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

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Project ID: ES035

Overview

Timeline

- Start: 10/01/2008
- End: 02/28/2012
- 100% completed

Budget

- Total project funding
  - DOE - $2175K
  - Contractor - $ 0
- Funding received in FY12
  - $325K
- Funding for FY13
  - DOE - $0K

Barriers

- Barriers addressed
  - Safety

Partners

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

Objectives of the work

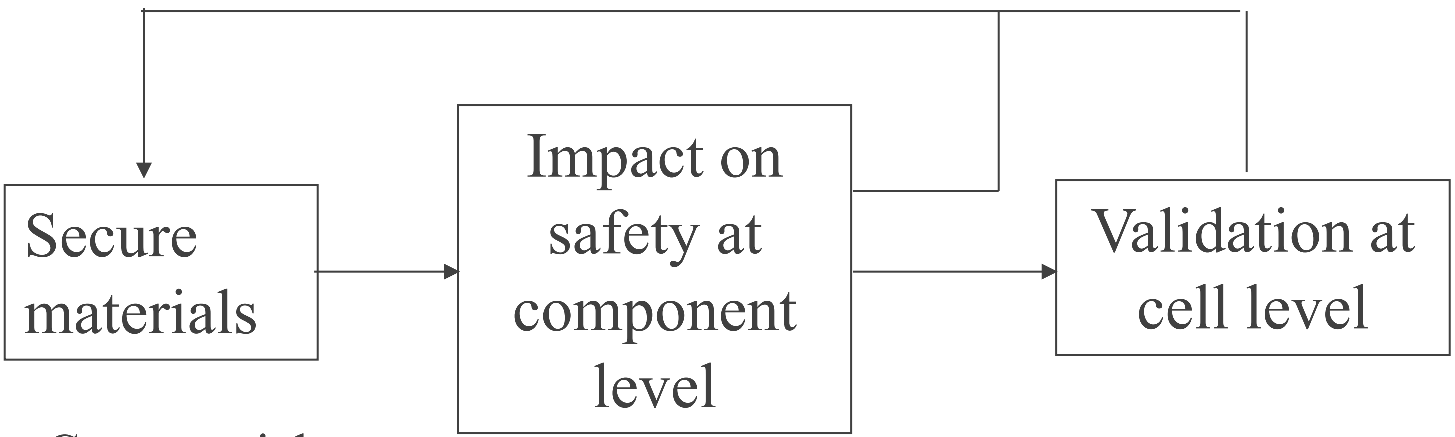
- Identify the role of each cell material/components in the abuse characteristics of different cell chemistries.

- 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

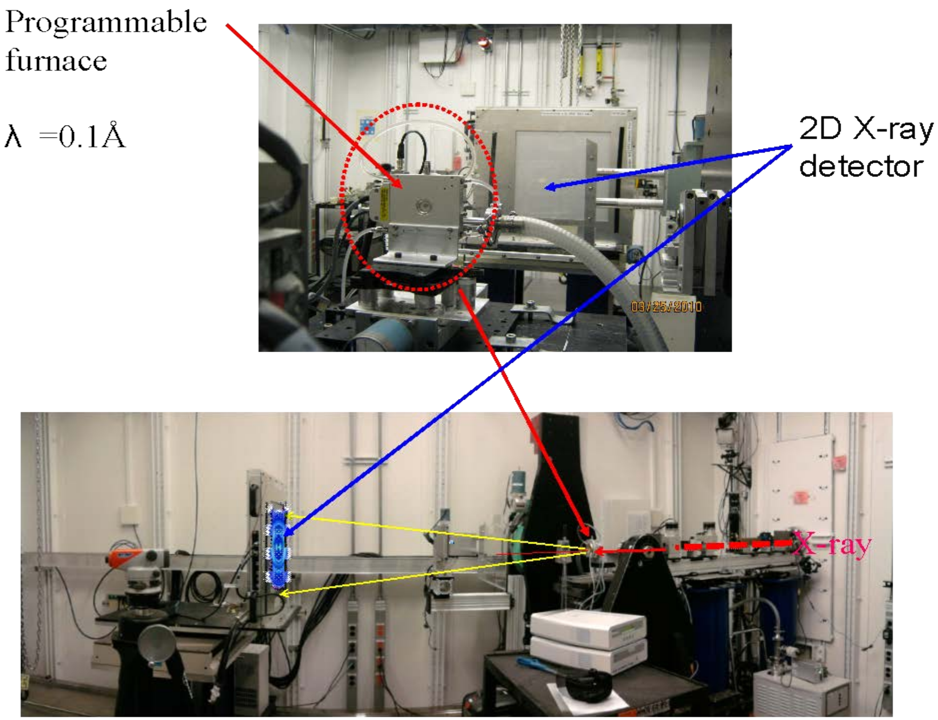
- **Thermal decomposition pathway of delithiated LMR-NMC**

