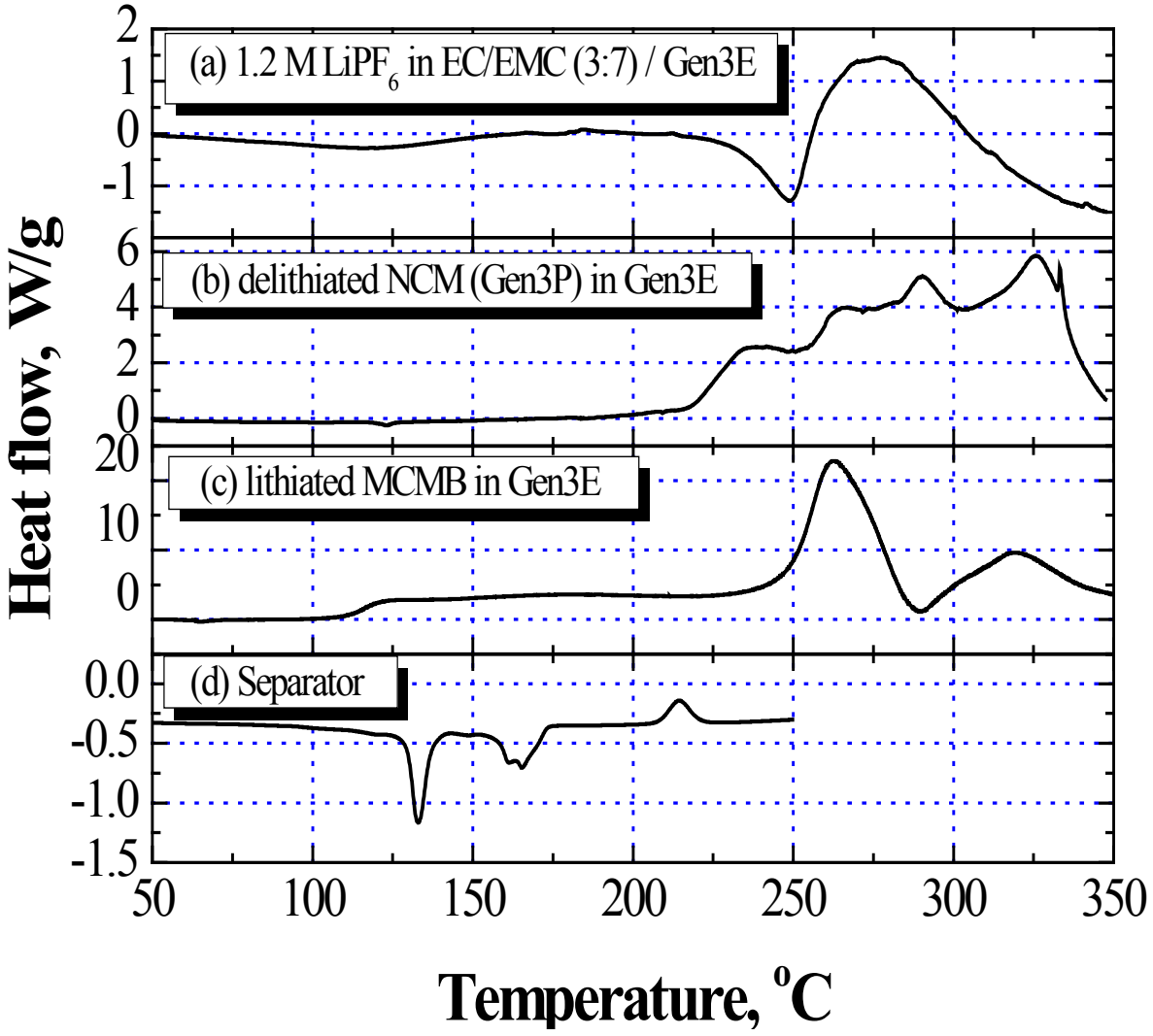
- **Thermal decomposition pathway of delithiated cathodes**
  - Confirmed poor reproducibility of DSC data for delithiated cathodes
  - Developed in situ high energy X-ray diffraction (HEXRD) and applied to investigate the thermal decomposition of delithiated cathodes
  - Identified different decomposition pathway of $Li_{1-x}(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ at various conditions.
  - Investigated the effect of salts ($LiPF_6$ $LiBF_4$, LiTFSI and $Li_2B_{12}F_{12}$) as well as pure solvents on safety. ($LiPF_6$ has negative impact on safety of cathode by reducing the onset temperature from ~310^{o}C to about ~200^{o}C).

Recent Accomplishments and Progress (cont'd)

- **Impact of ANL-2 redox shuttle on electrochemical performance**
  - Studied cell chemistry: MCMB/$LiFePO_4$ using 1.2 M $LiPF_6$ in EC/EMC (3:7, by weight) with and without 0.3 M ANL-2 as electrolyte.
    -The addition of 0.3 M ANL-2 slightly increases the impedance of the cell, but not major difference was observed on rate capability.
    -Life testing is ongoing. No major difference was observed on capacity retention.
    -No oral discussion about above topics due to the time limitation.

