Li-CF$_x$/MnO$_2$ Hybrid D-cell with Wide Operating Temperature Range for Military Batteries

Xinrong (Ron) Wang and David Modeen
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- Phase I D-Cell Performance
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Introduction

Design, Manufacture, Install & Maintain Power and Communications Systems

- Battery & Energy Products
- Communications Systems

Government, Defense & Commercial Markets

Ultralife Batteries, ABLE McDowell, RedBlack, AMTI

Headquarters in Newark, NY
Sales & Operations in US, Europe and Asia
Objective

- Develop Li-CF$_x$/MnO$_2$ Hybrid D-cells into Different Formats of Military Batteries

Goal:
1) High Capacity
2) High Power
3) Light Weight (High Energy Density)
4) Wide Operating Temperature Range
5) Long Shelf Life
6) Cost Effective
7) Safe (Robust)
Objective

D-cell in BAxx90 Battery

BA5590: 200 Wh, 2.2 lbs, Li-SO$_2$
BA5390: 300 Wh, 2.9 lbs, Li-MnO$_2$

Target:
1) 400 Wh, 2.2 lbs in same footprint
2) 200 Wh, 1.1 lbs in half size
   400 Wh/kg
# Chemistry Comparison

## Comparison of D-cells with Different Chemistries

<table>
<thead>
<tr>
<th>Lithium – Cathode Chemistry System</th>
<th>Theoretical specific capacity (mAh/g)</th>
<th>Safety Concern</th>
<th>Specific power (W/kg)</th>
<th>2A Discharge Capacity (Ah)</th>
<th>Voltage Delay</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF&lt;sub&gt;x&lt;/sub&gt;</td>
<td>864</td>
<td>Safe</td>
<td>~15</td>
<td>15.5; 16.8</td>
<td>Yes</td>
<td>Very High</td>
</tr>
<tr>
<td>SOCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>480</td>
<td>Yes</td>
<td>140</td>
<td>7.0</td>
<td>Yes</td>
<td>Medium</td>
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<tr>
<td>SO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>418</td>
<td>Yes</td>
<td>680</td>
<td>7.5</td>
<td>Yes</td>
<td>Low</td>
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<tr>
<td>MnO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>308</td>
<td>Safe</td>
<td>300</td>
<td>10.5, 13</td>
<td>No</td>
<td>Low</td>
</tr>
<tr>
<td>CF&lt;sub&gt;x&lt;/sub&gt;/MnO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>308~864</td>
<td>Safe</td>
<td>15~300</td>
<td>≥ 15</td>
<td>No</td>
<td>Medium</td>
</tr>
</tbody>
</table>
Design of Li-CF$_x$ / MnO$_2$ Hybrid Chemistry

Hybrid Advantages

- Flexibility of cell design
- Lower self-discharge rate
- Higher energy density
- Lower overall thermal signature
- Without voltage delay at LT
- Relatively low cost
Design Considerations

1) D-cell (34605)
2) Anode limited design
3) Cathode hybrid structure of CF$_{x}$ and MnO$_{2}$
4) Thermal shutdown separator
5) Common components of UBI existing Li-MnO$_{2}$ production D-cell
Phase I Li-CF$_x$/MnO$_2$ Hybrid D-cell

Goal was: Operating T range: -30°C to +55°C

1) Different anode

2) Different cathode with hybrid mixture of CF$_x$ and MnO$_2$

3) All other parts as same as existing Ultralife Li-MnO$_2$ D-cell
   - Shutdown separator
   - Electrolyte
   - Cell enclosure
Phase I D-Cell Performance

Phase I Li-CFₓ/MnO₂ hybrid D-cell discharge under 250mA constant current at 23°C, 55°C, -10°C and -30°C

Capacity to 2V cutoff
- 23°C: 16.06 Ah
- 55°C: 15.89 Ah
- -10°C: 15.11 Ah
- -30°C: 11.30 Ah

Li-MnO₂:
- 23°C: 11.20 Ah
- -30°C: 5.90 Ah
Phase I D-Cell Performance

Phase I Li-CFₓ/MnO₂ hybrid D-cell discharge under 2 A constant current at 23°C, 55°C, -10°C and -30°C

Capacity to 2V cutoff
- 23°C: 15.50 Ah
- 55°C: 15.20 Ah
- -10°C: 13.23 Ah
- -30°C: 1.85 Ah

