Calorimetric Evaluation

of

Commercial Ni-MH Cells and Chargers

with
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The test objectives are to evaluate the electrical and thermal performance of commercial Ni-MH cells and to evaluate the effectiveness of commercial charge control circuits. The ultimate design objectives are to determine which cell designs are most suitable for scale-up and to guide the design of future Shuttle and Station based battery chargers.
• Description of Ni-MH cells and chargers
• Cycling experiment using Taguchi techniques
• Calorimetric comparison of best performing cells
• Summary conclusions
The cells tested were those most readily available. Some were purchased while others were sampled to us. The most notable exclusion are Panasonic cells. Efforts are under way to obtain these for future evaluation.
<table>
<thead>
<tr>
<th>Cell Manufacturer</th>
<th>Cell Size</th>
<th>Ah rating</th>
<th>DoM</th>
<th>Hydride formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ovonic</td>
<td>C</td>
<td>3.25</td>
<td>92</td>
<td>AB$_2$</td>
</tr>
<tr>
<td>Harding*</td>
<td>A</td>
<td>1.8</td>
<td>93</td>
<td>AB$_2$</td>
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<tr>
<td>Gold Peak*</td>
<td>7/5A</td>
<td>2.5</td>
<td>94</td>
<td>AB$_2$</td>
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<tr>
<td>Maxell</td>
<td>4/3A</td>
<td>2.3</td>
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<tr>
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<td>2.3</td>
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<td>Toshiba*</td>
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<td>93</td>
<td>AB$_5$</td>
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<tr>
<td>Furukawa</td>
<td>Prismatic</td>
<td>0.55</td>
<td>93</td>
<td>AB$_5$</td>
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<tr>
<td>Yuasa*</td>
<td>Prismatic</td>
<td>3.0</td>
<td>94</td>
<td>AB$_5$</td>
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<tr>
<td>Yuasa*</td>
<td>4/3A</td>
<td>2.4</td>
<td>94</td>
<td>AB$_5$</td>
</tr>
</tbody>
</table>

* have limited cycling performance data.
This Austrian product uses a novel fast charge approach which starts fast and declines in a stair-step manner. The technique reduces the maximum charge voltage (power) needed. Unfortunately, this charger sometimes failed to terminate when the current was adjusted from its factory setting. Thus, only C-cells where tested with this charger.
Model # - ECS-II by Enstore, Inc.

Input - constant voltage AC (110 V or 220V) or DC (11 V)

Output - continuously pulsing charge current with 4 step sequence.
  • Step 1 - 100% of initial setting to about 75% SOC
  • Step 2 - 75% of initial setting to about 95% SOC
  • Step 3 - 38% of initial setting to about 100% SOC
  • Step 4 - lower duty cycle of pulses at step 3 level maintained indefinitely

Charge Rates - 2 to 8 A, but with Evaluation Board only successful at 4 A

Charge Termination Methods
  • proprietary voltage inflection
  • maximum voltage
  • maximum temperature

Other Features/Limits
  • can be set to charge Ni-Cd and Pb/PbO₂ batteries
  • termination was inconsistent at any setting other than 4 A.
  • requires a 6 kΩ NTC thermistor.
This declining stair-step current profile results in a camelback heat profile which minimizes peak charge voltage and heat. Enstore, Inc., acknowledged this termination problem and is performing further development to correct it.
The Benchmark charger uses a negative slope algorithm, which has proven successful with Ni-Cd cells, and couples it with a cell temperature rise algorithm. Besides the Enstore charger, it has the least amount of current rate settings. The chip has an input pin to activate discharge of a battery before initiating charge.
Model # - bq2003 by Benchmarq Microelectronics, Inc.

Input - constant voltage of 11 V (or constant current with additional circuitry)

Output - constant current set by user with resistors

Charge Rates - C/4, C/2, C, 2C, and 4C

Primary Charge Termination Methods
- temperature rise ($\Delta T/\Delta t$)
- negative voltage slope ($-\partial V/\partial t$)

Secondary Charge Termination Methods
- maximum temperature (user tweakable)
- maximum voltage (user tweakable)
- timer (360, 180, 90, 45, and 23 minutes)

Top-off and Trickle Charge
- top-off is set equivalent to 1/10 the duty cycle of fast charge
- trickle rate constant (user configurable with resistors)

Other Features/Limits
- discharge before charge initiation
The Maxim charger is the simplest tested. It has the least amount of features. Charge current fluctuations can occur if the power transistor is not carefully matched to the control circuit. The resulting voltage fluctuations troubles the zero slope algorithm.
Maxim Charger

Model # - Max 712 by Maxim Integrated Products

Input - Constant voltage of 11 V (No constant current capability)

Output - Constant current set by user with resistor(s)

Charge Rates - 3C, 2C, 1.5C, 1C, C/2, C/2.5, and C/4

Primary Charge Termination Methods
  • maximum voltage point (ΔV/Δt ≤ 0)
  • max temperature (user tweakable)

Secondary Charge Termination Methods
  • max voltage (user tweakable)
  • timer (22, 33, 45, 66, 90, 132, 180, and 264 minutes)

Trickle Charge
  • built-in trickle set to 1/8 of fast charge rate.
  • can be set to other values with additional circuitry

Other Features/Limits
  • Power transistor must be carefully matched to the control circuit to prevent instabilities in the output.
The ICS charger is the most complex and feature-packed of the lot tested. An important feature is its acceptance of constant current input. This feature exists with the Benchmark charger with some reworking of the circuitry around the chip, but is not available with the Maxim or Enstore chargers.
Model # - ICS 1702 by Integrated Circuits Systems, Inc.