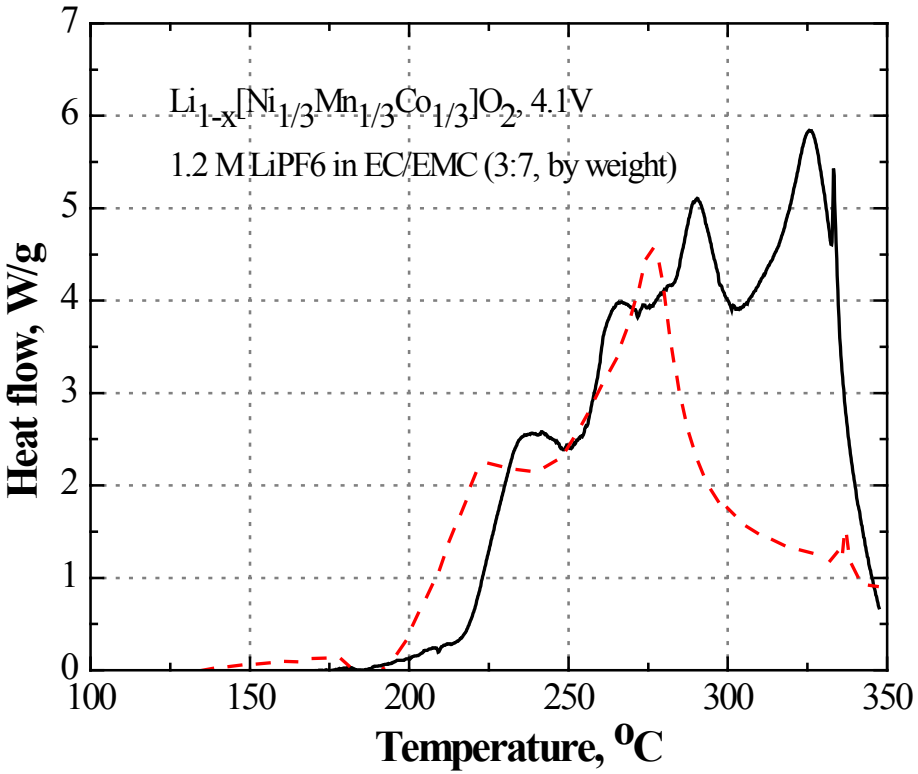
- **Impact of surface chemistry on graphite**
  - Secured nature graphite coated with amorphous carbon source from Superior Graphite.
    -Heat treated the nature graphite at various temperatures from 700°C to 1080°C in glove box to introduce variation on the surface chemistry.
    -Physical, electrochemical, and thermal characterization of resulted materials are ongoing.
    -No oral discussion due to the time limitation.

Thermal response of battery components



- SEI decomposition occurs at the low temperature at about 110°C.
- Delithiated cathode generated largest amount of heat at above 200°C.
- Focus of FY12 is the thermal decomposition mechanism of delithiated cathodes.

Typical thermal response of delithiated cathodes



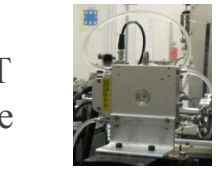
- The onset of exothermal reaction is about 200°C.
- Difficult to reproduce the data.
- Sensitive to the ratio of electrode material to the added electrolyte.
- Similar results were reported by Brian Barnett (TIAX) on $LiCoO_2$.
- XRD can help to study the change of cathode materials during heating.

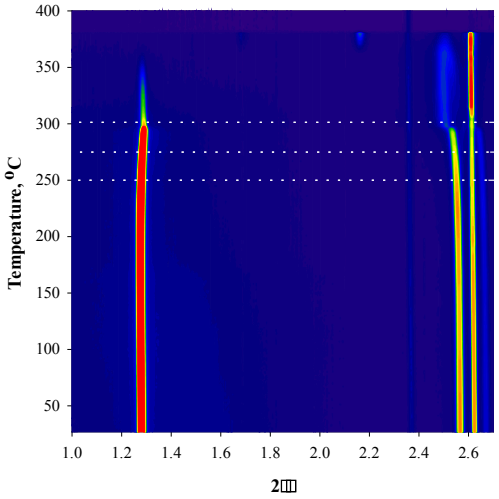
Why high energy X-ray diffraction (HEXRD)?

