Sealed Aerospace Metal-Hydride Batteries

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1991 NASA AEROSPACE BATTERY WORKSHOP

SEALED AEROSPACE
METAL-HYDRIDE BATTERIES

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ADVANCED SYSTEMS OPERATION
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Nickel-metal hydride and silver-metal hydride batteries are being developed for aerospace applications by Eagle-Picher. There is a growing market for smaller, lower cost satellites which require higher energy density power sources than aerospace nickel-cadmium at a lower cost than space nickel-hydrogen. These include small LEO satellites, tactical military satellites and satellite constellation programs such as Iridium and Brilliant Pebbles. Small satellites typically do not have the spacecraft volume or the budget required for nickel-hydrogen batteries. NiCd's do not have adequate energy density as well as other problems such as overcharge capability and memory effect. Metal hydride batteries provide the ideal solution for these applications. Metal hydride batteries offer a number of advantages over other aerospace battery systems.
SEALED METAL-HYDRIDE BATTERIES FOR AEROSPACE APPLICATIONS

NICKEL-METAL HYDRIDE

- TWICE GRAVIMETRIC ENERGY DENSITY OF AEROSPACE NICKEL-CADMIUM
- TWICE VOLUMETRIC ENERGY DENSITY OF SPACE NICKEL-HYDROGEN

SILVER-METAL HYDRIDE

- THREE TIMES ENERGY DENSITY OF NICKEL-METAL HYDRIDE
Nickel-metal hydride batteries offer twice the gravimetric and volumetric energy density of aerospace nickel-cadmium. They also achieve twice the volumetric energy density of space nickel-hydrogen. Silver-metal hydride batteries have the potential of three times the energy density of nickel-metal hydride.
SEALED METAL-HYDRIDE BATTERIES
FOR AEROSPACE APPLICATIONS

HERMETICALLY SEALED
OPERATE AT LOW PRESSURE
PRISMATIC GEOMETRY
EXCELLENT OVERCHARGE
EXCELLENT OVERDISCHARGE
EXCELLENT THERMAL
LOW COST
Metal hydride batteries are hermetically sealed, operate at low pressure and are prismatic in geometry. They exhibit excellent overcharge and overdischarge characteristics. Preliminary calorimetry testing indicates that the batteries have superior thermal performance as compared to nickel-cadmium and nickel-hydrogen. The cells are lower in cost than aerospace nickel-cadmium and much lower in cost than space nickel-hydrogen.
SOURCES OF HYDRIDE MATERIALS AND ALLOYS

Morton International
Trebacher-Austria
Rhone-Poulenc
Nissho-Iwai America
Sumitomo
Ergenics
HCl-Denver
Aesar/Johnson Matthey
Baotou Research

Tricoastal Lanthanides
Crucible
Goldschmidt AG
Indian Rare Earths
Molycorp/Unocal
REMACOR
Santoku Metal
Chori-Osaka
Japan Metals
There are currently a large number of companies interested in the metal hydride battery business. Nearly all of the commercial battery companies have either announced products or are in the development stage of a product. There are a lot of potential sources for hydride electrode materials. This table shows only the sources that I am aware of and is not necessarily complete. Materials from several of these sources are currently on test and other materials are either in-house or in-transit. A comprehensive development effort is currently underway at Eagle-Picher to evaluate as many prospective materials as possible.
Eagle-Picher has evaluated materials from several of the sources previously listed. The chart shows comparative data for Ovonics material, Treibacher material and material from Rhone-Poulenc. The materials are in various stages of testing. Other materials are in-house but have not been evaluated yet. Materials have not yet been obtained from some of the sources. It would not be appropriate at this stage to start making claims about whose material is better than whom's. However, it seems conclusive that there are several materials on the market which will provide adequate function in an electrochemical cell. The markets for the metal hydride system are varied and extensive enough that most likely a single material would not be able to satisfy all of the applications. It is important that parallel development work of metal hydride materials be continued.
Sealed Metal-Hydride Batteries for Aerospace Applications