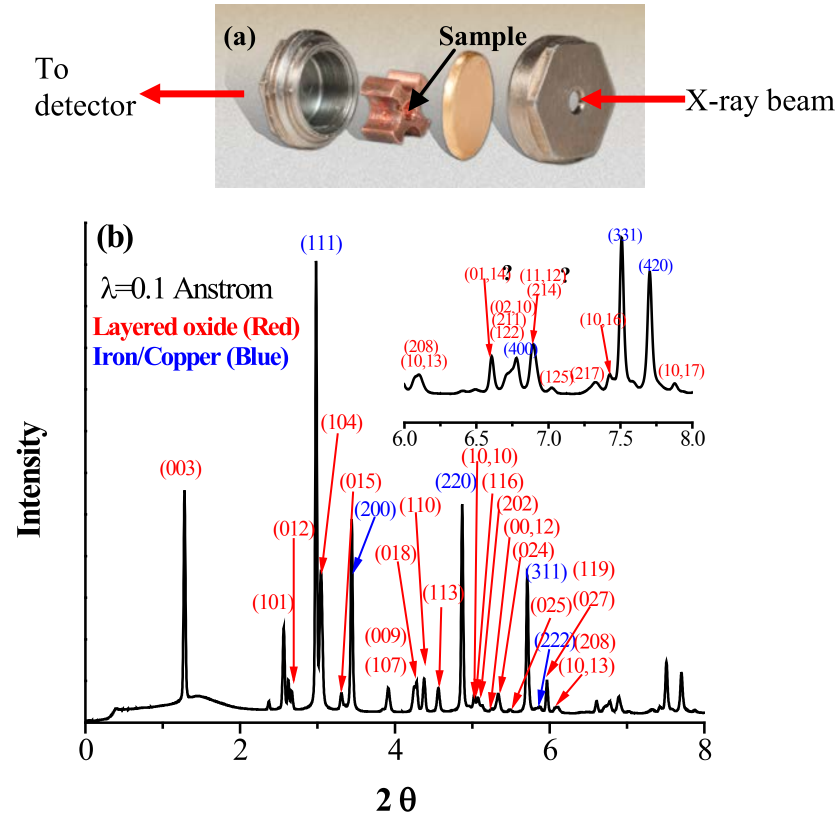
  - LMR-NMC = lithium-manganese-rich nickel manganese cobalt oxides
  - Materials investigated: HE5050, $0.5Li_2MnO_3 \cdot 0.5LiNi_{0.375}Mn_{0.375}Co_{0.25}O_2$
  - The thermal stability of delithiated HE5050 was investigated with in situ HEXRD
  - The decomposition pathway was highly dependent on the electrolyte as well as the state of charge (or degree of delithiation).

- **Localization of heat deposition for redox shuttles**

  - In situ HEXRD was deployed to monitor the temperature change inside the pouch cell
  - Lattice parameters of Cu and Al were traced as a temperature indicator for the anode and the cathode, respectively.
  - When redox shuttle was activated, heat deposition was found localized on anode side.
  - Thermal stable SEI is suggested to improve the performance of redox shuttle.

In situ HEXRD setup to study the safety of lithium-ion battery

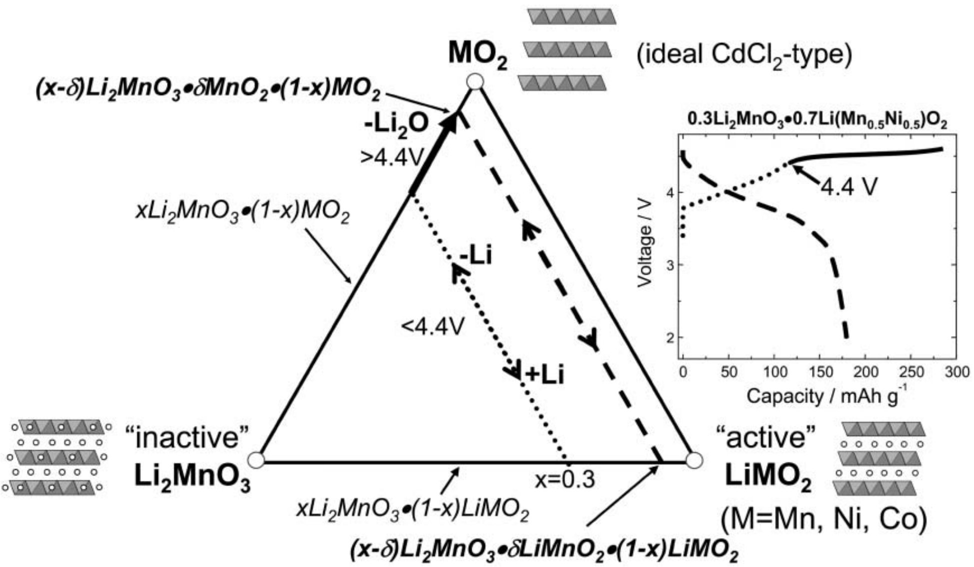


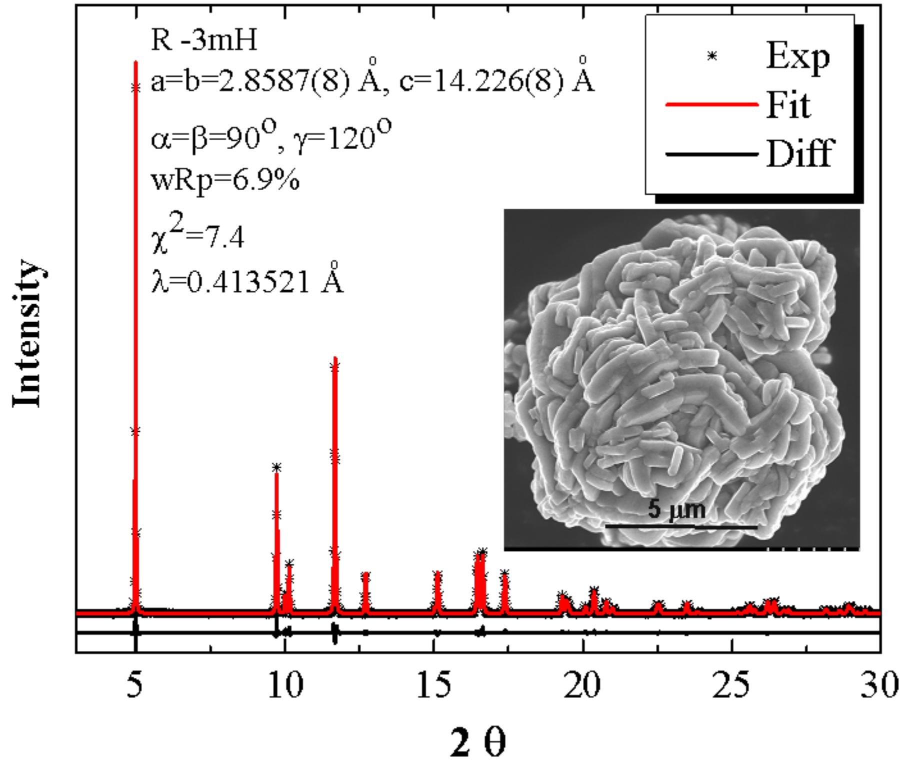


- Sector 11-ID-C at APS of ANL.
- High energy X-ray source is critic to penetrate through the stainless steel vessel that is used to seal the volatile solvents.