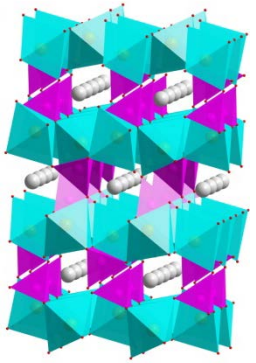
Real battery

High pressure sample

High-T furnace





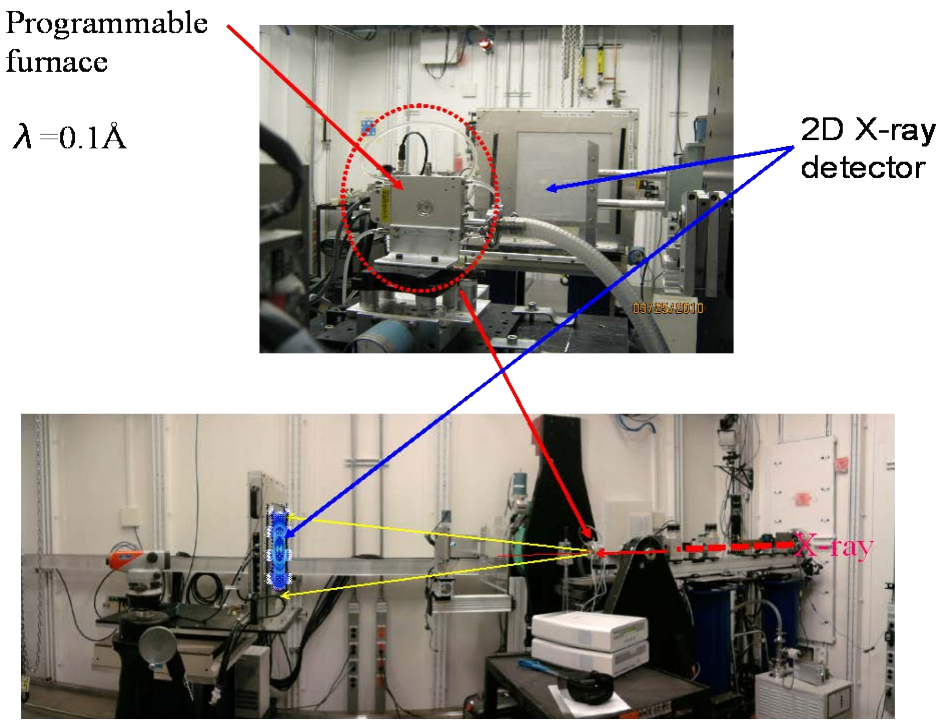


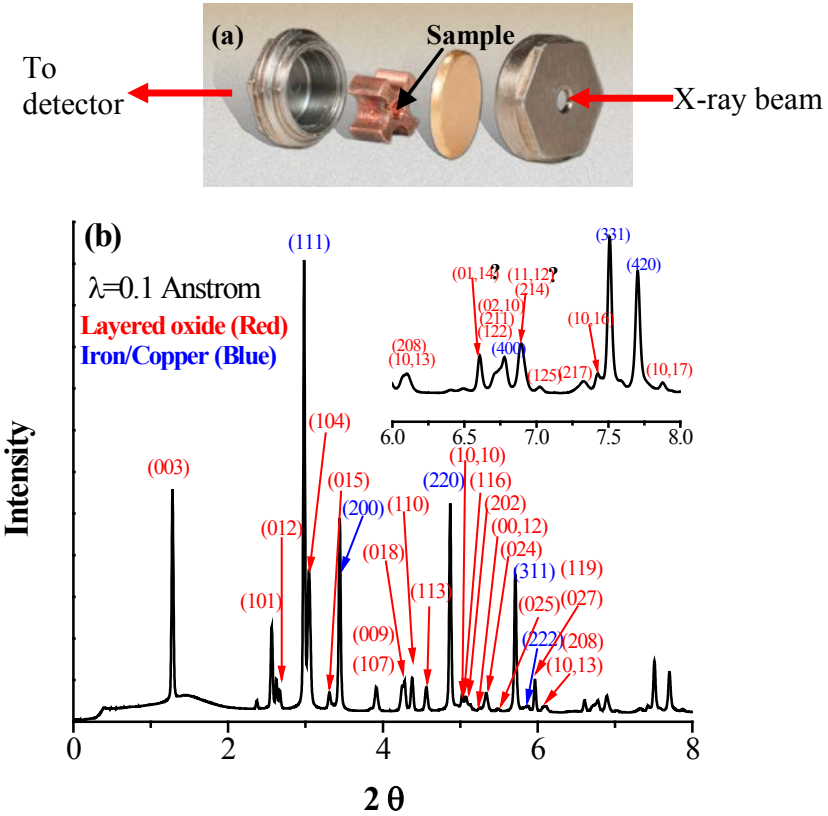
Structure
Defects

- Materials:
  - Process optimization
  - Quality control
  - Intercalation mechanism
  - Abuse tolerance
- Battery:
  - Nondestructive diagnosis
  - Failure analysis
  - Mechanical fatigue
  - Heat generation
  - Capacity and power fade

- **Thermal decomposition of material**
- Heat generation of redox shuttles
- LTO gassing
- **Voltage drop of high energy cathode**

