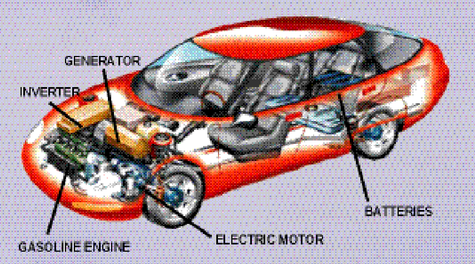
Diagnosis of Power Fade Mechanisms in High-Power Lithium-Ion Cells

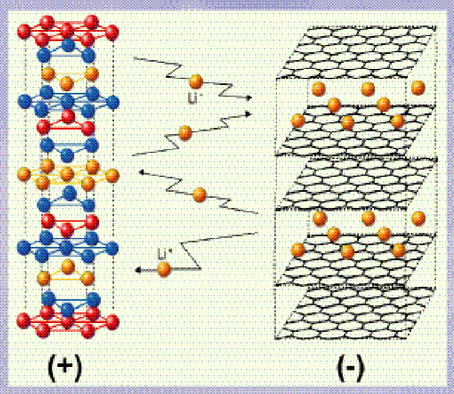
Intro

Program Goals

- Hybrid electric vehicles (HEV) need long-lived, high-power batteries as energy storage devices. Batteries based on lithium-ion cell technology can meet the high-power requirements but have been unable to meet HEV calendar-life requirements (15-year life).
- The goal of the diagnostic effort is to determine causes that limit the calendar and cycle life of high-power lithium-ion cells.

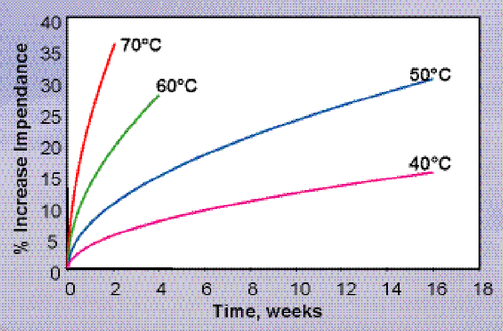


Generation 1 cells contain $LiNi_{0.8}Co_{0.2}O_2$ (+) and Graphite (-)



- During cell charging, lithium ions are extracted from $LiNi_{0.8}Co_{0.2}O_2$ and inserted into the graphite; the reverse reaction occurs during cell discharge.

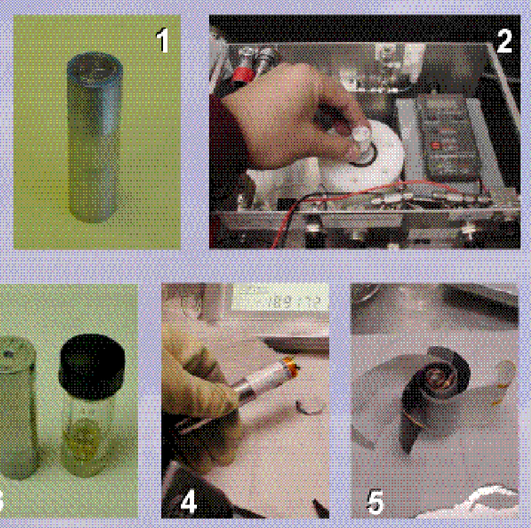
Cell Impedance Increases During Accelerated Testing



- Lithium-ion cells subjected to accelerated calendar-life and cycle-life tests display varying degrees of capacity and power fade.
- Test data extrapolation indicates that cell life will be less than 1 year under normal conditions.

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

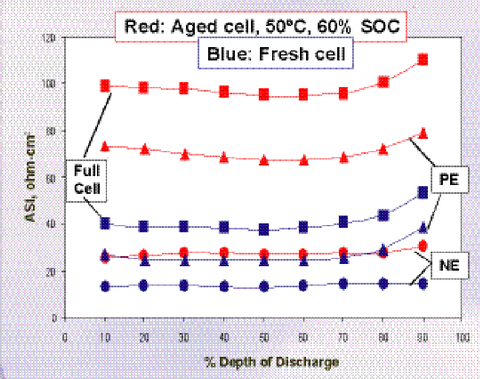
1. 18650 cell
2. Puncturing fixture for gas analysis
3. Electrolyte extraction
4. Electrodes/separator removal
5. Disassembled electrodes/separator



- 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.

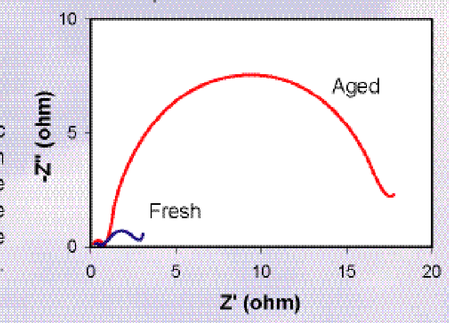
Results

The Positive Electrode is the Main Contributor to Cell Power Fade

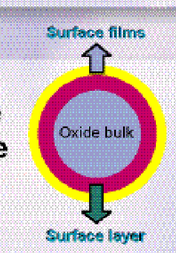


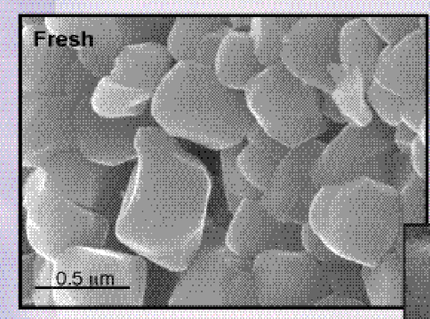
High-current pulse-charging and -discharging measurements (with Li-Sn reference electrode) have determined that the main contribution to cell impedance increase is from the positive electrode.

