The Design of VRLA Batteries for Successful Operation in a High-rate, Partial-state-of-charge Regime

The Advanced Lead–acid Battery Consortium

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ACKNOWLEDGMENTS

• Funded in part by the Energy Storage Systems Program of the U.S. Department Of Energy (DOE/ESS) through Sandia National Laboratories (SNL).
## Types of Hybrid Electric Automobile

<table>
<thead>
<tr>
<th></th>
<th>Micro-</th>
<th>Mild-</th>
<th>Medium</th>
<th>Full</th>
</tr>
</thead>
<tbody>
<tr>
<td>EV Drive</td>
<td></td>
<td></td>
<td></td>
<td>⭐</td>
</tr>
<tr>
<td>Motor assist</td>
<td>⭐</td>
<td>⭐</td>
<td>⭐</td>
<td>⭐</td>
</tr>
<tr>
<td>Regen. braking</td>
<td>⭐</td>
<td>⭐</td>
<td>⭐</td>
<td>⭐</td>
</tr>
<tr>
<td>Engine stop</td>
<td>⭐</td>
<td>⭐</td>
<td>⭐</td>
<td>⭐</td>
</tr>
<tr>
<td>Battery voltage</td>
<td>12</td>
<td>36</td>
<td>144</td>
<td>&gt;200</td>
</tr>
<tr>
<td>Battery capacity (Ah)</td>
<td>50 - 60</td>
<td>15 - 20</td>
<td>6 - 8</td>
<td>6</td>
</tr>
</tbody>
</table>
# HEV Power-assist Performance Requirements

<table>
<thead>
<tr>
<th></th>
<th>USABC Minimum P-A goals</th>
<th>NiMH use in Honda Insight</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Maximum wt (kg)</strong></td>
<td>40</td>
<td>~30*</td>
</tr>
<tr>
<td><strong>Power out (10s) kW</strong></td>
<td>25 kW (625W/kg)</td>
<td>14 kW (467W/kg)</td>
</tr>
<tr>
<td><strong>Power in (10s) kW</strong></td>
<td>20 kW (500W/kg)</td>
<td>7 kW (233W/kg)</td>
</tr>
<tr>
<td><strong>Energy available in HRPSoC (Wh)</strong></td>
<td>300 (7.5Wh/kg)</td>
<td>450 (15 Wh/kg)</td>
</tr>
<tr>
<td><strong>(% of Total Cap'y)</strong></td>
<td>~33% (of 900Wh)</td>
<td>~50% (of 900Wh)</td>
</tr>
<tr>
<td><strong>% of Capacity used in cycle test (25Wh)</strong></td>
<td>2.8%</td>
<td>?</td>
</tr>
<tr>
<td><strong>Cycle life</strong></td>
<td>300,000</td>
<td>?</td>
</tr>
<tr>
<td><strong>Production Price ($)</strong></td>
<td>500</td>
<td>1017^</td>
</tr>
</tbody>
</table>

Real-world HEV Battery Duty

Current pulses through 30 minutes driving - 2 to 5% of capacity discharged at up to 15C and charged at up to 8C.

Charge removal and return during the same period
Characteristics of high-rate partial-state-of-charge operation

1. High rate - up to 15 C discharge and 8 C charge
2. Long periods without approaching top-of-charge
3. Very large number of (small) cycles - 300,000 rather than < 1,000
Battery Capacity in HEV Duty

- Y-axis: Capacity (Ah)
- X-axis: Miles

Graph shows a downward trend in battery capacity as miles increase.
Discharge

\[ \text{PbO}_2 + 3\text{H}^+ + \text{HSO}_4^- + 2\text{e}^- = \text{PbSO}_4 + 2\text{H}_2\text{O} \]

\&

\[ \text{Pb} + \text{HSO}_4^- = \text{PbSO}_4 + \text{H}^+ + 2\text{e}^- \]

When current is limited by diffusion,

Flux, \( S = -D \frac{\delta c}{\delta x}, \quad \Delta x^2 = 2Dt \)

Peukert \( I^n \cdot t = k \quad \text{At low current} \: n = 1 \)

At high current (diffusion control) \( n = 2 \)

\( I = k' t^{0.5} \)
High Rate Peukert Plot (data from JPS 9 (1983) 19)