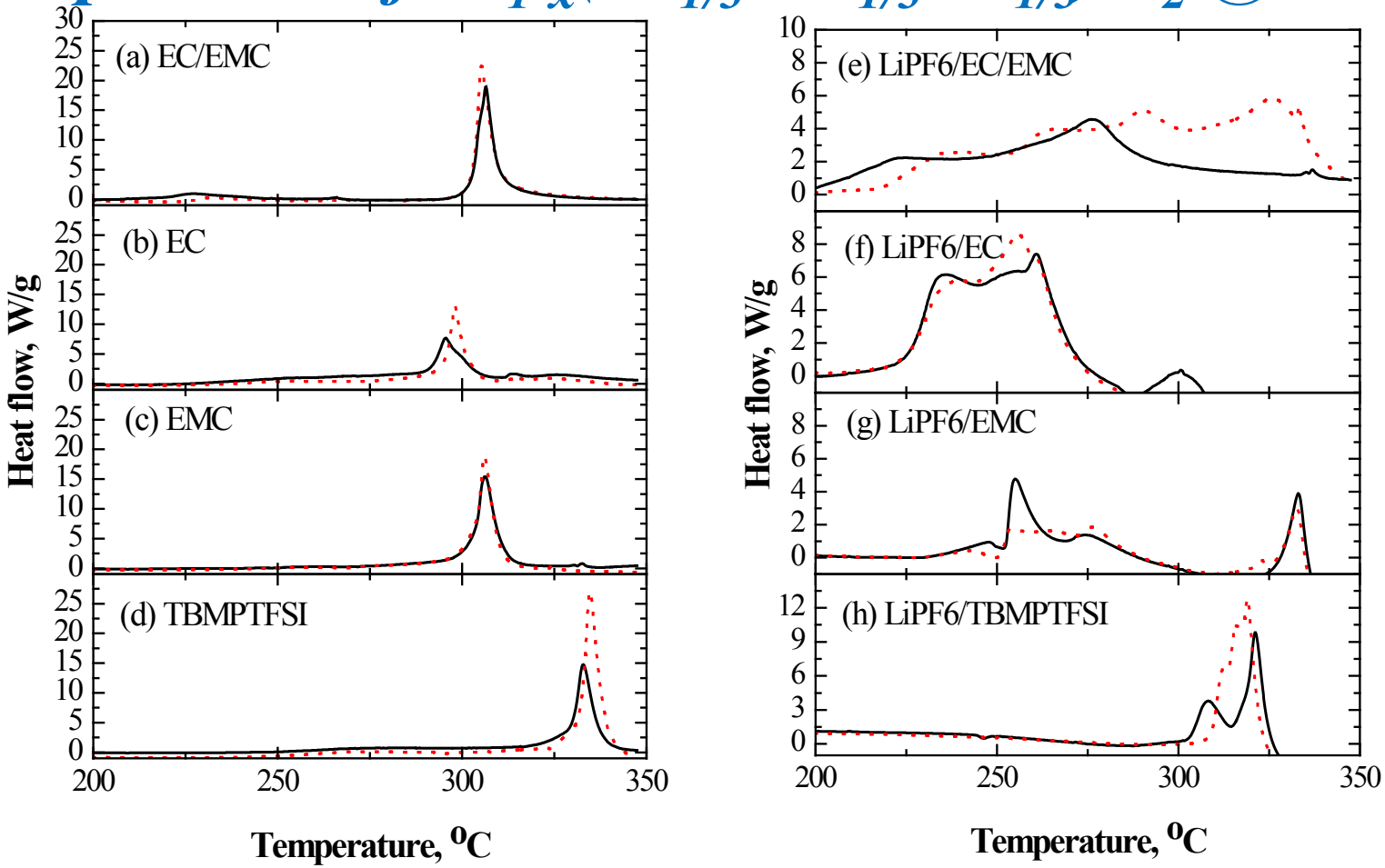
In situ HEXRD setup





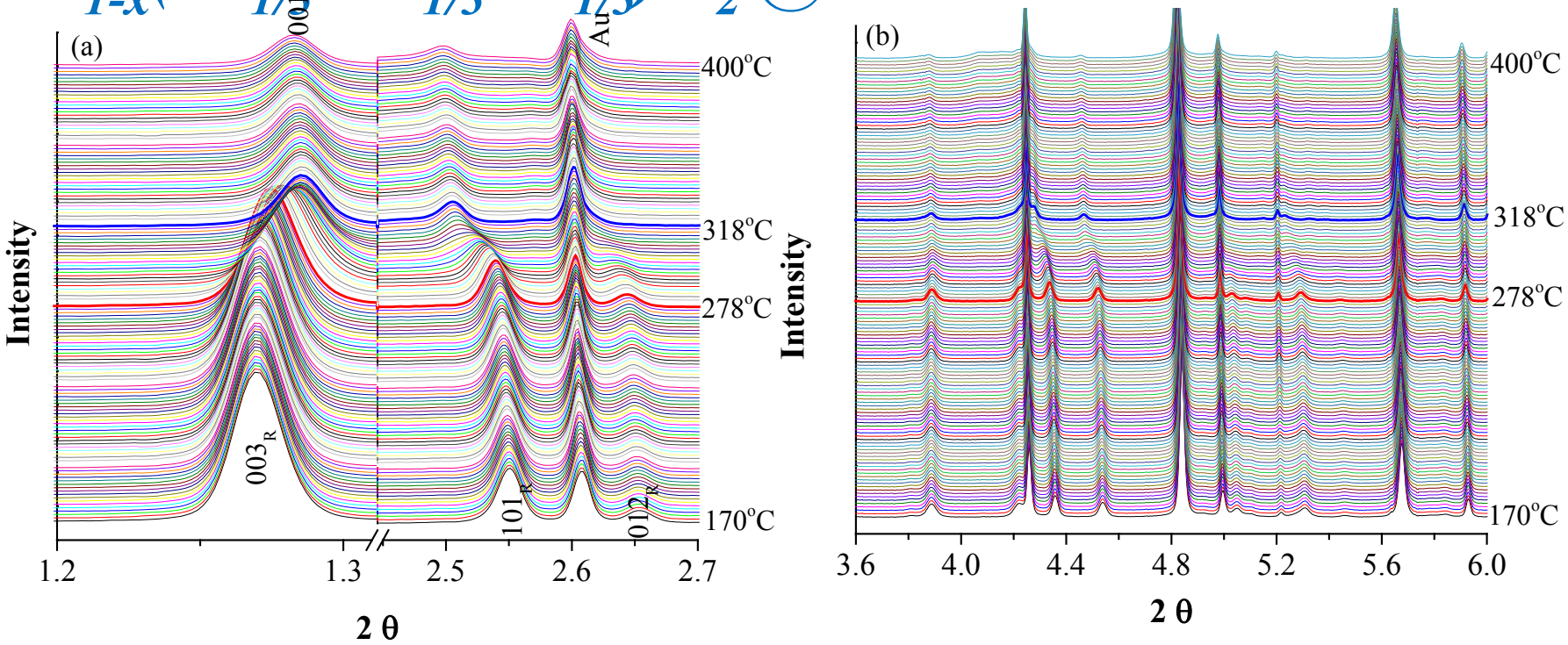
- Sector 11-ID-C at APS of ANL.
- High energy X-ray source is critic to penetrate through the stainless steel vessel that is used to seal the volatile solvents.

Impact of electrolyte components on thermal decomposition of $Li_{1-x}(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ @ 4.1 V.



- Solid line and dotted line represent two independent runs of the same charged electrode.
- Solvents do show some impact. But major influence comes from the addition of $LiPF_6$.