Input - Constant current or constant voltage of 11 V. Configured by user.

Output - Constant current with discharge pulses (Reflex). Current is limited by size of external transistor.

Charge Rates - C/4, C/3, C/2.5, C/2, C/1.5, 1C, 1.3C, 2C, and 4C

Primary Charge Termination Methods
- voltage inflection ($\frac{\partial^2 V}{\partial t^2} = 0$)
- temperature slope approximately = 0.7°C/min
- negative voltage slope ($-\frac{\partial V}{\partial t}$)

Secondary Charge Termination Methods
- maximum voltage (user tweakable)
- maximum temperature (user tweakable)
- timer (273, 242, 210, 142, 107, 73, 55, 37, and 19 minutes)

Trickle Charge - 2 hr topping and indefinite maintenance charge available

Other Features/Limits
- discharge pulse current is set by user
- 2 min soft start period prevents false voltage inflection termination
The typical Reflex current profile uses a discharge pulse level set at -2.5 times the charge current.
The objective of the experiment is to determine which combination of factors contribute to maximum discharge capacity as a % of nameplate capacity after 100 cycles. A secondary objective was to determine the Ah C/D ratios of each combination. All three Harding batteries (consisting of A-cells) failed within 80 cycles to deliver appreciable capacity. They were replaced with Gold Peak cells.
Cycling experiment using Taguchi techniques

Propulsion and Power Division
Eric Darcy
11/16/94

1st Performance Evaluation using L18 Taguchi Matrix
- 3 cell types - Harding A, Sanyo 4/3A, and Toshiba 4/5A
- 3 chargers - Benchmarq, ICS, and Maxim
- 3 charge rates - 3/C, C, and 2C
- 3 trickle charge rates - C/100, manufacturer setting, and C/10
- 3 trickle charge times - 5 min, 1 hr, and 2 hr
- 3 charge and discharge rest times - 2 min, 15 min, 30 min
- 2 temperatures - 25 and 5 deg C
- 1 discharge rate - C rate to 1 volt/cell

Performance criteria
- Discharge capacity (as % of nameplate) vs cycle number

After Harding cells failed, they were replaced with Gold Peak 7/5A cells.
This plot shows the cycling performance of Sanyo 4/3A batteries with 3 different chargers at room temperature. Sanyo cells performed very consistently. Benchmark terminated after 85-87% charge input at a C rate probably due to its sensitive temperature rise termination algorithm. Interestingly, ICS achieved a lower C/D Ah ratio at 2C than Maxim did at C/3, while discharge output was nearly identical.
Sanyo 4/3A cell cycling

Performance cycling of Sanyo NiMH Cells
Size = 4/3A, nameplate capacity = 2.3 Ah
Date = 5/94, temperature = 25 C

- Maxim discharge
- Maxim C/3 charge + 2 hr @ C/100
- Benchmark discharge
- Benchmark C charge + 5 min trickle
- ICS 2C discharge
- ICS 2C charge + 1 hr @ C/10
Toshiba batteries were also consistent performers with all the chargers. Curiously, the rate of charge did not effect the discharge output (90% of nameplate capacity). ICS inconsistencies were due to a "testing" bug.
Toshiba 4/5A cell cycling

Cycling Performance of Toshiba Ni-MH cells
Size = 4/5A, nameplate capacity = 1.5 Ah
Date = 8/29/94, temperature = 25 C
Gold Peak batteries did not perform much better than Harding cells. At C/3 rate, they faded. At C rate, they failed abruptly. At the 2C rate, they only accepted a 60% charge input.
Gold Peak 7/5A cell cycling

Cycling Performance of Gold Peak Ni-MH Cells
Size = 7/5A, nameplate capacity = 2.5 Ah
Date = 8/94, temperature = 25 C

- ICS discharge
- ICS C/3 charge + 1 hr pulse trickle
- Maxim discharge
- Maxim C charge + 2 hr @ C/10
- Benchmark discharge
- Benchmark 2C charge + 5 min @ C/100

Charge terminating by exceeding temp limit

% of nameplate capacity / 100

Cycle number
At 10 °C, Sanyo cells were consistent like at room temperature. Note that the discharge output of the Benchmark C/3 charge was identical to the Maxim 2C charge. Both benefited from C/100 trickle period. ICS terminated at 90% charge input, and thus, fared weakly at this lower temperature.
Sanyo 4/3A cell cycling at 10°C

Performance cycling of Sanyo Ni-MH cells
Size = 4/3A, nameplate capacity = 2.3 Ah
Date = 9/94, temperature = 10°C

Lost data hereafter

- Benchmarq discharge
- Benchmarq C/3 charge + 2 hr @ C/100
- ICS discharge
- ICS C charge + 5 min trickle
- Maxim discharge
- Maxim 2C charge + 1hr @ C/100