Figure 2
Prismatic Aerospace Nickel-Metal Hydride Cell
The advantage of the metal hydride cell over nickel-hydrogen is that the hydrogen is stored as a solid metallic hydride rather than as a gas. Therefore the cell operates at low pressure and a rectangular geometry can be used for the cell container. The volumetric energy density of the cell is much higher because no free volume is required in the cell to contain hydrogen gas. The cell is much simpler and cheaper to build than nickel-hydrogen because there are no complex internal components. Standard aerospace or commercial nickel-cadmium battery separators can be used. W.R.Grace is currently developing separator materials specifically for the nickel-metal hydride system. The cell design is essentially an aerospace nickel-cadmium design in which the cadmium electrodes have been replaced by hydride electrodes. Because the hydride electrode has a much higher energy density than the cadmium electrode the energy density of the cell is correspondingly higher. The cell design is such that the aerospace heritage of the parent NiCd system is retained. Current aerospace designs yield about 50 watt-hours per kilogram and 200 watt-hours per liter.
Sealed Metal-Hydride Batteries for Aerospace Applications

Figure 3
Prototype Nickel-Metal Hydride Aerospace Battery Design
Prismatic cells are much easier and more volume efficient to package into a battery than cylindrical cells. The cells are sandwiched between two lightweight endplates and held together by stainless steel connecting rods. The endplates are machined from aluminum and are painted with Chemglaze paint. The cells are insulated from each other and from the endplates with Kapton and Mylar. Nickel or silver foil is used as the intercell connectors. Connectors and on-board electronics can be integrated into the design as required by the application.
Sealed Metal-Hydride Batteries for Aerospace Applications

Figure 4
Nickel-Metal Hydride Alternative Battery Design
Another concept for an aerospace battery is to package commercial cylindrical cells into an aerospace battery pack. Some small satellite designers use this method rather than using aerospace cells. The Defense Advanced Research Projects Agency (DARPA) published a study which concluded that there was virtually no benefit in flying commercial cells rather than aerospace cells because of the extensive testing and cell matching required by the commercial cells. They also concluded that a redundant set of batteries had to be flown in order to achieve any level of reliability. This greatly reduces the effective energy density of the system and increases the cost.
Sealed Metal-Hydride Batteries for Aerospace Applications

Figure 7
Nickel-Metal Hydride Aerospace Cells

Voltage

RMH-10
Temperature: 22°C

Capacity (Ampere-Hours)

1.6
1.4
1.2
1.0
0.8
0.6
0.4
0
2
4
6
8
10
12

1.0 AMP
2.0 AMP
5.0 AMP
10 AMP
15 AMP
20 AMP
30 AMP
This is a set of discharge curves for a 10 amp-hour aerospace nickel-metal hydride cell. The cell was discharged at a variety of rates ranging from 1 amp to 30 amps. The data shows excellent rate capability for the aerospace nickel-metal hydride system. The cell delivered 11.5 amp-hours at the low rates and even at the 30 amp rate still did better than nameplate capacity. There is some discharge plateau voltage depression at the higher rates. However, all discharges were at room temperature with no active cooling so the effect is probably compounded by the larger amount of heat being generated at the higher rates.
Several metal hydride cells are currently on cycle life test. The cells are operating under a low-earth-orbit regime at 37 per cent depth-of-discharge. The cells are on charge for 55 minutes and then discharge 35 minutes. The charge return ratio is about 1.02. The cells are being cycled at room temperature with no active thermal control. There is significant end-of-discharge voltage depression at cycle number 4268 as compared to an earlier cycle, number 89. The cell was reconditioned in a manner similar to aerospace Nicd's and the EOD voltage immediately recovered to its original value. The trend of increased charge voltage is continuing with cycling. The charge-to-discharge return factor is being increased slightly to offset the EOD voltage degradation being observed.
Figure 9
Silver vs Nickel Hydride