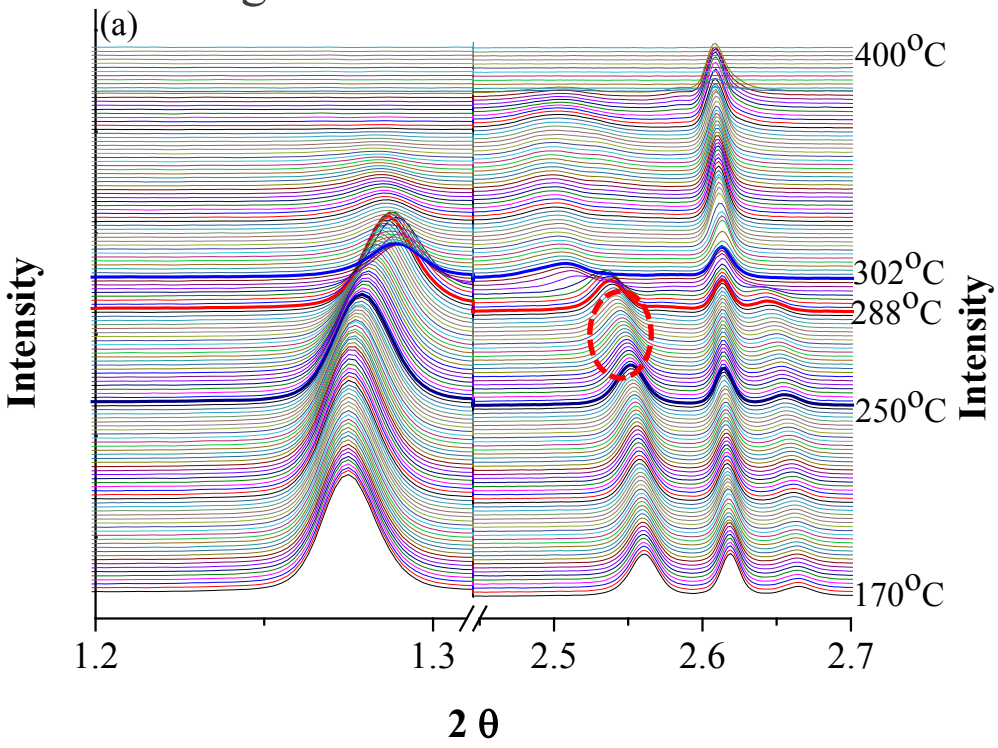
Structural evolution of "dry" $Li_{1-x}(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ @ 4.1 V



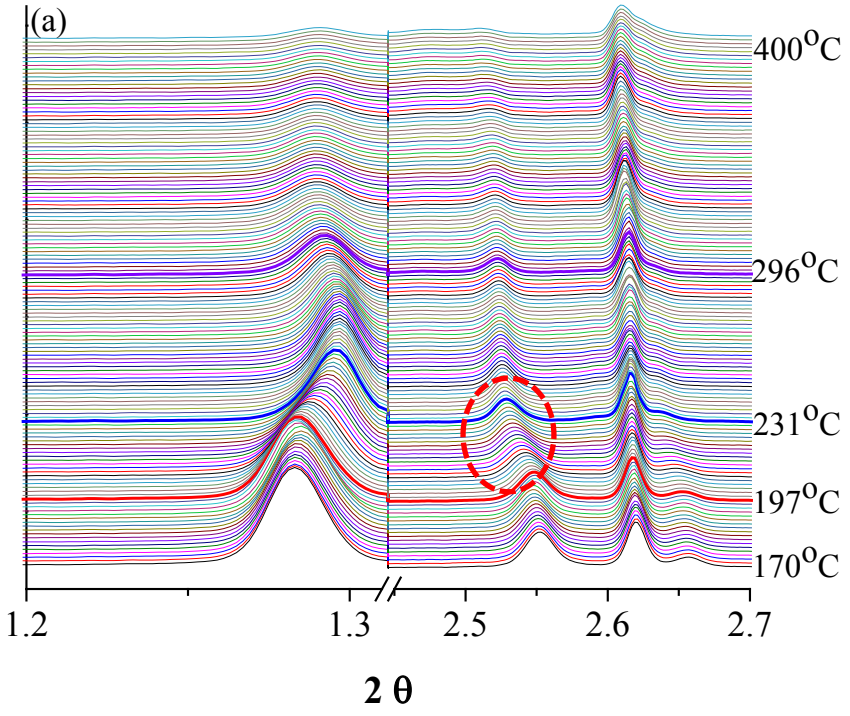
- "Dry" sample: (1) half cell containing $Li_{1.1}(Ni_{1/3}Mn_{1/3}Co_{1/3})_{0.9}O_2$ was charged to 4.1 V. (2) Open the cell in glove box and dry the electrode for 10 minutes. (3) Harvested about 3 mg electrode material and sealed in an in situ DSC high pressure vessel.
- "Dry" sample may contain delithiated NMC, carbon black, PVDF, and some $LiPF_6$.
- The sample was heated to 400°C with a heating rate of 5°C per minute, and XRD spectrum was collected every 20 seconds.
- The transformation of "dry" sample to O1 phase starts at about 278°C, and at about 318°C. No further decomposition was observed up to 400°C.

Mechanism changes when it is "wet"