Cycle number
Toshiba cells showed signs of capacity degradation. Note that these cycles were accumulated on top of those done at room temperature. ICS at a C rate has a good C/D ratio with a 85% discharge output.
Performance cycling of Toshiba NiMH cells
Size = 4/5A, nameplate capacity = 1.5 Ah
Date = 9/94, temperature = 10 °C

- Benchmark discharge
- Benchmark C/3 charge + 1 hr @ C/10
- ICS discharge
- ICS C charge + 2 hr @ C/100
- Maxim discharge
- Maxim 2C charge + 1 hr @ C/100
Gold Peak performance at 10 °C was dismal.
Gold Peak 7/5A cells at 10°C

Performance cycling of Gold Peak NiMH cells
Size = 7/5A, nameplate capacity = 2.5 Ah
Date = 9/94, temperature = 10°C

- Maxim discharge
- Maxim C/3 charge + 5 min trickle
- Benchmark discharge
- Benchmark C charge + 1 hr @ C/100
- ICS discharge
- ICS 2C charge + 2 hr @ C/10

% of nameplate capacity vs. Cycle number
Cell type was the overwhelming factor affecting discharge output after 100 cycles because the Gold Peak cells performed so poorly. The contribution attributed to experimental error was higher than all other factors.
- Cell type was the most important factor effecting % of discharge capacity
- All other factors were less important than experimental error
Experimental is needed with only one cell type to more accurately pin point the effects of the changes, charge rate, etc.

Strangely, the single-hour and 2C rates were better than C rate, Benchmark and IC3 charges being better than maximum. A future

Nevertheless, the effects of varying the levels of each factor can be observed. Room temperature was 20% better than 10°C.
The cells and chargers listed have been evaluated in the calorimeter. Only the best performing cells will be discussed today. The majority of the cells were tested with the ICS charger because of its performance and its constant current input made current adjustments very convenient. The cycling conditions included long rest periods after trickle charge and discharge to allow integration of the heat profile to calculate thermal energy.
Experimental Plan - Calorimetry

Cell types tested to date
- Ovonic C
- Sanyo 4/3A and 4/3AU
- Gold Peak 7/5A
- Yuasa 4/3A and prismatic
- Toshiba 4/5A
- Maxell 4/3A
- Sanyo Ni-Cd C

Chargers
- Benchmark Microelectronics, bq2300
- Integrated Circuit Systems, ICS-1702
- Maxim Integrated Products, Maxim712

Cycling conditions
- C charge and discharge rates
- 0.1 A trickle charge for 1 hour immediately after charge
- 2 hr rest after trickle charge and discharge
- 1 volt/cell discharge cut-off
- Room temperature water bath controlled environment
The Sanyo 4/3A cell had the lowest steady state heat rate on charge and discharge. However, it was significantly overcharged by the ICS charger as is evident by the severe heat spike. This overly influences the total charge thermal energy calculation. At a C rate this cell only delivered 94% of its 2.3 Ah nameplate capacity. Sanyo says that the cell N/P ratio is nearly 2.0 and that the nickel electrode is the sintered type. This is clearly a low impedance cell but with limited capacity delivery at higher rates.
Sanyo 4/3A cells with ICS charger

- 2.50 Ah charge + 0.11 Ah trickle
- 3.69 Wth charge
- 0.935 Wth charge
- 2.17 Ah discharge
- 2.63 Wth discharge
- 0.310 Wth discharge

Heat
voltage
current

Sanyo 4/3 A cells
ICS-1700A charger
C rate, room temp
cycle 7
The new Sanyo 4/3AU cell yields a 0.1 Ah more capacity at the same rate but runs very much hotter. Specifically, 1.85 times hotter, in terms of steady state heat, on discharge and 2.43 times hotter on charge. Sanyo says the nickel electrode is nonsintered. Clearly, impedance changes alone can not account for this difference. I suspect hydride modifications have changed the heat of hydriding and dehydriding. Interestingly, this cell suffered less overcharge heat than the 4/3A, maybe because temperature algorithms terminated the AU cell.
Sanyo 4/3AU cell with ICS Charger

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Sanyo 4/3AU cells
ICS-1702 charger
C-rate, RT cycle 10

2.53 Ah charge + 0.11 trickle
3.58 Wh charge
1.16 Wh charge
2.26 Ah discharge
2.75 Wh discharge
0.617 Wh discharge
Yuasa 4/3A cell capacity delivery is nearly identical with the Sanyo 4/3A. However, the Sanyo cell runs 1.16 and 1.91 times hotter (steady-state heat) during discharge and charge, respectively. Yuasa has informed me that the cell's N/P ratio is 1.5. This cell appears to suffer the least amount of overcharge heat compared to the Sanyo cells. Yuasa says that the nickel electrode uses a high surface area powder material doped with CoO and pasted onto a porous foam substrate. Again, the difference between heat rates of charge and discharge indicates that their hydride electrodes are different as well.
Yuasa 4/3A cell with ICS charger

