CAPACITY MANAGEMENT AND WALKDOWN DURING LEO CYCLING OF NICKEL-HYDROGEN CELLS AND BATTERIES

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OUTLINE OF PRESENTATION

• CAPACITY WALKDOWN DEFINED AND ILLUSTRATED
• IMPORTANCE OF CAPACITY WALKDOWN
• FOUR APPROACHES TO UNDERSTANDING THE PHENOMENON
  – Pressure Trend Studies
  – Charging Curve Studies
  – Electrochemical Voltage Spectroscopy Studies
  – Destructive Physical Analysis Studies
• RESULTS OF THE INTERRELATED STUDIES
• SUGGESTED MECHANISM FOR CAPACITY WALKDOWN
• CHARGING PROTOCOLS TO AVOID THE PROBLEM
• SUMMARY STATEMENTS
CAPACITY WALKDOWN

Characteristics

- Very Slow
- 2000 - 8000 Cycles
- Recoverable
- 30% to 40% Capacity Loss
- Monitored Using Strain Gauge
IMPORTANCE OF CAPACITY WALKDOW

• RESULTS IN A SIGNIFICANT REDUCTION IN THE RESERVE CAPACITY FOLLOWING A NORMAL DISCHARGE
  – The Gradual Drop in State of Charge for a Fixed Depth of Discharge will Result in Less and Less Reserve Capacity Following a Discharge

• WHEN THE CHARGEING PROTOCOL IS BASED ON A FIXED RECHARGE RATIO ADJUSTMENTS ARE REQUIED AS CYCLING CONTINUES
  – Accuracy to the Nearest One Tenth of a Percent May be Needed
APPROACHES USED TO QUANTIFY AND UNDERSTAND CAPACITY WALKDOWN

• PRESSURE TRENDS DURING LEO CYCLING AT THE NAVY FACILITY AT CRANE INDIANA
  – Air Force, NASA Glenn, and NASA Space Station Tests
• CHARGING CURVES OF SELECTED AIR FORCE AND NASA SPONSORED LEO TESTS
• ELECTROCHEMICAL VOLTAGE SPECTROSCOPY STUDIES OF SELECTED SAMPLES OF PLATE MATERIAL FROM A VARIETY OF SOURCES
• EXTENSIVE DESTRUCTIVE PHYSICAL ANALYSES ON SIMILAR CELLS
  – One Cycled Under Conditions With No Walkdown
  – One Cycled Under Conditions With Significant Amount of Walkdown
WALKDOWN AS A FUNCTION OF CYCLING CONDITIONS

- CELLS CYCLED AT 40% DOD AND -5°C DID NOT SHOW WALKDOWN
- CELLS CYCLED AT 40% DOD AND +10°C SHOWED VARIABLE AMOUNTS OF WALKDOWN
- CELLS CYCLED AT 60% DOD AND +10°C SHOWED NO WALKDOWN
- CELLS CYCLED AT 60% DOD AND -5°C SHOWED NO WALKDOWN BUT VERY SHORT CYCLE LIVES
CAPACITY LOSS AT 40% DOD AND +10°C

![Bar chart showing the distribution of capacity loss at 40% depth of discharge and 10°C. The x-axis represents the loss of capacity from maximum pressure in percent, ranging from 0-5% to 41-45%. The y-axis represents the number of classes with each group containing 5% increments. The chart indicates that the majority of samples fall within the 30-35% loss class.]
TYPICAL TEST SHOWING NO WALKDOWN

26% KOH, 40% DOD, AND -5°C
CHARGE CURVES FOR TWO CELLS:
ONE AT +10°C AND ONE AT -5°C

3214E Cell 1: Cycles 4000, 4100

3254E Cell 1: Cycles 4000, 4100

+10°C, 40% DOD, RR = 1.04

-5°C, 40% DOD, RR = 1.03

Electronics And Photonics Laboratory
Energy Technology Department
Differences in Charging Curves

• Cycle 4000 was near the minimum of pressure following walkdown for cells in Pack 3214E
• Cell #1 in Pack 3214E does not show the sharp rollup at the end of the charging process
• Cell #1 in Pack 3254E has a sharp rollup indicative of less oxygen evolution
  – This results in a higher charging efficiency and therefore a higher state of charge at the end of the charging process for the cell cycled at -5°C
ELECTROCHEMICAL VOLTAGE SPECTROSCOPY STUDIES

EVS Scan to 0.52 V
Cell 5402H  S/N 004  Plate #12

Capacity/Volt

Potential vs Hg/HgO

- Cycle 1  Cycle 2
EVS REVEALED THE SOURCE OF THE WALKDOWN PHENOMENON

• THE BETA MATERIAL DURING THE FIRST CYCLE IS MORE DIFFICULT TO CHARGE BY 30 TO 40 MILLIVOLTS

• AFTER CHARGING TO THE GAMMA PHASE AND ONE FULL DISCHARGE, THE BETA MATERIAL IS REFERRED TO AS BEING IN THE ‘ACTIVE’ FORM