3mg NMC + 3uL solvent



3mg NMC + 3uL electrolyte

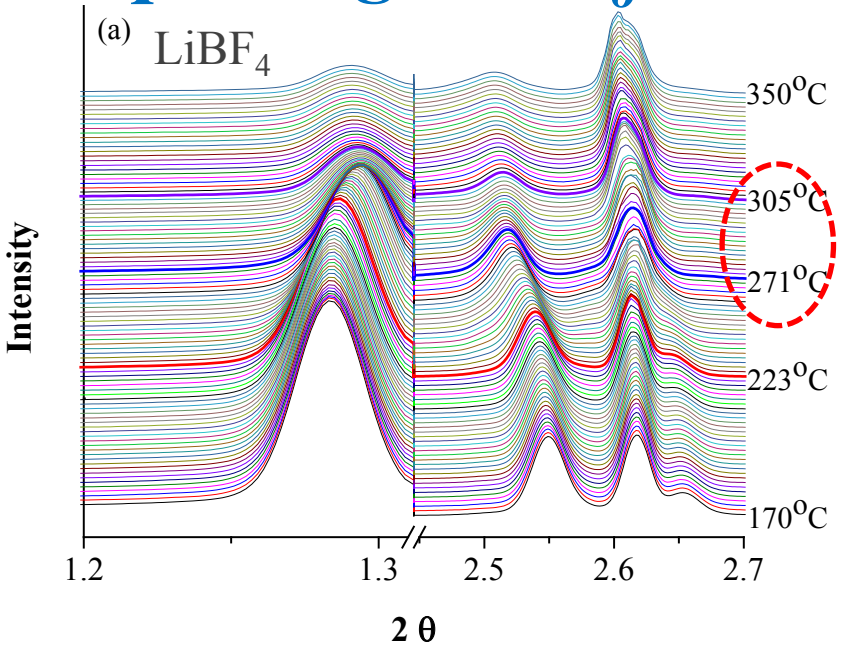


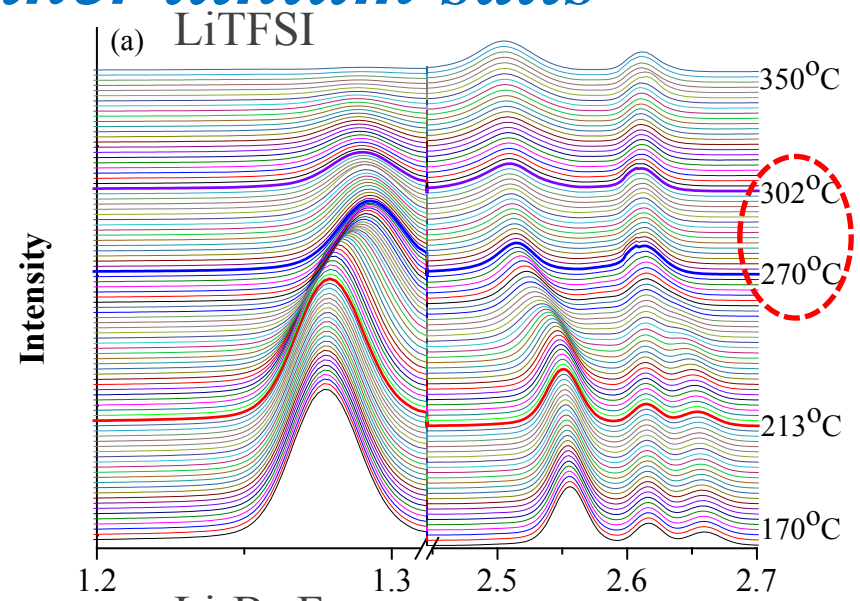
Major difference: 3-step reaction

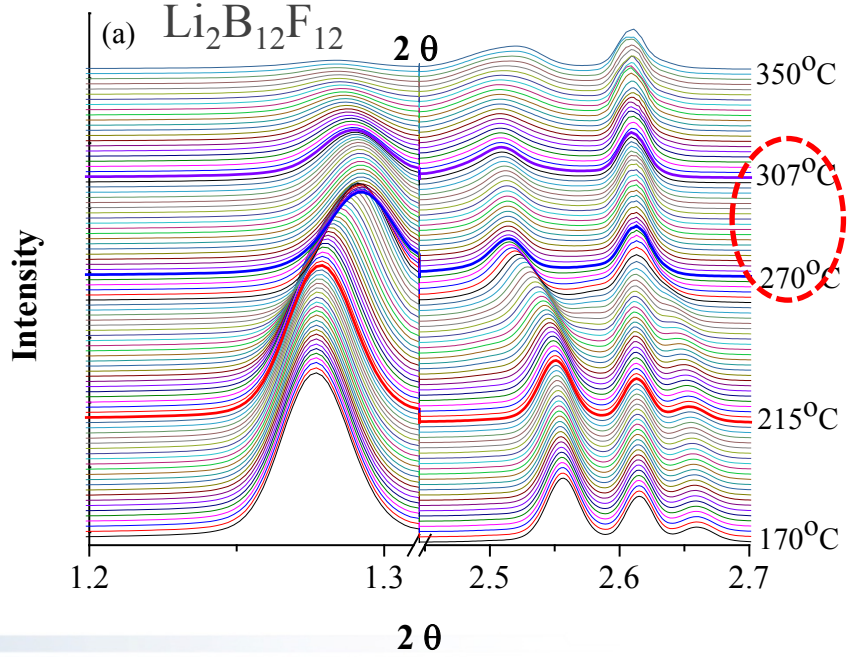
(a) Expansion of c axis from 250°C to 288°C.
(b) Conversion to O1 phase from 288°C to 302°C.
(c) Disappearance of O1 phase above 302°C.

The onset temperature for the first reaction is reduced to 197°C with the addition of $LiPF_6$.