Yuasa 4/3A cells
ICS-1700 charger
C-rate, RT
cycle 6

2.50 Ah charge + 0.11 Ah trickle
3.82 Wh charge
0.873 Wh_t charge

2.29 Ah discharge
2.78 Wh discharge
0.543 Wh_t discharge

Heat
voltage
current

W and V

2 1 0 -1 -2

Amps

time, hr
The Yuasa prismatic cell rated at 3.0 Ah delivered slightly less capacity than its cylindrical relative and was not as thermally efficient. This mostly likely due to the higher impedance of the prismatic construction. Yuasa says its N/P ratio is 1.75 and it received more overcharge than its 4/3A relative.
Yuasa prismatic cell with ICS charger

Yuasa prismatic cells
ICS-1700 charger
C-rate, RT
cycle 8

3.21 Ah charge + 0.11 Ah trickle
4.80 Wh charge
1.32 Wh_t charge
2.77 Ah discharge
3.35 Wh discharge
0.749 Wh_t discharge
This table compares the four best performing cells. Electrical and thermal potentials are parameters I devised to compare the integrated electrical and thermal energy on a per Ah delivered basis. This allows for comparing cells of varying capacity. On charge, the electrical potentials were nearly identical while the Sanyo 4/3AU clearly generated more heat per Ah than the others. On discharge, the Sanyo 4/3A cell generated less heat per Ah delivered. But the telling parameter is the midway heat rate value determined halfway during charge and discharge. Differences in midway voltage were minimal compared to the midway heat. This comparison demonstrates the wide difference in the thermal characteristics of Ni-MH cells all using similar hydride formulations (AB₃).
## Comparison of 4 best cells

<table>
<thead>
<tr>
<th></th>
<th>Sanyo 4/3A</th>
<th>Sanyo 4/3AU</th>
<th>Yuasa 4/3A</th>
<th>Yuasa Prismatic</th>
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<tbody>
<tr>
<td><strong>Charge characteristics</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ampere-hours, Ah</td>
<td>2.61</td>
<td>2.55</td>
<td>2.61</td>
<td>3.32</td>
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<tr>
<td>Watt-hours, Wh</td>
<td>3.82</td>
<td>3.69</td>
<td>3.69</td>
<td>4.8</td>
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<tr>
<td>Electrical potential Wh/Ah, V</td>
<td>1.46</td>
<td>1.45</td>
<td>1.41</td>
<td>1.45</td>
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<tr>
<td>Watt-hours thermal, Wht</td>
<td>0.935</td>
<td>1.26</td>
<td>0.873</td>
<td>1.32</td>
</tr>
<tr>
<td>Thermal potential Wht/Ah, V</td>
<td>0.358</td>
<td>0.494</td>
<td>0.334</td>
<td>0.398</td>
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<tr>
<td>Midway voltage, V</td>
<td>1.44</td>
<td>1.46</td>
<td>1.47</td>
<td>1.47</td>
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<tr>
<td>Midway heat, W</td>
<td>0.36</td>
<td>0.875</td>
<td>0.459</td>
<td>0.65</td>
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<td><strong>Discharge characteristics</strong></td>
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<tr>
<td>Ampere-hours, Ah</td>
<td>2.17</td>
<td>2.26</td>
<td>2.29</td>
<td>2.77</td>
</tr>
<tr>
<td>Watt-hours, Wh</td>
<td>2.63</td>
<td>2.8</td>
<td>2.78</td>
<td>3.35</td>
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<tr>
<td>Electrical potential Wh/Ah, V</td>
<td>1.21</td>
<td>1.24</td>
<td>1.21</td>
<td>1.21</td>
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<tr>
<td>Watt-hours thermal, Wht</td>
<td>0.31</td>
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<tr>
<td>Thermal potential Wht/Ah, V</td>
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<td>0.237</td>
<td>0.27</td>
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<tr>
<td>Midway voltage, V</td>
<td>1.23</td>
<td>1.219</td>
<td>1.21</td>
<td>1.2</td>
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<tr>
<td>Midway heat, W</td>
<td>0.295</td>
<td>0.547</td>
<td>0.472</td>
<td>0.78</td>
</tr>
</tbody>
</table>
Sanyo 4/3A vs Sanyo 4/3AU
- AU cell yields 0.1 Ah more on discharge at C rate
- AU cell runs 1.85 and 2.43 times hotter during discharge and charge
- impedance changes alone can not account for this difference
- difference probably due to a change in $\Delta H$ of hydriding/dehydriding

Yuasa 4/3A vs Sanyo 4/3AU
- capacity delivery is nearly identical
- Sanyo cell runs 1.16 and 1.91 times hotter during discharge and charge

Yuasa Prismatic vs Yuasa 4/3A
- Prismatic delivered slightly less Ah relative to its nameplate (3 Ah)
- Prismatic not as thermally efficient due to higher impedance

Most thermally efficient cells
- Yuasa 4/3A cell during charge (0.78)
- Sanyo 4/3A cell during discharge (0.88)
Performance Cycling  
- $AB_5$ (Sanyo, Yuasa, Toshiba) cells cycled more consistently than $AB_2$ cells  
- Yuasa 4/3A and Sanyo 4/3AU yielded best energy (56 Wh/kg, 193 Wh/L)

Taguchi Experiment  
- Cell Design was most important factor due to poor performance of $AB_2$ cell  
- ICS and Benchmarq chargers are better than Maxim charger