Thermal stability of delithiated HE5050

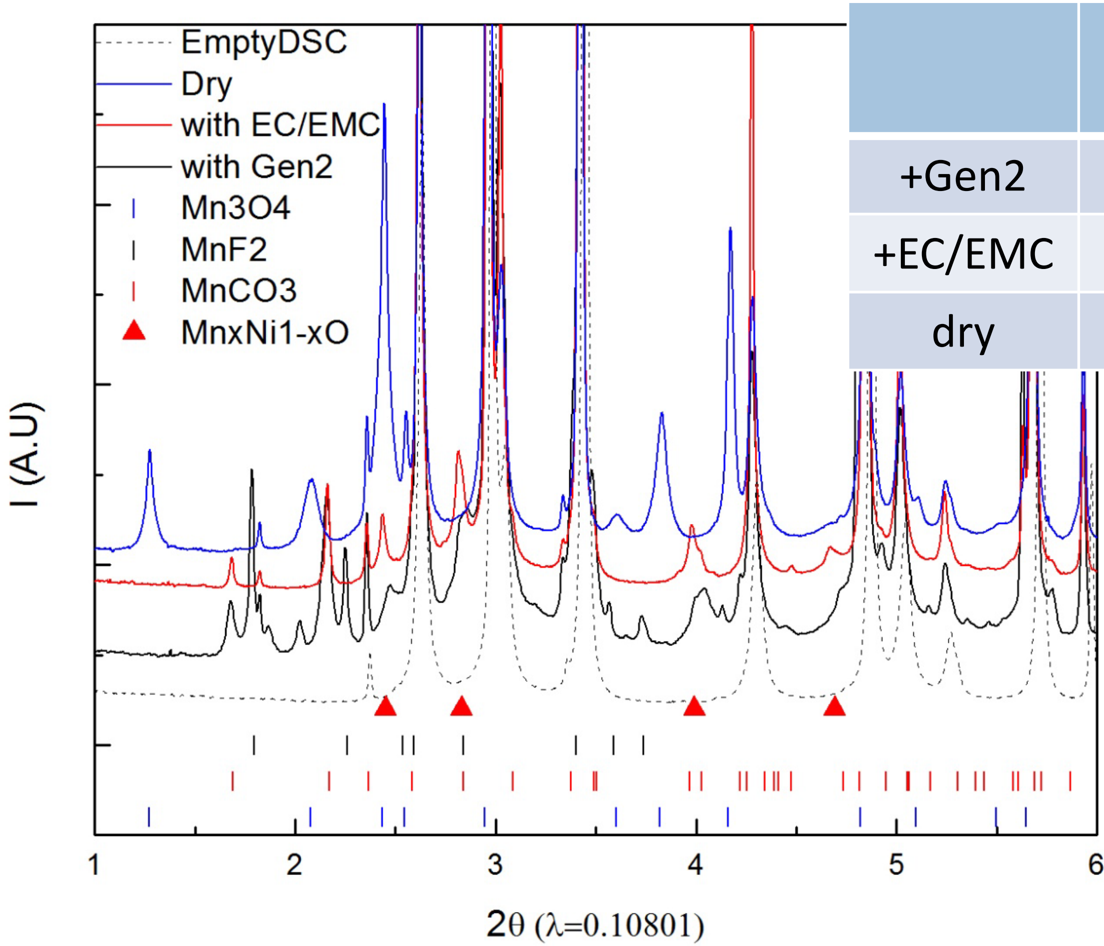
LMR-NMC as a high voltage and high capacity cathode





- LMR-NMC can deliver a reversible capacity of >200 mAh/g when cycled up to 4.6 V.
- Thermal stability of the delithiated LMR-NMC needs to detailed investigation at such a high potential.
- HE5050 = $0.5Li_2MnO_3 \cdot 0.5LiNi_{0.375}Mn_{0.375}Co_{0.25}O_2$

