Performance and Safety Evaluations of Moli Spinel Lithium-ion Cells

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Introduction

- LiMn$_2$O$_4$ is a spinel oxide.
- Co and Ni are more expensive and toxic than Mn.
- Performance of the LiMO$_2$ is influenced strongly by the ordering of the Li$^+$ and M$^{3+}$ ions.
- Cation disordering is a major drawback in LiCoO$_2$ cathodes. Presence of Co in the Li planes leads to the extraction of Co into the solution leading to higher levels of cell failure.
- However, LiMn$_2$O$_4$ exhibits capacity fading. Due to the Jahn-Teller distortion associated with the Mn$^{3+}$ ions.
Electrode Potential Ranges of Lithium Insertion Compounds

Voltage (V) vs. Insertion Compounds:
- $\text{Li}_x\text{CoO}_2$
- $\text{Li}_x\text{NiO}_2$
- $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$
- $\text{Li}_x\text{Fe}_2(\text{SO}_4)_3$
- $\text{Li}_x\text{MnO}_2$
- $\text{Li}_x\text{TiS}_2$
- $\text{Li}_x\text{WO}_2$
- $\text{Li}_x\text{MoO}_2$
- $\text{Li}_x\text{Graphite}$
- $\text{Li}_x\text{Coke}$
- $\text{Li Metal}$
- $\text{LiAl}$
LAYEROED (2-D) LiMO$_2$ (M = Co, Ni)
SPINEL (3-D) LiMn$_2$O$_4$
Physical and Electrochemical Characteristics

Physical Characteristics:
Diameter: 18 mm
Height: 65 mm
Weight: 41.8 g

Electrochemical Characteristics:
OCV: 3.88 V (as recd.)
CCV: 3.5 V
Capacity: 1.27 Ah (1.4 Ah)
Typical Discharge Profiles for the Moli Spinel 18650 Cell

Figure A1.2 - Voltage vs. Discharge Capacity of Moli Spinel 18650 Li-ion Cell
For 1 C Rate Charge to 4.2V with Taper to 50mA and -1C Rate Discharge to 3.0V

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Typical Discharge Profiles for the Moli Spinel 18650 Cell

Figure A3.2 - Voltage vs. Discharge Capacity of Moli Spinel 18650 Li-Ion Cell
For 1C Rate Charge to 4.2V with Taper to 50mA and 0.25C Rate Discharge to 3.0V

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## Summary of Rate Capability Tests

<table>
<thead>
<tr>
<th>Charge/Discharge Rate</th>
<th>Capacity 5\textsuperscript{th} Cycle [Ah]</th>
<th>Capacity 200\textsuperscript{th} Cycle [Ah]</th>
<th>Capacity Change [Ah]</th>
<th>% Capacity Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>1C/1C</td>
<td>1.071</td>
<td>1.023</td>
<td>-0.048</td>
<td>4.5 %</td>
</tr>
<tr>
<td>1C/0.5 C</td>
<td>1.173</td>
<td>1.117</td>
<td>-0.056</td>
<td>4.8 %</td>
</tr>
<tr>
<td>1C/0.25 C</td>
<td>1.202</td>
<td>1.154</td>
<td>-0.048</td>
<td>4.0 %</td>
</tr>
<tr>
<td>0.5 C/1C</td>
<td>1.044</td>
<td>1.034</td>
<td>-0.010</td>
<td>0.95 %</td>
</tr>
<tr>
<td>0.5 C/0.5 C</td>
<td>1.156</td>
<td>1.117</td>
<td>-0.039</td>
<td>3.4 %</td>
</tr>
<tr>
<td>0.5 C/0.25 C</td>
<td>1.188</td>
<td>1.134</td>
<td>-0.054</td>
<td>4.5 %</td>
</tr>
<tr>
<td>0.25 C/1 C</td>
<td>1.049</td>
<td>1.046</td>
<td>-0.003</td>
<td>0.3 %</td>
</tr>
<tr>
<td>0.25 C/0.5 C</td>
<td>1.187</td>
<td>1.097</td>
<td>-0.090</td>
<td>7.6 %</td>
</tr>
<tr>
<td>0.25 C/0.25 C</td>
<td>1.191</td>
<td>1.108</td>
<td>-0.083</td>
<td>6.9 %</td>
</tr>
</tbody>
</table>
Internal Resistance vs SOC for the Moli Spinel 18650 Li-ion Cells

Figure 3 - Effective Internal Resistance of Moli 18650 Li-Ion Cells
Performance of the Moli Spinel 18650 Li-ion Cells at Different Temperatures

