Factors Governing Life of High-Energy Lithium-Ion Cells

D.P. Abraham

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Diagnostics Overview

- Use of characterization tools (electrochemical, physicochemical, mechanical, acoustic) to explain the electrochemical behavior of materials, electrodes, and cells
  - Every part of the cell is examined – electrodes (active and inactive components in coating, current collector, tabs), electrolyte, separator, etc.

- To identify constituents and mechanisms responsible for cell performance and performance degradation
  - To recommend solutions that improve performance and minimize performance degradation of materials, electrodes, and cells
Electrochemical couples examined

<table>
<thead>
<tr>
<th></th>
<th>Chemical Composition</th>
<th>Technology</th>
<th>Energy Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATD-1</td>
<td>LiNi$<em>{0.8}$Co$</em>{0.2}$O$_2$/MCMB-6 graphite</td>
<td>HEV</td>
<td></td>
</tr>
<tr>
<td>ATD-2</td>
<td>LiNi$<em>{0.8}$Co$</em>{0.15}$Al$<em>{0.05}$(Al$</em>{0.1}$)O$_2$/Mag-10 graphite</td>
<td>HEV</td>
<td>150 Wh/kg</td>
</tr>
<tr>
<td>ATD-3</td>
<td>Li$<em>{1.04}$Ni$</em>{1/3}$Mn$<em>{1/3}$Co$</em>{1/3}$O$_2$/MCMB-10 graphite</td>
<td>HEV</td>
<td></td>
</tr>
<tr>
<td>ABR-1</td>
<td>Li$<em>{1.2}$Ni$</em>{0.15}$Mn$<em>{0.55}$Co$</em>{0.1}$O$_2$/A-12 graphite</td>
<td>PHEV</td>
<td>300 Wh/kg</td>
</tr>
</tbody>
</table>

EC:EMC (3:7 by wt.) + 1.2M LiPF$_6$ electrolyte

$0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.375}\text{Mn}_{0.375}\text{Co}_{0.25}\text{O}_2$

Integration and interconnection of LiMO$_2$-like (rhombohedral) and Li$_2$MnO$_3$ (monoclinic) structures at atomic level
LiMO₂ (M=Ni, Co, Al) Crystal Structure

Li atoms enter and exit through edge planes (2-D motion)

Z-contrast STEM images that show Li ordering in TM planes of Li₂MnO₃

Li₂MnO₃ = Li(Li₁/₃Mn₂/₃)O₂

D.P. Abraham, Advanced Materials 22 (2010) 1122-1127
Electronic conductivity of ABR-1 oxide powder is more than 3 orders of magnitude lower than that of NCA, and about 2 orders of magnitude lower than that of NMC.

Electrode preparation with HE5050 oxide powder is expected to be more challenging than that for NCA and NMC333 oxide powders.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCA</td>
<td>LiNi$<em>{0.8}$Co$</em>{0.15}$Al$_{0.05}$O$_2$</td>
</tr>
<tr>
<td>NMC333</td>
<td>Li$<em>{1.04}$Ni$</em>{1/3}$Mn$<em>{1/3}$Co$</em>{1/3}$O$_2$</td>
</tr>
<tr>
<td>NMC992</td>
<td>Li$<em>{1+x}$Ni$</em>{0.45}$Mn$<em>{0.45}$Co$</em>{0.1}$O$_2$</td>
</tr>
<tr>
<td>HE5050</td>
<td>Li$<em>{1.2}$Ni$</em>{0.15}$Mn$<em>{0.55}$Co$</em>{0.1}$O$_2$</td>
</tr>
</tbody>
</table>
# Chemistry of ABR-1 cells

<table>
<thead>
<tr>
<th>ABR-1S(+)</th>
<th>ABR-1S(-)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Positive Electrode:</strong></td>
<td><strong>Negative Electrode:</strong></td>
</tr>
<tr>
<td>86%wt Li$<em>{1.2}$Ni$</em>{0.15}$Mn$<em>{0.55}$Co$</em>{0.1}$O$_2$</td>
<td>89.8 %wt ConocoPhillips A12 graphite</td>
</tr>
<tr>
<td>8%wt Solvay 5130 PVDF binder</td>
<td>6%wt KF-9300 Kureha PVDF binder</td>
</tr>
<tr>
<td>4%wt Timcal SFG-6 graphite</td>
<td>4 %wt Timcal Super P</td>
</tr>
<tr>
<td>2%wt Timcal Super P</td>
<td>0.17 %wt Oxalic Acid</td>
</tr>
<tr>
<td>6.64 mg/cm$^2$ active-material loading density</td>
<td>5.61 mg/cm$^2$ active-material loading density</td>
</tr>
<tr>
<td>37.1% electrode porosity</td>
<td>26% electrode porosity</td>
</tr>
<tr>
<td>35-µm-thick coating</td>
<td>40-µm-thick coating</td>
</tr>
<tr>
<td>15-µm-thick Al current collector</td>
<td>10-µm-thick Cu current collector</td>
</tr>
</tbody>
</table>

$\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2 = 0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.375}\text{Mn}_{0.375}\text{Co}_{0.25}\text{O}_2$

- Oxide primary particles consist of randomly oriented plate-like grains
- A12 graphite particles, potato-shaped morphology; surface-treated
Identifying sources of performance degradation is the first step to designing long-life cells

- **Significant impedance rise during cell cycling/aging**
  - Arises mainly from the positive electrode

- **Significant capacity fade during cell cycling/aging**
  - Originates at the positive electrode
  - Manifests itself at the negative electrode – thick negative electrode SEI

- **Voltage profile changes observed during cell cycling/aging**
  - Arises from crystal structure changes
Positive electrode has to be cycled over a wider voltage window to obtain higher capacities.