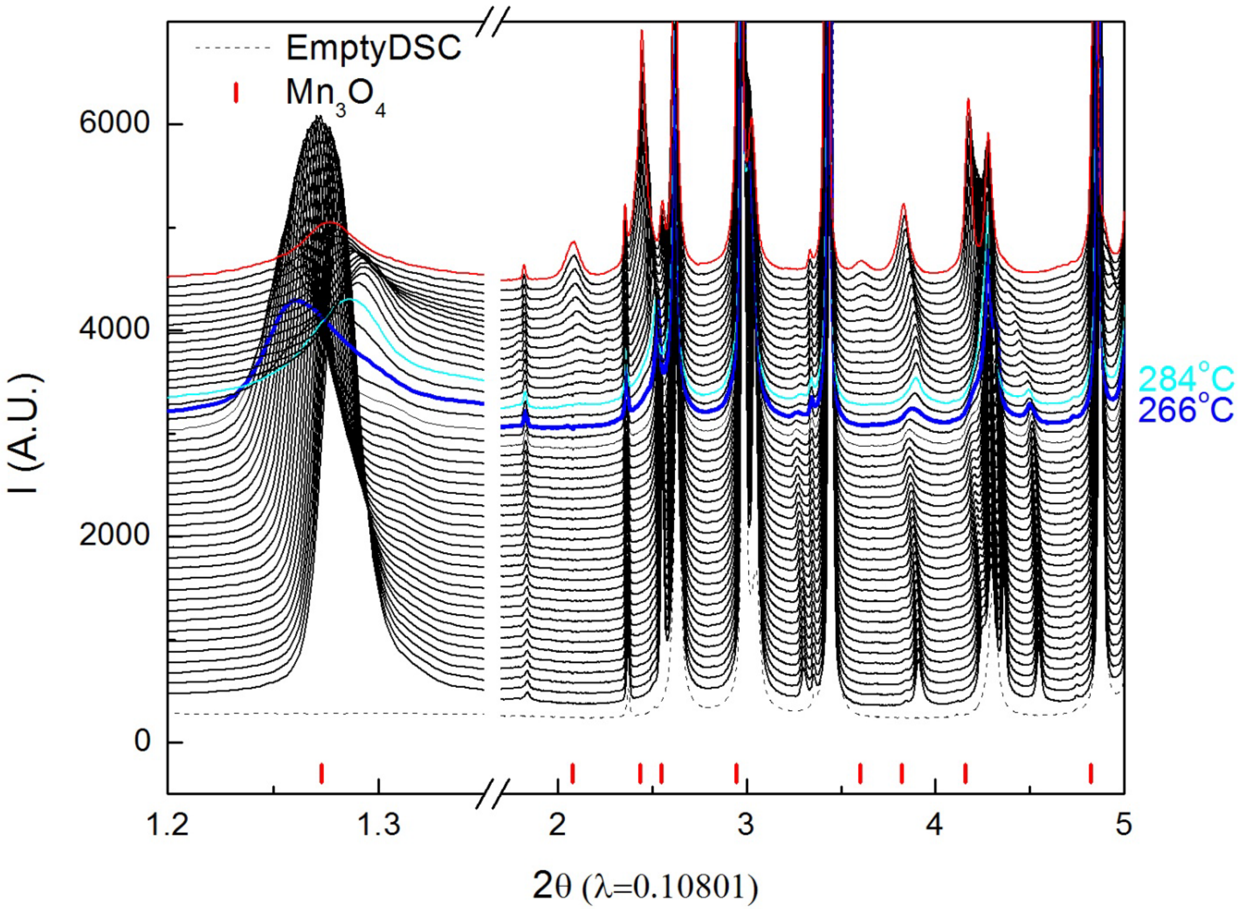
Dependence of decomposition products of delithiated HE5050 on exposure environment



	$Mn_xNi_{1-x}O$	$MnCO_3$	MnF_2	M_3O_4 – type
+Gen2	Yes	Yes	Yes	No
+EC/EMC	Yes	Yes	No	No
dry	No	No	No	Yes

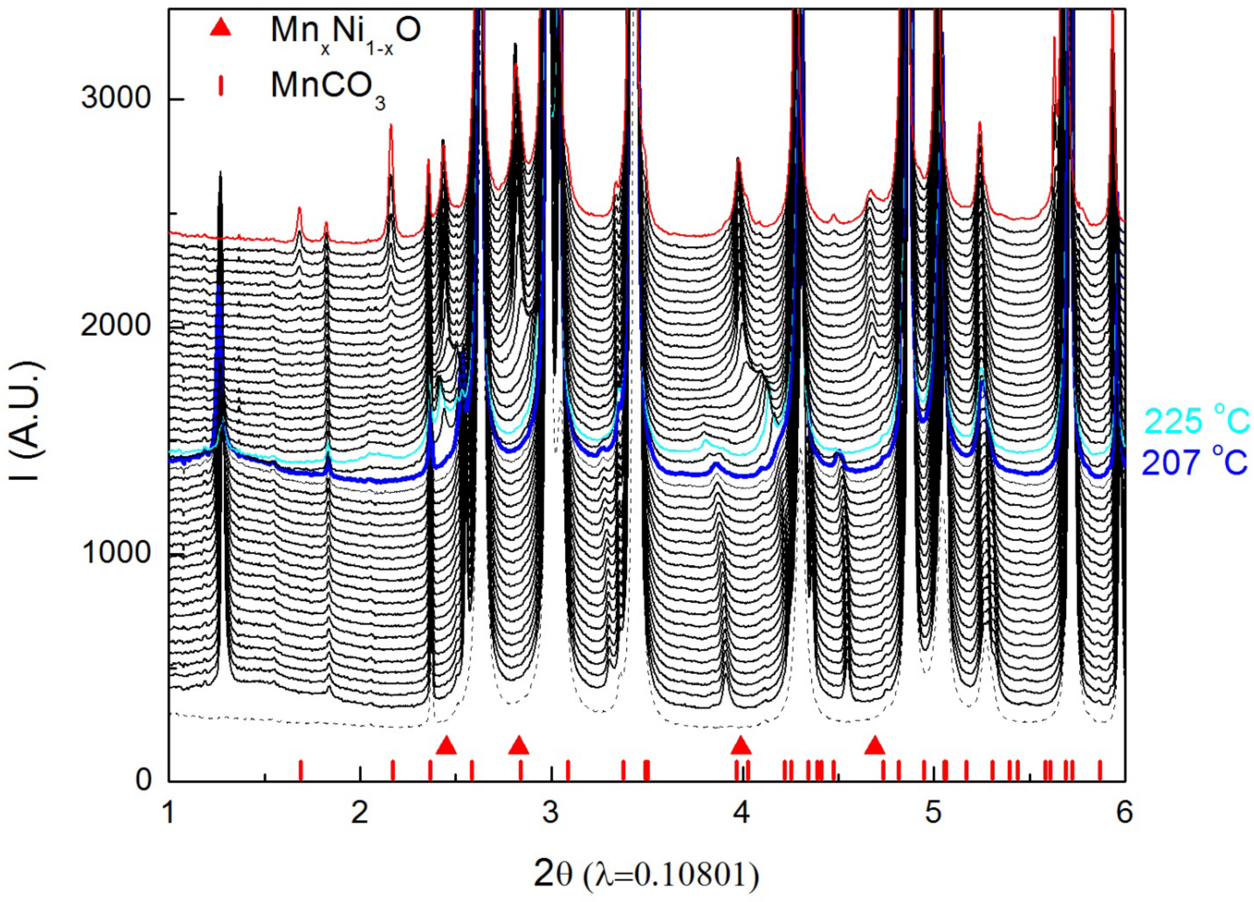
- The cathode was charged to 4.6 V.
- Dry sample converted to M_3O_4 spinel without further decomposition.
- Transition metal was reduced to +2 state when electrolyte or solvent is present.