Both cells discharged at C/4 Rate: 22°C

- NiMH
- AgMH

Capacity (mAh/g)
This graph directly compares the nickel-metal hydride system with the silver-metal hydride system. The silver electrode has a much higher energy density than the nickel electrode. The silver-metal hydride system delivers about three times the electrical capacity of the nickel-metal hydride system, although at a slightly lower voltage. The silver-metal hydride system has a number of applications where the higher energy density available offsets the lower cycle life. This could include laptop computers and cellular telephones where increased run time is a valuable premium to the user. Military and aerospace applications include portable battlefield computers, portable communications equipment, lightweight weapons systems and tactical satellites.
NICKEL-METAL HYDRIDE DISCHARGE

1.0 AMP RATE

VOLTAGE

CAPACITY (AHR)

1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0

\[ \text{Voltage} \]

\[ \text{Capacity (AHR)} \]

\[ \Delta \ 10 \text{ DEG. C} \]

\[ \circ \ 30 \text{ DEG. C} \]
This graph shows the temperature dependence of the nickel-metal hydride system. Two discharges were done at the same rate, one at 10 degrees C and the other at 30 degrees C. The cell yields the same capacity at either temperature, however, there is a depression of the discharge plateau voltage at the colder temperature. Warm temperature performance is slightly better than NiCd and much better than NiH2.
NiMH BUTTON CELL

S/N 477

1991 NASA Aerospace Battery Workshop -564- Advanced Technologies Session
This data was included to illustrate the design versatility of the metal hydride system. Cells can be constructed in virtually any size or shape. This is a small diameter nickel-metal hydride button cell design. The cell is assembled and die-crimped such that it is a sealed cell. About 40 of these cells have been assembled. The cell was discharged at four different rates and yields around 200 milliamp-hours. The depression in the discharge voltage occurs because this is a low rate cell design such as that used in a wristwatch.
Some preliminary calorimetry testing is being done with aerospace nickel-metal hydride cells in conjunction with Chris Johnson at Boeing. Initial data shows that nickel-metal hydride should be thermally superior to both nickel-cadmium and nickel-hydrogen. The chart shows that heat flow is negative on charge until 100% state-of-charge is reached. As more and more oxygen is being generated on the nickel electrodes the heat output of the cell gradually increases. The heat output increases more rapidly going into discharge with a plateau that corresponds to the discharge voltage plateau. As the cell state-of-charge decreases towards reversal the heat output again increases.
AC Impedance Data Acquisition System

1991 NASA Aerospace Battery Workshop

Advanced Technologies Session
Eagle-Picher is currently collaborating with TRI-Austin under a contract with the U.S. Air Force, Phillips Laboratory, Edwards Air Force Base, for impedance spectroscopy analysis of nickel-hydrogen and nickel-metal hydride batteries. The purpose of the study is to evaluate indicators of cell and battery aging and performance which are more readily determined and appear earlier than the traditional voltage and capacity degradation which occurs on long term cycling. Preliminary impedance spectral data ranging from 3 milliHertz to 30 kiloHertz has been acquired on approximately 100 cells. Data interpretation and a mathematical battery modeling effort is currently underway. The measurement test set-up includes a Schlumberger 1260 Impedance Analyzer interfaced with a PC. An extensive software package was developed by TRI for data acquisition and management.
# Summary of the Significant Groups of Cells for which AC Impedance Data Were Collected

