Effect of electrolyte and additives on performance of \( \text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \)

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Source of Energy Fade of Lithium-ion Batteries

Poor calendar life and performance loss upon thermal abuse, accelerated aging, or extended cycling of Lithium-ion batteries

Three primary sources have been reported

- Thermal decomposition of the electrolyte (LiPF$_6$/Carbonate)
- Thermal deterioration of protective SEI on anode and reactions of electrolyte with anode
- Reaction of electrolyte with cathode to form surface films composed of LiF/Li$_x$PF$_y$/Li$_x$POF$_y$, PEO, Polycarbonate, ROCO$_2$OLi

Aurbach, D. J. Power Sources 119-121, 497 (2003)
Investigation of Electrolytes for HV Spinel

Research suggests two primary mechanisms of performance loss due to electrolyte (LiPF$_6$ in Carbonates)

- Oxidation of the electrolyte on cathode surface
- Metal ion dissolution due to acidic electrolyte decomposition products

Investigation of novel electrolytes to Improve Performance of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathodes cycled to high Voltage

- Cathode Film forming additives which generate a passivation layer inhibiting electrolyte oxidation
- Lewis Basic Additives which inhibit Mn dissolution

Very little capacity fade at RT followed by dramatic capacity fade at 55 °C for graphite/LiNiMnO$_4$ cells

Cathode laminate may be damaged (Oh J. Power Sources 215, 312, 2012)
Storage Experiments of $\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_3$ with Electrolyte

Investigation of the reactions of the electrolyte with the cathode surface.

$\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_3$/Li cells were stored at various voltages between 4.0 and 5.3 V vs Li for one week.

At low voltages, below 4.7 V, there is very little current flow through the cells. As the voltage surpasses 4.7 V vs Li there is a significant increase in charge flow through the cells.

The increased charge flow is consistent with electrolyte oxidation on the surface of the cathode at high potential.

Similar results were observed for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ /Li half cell.

Oxidation of the electrolyte solution (1 M LiPF$_6$ in 1:1:1 (EC:DEC:DMC) at various potentials with a $\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_3$ /Li half cell.

Ex-Situ Surface Analysis of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathodes with LiPF$_6$ in EC/DMC/DEC (1/1/1 vol)

XPS Suggests Metal oxide covered with polyethylene carbonate (PEC) at high voltage.

Polyethylene carbonate and oxalate generation supported by IR.
Impedance before and after cycling at elevated temperature.

Half cells were prepared from electrode extracted from cells cycled at ET.

Most of the impedance growth occurs on the cathode.
XPS Spectra of Cycled Cathodes

Significant electrolyte decomposition occurs upon cycling at 55 °C

Decomposition products include polyethylene carbonate and lithium alkyl carbonates and lithium oxalate

Mn and Ni content at surface is decreased
SEM Images of Cathodes

The changes to the morphology of the bulk cathodes upon cycling is small.
**XPS Spectra of Anodes**

Significant electrolyte decomposition occurs upon cycling at 55 °C

Decomposition products include lithium alkyl carbonates, Li$_2$CO$_3$, LiF, and Li$_x$PF$_y$O$_z$

No change to bulk material by SEM, but delamination is observed

Mn is also present on the anode surface (ICP-MS)
Incorporation of electrolyte additive(s) results in dramatic decrease in capacity fade upon cycling at 55 °C for graphite/LiNi_{0.5}Mn_{1.5}O_{4} cells.
Changes to cathode surface are small upon incorporation of additive
Additive inhibits LiF formation on Anode

Mn deposition is also inhibited
Investigating the performance of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathodes cycled to high voltage

- Discovered that the two leading sources of performance fade are electrolyte oxidation and Mn dissolution.

- Electrolyte oxidation below 4.9 V lesser contributor, thermal effects are larger contributor.

- Both the anode and cathode are damaged from cycling at 55 °C.

- Additives have been developed that inhibit Mn dissolution and improve performance of high voltage cathodes.

- Novel electrolyte formulations can improve the cycling performance of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathodes at high voltage (4.9 V vs Li).
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