Phase transformation of dry delithiated HE5050 during thermal abuse



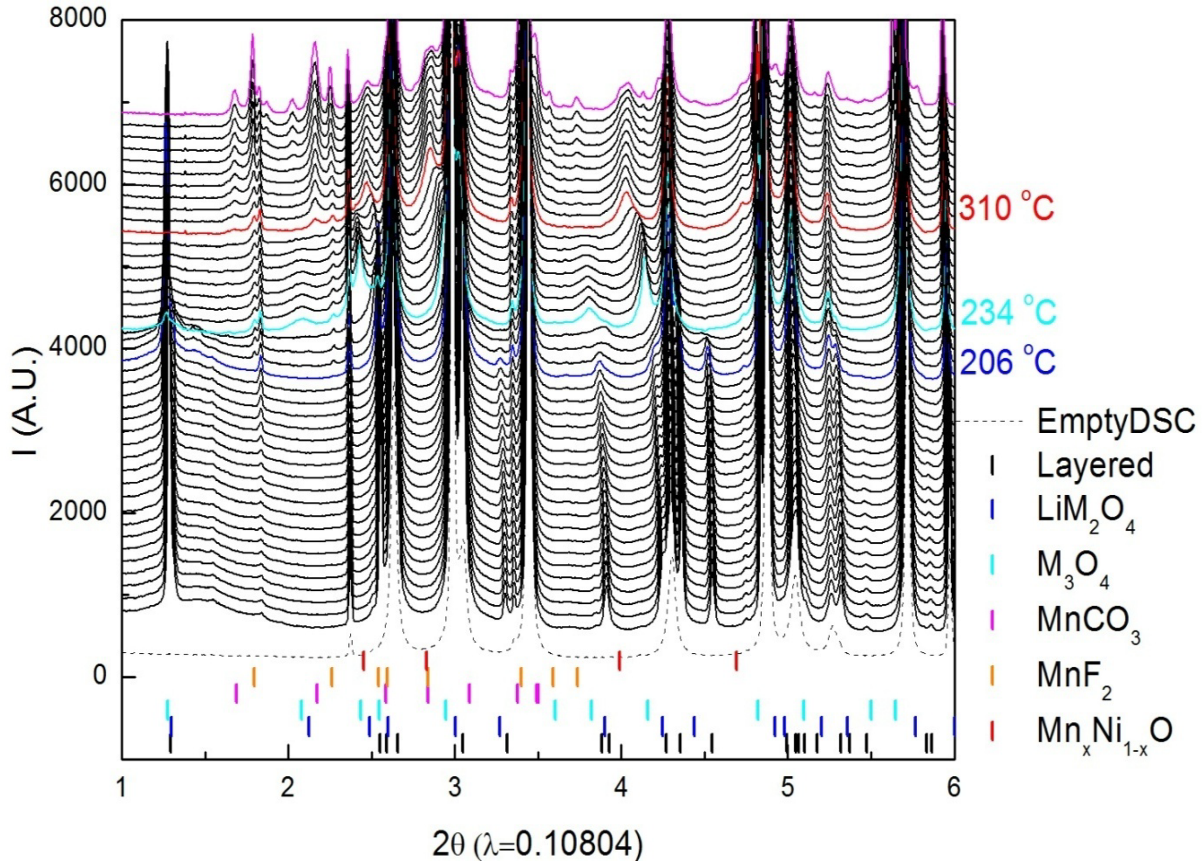
- HE505 was charged to 4.6 V.
- DSC sample composed of dry delithiated HE5050.
- Phase transformation of layered structure to M_3O_4 occurred at about 266^{o}C.
- No follow-up reaction was observed due to the lack of reducing agent.

Decomposition of delithiated HE5050 with the presence of the solvent (EC/EMC)