<table>
<thead>
<tr>
<th>Cell Type</th>
<th>Capacity (Amp-Hrs)</th>
<th>No. of Cells Measured</th>
<th>Storage Time (Years)</th>
<th>No. of Aging Cycles</th>
<th>Type of Life Test</th>
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<tbody>
<tr>
<td>NiH₂</td>
<td>30</td>
<td>1</td>
<td>7</td>
<td>10,800</td>
<td>Real-Time LEO</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1</td>
<td>0</td>
<td>10,800</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>2</td>
<td>0</td>
<td>3,800</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>9</td>
<td>0</td>
<td>38,000</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>9*</td>
<td>7</td>
<td>1,500</td>
<td>Real-Time LEO</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>1</td>
<td>5-6</td>
<td>0</td>
<td>None</td>
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<tr>
<td></td>
<td>50</td>
<td>4</td>
<td>0</td>
<td>23,309</td>
<td>Proprietary</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>18</td>
<td>0</td>
<td>62,000</td>
<td>Accel. LEO</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>Real-Time GEO</td>
</tr>
<tr>
<td></td>
<td>65</td>
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<td>0</td>
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<td>&quot;</td>
</tr>
<tr>
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<td>76</td>
<td>4</td>
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<td>3,057</td>
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<tr>
<td></td>
<td>76</td>
<td>2</td>
<td>?</td>
<td>23,309</td>
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</tr>
<tr>
<td></td>
<td>76</td>
<td>2</td>
<td>?</td>
<td>43,000</td>
<td>Accel. LEO</td>
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<tr>
<td>NiMH</td>
<td>4</td>
<td>8</td>
<td>0</td>
<td>3,801</td>
<td>Real-Time LEO</td>
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<tr>
<td></td>
<td>4</td>
<td>2</td>
<td>0.33</td>
<td>0</td>
<td>&quot;</td>
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<tr>
<td></td>
<td>8</td>
<td>2</td>
<td>0</td>
<td>3,801</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>C-cell</td>
<td>3</td>
<td>0</td>
<td>2,001</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>C-cell</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

* A number of fabrication variations
Data was acquired on a large number of life test cells including aerospace nickel-metal hydride cells, commercial nickel-metal hydride cells and space nickel-hydrogen cells. The cells are being tested under several regimes including a real-time low-earth-orbit (LEO) regime, an accelerated LEO regime and a real-time geostationary-earth-orbit (GEO) regime. A number of cell designs are represented in sizes ranging from 3.5 amp-hours to 76 amp-hours.
5 REPEATED MEASUREMENTS OF A 50 AMP-HR NICKEL HYDROGEN CELL (62,000 CYCLES)

Graph showing impedance magnitude (ohms) versus log(10) frequency with a note about test lead inductance artifact.
A typical scan ranges from 3 milliHertz to 30 kiloHertz. Multiple runs were frequently made on the same cell at random intervals to evaluate the reproducibility of the method. This data represents five runs on the same cell made at various times during a two week period. The data shows excellent reproducibility.
RAW IMPEDANCE DATA FOR 76 AMP-HR NICKEL HYDROGEN CELLS

3057 Cycles (2-Cell Average)

43,000 Cycles (3-Cell Average)

Failed Cell (2-Cell Average)
A plot of impedance versus the base ten log of frequency shows some interesting characteristics in the low frequency region below 1 Hertz. This is the Warburg region where the availability of charge carriers is diffusion controlled. The AC impedance in this frequency range decreases with the age of the cell. The graph shows spectral data for cells of identical design with 3000 cycles, 43,000 cycles and a cell which had been cycled to failure. The trend in the data is decreased impedance with age.
The Argand diagram for two 30 amp-hour Intelsat V type cells also shows a definite trend. Two cells are compared, one with 3800 cycles and the other with 38,000 cycles. The capacitive to Warburg transition is significantly frequency shifted for the aged cell.
COMPARISON OF RESISTANCE AND REACTANCE OF TWO NICKEL METAL HYDRIDE CELLS

One Year Storage, Zero Aging Cycles
2001 Cycles

(OMS)

LOG(10) FREQUENCY

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Comparisons of resistance and reactance also show some trends with cell aging. The gap between the two decreases as the cell is cycled. The uncycled cell shows a much larger delta between resistance and reactance than the cell with 2001 cycles. This relationship also hold true for nickel-hydrogen cells.
THE FUTURE

BASIC ELECTRODE MATERIALS

FABRICATION TECHNIQUES

CYCLE LIFE TESTING

IMPROVEMENTS:

ENERGY DENSITY

PERFORMANCE

CYCLE LIFE
The idea for a metal hydride battery has been around for a long time. However, practical batteries have only come about recently. So recently that they are still not generally available. The development of the metal hydride chemistry is still in the early stages particularly for aerospace applications. Future efforts will be aimed at the further refinement of the nickel and silver metal hydride battery chemistry. Work is being continued on developing and improving hydride electrode materials and fabrication techniques. Life cycle testing will be continued. The system will be optimized to yield improved energy density, improved performance and longer cycle life.