Long Life, High Energy Silver/Zinc Batteries

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NASA Aerospace Workshop
Huntsville, AL
November 19, 2002
Presentation Outline

- Introduction to RBC Technologies

- Rechargeable Zinc Alkaline (RZA™) Systems
  - MnO₂/Zn
  - Ni/Zn
  - Ag/Zn
  - Zn/Air

- RZA Silver/Zinc Battery Developments
  - NASA Phase I and Phase II SBIR goals and results
  - Other silver/zinc opportunities
RBC Background

• Founded in 1989 to commercialize battery technology based on Ford discovery of rechargeable form of manganese-dioxide

• In 1999, RBC was awarded $3.8 million Advanced Technology Program by US Dept. of Commerce, NIST to accelerate RZA development

• Core competencies, rechargeable zinc, stable ion-blocking separator and cathode active materials

• In 2000, expanded RZA technology family to include nickel-zinc and silver-zinc

• RBC commercializes technologies through licensing and joint-venture agreements

www.rbctx.com
Facilities and Staff

- College Station, Texas facility encompasses 10,000 square feet
  - full development capabilities to support the design and processing of batteries and materials
  - 400 channels of computer controlled electrical testing stations

- Battery Industry Depth - Over 110 years of professional battery industry experience: R&D, Engineering, Applications, Manufacturing, Marketing
- Extensive Corporate relationships: Electronics OEMs, battery manufacturers, materials suppliers, universities, National laboratories, agencies
Commercialization Activity Focused on Two RZA Systems

<table>
<thead>
<tr>
<th>RZA System</th>
<th>Mn/Zn Manganese/Zinc</th>
<th>Ni/Zn Nickel/Zinc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positive electrode (cathode)</td>
<td>Bismuth-modified manganese-dioxide (BMD)</td>
<td>Nickel hydroxide</td>
</tr>
<tr>
<td>Specific energy (wh/kg)</td>
<td>70-90</td>
<td>50-75</td>
</tr>
<tr>
<td>Product Formats</td>
<td>Cylindrical AAA, AA, C and D, small (0.5 – 3 Ah) prismatic cells</td>
<td>15 Ah+ Ah prismatic cells and 12-volt batteries</td>
</tr>
<tr>
<td>Applications</td>
<td>Portable electronics, cameras, toys and games, radios and CD players, PDA’s</td>
<td>42-volt hybrid and electric vehicles, standby power.</td>
</tr>
</tbody>
</table>
Spiral Wound RZA Ni/Zn Battery

- Being developed with manufacturing partner
- Wide range of potential applications with performance/cost attributes intermediate between nickel-metal hydride and lead-acid batteries
- Higher cell voltage means fewer cells in series for a given battery voltage, (eg. 12 Volt battery uses 7 Ni/Zn cells vs 10 cells for either NiCd or NiMH)

### TABLE: COMPARISON OF D SIZE CELLS in 3 NICKEL ELECTROCHEMISTRIES

<table>
<thead>
<tr>
<th></th>
<th>NiCd</th>
<th>RZA NiZn</th>
<th>NiMH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity (ampere-hours)</td>
<td>4.6</td>
<td>5.0</td>
<td>6.5</td>
</tr>
<tr>
<td>Operating Voltage (Volts)</td>
<td>1.2</td>
<td>1.65</td>
<td>1.2</td>
</tr>
<tr>
<td>Weight (g)</td>
<td>139</td>
<td>139</td>
<td>170</td>
</tr>
<tr>
<td>Watt-hours per kg</td>
<td>40</td>
<td>59</td>
<td>46</td>
</tr>
<tr>
<td>Watt-hours per liter</td>
<td>106</td>
<td>158</td>
<td>150</td>
</tr>
</tbody>
</table>

- For a given energy content an RZA Ni/Zn battery can be lighter, smaller and lower cost than the other nickel chemistries.
RBC-Ni/Zn Technical Innovation

- Anode formulation for minimal shape change, no dendrites, 1,000 cycles.
- Advanced low cost separator designs for dendrite prevention
- Charging algorithms to facilitate maintenance-free operation
- Developed innovative processes for continuous, uniform electrode manufacture

![Graph showing normalized capacity over cycle number with rated capacity of 0.9Ah, discharge at 0.45A (C/2), and charge at 0.225A (C/4)]
## RZA Systems - Specific Energy