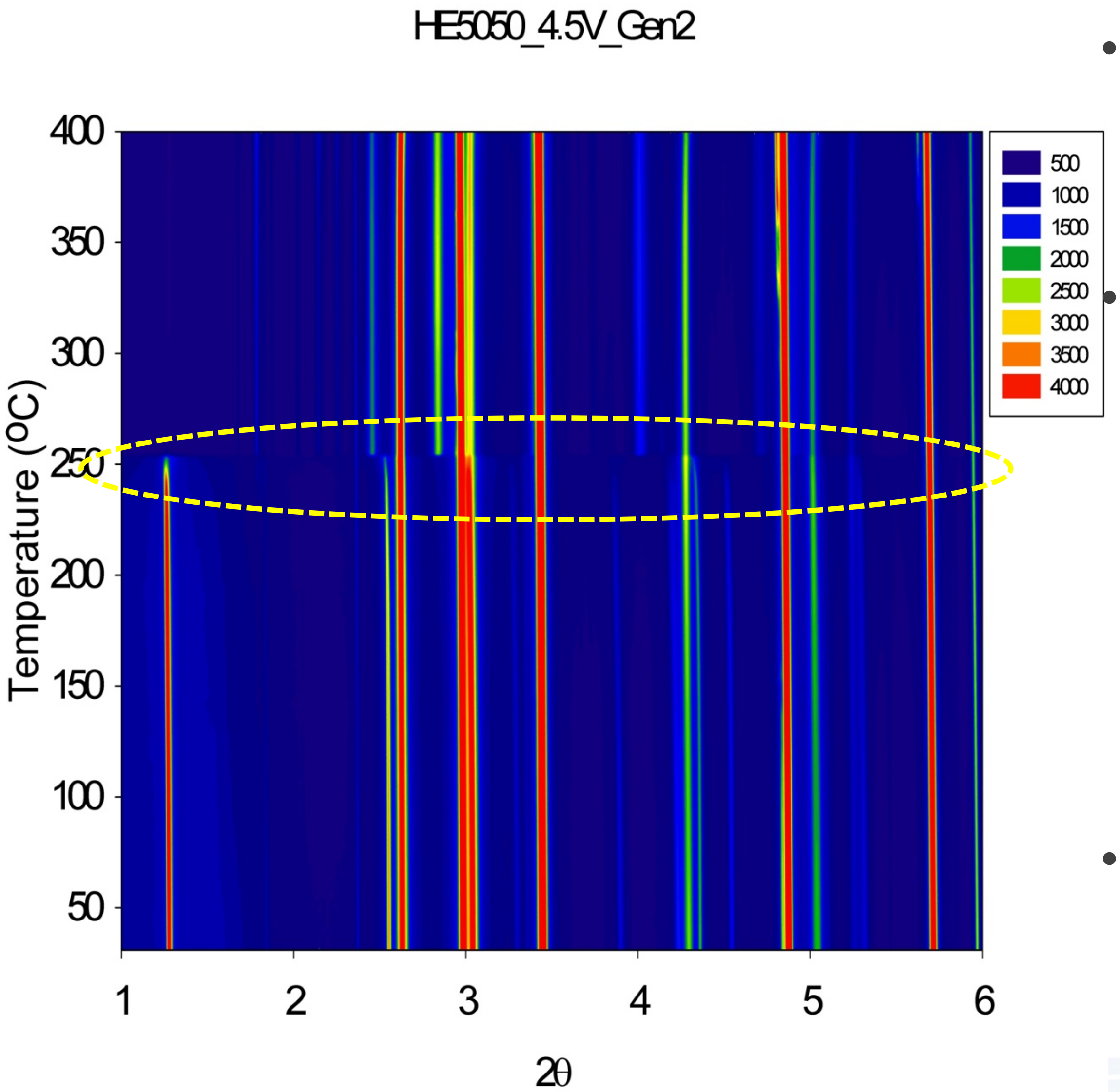
- Thermal decomposition started at 207°C.
- The oxides were reduced by the solvent and formed transition metal oxides, and transition metal carbonates.
- M_3O_4 type spinel was not observed

Decomposition of delithiated HE5050 with the presence of the electrolyte ($LiPF_6$/EC/EMC)



- Thermal decomposition started at 206°C.
- The oxides were reduced by the solvent and formed transition metal oxides, transition metal carbonates, and transitional metal fluorides.
- M_3O_4 type spinel was not observed

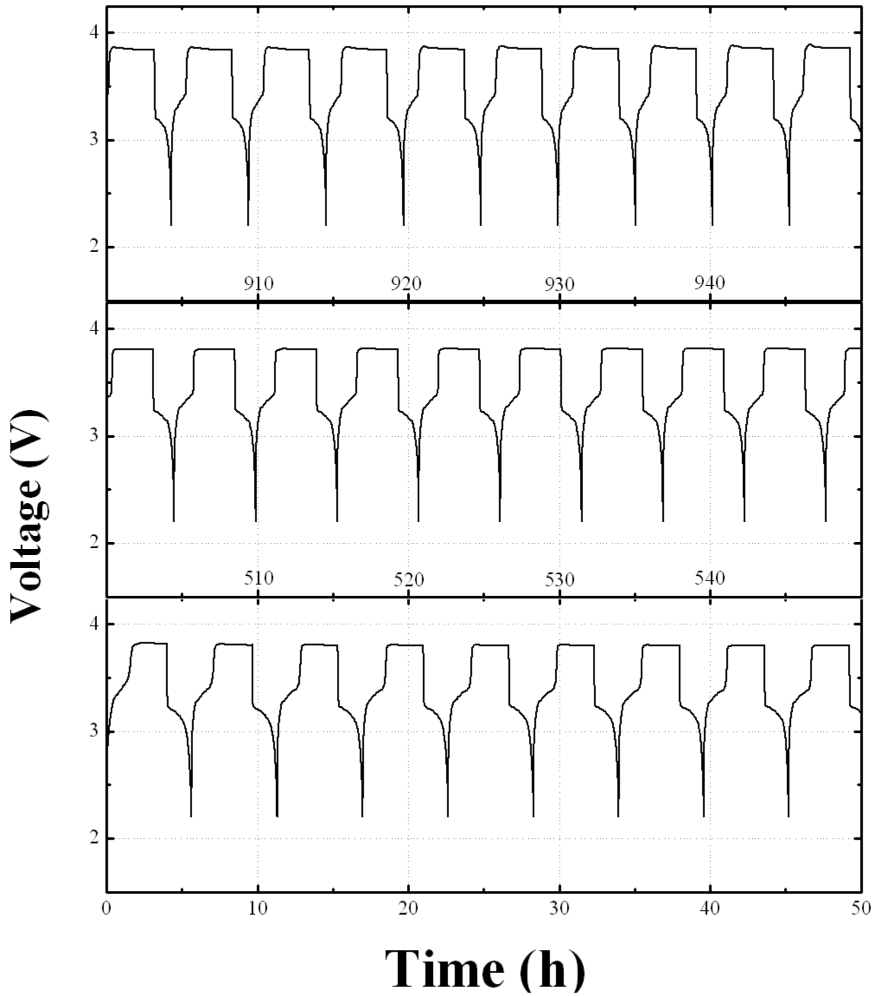
Impact of upper cutoff potential on thermal decomposition of delithiated HE5050

