Diagnostic Analysis of Lithium-Ion Cells

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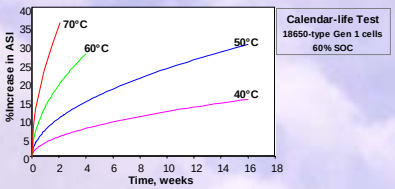
Introduction

Hybrid electric vehicles need long-life high-power batteries as energy storage devices. Batteries based on lithium-ion technology can meet the high-power requirements but have been unable to meet the 15-year calendar life goal.

The goal of the diagnostic analysis effort is to determine causes that limit the calendar and cycle life of high-power lithium-ion cells.

Challenge

The high-power lithium-ion cells contain $LiNi_xCo_yAl_zO_2$-based cathodes, graphite-based anodes, and $LiPF_6$-based electrolytes. These cells show a loss of capacity and a rise in area-specific impedance (ASI) during accelerated testing at elevated temperatures.



The electrochemical performance of electrodes harvested from these cells are being studied to identify the sources of this loss. The electrolyte, separator and electrode materials are being examined by spectroscopy, microscopy and diffraction techniques to delineate fundamental mechanisms that are responsible for degradation of cell performance. Identifying and optimizing components responsible for cell degradation should enable the development of long-life high-power lithium-ion cells.

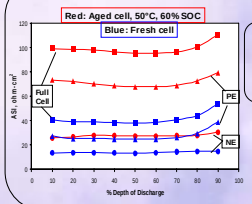
Argonne's Approach

Tested cells are disassembled and cell components examined to determine sources of impedance rise

1. 18650 cell
2. Puncturing fixture for gas analysis
3. Electrolyte extraction
4. Electrodes/separator removal
5. Disassembled electrodes/separator

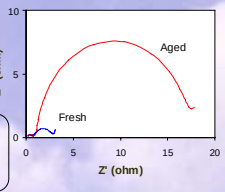
- Gas chromatography identifies and quantifies gases generated during testing.
- High-performance liquid chromatography quantifies electrolyte changes.
- AC impedance and other electrochemical techniques quantify changes in electrode material characteristics.
- X-ray photoelectron spectroscopy (XPS) and other surface analysis techniques characterize films formed on electrode materials.
- Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and electron energy loss spectroscopy (EELS) determine changes in composition and crystal structure of electrode materials.

The Positive Electrode is the Main Contributor to Cell Power Fade

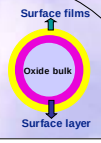


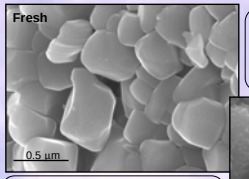
High-current pulse-charging and -discharging measurements in a cell with a Li-Sn reference electrode have determined that the main contribution to cell impedance increase is from the positive electrode.

AC impedance data on symmetric cells have shown that an increase in charge-transfer resistance at the positive electrode-electrolyte interface is primarily responsible for the impedance increase.

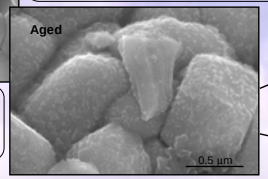


Surface films (from electrode-electrolyte interactions) and surface layers on oxide particles cause positive electrode impedance rise

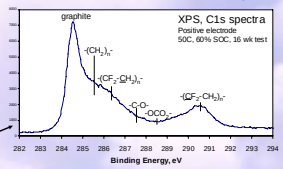


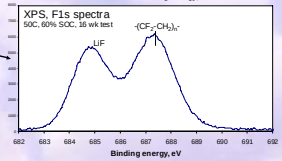


Surface films (identified by XPS) on the oxide particles contain polymeric compounds, LiF, Li_xPF_y- and Li_xPO_y-type compounds. Surface film compositions do not change, but surface film thickness appears to increase during aging.



SEM images show surface films on the oxide particles that result from electrode-electrolyte interactions during aging.

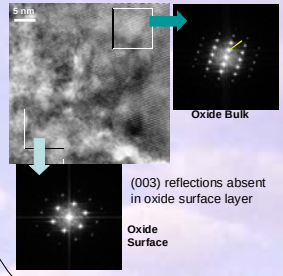




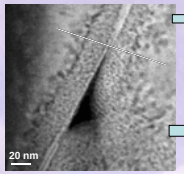
TEM-EELS data

A $Li_xNi_{1-x}O$-type surface layer, ~2-4 nm thick, is observed on the $LiNi_{0.8}Co_{0.2}O_2$ powder.

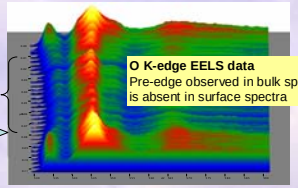
The thickness of this surface layer appears to increase on aging (~35 nm thick on oxide particles from a cell that showed 45% power fade). Initial data suggest that composition and crystal structure of this surface layer are also altered on aging.



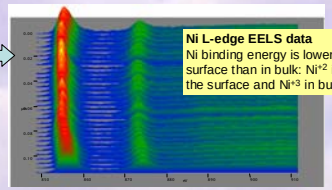
(003) reflections absent in oxide surface layer



Area selected for EELS study
Annular DF image
60°C, 60% state-of-charge cycle life sample



O K-edge EELS data
Pre-edge observed in bulk spectra is absent in surface spectra



Ni L-edge EELS data
Ni binding energy is lower in surface than in bulk: Ni^{+2} is in the surface and Ni^{+3} in bulk.

Conclusions

The positive electrode is the dominant contributor to impedance rise observed during accelerated aging of high-power lithium ion cells. This impedance rise is apparently caused by (a) composition changes in surface films present on the oxide particles, and (b) surface structure changes produced by oxygen loss from the oxide. Cell capacity loss results from (a) decrease in cyclable lithium resulting from processes that include the growth of the graphite solid electrolyte interface layer, and (b) reduction in rate capability for the cell caused by the increasing impedance at the positive electrode.

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FreedomCAR

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