<table>
<thead>
<tr>
<th>System</th>
<th>Specific Energy (Wh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/Zn</td>
<td>55-80</td>
</tr>
<tr>
<td>MnO₂/Zn</td>
<td>70-90</td>
</tr>
<tr>
<td>Ag/Zn</td>
<td>100-200</td>
</tr>
</tbody>
</table>
Silver-Zinc Electrochemistry

\[\text{discharge}\]

\[
2\text{AgO} + \text{H}_2\text{O} + 2\text{e} \rightarrow \text{Ag}_2\text{O} + 2\text{OH}^- \]

\[
\text{Ag}_2\text{O} + \text{H}_2\text{O} + 2\text{e} \rightarrow 2\text{Ag} + 2\text{OH}^- \]

\[
\text{Zn} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 + 2\text{e} \]

\[
\text{Zn(OH)}_2 + 2\text{OH}^- \rightarrow \text{Zn(OH)}_4^{2-} \]

\text{Overall Reaction}

\[
\text{AgO} + \text{Zn} + \text{H}_2\text{O} \rightarrow \text{Ag} + \text{Zn(OH)}_2 \]
Silver-Zinc Applications
*(primary as well as secondary)*

<table>
<thead>
<tr>
<th>Space</th>
<th>Launch-vehicle guidance and control, telemetry, NASA vehicles Lunar Rover and Mars Rover, space shuttle payload launch and power for the life-support equipment used by the astronauts during EVA’s.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Military</td>
<td>Missle systems, Navy: mines, buoys, deep submergence and rescue vehicles, torpedo propulsion, drones and submarines.</td>
</tr>
</tbody>
</table>
Silver/Zinc Problems and Opportunities

- Highest specific energy and energy density
- High discharge rate capability
- Good charge retention
- Flat discharge voltage curve

BUT

- Relatively low cycle life
- Limited wet life (3-18 months, fill/activate prior to use)
- Sensitivity to overcharge
Technical Issues

- Zincate migration from electrode following discharge, non uniform charging leading to shape change
- Zinc dendrite formation which can penetrate the separator causing shorting
- Cellophane separators chemically attacked by colloidal silver and KOH
- Silver goes into solution and can pass through the separator

Note:

- RBC has developed separator system which inhibits cross over of selective ions in alkaline electrolyte (U.S. 5,952,124)
NASA SBIR Phase I, Technical Objectives

- Collaborate with Eagle-Picher Technologies, an established supplier of mission-critical silver/zinc batteries to:
  - construct silver/zinc cells using RBC’s advanced anode and separator components
  - evaluate the ability of these components to render improvements in: specific energy, cycle life and wet-life of rechargeable silver/zinc batteries
# Design Variables

- **Separators Evaluated:**

<table>
<thead>
<tr>
<th>Separator Type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microporous polyolefin separator</td>
<td>Continuous polyolefin membrane, approximately 1 mil thick, with carboxylic surface functionality</td>
</tr>
<tr>
<td>SPPO coated microporous polyolefin separator</td>
<td>As above, but dip-coated with sulphonated polyphenylene oxide per U.S. 5,952,124</td>
</tr>
<tr>
<td>Cellophane laminate</td>
<td>Cellophane laminated to a non-woven polyamide, approximately 6 mils thick</td>
</tr>
<tr>
<td>AMS</td>
<td>A mineral filled polyolefin supplied by Advanced Membrane Systems.</td>
</tr>
</tbody>
</table>

- **Electrolyte compositions evaluated:**
  - 20%KOH
  - 45%KOH
1Ah Cell - Standard RZA Separator & Electrolyte

Rated Capacity - 1Ah
Microporous Separator
20% KOH

Silver migration through uncoated microporous separator leads to early failure.
1Ah Cell - Standard RZA Separator & Electrolyte

Microporous Separator
20% KOH

Cell Voltage (V) vs. Time (hr)
1 Ah Cell - SPPO Coated Separator 20% KOH

- SPPO coating blocks silver migration
- Capacity utilization lower in 20% KOH electrolyte
- Fade is lower
- Wet life 4 months +
1 Ah-Cellophane Laminate Separator, 20% KOH

- RZA zinc anode cycles well
- Capacity utilization low in 20% KOH
1 Ah Cell - Cellophane Laminates, 45% KOH

- Capacity utilization - higher with 45% KOH
- Cellophane laminate fails (cracking) at 90 cycles
1Ah Cell - AMS Separator, 45% KOH
Silver-Zinc 10 Ah Cell

Cellophane Laminate
45% KOH

Nominal Capacity (%) vs. Cycle Number

RBC Technologies
Quality Battery Solutions
5 Ah Silver-Zinc Cells, 45% KOH

Nominal Capacity (%) vs. Cycle Number

- Cellophane Laminate Separator
- SPPO Coated Microporous Separator
- Space Suit Battery (45 Ah)
Phase I Conclusions

- Use of RBC anode in Silver-Zinc cells enhanced cycle life substantially.