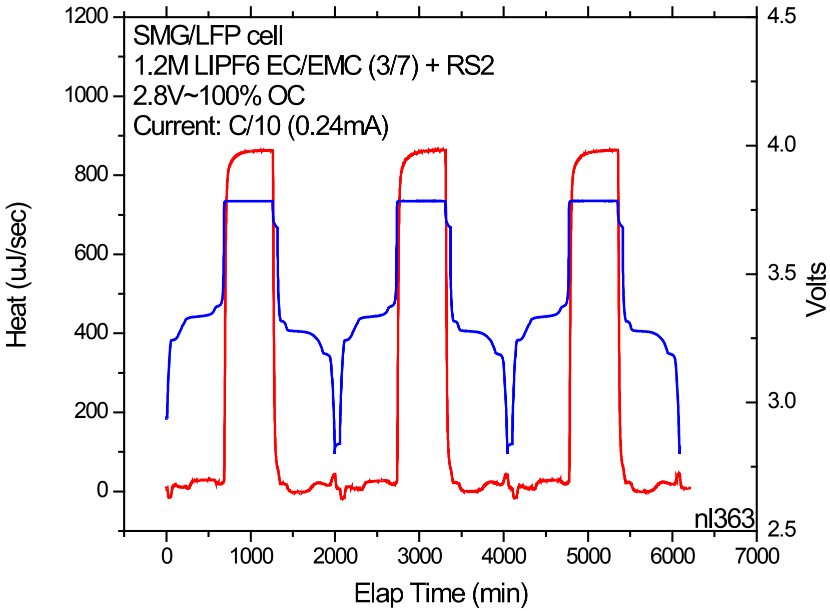


- HE505 was charged to 4.4V, 4.5 V, 4.6 V and 4.8 V, respectively.
- The onset temperature of thermal decomposition decreased with the upper cutoff voltage as following.
  ~ 262°C @ 4.4 V
  ~ 238°C @ 4.5 V
  ~ 206°C @ 4.6 V
  ~ 186°C @ 4.8 V
- It can be of big safety advantage by reducing the upper cutoff potential to 4.5 V.

Localizing the heat deposition of redox shuttles

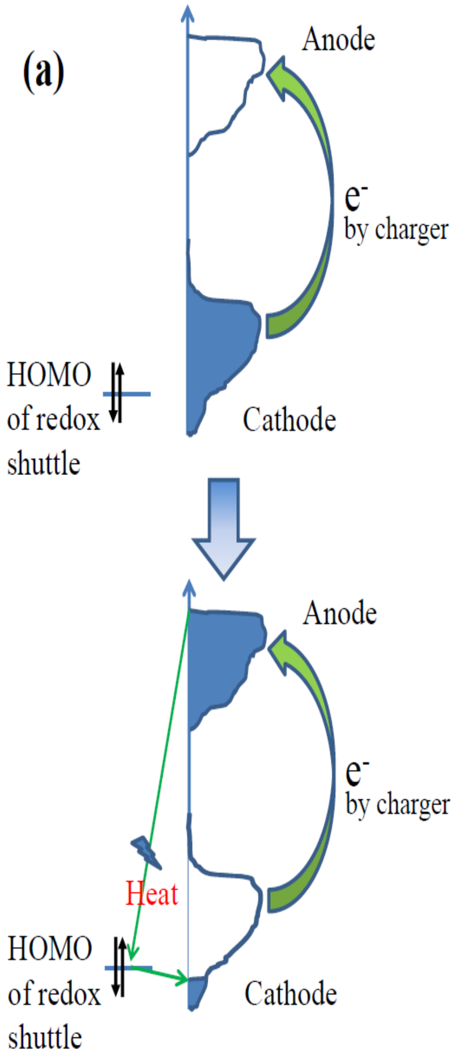
Redox shuttles are cool for overcharge protection, but heat deposition is an issue.



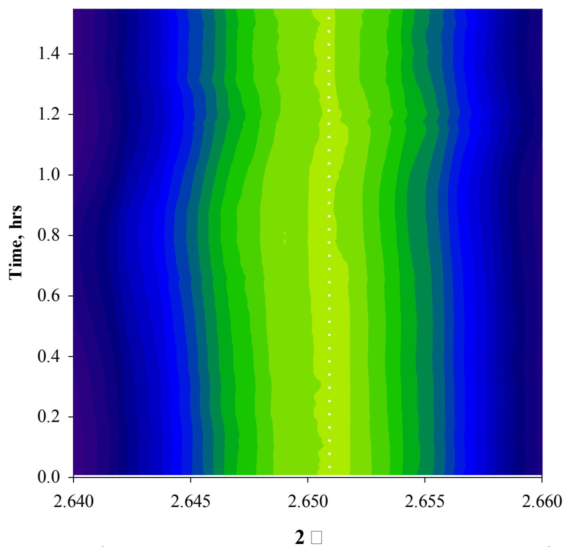


- Large amount of heat was deposited on the cell.
- Where is the heat deposition?
- What's the impact on electrochemical performance?