Replacing $LiPF_6$ with other lithium salts

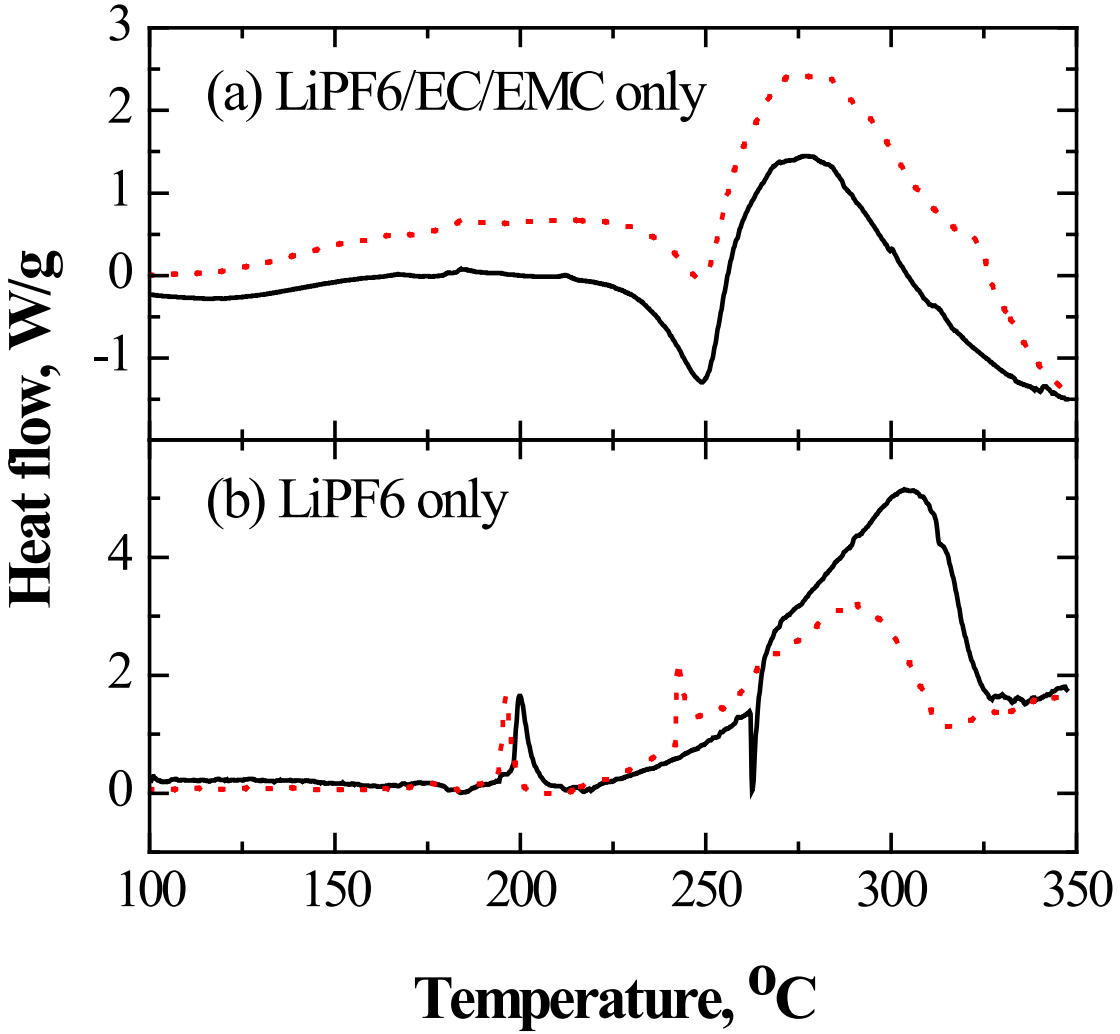






- The lithium salt shows significant impact on the first step reaction. The onset temperature increases in the order of $LiPF_6$<LiTFSI~$Li_2B_{12}F_{12}$<$LiBF_4$.
- The onset temperature for the second reaction is 231°C for $LiPF_6$ and 270°C for $LiBF_4$, LiTFSI and $Li_2B_{12}F_{12}$.
- The mechanism will be further investigated using density function theory.

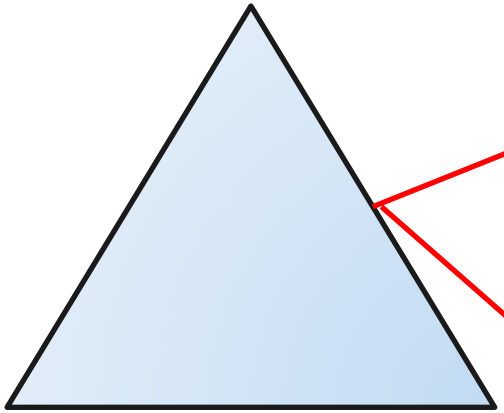
Thermal decomposition of $LiPF_6$



- $LiPF_6$ start to decompose at 200°C.
- Electrolyte starts at about 220°C.
- What's the product of electrolyte decomposition?
- What's the impact of $LiPF_6$?
- DFT calculation is ongoing.

How about high energy cathodes?

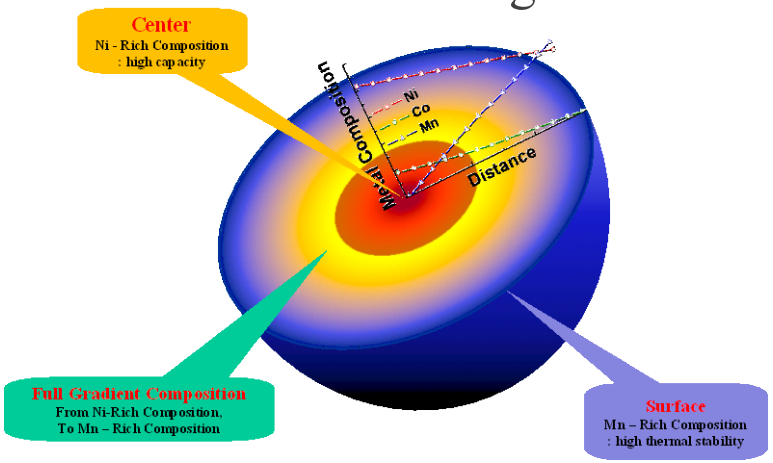
$LiCoO_2$
High cost
Limited resource
Low lithium utilization