Calorimetric Study  
- $AB_5$ cells are more thermally efficient than $AB_2$ cells  
- Nevertheless, thermal performance varies widely within $AB_5$ cell designs.
Future tests

- Calorimetric evaluation of other viable cells and chargers

- Convert test stand to ICS chargers and cycle test the following cells
  - Yuasa 4/3A
  - Yuasa Prismatic
  - Sanyo 4/3AU
  - improved Toshiba 4/3A cells
  - Furukawa prismatic cells

- DPA’s to correlate performance to cell design
Back-up charts
Purpose: Determine why Yuasa cells are thermally different from Sanyo cells

Part I - Determine general cell design characteristics
- Cell gas composition and pressure (gas chromatograph)
- KOH conc of electrolyte (titration) and ion composition (ion chromatography)
- Weight and volume distribution of dry cell components

Part II - Analysis of the negative
- Grain structure (optical and SEM techniques)
- Elemental composition (Mass Spectroscopy)
- Specific surface area (BET)
- Porosity and pore distribution (Hg porosimetry)
- Elemental and molecular composition of surface (XPS)
- Composition depth profiling of the surface (AES)
- Electrochemical capacity, mAh/g (electrode test)
- Heat of hydriding/dehydriding (calorimetry)

Part III - Analysis of the positive
- Electrochemical capacity, mAh/g (electrode test)
- Porosity and pore distribution (Hg porosimetry)
Automated Battery Cycler Capabilities
- 10 independent battery cycling stations
- Each station equipped with bipolar power supply = 20 V and ±10 A
- Charge control options for each station
  - user software controlled with power supply as source, or
  - controlled by IC chargers using battery voltage and temperature inputs
- Data Acquisition = 40 channels, 15 to 30 sec single scan rate
- Stand Computer is a Macintosh IIci, 20 MB RAM, 100 MB HD, 25 MHz
- LabVIEW software for stand control and data acquisition
  - 5 state cycle; discharge, discharge rest, charge, trickle charge, charge rest
  - Charge parameters = current with time, voltage, and temperature limits
  - Discharge parameters = current with voltage and time limits
  - Trickle charge parameters = current with time, voltage, and temp limits
  - Number of cycles entered by user
- LabVIEW for datalogging
  - Battery state time, voltage, current and temperature read each scan
  - Uses fencepost and deadband features to minimize stored data.
  - Logs battery state t, V, I, and T at the end of each state.

Battery environment maintained with water and air bath
- 1355 cc (83 in³) available for all ten batteries
- range; 0 to 100 °C
Twin Cell Heat Conduction Calorimeter
- made by Hart Scientific, Inc.
- can accommodate D-cells or smaller
- no messy immersion of battery in heat conductive liquids needed
- water bath temperature range is 0 to 100 °C
- water bath stabilizes temperature to ± 0.01 °C
- walls of twin cells measure heat with thermoelectric sensors
- 200 second time constant
- 100 μW resolution
- 10 channel data acquisition; bath temp, heat, and 8 other user selected
- twin cell design cancels effects of external undesired thermal inputs
- other measurement cell is used for calibration, or
- two batteries can be tested simultaneously with lower resolution
Yuasa 4/3A and prismatic cell cycling

Cycling Performance of Yuasa Ni-MH cells
YuA = 4/3A : 2.3 Ah nameplate
YuP = prismatic: 3.0 Ah nameplate

- YuA-BQ C/6 discharge
- YuA-BQ 1C charge
- YuP-Max C/6 discharge
- YuP-Max C/2 charge
- YuA-ICS 1C discharge
- YuA-ICS 1C charge
- YuA-ICS C/6 discharge
- YuA-ICS C/3 charge
### Tabular comparison of all cells tested

<table>
<thead>
<tr>
<th></th>
<th>AB2</th>
<th>AB5</th>
<th>AB5</th>
<th>AB5</th>
<th>AB5</th>
<th>AB2</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Ni-Cd</td>
<td>Oronic C</td>
<td>Sanyo 4/3A</td>
<td>Sanyo 4/3AU</td>
<td>Yuasa 4/3A</td>
<td>Yuasa P</td>
<td>Toshiba 4/5A</td>
</tr>
<tr>
<td>Nominal cell weight (g)</td>
<td>80</td>
<td>84</td>
<td>49.2</td>
<td>50.6</td>
<td>49.9</td>
<td>75.7</td>
<td>32</td>
</tr>
<tr>
<td>Nominal cell volume (L)</td>
<td>0.0241</td>
<td>0.0241</td>
<td>0.014</td>
<td>0.0145</td>
<td>0.0147</td>
<td>0.0202</td>
<td>0.00976</td>
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<tr>
<td><strong>Benchmark bg2300 charger</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Discharge output (% of nameplate)</td>
<td>1.07</td>
<td>0.78</td>
<td>0.87</td>
<td></td>
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<tr>
<td>Ah C/D ratio</td>
<td>1.15</td>
<td>1.23</td>
<td>1.12</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Wh C/D ratio</td>
<td>1.35</td>
<td>1.83</td>
<td>1.38</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Wh t C/D ratio</td>
<td>0.96</td>
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<td>Wh C/D ratio</td>
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Note: All figures obtained while charging/discharging at C rates.
Abuse Tolerance Determination