• THE POSITION OF THE CHARGING PEAKS OF THE SECOND CYCLE IS INDICATIVE OF A DIFFERENT ACTIVE SPECIE

• IT HAS BEEN SUGGESTED THAT THEY ARE DIFFERENT CRYSTALINE FORMS OF BETA NICKEL HYDROXIDE

• WE HAVE NOT BEEN ABLE TO DESCERN ANY IDENTIFIABLE DIFFERENCES IN THE TWO DIFFERENT FORMS
RESULTS OF EVS SCANS TO DIFFERENT END OF CHARGE VOLTAGES

• MULTIPLE ~1.0 CM² SAMPLES SELECTED FROM THE SAME PLATE TAKEN FROM A GOOD CELL WITH ONLY 100 CYCLES

• TWO COMPLETE CHARGE DISCHARGE CYCLES WERE USED AS PER THE PREVIOUS CHART

• THE END OF CHARGE VOLTAGE RANGED FROM 0.48 V vs. Hg/HgO REFERENCE ELECTRODE TO 0.54 V

• THE VOLTAGE PEAK FOR CHARGING THE BETA Ni(OH)₂ DURING THE SECOND CYCLE WAS RECORDED

• IT WAS FOUND THAT IF THE END OF CHARGE VOLTAGE WAS BELOW A CERTAIN VALUE, THE DISCHARGED FORM OF THE ACTIVE MATERIAL WAS NOT CONVERTED TO THE ACTIVE FORM

• FOR THIS ELECTRODE THE DIFFERENCE IN POTENTIAL OF THE TWO FORMS WAS 20 MILLIVOLTS
POSITION OF THE BETA PEAK DURING THE SECOND EVS SCAN

Position of Beta Charge Peaks During Second EVS Cycle

Position of Beta Peak vs. Hg/HgO-Volts

End-of-Charge Voltage vs. Hg/HgO-Volts
EXTENSIVE EVS STUDIES REVEALED THE FOLLOWING

• THE DEACTIVATED FORM OF NICKEL HYDROXIDE IS THE THERMDYNAMICALLY STABLE FORM
• THE ACTIVATED FORM OF NICKEL HYDROXIDE CAN BEGIN TO CONVERT BACK TO THE STABLE INACTIVE FORM IN ONLY A FEW DAYS
• ONCE IN THE ACTIVATED FORM, THE MATERIAL WILL REMAIN IN THE ACTIVATED FORM AS LONG AS IT IS CHARGED ABOVE THE CRITICAL TRANSITION VOLTAGE
• THE DISCHARGE BETA AND GAMMA PEAKS SEPARATE AS ONE OR THE OTHER MATERIAL DOMINATES THE DISCHARGE TRACE
POST TEST AND DPA STUDIES ON SIMILAR CELLS

• CELL FROM PACK 3214E
  – +10 Degrees, 1.04 Recharge Ratio, 26% KOH
• CELL FROM PACK 3254E
  – -5 Degrees, 1.03 Recharge Ratio, 26% KOH
• CELLS WERE 50 Ah, DOUBLE LAYER ZIRCAR, SLURRY, BACK TO BACK CELLS CYCLING UNDER AIR FORCE SPONSORSHIP
• CELLS WITHDRAWN FROM ONGOING TESTS FOR OUR FURTHER STUDIES
• CRANE CONDUCTED TWO POST CEST CYCLES
### SUMMARY OF CRANE POST TEST EVALUATION

<table>
<thead>
<tr>
<th>Discharge</th>
<th>Charge</th>
<th>+10°C Cells</th>
<th>-5°C Cells</th>
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<tbody>
<tr>
<td>Normal</td>
<td>1.04 recharge ratio</td>
<td>1.03 recharge ratio</td>
<td></td>
</tr>
<tr>
<td>C-rate</td>
<td>21.7 Ah discharged</td>
<td>46.8 Ah discharged</td>
<td></td>
</tr>
<tr>
<td>C/10-rate</td>
<td>11.3 Ah discharged</td>
<td>7.7 Ah discharged</td>
<td></td>
</tr>
<tr>
<td>Total 1&lt;sup&gt;st&lt;/sup&gt; discharge</td>
<td>33.0 Ah discharged</td>
<td>54.5 Ah discharged</td>
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</tr>
<tr>
<td>C/2-rate</td>
<td>48.9 Ah charged</td>
<td>48.9 Ah charged</td>
<td></td>
</tr>
<tr>
<td>C/10-rate</td>
<td>14.8 Ah charged</td>
<td>14.9 Ah charged</td>
<td></td>
</tr>
<tr>
<td>Total 1&lt;sup&gt;st&lt;/sup&gt; charge</td>
<td>63.7 Ah charged</td>
<td>63.8 Ah charged</td>
<td></td>
</tr>
<tr>
<td>C-rate</td>
<td>49.9 Ah discharged</td>
<td>50.2 Ah discharged</td>
<td></td>
</tr>
<tr>
<td>C/10-rate</td>
<td>7.7 Ah discharged</td>
<td>9.0 Ah discharged</td>
<td></td>
</tr>
<tr>
<td>Total 2&lt;sup&gt;nd&lt;/sup&gt; Discharge</td>
<td>57.6 Ah discharged</td>
<td>59.2 Ah discharged</td>
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AEROSPACE DPA ACTIVITIES

