Materials-Level Thermal Abuse and Mitigation Study: Toward Safe Lithium-Ion Batteries

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Introduction

The U.S. auto industry is in search of improved energy storage devices for use in hybrid electric vehicles (HEVs) and fuel cell electric vehicles (FCEVs). Commercial HEVs use nickel metal hydride batteries that are very expensive, heavy, and lack sufficient calendar life. High-power lithium-ion batteries offer promise for replacing nickel metal hydride batteries, but significant improvements in their abuse tolerance characteristics are needed.

Challenge

- Improve the inherent thermal stability of high-power lithium-ion cells to help in meeting the abuse tolerance requirements established by the auto industry for large-scale HEV batteries.

Argonne's Approach

- Conduct detailed thermal characterization studies on each component of our baseline high-power cell chemistry to understand the mechanisms responsible for the thermal instability of cells that employ this chemistry.
- Develop advanced cell materials and cell chemistries that possess enhanced stability:
  - Use chemical delithiation technique to evaluate the safety of different charged cathode powders independently from other cell components.
  - Investigate oxygen release from the oxide active cathode materials and quantify its impact on the oxidation of electrolytes.
  - Study effects of flame retardants on the safety of lithium-ion cells

Thermal Mitigation Study Tools

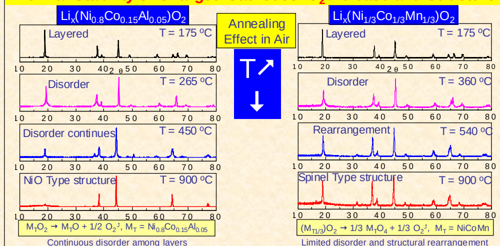
- Differential scanning calorimetry (DSC)
- Accelerated rate calorimetry (ARC)
- Gas chromatography/mass spectrum (GC-MS)
- Thermo-gravimetric analysis (TGA)
- Structural investigation: X-ray diffraction


GC-MS Instrument: Gas Collection and Analysis


Designed Cell Holder: Open and closed designs


ARC Cell: Allows temperature and pressure recording

Thermal Stability of Charged Cathodes: O_2 Release and Structure

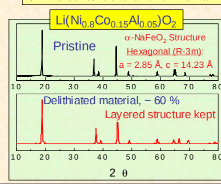


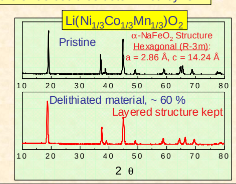
The limited O_2 release from charged $Li_x(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ material is blocked by the formation of a spinel type structure

Chemical Delithiation of Cathodes Using NO_2BF_4

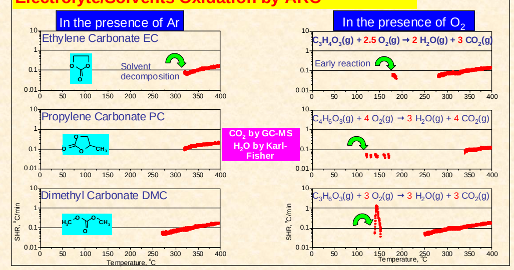
$Li(Ni_xCo_yMn_z)O_2$ reacts with a strong oxidizer NO_2BF_4 in acetonitrile solution for different reaction times: $LiM_TO_2 + \alpha\, NO_2BF_4 \rightarrow Li_{1-\alpha}M_TO_2 + \alpha\, NO_2^{\uparrow} + \alpha\, Li^+, BF_4^-{}_{aq}$

- α = 1 and same reaction time (24 h).
- The powders were recovered after filtration and were rinsed with acetonitrile several times and then dried under vacuum at 80 °C.
- The content of the lithium remaining in the oxide could be determined by ICP

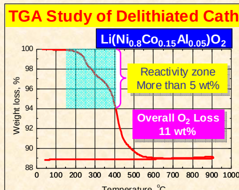


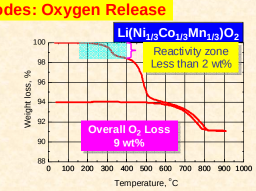


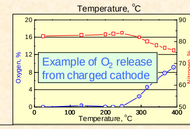
Why Is O_2 Release From a Cathode So Important ? Electrolyte/Solvents Oxidation by ARC



TGA Study of Delithiated Cathodes: Oxygen Release





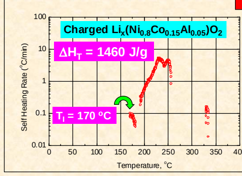


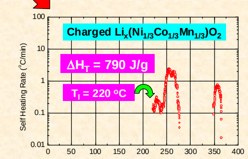
In the zone of reactivity where charged cathodes are expected to vigorously react with electrolytes, $Li_{1+x}(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ material exhibits a limited oxygen release compared with $Li(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$ cathode, which also shows an anticipated thermal degradation.

Reactivity of Charged Cathodes With Electrolytes

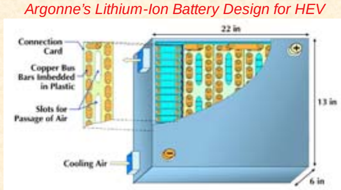
If no electrolyte present, both charged cathodes show no heat generation by ARC

If the presence of an electrolyte 1.2 $MLiPF_6$ in (EC:EMC) (3:7 wt%)/





Argonne's Lithium-Ion Battery Design for HEV



Conclusions

- Oxygen release from cathodes plays a significant role in the safety of lithium batteries.
- Highly stable cathodes, such as $Li_{1+x}(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$, with a limited oxygen release, have much better safety characteristics than $Li(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$.

Future Work

- Investigate new flame retardants and electrolyte additives to stabilize the electrodes and further improve the safety of lithium-ion batteries.

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