of

Commercial Ni-MH cells
<table>
<thead>
<tr>
<th>Outline</th>
<th>Propulsion and Power Division</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Eric Darcy</td>
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- Objectives
- Test Matrix
- Overcharge
- Reversal
- Short Circuit
- Heat-to-Vent
- Conclusions
<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Shape</th>
<th>Capacity, Ah</th>
<th>Overcharge</th>
<th>Reversal</th>
<th>Short Circuit</th>
<th>Heat-to-Vent</th>
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<td>Furukawa</td>
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<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>Goldpeak</td>
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<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>Harding</td>
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<td>1.1</td>
<td>x</td>
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<td>x</td>
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<td>x</td>
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<td>x</td>
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<tr>
<td>Harding</td>
<td>C</td>
<td>3.25</td>
<td>x</td>
<td>x</td>
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<td>x</td>
</tr>
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<td>4/3A</td>
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<td></td>
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<td>x</td>
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<td>x</td>
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<td>x</td>
</tr>
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<td>x</td>
<td>x</td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>Yuasa</td>
<td>4/3A</td>
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<td></td>
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<td>x</td>
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<tr>
<td>Yuasa</td>
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Overcharge Tests

<table>
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<tbody>
<tr>
<td>Eric Darcy</td>
</tr>
<tr>
<td>11/16/94</td>
</tr>
</tbody>
</table>

Overcharge reactions

- Negative MH electrode:
  \[ 2 \text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \rightarrow 4 \text{OH}^- \]

- Positive NiOOH electrode:
  \[ 4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \]

**Conditions**
- Charge input > 200% of nameplate capacity
- 4 tests run per cell type
  - low rate (C/3) at room temperature (RT) and at 0 °C
  - high rate (2C) at RT and at 0 °C

**Results**
- At C/3 and RT, no cells leaked and found no evidence of leaking
- At C/3 and 0 °C, only Toshiba and Harding C cell leaked a bit of KOH
- At 2C rate, only the Harding C cell leaked at both temperatures
- Max cell temp = 88 °C by Sanyo and Ovonic cells at high rate, RT
- None of the cells leaked profusively or ruptured
Overdischarge reactions

negative MH electrode; \[ H_2 + 2OH^- \rightarrow 2e^- + H_2O \]

positive NiOOH electrode; \[ 2H_2O + 2e^- \rightarrow 2OH^- + H_2 \]

Conditions
- Forced discharge > 200% of nameplate capacity
- 4 tests run per cell type
  - low rate (C/3) at room temperature (RT) and at 0 °C
  - high rate (2C) at RT and at 0 °C

Results
- All the cells leaked some electrolyte
- Max cell temp = 95 °C with Sanyo cell at high rate, RT
- None of the cells leaked profusively or ruptured
Short Circuit Tests

Conditions
- 4 tests run per cell type
  - low rate (0.1 Ω) at room temperature (RT) and at 0 °C
  - high rate (<0.05 Ω) at RT and at 0 °C

Results
- None of the cells leaked detectable amounts of electrolyte during all tests
- Max cell temp (91 °C) with Harding A cell at high rate, RT (peak I = 12.4A)
- Max peak current was 28.4 A (max T = 79 °C) with Sanyo cell at high rate, RT
Harding A cell

Propulsion and Power Division

Eric Darcy   11/16/94

Short Circuit Abuse Test
Cell: Harding A (S/N 24)
Resistance: <0.05 Ω
Temperature: Ambient

Cell Temperature, F

0 100 120 140 160 180

Time, seconds

-407.

Cell Voltage, V, and Current, A

-407.

Advanced Technologies Session

voltage

current

temperature

NASA Aerospace Battery Workshop
Sanyo 4/3A cell

Short Circuit Abuse Test
Cell: Sanyo 4/3A (S/N 14)
Resistance: <0.05 Ω
Temperature: Ambient

- voltage
- current
- temperature

Time, seconds

Cell Voltage, V, and Current, A

0 200 400 600 800

0 25

100 120 140 160

Cell Temperature, °F
Heat-to-Vent Tests

Propulsion and Power Division
Eric Darcy | 11/16/94

Conditions
- cells pre-charged at C/2 for 130 min within 48 hours of oven test.
- cell were placed in evacuated pressure vessel
- pressure vessel and cell were heated in thermal chamber
- Temperature profile
  - RT to 177 °C in 4-5 hours
  - > 1 hour at 177 °C
  - 177 °C to RT overnight
- Vents detected as small sudden increases in vessel pressure

Results
- All cells vented, some gradually, other discreetly from 130 °C to 171 °C
- Prismatic cells and Ovonic’s C-cell lost the most electrolyte
- Outer insulation of all cells was burnt and cracked
- None of the cells ruptured
# Heat-to-Vent Results