• CELLS PUNCTURED IN SPECIAL CHAMBER TO MEASURE RESIDUAL GAS PRESSURE AND COMPARE WITH STRAIN GAUGE READINGS OF OTHER CELLS WITHIN THE PACK
• RESIDUAL GAS SAMPLES SENT FOR MASS SPEC. ANALYSIS
• FLOODED UTILIZATION AND EVS TESTING OF PLATE SAMPLES FROM FOUR SECTORS OF THE CELLS
• CHEMICAL ANALYSIS CARRIED OUT ON SINTER AND ACTIVE MATERIAL
# RESIDUAL PRESSURE AND GAS ANALYSIS

<table>
<thead>
<tr>
<th></th>
<th>3214 E</th>
<th>3254 E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell Pack</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cycling Temp. - °C</td>
<td>+10</td>
<td>-5</td>
</tr>
<tr>
<td>Residual Pressure - psia</td>
<td>118.0</td>
<td>1.3</td>
</tr>
<tr>
<td>Composition - %</td>
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<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td>97.8</td>
<td>3.0</td>
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<tr>
<td>Water Vapor</td>
<td>1.8</td>
<td>16.3</td>
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<tr>
<td>Nitrogen</td>
<td>0.3</td>
<td>77.9</td>
</tr>
<tr>
<td>Average Plate Expansion - %</td>
<td>15.7</td>
<td>15.0</td>
</tr>
</tbody>
</table>
SUGGESTED MECHANISM

• CHARGING TO HIGHER VOLTAGES CONVERTS BETA NICKEL OXYHYDROXIDE TO THE GAMMA PHASE

• UPON DISCHARGE, THE UNSTABLE ALPHA FORM OF NICKEL HYDROXIDE IS FORMED

• THIS MATERIAL DISSOLVES IN KOH AND PRECIPITATES AS A VERY SMALL CRYSTALINE FORM OF BETA NICKEL HYDROXIDE

• THIS IS THE ACTIVATED FORM AND CAN EASILY BE CHARGED TO THE GAMMA FORM VIA THE BETA NICKEL OXYHYDROXIDE

• OSTWOLD RIPENING CONVERTS THE ACTIVATED FORM BACK TO THE DEACTIVATED FORM

• LOWER TEMPERATURES FACILITATE THE CHARGING TO THE GAMMA PHASE AND RETARDS THE RATE OF COVERSION BACK TO THE DEACTIVATED FORM
SUGGEST RECHARGE PROTOCOL TO AVOID OR MINIMIZE WALKDOWN

• CYCLING TEMPERATURE MUST BE LOW ENOUGH TO PERMIT CHARGING TO THE GAMMA PHASE
• DETERMINE MINIMUM VOLTAGE REQUIRED TO CONVERT MATERIAL TO THE ACTIVE FORM
• CHARGE TO A CUTOFF PRESSURE OR MONITOR THE END OF CHARGE PRESSURE
• CORRECT PRESSURE READING FOR STRAIN GAUGE DRIFT AND SINTER CORROSION VIA RECONDITIONING
SUMMARY

- CAPACITY WALKDOWN A CONSEQUENCE OF THE INABILITY TO MAINTAIN A HIGHT STATE OF CHARGE
- CAPACITY LOSS IS TYPICALLY 35% WHICH WOULD BE EXPECTED BY THE VALENCE DIFFERENCE BETWEEN GAMMA AND BETA NICKEL OXYHYDROXIDE
- CYCLING AT -5 DEGREES FACILITATES THE FORMATION OF THE GAMMA PHASE
- EXCESSIVE OVERCHARGE CAN ALSO FACILITATE GAMMA PHASE FORMATION AT THE EXPENSE OF CYCLE LIFE
- CONDITIONS CAN NOW BE SUGGESTED TO HELP MINIMIZE CAPACITY WALKDOWN