- Within the limited time period of the project, wet life exceeding 4 months was demonstrated with the cell still operating satisfactorily.

- Coated microporous separators inhibit silver migration. Coated and filled polyolefin separators allow for greater wet-life stability than cellulose and cellulose laminates.

- All the cells were assembled in the charged state and did not need formation.

- KOH concentration must be optimized for cycle life, capacity and wet life.
NASA SBIR PHASE II
Technical Objectives

Application Demonstration: EMU-PLSS Battery

- Optimize separator and electrolyte for wet life/cycle life
- Scale to 5Ah, 17V battery (11 cells in series)
- Scale to 40Ah cells and a 17V battery
- Deliver two (2) 17V, 40Ah equivalent batteries to NASA, which will exceed the performance of current batteries.
Phase II SBIR Goals

Application Demonstration: EMU-PLSS Battery

<table>
<thead>
<tr>
<th>Item</th>
<th>Existing</th>
<th>Phase II Goal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conditioning</td>
<td>Fill and electrically charge</td>
<td>Fill and go</td>
</tr>
<tr>
<td>Volume (L)</td>
<td>2.27</td>
<td>2.12</td>
</tr>
<tr>
<td>Weight (Kg)</td>
<td>4.4-6.4</td>
<td>5.2</td>
</tr>
<tr>
<td>Capacity</td>
<td>26.6 Ah minimum @3.8A</td>
<td>26.6 Ah minimum @3.8A</td>
</tr>
<tr>
<td>Number of cycles to 26.6</td>
<td>7-32</td>
<td>50 minimum</td>
</tr>
<tr>
<td>Ah cut-off</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Operation</td>
<td>Rugged, Vented maintenance free</td>
<td>Rugged, vented maintenance free</td>
</tr>
<tr>
<td>Charging</td>
<td>With existing charger</td>
<td>Ability to interface with existing charging systems</td>
</tr>
<tr>
<td>Wet-life</td>
<td>170-420 days</td>
<td>450 days minimum</td>
</tr>
<tr>
<td>Electrical</td>
<td>16.5 volts</td>
<td>16.5 volts</td>
</tr>
</tbody>
</table>
Phase II - Current Status

- Program started Sept. 2002

- Evaluating separators, absorbers and electrolytes to optimize wet/cycle life

- 12V batteries have been assembled and are being tested

- More than 40 cycles and at least two months wet life demonstrated
Average Working Voltage vs Cycle number for 1 Ah, 12V Silver/Zinc Battery
Capacity vs Cycle number for 1 Ah, 12V Silver/Zinc Battery

Normalized Capacity (%) vs Cycle Number
Discharge/Charge Profile for 1 Ah, 12V Silver/Zinc Battery
### Opportunity - Spiral Wound RZA Silver/Zinc Battery

**TABLE: Comparison of Cylindrical Cells in Various Rechargeable Electrochemistries**

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Cell config.</th>
<th>Capacity (Ah)</th>
<th>Cell voltage</th>
<th>Wh/kg</th>
<th>Wh/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCd</td>
<td>D</td>
<td>4.6</td>
<td>1.2</td>
<td>40</td>
<td>106</td>
</tr>
<tr>
<td>RZA-NiZn</td>
<td>D</td>
<td>5.0</td>
<td>1.65</td>
<td>59</td>
<td>158</td>
</tr>
<tr>
<td>NiMH</td>
<td>D</td>
<td>6.5</td>
<td>1.2</td>
<td>46</td>
<td>150</td>
</tr>
<tr>
<td>Li-ion</td>
<td>18650</td>
<td>2.0</td>
<td>3.7</td>
<td>130</td>
<td>410</td>
</tr>
<tr>
<td>RZA-Ag/Zn</td>
<td>D</td>
<td>10.2</td>
<td>1.5</td>
<td>110</td>
<td>300</td>
</tr>
</tbody>
</table>
Conclusions

- Issues with long term wet life and cycle life of the silver/zinc battery system are being overcome through the use of new anode formulations and separator designs.

- Performance may exceed 200 cycles to 80% of initial capacity and ultimate wet-life of > 36 months.

- Rechargeable silver/zinc batteries available in prismatic and cylindrical formats may provide a high energy, high power alternative to lithium-ion in military/aerospace applications.
Acknowledgements

NASA, SBIR S4.07-0679

US Dept of Commerce, NIST
Advanced Technology Program
#70NANB9H3031