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Shape</th>
<th>mass, g</th>
<th>mass lost, %</th>
<th>Vent temperatures, deg F</th>
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<tr>
<td>Furukawa</td>
<td>prismatic</td>
<td>17.4</td>
<td>4</td>
<td>340</td>
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<tr>
<td>Furukawa</td>
<td>AA</td>
<td>27.5</td>
<td>0.7</td>
<td>304, gradual vent</td>
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<tr>
<td>Gates</td>
<td>4/5A</td>
<td>33.4</td>
<td>1.1</td>
<td>gradual vent</td>
</tr>
<tr>
<td>Goldpeak</td>
<td>7/5A</td>
<td>47.5</td>
<td>0.6</td>
<td>300</td>
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<td>1.2</td>
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<td>C</td>
<td>82.7</td>
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<td>49.9</td>
<td>1.8</td>
<td>266, 276, and 284</td>
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<td>prismatic</td>
<td>75.8</td>
<td>3.8</td>
<td>gradual vent</td>
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</table>
• Commercial Ni-MH cells are very tolerant to short circuits
• Overcharge and reversal tests resulted in very benign KOH leakage
• Cells vent noticeably and benignly at temperatures over 130 °C
Summary of Commercial Ni-MH Cell Abuse Test Results

Introduction
The purpose of this test was to determine the abuse tolerance characteristics of various commercially available nickel-metal hydride (Ni-MH) cells. Cells from Furukawa, Gold Peak, Gates, Harding, Maxell, Ovonic, Sanyo, Toshiba, and Yuasa were tested. The tests were conducted as sub portion of test number 2P807 at B352 of the Thermochemical Test Area and included overcharge, overdischarge, short circuit, and heat-to-vent cell tests. The tests were started on 4/14/94 and finished on 8/26/94. Table 1 describes the type of cells evaluated and which tests each type was submitted to.

Table 1

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Shape</th>
<th>Capacity, Ah</th>
<th>Overcharge</th>
<th>Reversal</th>
<th>Short Circuit</th>
<th>Heat-to-Vent</th>
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<td>prismatic</td>
<td>3.0</td>
<td></td>
<td></td>
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Overcharge Test
A total of four overcharge tests were performed covering two rates, C/3 and 2C, and two temperatures, room and 0 °C. Each test lasted until a 200% charge input into each cell was achieved. At the C/3 rate, only the low temperature run caused the Toshiba 4/5 A and Harding C cells to lose weight indicating a small venting of electrolyte. At the higher 2C rate only the C cells leaked at both temperature. During the high rate, room temperature test, the Sanyo 4/3A and Ovonic C reached temperatures over 88 °C all others were lower. None of the cells leaked profusely or ruptured.

Reversal Test
A total of four cell reversal test were performed covering two rates, C/3 and 2C, and two temperatures, room and 0 °C. Each test lasted until a >100% reverse charge was drawn from the cell from the point of voltage reversal. Nearly all the cells lost a bit of weight during the tests indicating a venting of some electrolyte. During the high rate, room temperature tests the Sanyo 4/3A and Ovonic C reached temperatures over 88 °C all others were lower. None of the cells leaked profusely or ruptured.

Short Circuit Test
A total of four cell short circuit test were performed covering two loads, 0.12Ω and >0.05Ω, and two temperatures, room and 0 °C. None of the cells leaked or ruptured during any of the short circuit tests. At the high rate and room temperature, the Harding A cell reached the highest temperature of the all the cells, 91 °C, and its peak current was 12.4 A. Under the same conditions, the Sanyo 4/3A cell had a peak current of 28.4 A while attaining 79 °C.
Heat-to-Vent Test

All the cells listed in Table 1 were charged at C/2 rate for 2 hr and 10 min. and then submitted to this test within 48 hours. This test was performed by placing the cell in a pressurized vessel equipped with feed-throughs for cell voltage and temperature measurements. A roughing pump was used to pull a light vacuum on the cell so as best detect changes in pressure from a transducer connected to the vessel. The vessel was placed in an automated thermal chamber. This massive vessel took about 4-5 hours to heat to 177 °C (350 °F) from room temperature. It was maintained there for an hour before letting the vessel naturally cool off. Prior to opening the vessel, it was purged with nitrogen for over 5 min.

All the cells vented, presumably hydrogen, and varying amounts of electrolyte. These vents were sometimes very gradual over the entire heating process, while some cells vented in very discreet events easily associated with a particular temperature. Table 2 lists the weight loss incurred during the test and any discreet vent temperatures for all the cells tested. Exempting the Ovonic C-cell which is an obsolete cell design, the prismatic cells lost the most weight percent during the ventings. Outer insulation of all the cells was burnt and cracked, but none of the cells ruptured. The Sanyo and Toshiba cells showed evidence of forceful vents. The Sanyo cell’s terminal insulator cap on its positive was separated from the lid of the case during the vent. The Toshiba cell’s vent products left white deposits covering the positive end of the cell. Including these last two cells, the venting were very benign and uneventful.

