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

- Secure materials
  - Commercial source
  - Partners
  - In-house synthesis

- Impact on safety at component level
  - Thermal analysis
  - Electrochemical analysis

- Validation at cell level
  - 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 \( \text{Li}_{1-x}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2 \) at various conditions.
  - Investigated the effect of salts (\( \text{LiPF}_6, \text{LiBF}_4, \text{LiTFSI} \) and \( \text{Li}_2\text{B}_{12}\text{F}_{12} \)) as well as pure solvents on safety. (\( \text{LiPF}_6 \) has negative impact on safety of cathode by reducing the onset temperature from \(~310^\circ\text{C}\) to about \(~200^\circ\text{C}\).)
Recent Accomplishments and Progress (cont’d)

- **Impact of ANL-2 redox shuttle on electrochemical performance**
  - Studied cell chemistry: MCMB/LiFePO₄ using 1.2 M LiPF₆ 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 a 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 LiCoO₂.
- XRD can help to study the change of cathode materials during heating.

![Graph showing heat flow against temperature for Liₓ[Li₁/₃Mn₁/₃Co₁/₃]O₂ with 1.2 M LiPF₆ in EC/EMC (3:7, by weight).](image-url)
Why high energy X-ray diffraction (HEXRD)?

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

- **Materials:**
  - Process optimization
  - Quality control
  - Intercalation mechanism
  - Abuse tolerance

- **Battery:**
  - Nondestructive diagnosis
  - Failure analysis
  - Mechanical fatigue
  - Heat generation
  - Capacity and power fade
In situ HEXRD setup

- Sector 11-ID-C at APS of ANL.
- High energy X-ray source is critical to penetrate through the stainless steel vessel that is used to seal the volatile solvents.
Impact of electrolyte components on thermal decomposition of $\text{Li}_{1-x}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ @ 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 LiPF₆.
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$\sim$Li$_2$B$_{12}$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$_2$B$_{12}$F$_{12}$.

• The mechanism will be further investigated using density function theory.
Thermal decomposition of LiPF$_6$

- LiPF$_6$ starts 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

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- 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.
- $\text{Li}_{1-x}\text{Ni}_{0.90}\text{Co}_{0.10}\text{O}_2$ started converting to spinel phase even at RT, and the conversion completed at about $110^\circ{\text{C}}$, leading to poor capacity retention.
- The newly formed phase reacted with electrolyte at about $200^\circ{\text{C}}$.
- The gradient material didn’t convert to spinel phase at RT, and small portion of spinel phase was observed at $150^\circ{\text{C}}$. The exothermal reaction between cathode and the electrolyte started at about $240^\circ{\text{C}}$. 
**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.
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