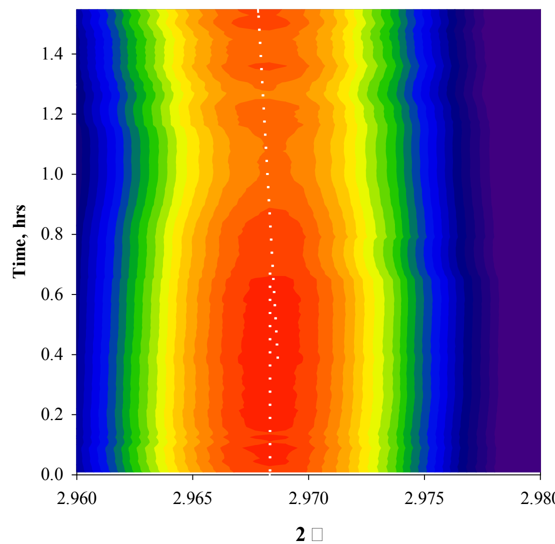
Locating the heat deposition when redox shuttle is activated



(111) Peak of Al

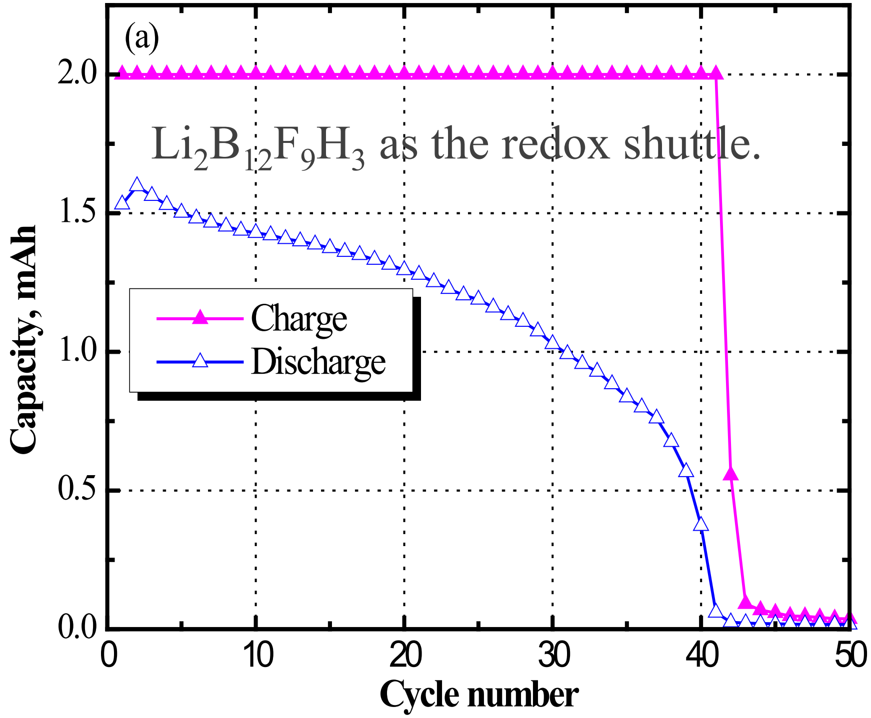


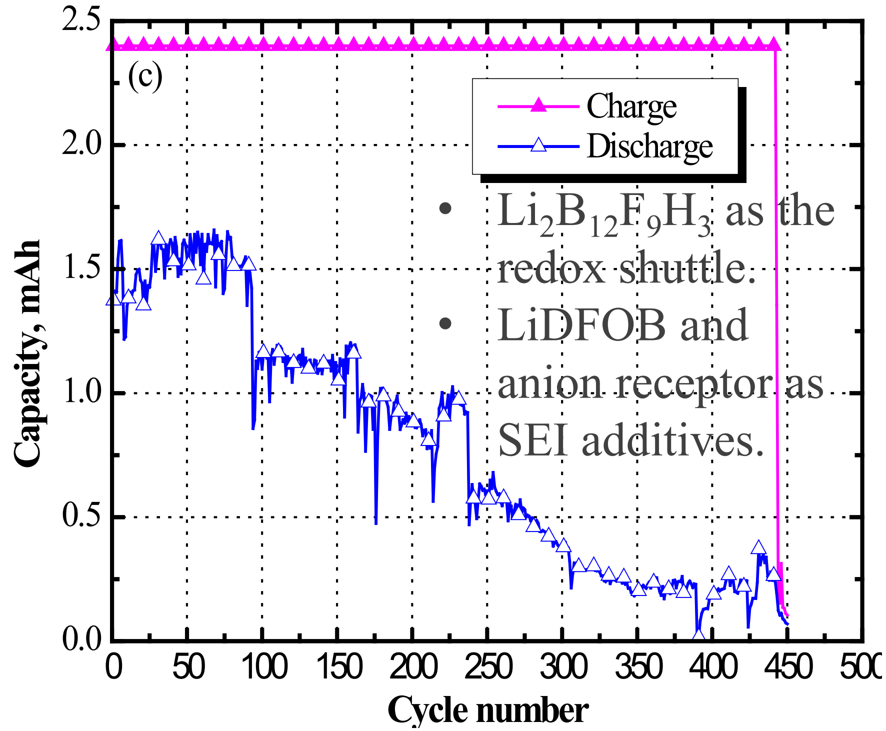
(111) Peak of Cu



- In situ HEXRD was carried out during overcharge test of pouch cell comprising a redox shuttle.
- Cu expanded when the redox shuttle was activated while Al had no change on cell parameters.
- It is heat deposition from redox shuttle caused the expansion of Cu.
- The thermal stability of SEI is challenged when the redox shuttle is activated.

Positive impact of a stable SEI layer on performance of redox shuttles





- **Forming a thermally stable SEI is the key to maximize the performance of the redox shuttle.**

Summary

- In situ high-energy X-ray diffraction technique was deployed to investigate the thermal decomposition of delithiated LMN-MNC.
    - The decomposition mechanism changes with the electrolyte environment.
    - The onset temperature decreases with the upper cutoff potential.
    - It is suggested, from the safety perspectives, to reduce the cutoff potential to 4.5 V vs. Li^+/Li.

- Heat deposition of redox shuttle at anode side was confirmed with in situ HEXRD.

- A thermally stable SEI is needed to maximize the performance of redox shuttles.

Acknowledgment

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