NCA(+) / Gr(-) cells yield a discharge capacity of 165 mAh/g (3-4.1V).
NMC333(+) / Gr(-) cells yield a discharge capacity of 140 mAh/g (3-4.1V).

Cells show capacity loss on aging
After 30° cycling in the 2.5-4.4V voltage window - up to 1500 cycles

Performance degradation is faster at higher upper-cutoff voltages, at higher temperatures, and for wider voltage windows

Cells show impedance rise on aging
After 30° cycling in the 2.5-4.4V voltage window - up to 1500 cycles

Mid-frequency arc increases when the UCV is higher (4.6V for example)
Capacity data obtained at high rates is strongly affected by cell impedance

Full cell impedance increase is mainly from the positive electrode

The positive electrode impedance rise arises from the oxide-carbon (high-frequency arc) and oxide-electrolyte (mid-frequency arc) interfaces.

Data from harvested electrodes (vs. Li) shows that positive electrode contribution to “true” capacity fade is small.

The “small” capacity loss could be due to oxide particle isolation that may result from loss of electronic connectivity (loss of oxide-carbon contact) or ionic connectivity (particle surface films or surface structure changes).

Data from harvested negative electrodes (vs. Li) shows that the graphite bulk is not damaged by cycling/aging.

The small capacity loss could be due to active particle isolation that may result from thick SEI films.

Cells containing the Li$_4$Ti$_5$O$_{12}$(-) electrodes (coupled with the baseline positive electrode) show negligible capacity fade on cycling: 0.75–3.15V, 30°C

These data confirm that the graphite-based negative electrode is the main contributor to capacity fade in our baseline cells.

SEI formation/dissolution/reformation reactions during cell cycling results in Li trapping

Transition metals (Mn, Ni, Co) from the oxide(+) electrode accumulate at the graphite(-) electrode and are believed to accelerate capacity fade

Positive and Negative Electrodes were reconstituted by altering oxide/carbon/binder ratios and calendaring conditions

<table>
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<tr>
<th>Electrodes were prepared at CFF in 2012</th>
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<tbody>
<tr>
<td><strong>L7(C45+)</strong></td>
<td><strong>A002 (CFF)</strong></td>
</tr>
<tr>
<td><strong>Positive Electrode:</strong></td>
<td><strong>Negative Electrode:</strong></td>
</tr>
<tr>
<td>92 wt% Li$<em>{1.2}$Ni$</em>{0.15}$Mn$<em>{0.55}$Co$</em>{0.1}$O$_2$ (HE5050)</td>
<td>91.8 %wt ConocoPhillips: CGP-A12 graphite</td>
</tr>
<tr>
<td>4 wt% Solvay 5130 PVDF binder</td>
<td>6%wt KF-9300 Kureha PVDF binder</td>
</tr>
<tr>
<td>4 wt% Timcal C45</td>
<td>2 %wt Timcal C45</td>
</tr>
<tr>
<td>5.89 mg/cm$^2$ active-material loading density</td>
<td>5.16 mg/cm$^2$ A12 graphite loading density</td>
</tr>
<tr>
<td>36.1% electrode porosity</td>
<td>38.8% electrode porosity</td>
</tr>
<tr>
<td>26-µm-thick coating</td>
<td>43-µm-thick coating</td>
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<td>20-µm-thick Al current collector</td>
<td>10-µm-thick Cu current collector</td>
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- **Only 4wt% carbons and 4 wt% binder**
- **Only 2 wt% carbons**

Electrolyte: EC:EMC (3:7 by wt.) + 1.2M LiPF$_6$
Separator: Celgard 2325

B. Polzin, S. Trask, A. Jansen, Argonne
By modifying electrode constitution and by using electrode additives we can dramatically reduce cell impedance rise.

Cell impedance rise is reduced by an order of magnitude (relative to baseline cell chemistry)

Full Cell: L7(C45)+/A002-
2.5–4.4V, 30° C
~C/2, 1000 cycles

2 wt% LiDFOB added to baseline electrolyte

Related to information from previous slide
XPS data show that LiDFOB generates surface films on the positive electrode that inhibits cell impedance rise.

Our data indicate that LiDFOB also reduces on the graphite negative electrode, enhances the negative electrode SEI, and inhibits cell capacity fade.

Alumina-coating of positive electrode and/or alumina addition to positive electrode improves cell capacity retention

Alumina reduces dissolution of Mn, Ni, and Co from the positive electrode by acting as a HF-getter. Incorporation of Al-bearing species may further help stabilize the SEI.

Ref: Bettge et al., J. Power Sources 233 (2013) 346
Positive electrode potential “fades” on cycling

- Voltage Fade – not a kinetic phenomenon
- Voltage Fade (VF) is non-uniform
- VF on charge is greater than that on discharge

Voltage fade is accelerated by higher temperature/upper cutoff voltage
Voltage profile changes on cycling caused by intermixing of Li and TM atoms

Li-Mn ordering in TM planes results in Li$_2$MnO$_3$-like and LiCoO$_2$-like areas

Periodic intensity in Li layers is characteristic of spinel structure
Approaches to designing long-life cells

- **Significant impedance rise during cell cycling/aging**
  - Can be reduced by reformulating positive electrode constitution, modifying oxide surface through coatings (pre-treatment), using electrolyte additives (in-situ), and by altering the cycling window.

- **Significant capacity fade during cell cycling/aging**
  - Can be minimized by “fixing problems at the positive electrode”, such as transition metal dissolution from the oxide.

- **Voltage profile changes observed during cell cycling/aging**
  - Solutions may include oxide surface modification, alternative synthesis techniques, oxide composition modification.
Acknowledgements

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- Argonne colleagues

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