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.

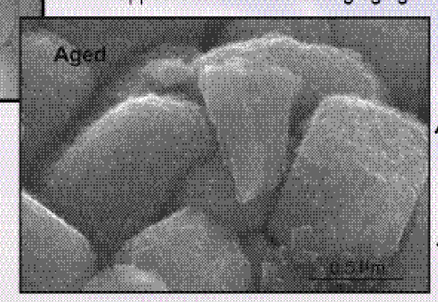


Surface films from electrode-electrolyte interactions and surface layers on oxide particles cause positive electrode impedance rise

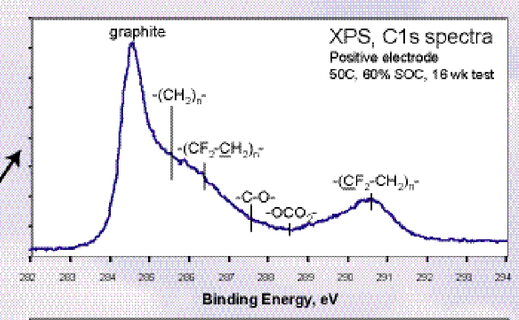


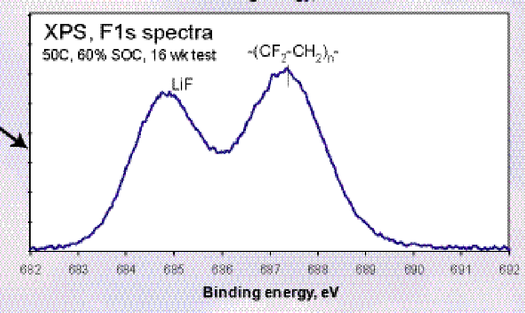


SEM images show surface films on the oxide particles that result from electrode-electrolyte interactions during aging.



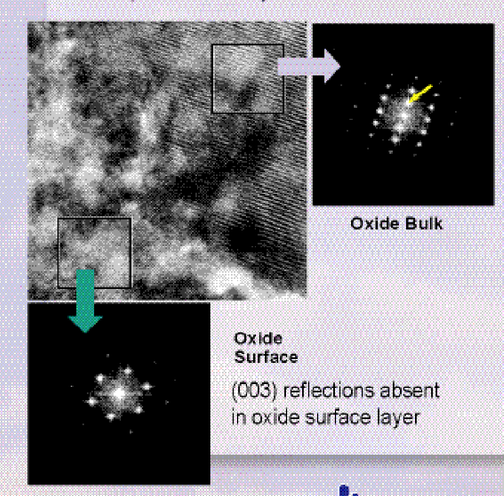
Surface films (identified by XPS) on the oxide particles contain polymeric compounds, LiF, Li_xPF_y- and Li_xPO_y-type compounds. Surface film compositions do not change, but surface film thickness appears to increase during aging.



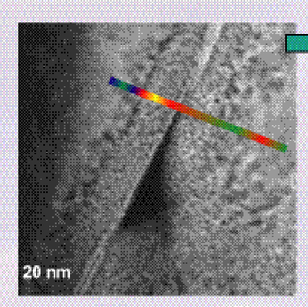


TEM-EELS data

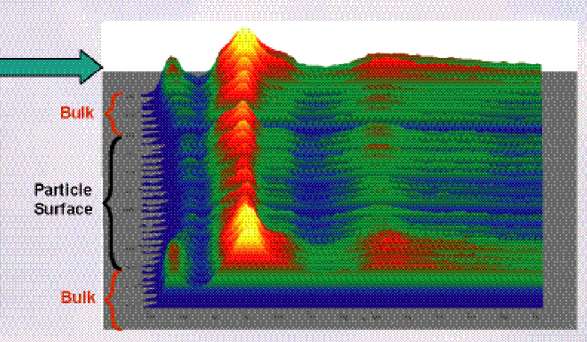
- A $Li_xNi_{1-x}O$-type surface layer, ~2-4 nm thick, is observed on the raw $LiNi_{0.8}Co_{0.2}O_2$.
- The thickness of this surface layer appears to increase on aging (~35 nm thick on oxide particles from a cell that showed 45% power fade). Initial data suggest that composition and crystal structure of this surface layer are also altered on aging.



(003) reflections absent in oxide surface layer

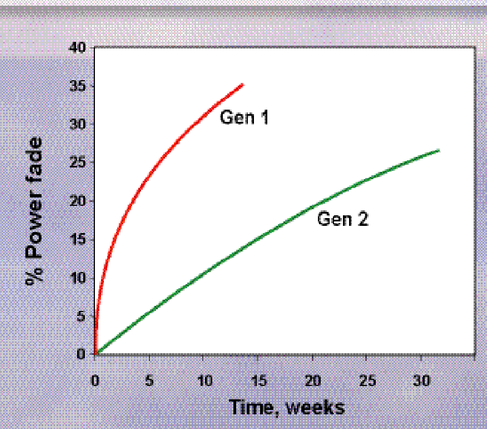


Area selected for EELS study
Annular DF image
60°C, 60% SOC cycle life sample



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

Current Work

Generation 2 cells show significantly lower rate of power fade

- Oxide stability was enhanced by replacing $LiNi_{0.8}Co_{0.2}O_2$ with $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ in Gen 2 cells.
- Capacity and power fade mechanisms in these cells are being studied.