Li-MnO₂:
- 23°C: 10.51 Ah
- -30°C: 2.63 Ah
# Phase I D-Cell Safety Performance

<table>
<thead>
<tr>
<th>No</th>
<th>Name</th>
<th>Description</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>UNTR-T1</td>
<td>Altitude</td>
<td>Pass</td>
</tr>
<tr>
<td>2</td>
<td>UNTR-T2</td>
<td>Thermal Test</td>
<td>Pass</td>
</tr>
<tr>
<td>3</td>
<td>UNTR-T3</td>
<td>Vibration</td>
<td>Pass</td>
</tr>
<tr>
<td>4</td>
<td>UNTR-T4</td>
<td>Shock</td>
<td>Pass</td>
</tr>
<tr>
<td>5</td>
<td>UNTR-T5</td>
<td>External Short Circuit</td>
<td>Pass</td>
</tr>
<tr>
<td>6</td>
<td>UNTR-T6</td>
<td>Impact</td>
<td>Pass</td>
</tr>
<tr>
<td>7</td>
<td>UNTR-T8</td>
<td>Forced Discharge</td>
<td>Pass</td>
</tr>
<tr>
<td>8</td>
<td>UL</td>
<td>Crush</td>
<td>Pass</td>
</tr>
<tr>
<td>9</td>
<td>SAR</td>
<td>Nail Penetration</td>
<td>Pass</td>
</tr>
</tbody>
</table>
Phase II Li-CF$_x$/MnO$_2$ Hybrid D-cell

Goal was: Operating T range: -40°C to +100°C

Worked on engineering for

1) Anode

2) Cathode using hybrid mixture of CF$_x$ and MnO$_2$
   with different particle size

3) Electrolyte

4) Separator
Phase II D-Cell Performance

Phase II Li-CFₓ/MnO₂ hybrid D-cell discharge under 250mA constant current at 72°C, 55°C, 23°C, -10°C, -30°C and -40°C

Capacity to 2V cutoff

23°C: 16.05 Ah
55°C: 15.57 Ah
72°C: 15.67 Ah
-10°C: 15.13 Ah
-30°C: 12.16 Ah
-40°C: 8.15 Ah
Phase II D-Cell Performance

Phase II Li-CFₓ/MnO₂ hybrid D-cell discharge under 2 A constant current at 72°C, 55°C, 23°C, -10°C, -30°C and -40°C

Capacity to 2V cutoff

- 23°C: 15.13 Ah
- 55°C: 15.36 Ah
- 72°C: 12.66 Ah
- -10°C: 13.66 Ah
- -30°C: 9.80 Ah
- -40°C: 0.59 Ah
Phase II D-Cell Performance

Phase II Li-CF$_x$/MnO$_2$ hybrid D-cell discharge under 250mA constant current at 95°C

2V Cutoff
Capacity: 14.92 Ah
Energy: 43.59 Wh
Max. Skin T: 96.8°C
## Phase II D-Cell Safety Performance

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<td>Thermal Test</td>
<td>Pass</td>
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</tbody>
</table>
Acceleration Testing for Shelf Life

Li-CFₓ/MnO₂ hybrid D-cells (Phase I) discharge 250 mA after storage 50 days or 100 days at different acceleration temperatures

<table>
<thead>
<tr>
<th>Equivalent storage terms at 23°C by that at acceleration temperatures</th>
<th>Capacity to 2V cutoff (Ah)</th>
<th>Percentage of capacity remain</th>
<th>Self-discharge rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 days at 23°C</td>
<td>15.44</td>
<td>100%</td>
<td>0</td>
</tr>
<tr>
<td>5 years at 23°C</td>
<td>15.32</td>
<td>99%</td>
<td>0.4%/year</td>
</tr>
<tr>
<td>10 years at 23°C</td>
<td>14.45</td>
<td>94%</td>
<td>0.6%/year</td>
</tr>
<tr>
<td>20 years at 23°C</td>
<td>14.15</td>
<td>92%</td>
<td>0.4%/year</td>
</tr>
</tbody>
</table>

Initial Shelf Life Testing

92% of capacity remains for 20 years by acceleration testing
Summary

Li-CF$_x$/MnO$_2$ Hybrid D-cell

- 15 Ah under 2A constant discharge for both Phase I & Phase II
- Specific energy density increases 47% more than Li-MnO$_2$ D-cell
- Pass UNTR and other SAR tests for both Phase I & Phase II
- Phase I has operating temperature range from -30°C to 55°C
- Phase II has operating temperature range from -40°C to 72°C
- Initial shelf life tests indicate up to 20 years with 92% capacity remain
- Ready to be used for different formats of military batteries, such as xx47, half size xx90, full size xx90 and large size xx90, some in progress
Acknowledgement

Li-CF\textsubscript{x}/MnO\textsubscript{2} Hybrid D-cell Development Is Also Under Support of Contract W15P7T-05-D-C002/002 With US Army CERDEC

- Special Thanks to Mr. Michael Brundage & Mr. Chris Hurley of US Army RDECOM
Thank You for Your Attention