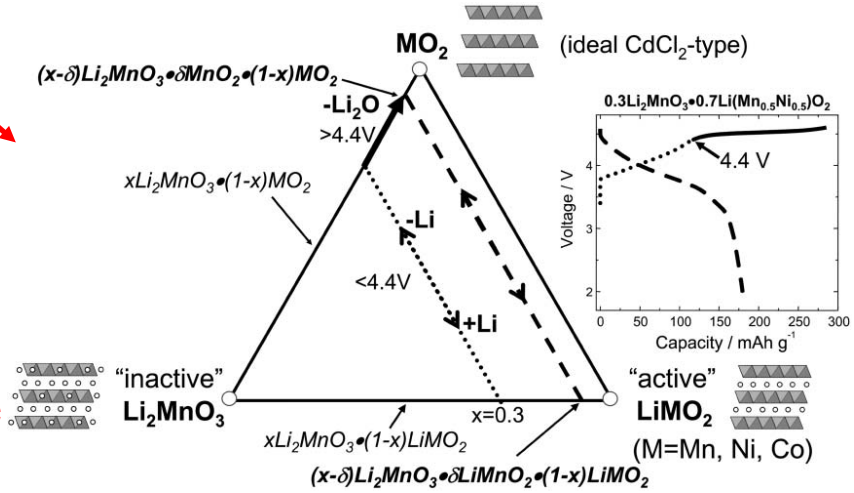


$LiMnO_2$
Low cost
Abundant
High thermal stability
Low energy density

$LiNiO_2$
High energy density
Poor thermal stability

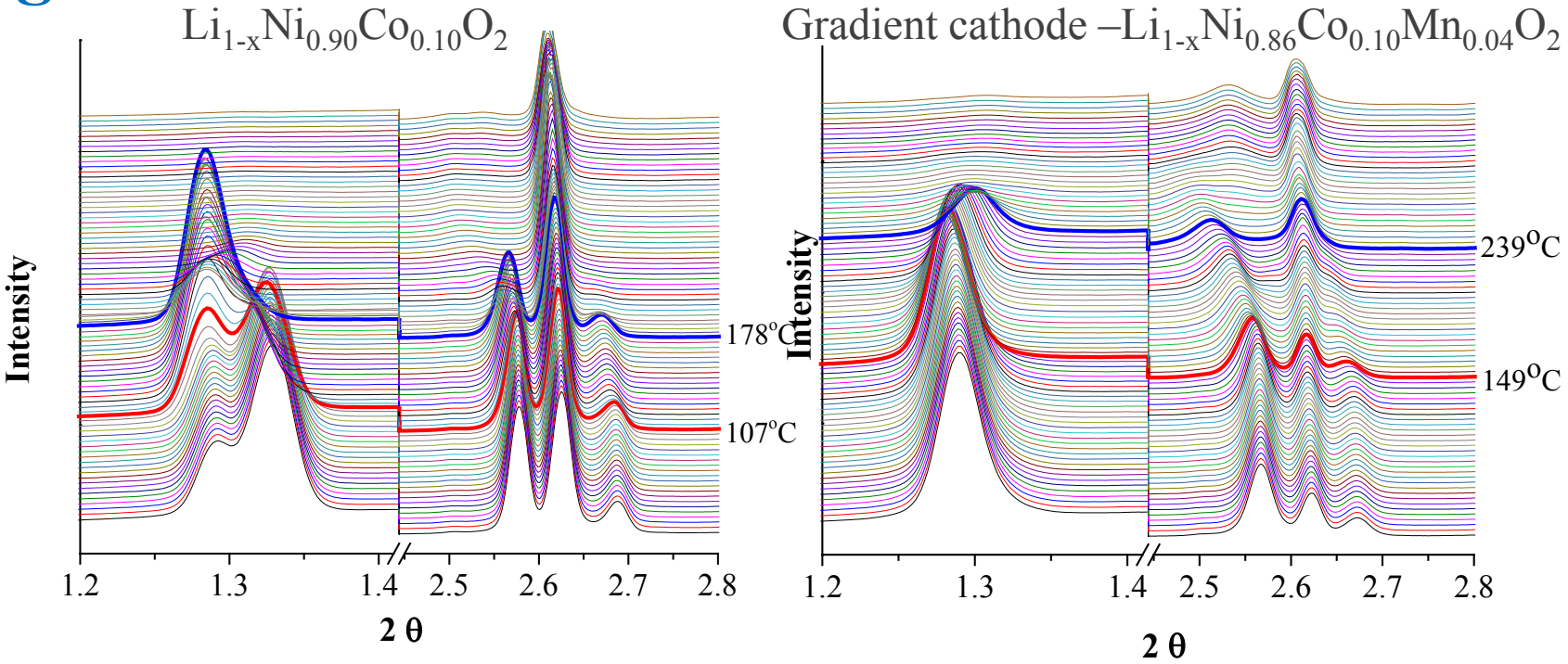
Concentration gradient





- Major effort has been devoted to searching high energy cathode in Ni-Mn-Co ternary system.
- Both concentration gradient cathodes and composite materials are promising for PHEV applications.
- How about the thermal stability of these materials?

Preliminary results on full concentration gradient cathode



- The thermal decomposition mechanism is different from that of composite NMC cathode.
- $Li_{1-x}Ni_{0.9}Co_{0.1}O_2$ started converting to spinel phase even at RT, and the conversion completed at about 110°C, leading to poor capacity retention.
- The newly formed phase reacted with electrolyte at about 200°C.
- The gradient material didn't convert to spinel phase at RT, and small portion of spinel phase was observed at 150°C. The exothermal reaction between cathode and the electrolyte started at about 240°C.

Proposed Future work

- Due to the re-scoping of ABR program the future effort will be rebalanced between the safety and the voltage fade of lithium-manganese-rich NMC materials.

- Initiate effort to investigate the structural evolution of LMR-NMC during and after electrochemical activation using synchrotron-based in situ techniques.

- Continue investigate the thermal decomposition mechanism of high energy cathodes and identify safer materials for automobile application.

- Finishing the effort to identify the impact of the surface chemistry on thermal stability of SEI layer and thus cell safety.

Summary

•In situ high-energy X-ray diffraction technique was developed to study the structural change of delithiated cathodes during thermal decomposition in the presence of the electrolyte.

•Lithium salt has significant impact on the decomposition pathway of delithiated cathodes.

•Full concentration gradient cathode has shown to have advantage on the thermal stability.

Acknowledgment

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