Figure 7 - Voltage vs. Discharge Capacity Curves of Moli 18650 Li-Ion Cells
For 0.5C Rate Charge at +25°C and -0.5C Rate Discharge at Different Temperatures

- $R_e$: 0 °C: 0.079 ohm
- 25 °C: 0.083 ohm
- 45 °C: 0.117 ohm
- 65 °C: 0.264 ohm

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Abuse Tests
Fast Charge Test of the Moli Spinel 18650 Cells

3C charge to 4.2 V with current taper/discharge with 0.5 C rate to 2.7 V
Overvoltage Test on the Moli Spinel 18650 Cells

CID activation (0.7 Ah charge rate)

Voltage (V) and Current (A)

Temperature (°C)

Test Time (Hr)
Overcharge of the Moli Spinel Cells to 12 V for 50 minutes

1C charge rate; CID activation in 15 minutes; Max temp: 57 °C
Overcharge to 12 V on the Moli Spinel Cells

- Charge with C/5 current to 12 V for 50 minutes
  No occurrences; max temp: 37 °C
- Charge with C/2 current to 12 V for 50 minutes
  CID activation occurred at approximately 30 minutes; max temp: 43 °C
- Charge with 2 C current to 12 V for 50 minutes
  CID activation occurred in 7 minutes; max temp. 78 °C
Fast Rate Discharge Test on the Moli Spinel 18650 Cells

3C current discharge to 2.7 V; cap: 0.9 Ah; max temp. 50 °C

![Graph showing voltage, current, and temperature over time.](image-url)

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Overdischarge into Reversal Test of the Moli Spinel 18650 Li-ion Cells
Discharge: 0.5 C; max temp: 29 ºC
Overdischarge into Reversal on the Moli Spinel 18650 Li-ion Cells

- Discharge current: 1C; max temp: 40 ºC
- Discharge current: 2C; max temp: 50 ºC
External Short Circuit Test on the Moli Spinel 18650 Cells

0.01 ohm load; 8.2 A current spike; max temp: 31 °C
External Short Circuit Test on Moli Spinel 18650 li-ion Cells

• 0.05 ohm load; 5.8 A current spike, max temp: 35 °C

• 0.01 ohm load to cells charged to 50 % SOC; 8 A current spike; no significant changes in temp.
Simulated Internal Short/Crush Test on the Moli Spinel 18650 Li-ion Cells

Fully charged cells: max temp: 77 ºC (electrolyte leakage; no venting or fire)
50 % charged cells: max temp: 57 ºC (no venting or fire)
Heat-to-vent Test on the Moli Spinel 18650 Li-ion Cells

100 % charged cells: Onset of thermal runaway: 217 °C; max temp 424 °C
Heat-to-vent Test on the Moli Spinel
18650 Li-ion Cells

50 % charged cells: Voltage drop at 168 °C; max temp 287 °C; no rapid increase in temp.
Vibration of Moli Spinel 18650 li-ion cells

20 to 80 Hz + 3 db/oct
80 to 350 Hz 0.1 g2/Hz
350 to 2000 Hz - 3 db/oct

15 minutes in each independent axis.

No change in capacity on subsequent cycling of the cells.
Drop Test on the Moli Spinel 18650 Li-ion Cells

Drop from 6 ft. Cells gained 11 % capacity after the drop.
Vent and Burst Pressure Test on Moli Spinel Li-ion Cells

Vent Pressure: 250 psi-300 psi
Burst Pressure: 1650 psi
Conclusions

• Moli spinel cells show similar performance under the rate protocols tested.
• The $R_e$ for the cells varies between 100 and 120 mohms for the cells.
• The overcharge on the cells shows that the cells do not perform well under fast charge conditions.
• Under conditions of high rate overcharge, the CID gets activated faster than under low charge rates.
• The fast rate discharge shows that the cells can tolerate it.
• The overdischarge into reversal tests show that the cells die benignly.
Conclusions

• The current spike obtained during the hard external short test is small (8.2 A) compared to those obtained from a LiCoO$_2$ system (60 to 80 A).
• The simulated internal short did not result in an explosion or fire as it does with the LiCoO$_2$ systems.
• The temperatures obtained during the heat-to-vent test are not very high compared to the cobaltate cells.
• The cells do not retain capacity very well, but the capacity can be recovered with cycling.
• The spinel cells are much safer under abuse conditions than the lithium-ion cells with other transition metal oxides.
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