(I/A)-1

0 0.005 0.01 0.015 0.02 0.025 0.03 0.035

-0.2 0 0.2 0.4 0.6 0.8 1 1.2 1.4

0 0.67 C

1 C

1.38 C

2 C

4 C

15 C (calculated)
Mechanism & solution:

1. Grid design
## Change of failure mode of a standard VRLA (15 Ah, flat plate) cell with operating rate

<table>
<thead>
<tr>
<th>Condition</th>
<th>PAM Porosity %</th>
<th>NAM Sulfate % Top</th>
<th>NAM Sulfate % Bottom</th>
<th>Failure mode(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>After formation</td>
<td>48.9</td>
<td>4.9</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td>Low-rate (C/10) deep cycle</td>
<td>61.4</td>
<td>3.4</td>
<td>20.0</td>
<td>PCL2 Strat.</td>
</tr>
<tr>
<td>Moderate rate (C/3) PSoC</td>
<td>58.2</td>
<td>4.2</td>
<td>38.5</td>
<td>PCL2 Strat.</td>
</tr>
<tr>
<td>High rate (5C) PSoC</td>
<td>54.1</td>
<td>79.6</td>
<td>7.4</td>
<td>PCL3</td>
</tr>
</tbody>
</table>

Soria et al., Exide Technologies, 9ELBC, Berlin, 2004
Current density contours on twin tab arrangements
Spiral Wound Cell with Dual Tabs
2V 8Ah Cell Discharged at 250A

Time in seconds

Voltage

- Twin Tab Connection
- Single Tab Connection
- Poly. (Twin Tab Connection)
- Poly. (Single Tab Connection)
Dual-tab spiral wound cell

Discharges up to 28 seconds at 250 A
At 1.4 V.

Weight 578 g.

Specific power: 605 W/kg
**RHOLAB test procedure** – cell comparison

*Normal Cyclon 36V pack*  
*Dual-tab Cyclon 36V pack*
Effect of continuous cycling (40 hours)

The drift of pack voltage over 65 RHOLAB cycles

The effect of conditioning on the evolution of cell capacity
Configuration with Most Uniform Current Distribution
Pasted Plates
Plates Wrapped with Separator in Case
High-rate performance of

1) Conventional cells

275 A for 120 s at -18 °C to 1.0 V.

2) Cells with selvage current collection

420 A for 121 s at -18°C to 1.0 V.
EXIDE battery on RHOLAB profile

time /s

battery current /A
Mechanism & Solution:

2. Expander Composition
HEV duty: sulfate build-up in negative plates – PCL-3!

- 0 cycles
- 1735 cycles
- 3191 cycles

Potential / V

HEV cycles

H₂ evolution

50 ± 3 % SoC

H₂ evolution
Diffusion of acid in and out of the plate is impeded by PbSO$_4$
Carbon - an element with variable properties

1. Ratio of $sp^2$ to $sp^3$ carbon atoms.
2. Surface groups.
3. Hexagonal/ rhombohedral stacking - faults.
4. Particle size - from Å to mm.
5. Shape.
Cycling Behavior of VRLA Cells With Enhanced Levels of Carbon Black and Graphite in the Negative Active Material

Composition: 0.6% Vanisperse-A
2.0% Carbon Black
2.0% Graphite

Total Cycles: 71880
Distribution of sulfur for a cell with 2% graphite and 2% carbon black
Extension of Life Under High Rate PSoC Cycling

**Failure Modes:**
- Early Gassing
- Negative Sulfation
- Recharge Resistance

**Solutions:**
- Carbon added to Negative
- Grid Design
- Pulses
the test vehicle...
Lead–acid battery in position
Insight on road-test with its lead–acid battery
Road test data with the lead-acid battery voltage/current readings

String Driving test 4/5/04 #2

String voltage (V) / String current (A)
ALABC Demonstration phase vehicles

- **RHOLAB**
  - Honda ‘Insight’
  - 144 V, 8 Ah

- **ISOLAB**
  - Ford ‘Focus’
  - 36 V, 25 Ah

- **Project DP 1.2**
  - Ford/PSA/VW
  - 12 V, 36 V

- **Project DP 1.3**
  - Hybrid electric bus*
  - 400+ V, 50-60 Ah

- **Project DP 1.6**
  - Chevrolet ‘Silverado’
  - 36 V, 52 Ah

- **Project DP 1.6**
  - Hybrid electric bus*
  - 400+ V, 52 Ah