Table 2

<table>
<thead>
<tr>
<th>Cell</th>
<th>Size</th>
<th>Weight, g</th>
<th>Weight loss</th>
<th>Vent temperatures, °F</th>
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<tbody>
<tr>
<td>Furukawa</td>
<td>prismatic</td>
<td>17.4</td>
<td>4.0%</td>
<td>340</td>
</tr>
<tr>
<td>Furukawa</td>
<td>AA</td>
<td>27.5</td>
<td>0.7%</td>
<td>304, gradual</td>
</tr>
<tr>
<td>Gold Peak</td>
<td>7/5A</td>
<td>47.5</td>
<td>1.1%</td>
<td>gradual vent</td>
</tr>
<tr>
<td>Gates</td>
<td>4/5A</td>
<td>33.4</td>
<td>0.6%</td>
<td>300</td>
</tr>
<tr>
<td>Harding</td>
<td>AA</td>
<td>23.9</td>
<td>0.4%</td>
<td>gradual vent</td>
</tr>
<tr>
<td>Harding</td>
<td>A</td>
<td>34.8</td>
<td>0.6%</td>
<td>gradual vent</td>
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<tr>
<td>Harding</td>
<td>C</td>
<td>83.0</td>
<td>0.1%</td>
<td>269, 272, 281, 328, 330, 331, 332, 334, 336, and 340</td>
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<tr>
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<td>4/3A</td>
<td>49.3</td>
<td>1.2%</td>
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<tr>
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<td>82.7</td>
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<tr>
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<td>prismatic</td>
<td>75.8</td>
<td>3.8%</td>
<td>gradual vent</td>
</tr>
</tbody>
</table>

Conclusions

The commercial Ni-MH cells tested behave very benignly when abused electrically and thermally. Their main hazards are the vent of a small amount of hydrogen (>0.1g for the largest cell which is equivalent to 2.5 liters at ambient pressure and temperature) and the leakage of KOH electrolyte. These hazards were not present during the short circuit tests. Overall, these cells are very safe to use in well ventilated applications.
Measurement

of

Thermal properties of Space Ni–MH cell

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S. Kuwajima & K. Koga
National Space Development Agency of Japan
Ni–MH Cell evaluation test : An Update

Measurement of Thermal Properties of Space Ni–MH Cell

Objectives
Experimental Method
Test Condition
Measurement result
Findings
Summary and Future Work
### 35Ah Ni-MH BBM Evaluation Test

#### Test Conditions

<table>
<thead>
<tr>
<th></th>
<th>25% DOD–LEO</th>
<th>40% DOD–LEO</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cell</strong></td>
<td>3 BBM–A + 3 BBM–B</td>
<td>2 BBM–A + 2 BBM–B</td>
</tr>
<tr>
<td><strong>Charge</strong></td>
<td>0.3C, 52.5 min.</td>
<td>0.48C, 52.5 min.</td>
</tr>
<tr>
<td><strong>Discharge</strong></td>
<td>0.5C, 30 min.</td>
<td>0.8C, 30 min.</td>
</tr>
<tr>
<td><strong>DOD</strong></td>
<td>25%</td>
<td>40%</td>
</tr>
<tr>
<td><strong>Charge Return</strong></td>
<td>105%</td>
<td></td>
</tr>
<tr>
<td><strong>Cell Temp.</strong></td>
<td>20°C (Maintained by Chamber)</td>
<td></td>
</tr>
<tr>
<td><strong>Capacity check</strong></td>
<td>Residual Capacity, Full-Charged Capacity at 1,000 cycles 3,000 cycles and then about every 5,000 cycles</td>
<td></td>
</tr>
</tbody>
</table>
Trend of EOCV, EODV, EOCP & EODP

All cells have good performance.

35Ah Ni-MH BBM LEO Cycle Test (DOD 25%)
Trend of EOCV, EODV, EOCP & EODP

BBM-A: EOCV and EOCP increased from about 7,000 cycle
BBM-B: One cell was subjected to DPA at 5294cyc to examine degradation mechanism
The other cell was added electrolyte at 5893cyc and continue cycle.
35Ah Ni-MH BBM LEO Cycle Test

Trend of Capacities

25% DOD

40% DOD

Plot of 6 Cells

Plot of 4 Cells

White-mark: Full-Charged Capacity
Black-mark: Residual Capacity
Current Status of Cycling test

LEO (DOD 25%)
EOCV, EODV, EOCP and EODP are all stable.
So far, capacity trend are better than Ni–Cd Cell

LEO (DOD 40%)
BBM–B
Before DPA, we added electrolyte tentatively, and then capacity, EOCV and
EODV were restored. From result of DPA, there isn’t another cause of
degradation. So that the degradation was caused by dryout of electrolyte.
Then we added electrolyte to the cell at 5893cyc and continued cycling test, and
it works well after that.

BBM–A
EOCV and EOCP increased from about 7000cyc, and it seems like phenomenon
of electrolyte dryout.
We added electrolyte at 8799cyc.
Objectives

NASDA has been developing space Ni–MH cell on contract with SANYO.

1st manufactured cell shows initial capacity of over 35Ah and specific energy of about 50 Wh/kg (about 860g of weight).

Ni–MH cell was decided to be used for OICETS (Optical Inter-orbit Communications Engineering Test Satellite) to be launched in 1998.

When applying new cell to satellite, we have to know the thermal properties of the cell.

Therefor we survey the thermal property of space Ni–MH cell and compare with Ni–Cd cell.
Experimental Method

Using thermopile-type heat sensor for evaluating the calorie from the cell.

Thermopile-type heat sensor measures temperature difference, and it generates a dc voltage directly proportional to the rate of heat flow by using "mV/W·m⁻²"

Insulating thermally from open air by using formed styrene.

Almost heat from the cell goes through the heat sensor along the aluminum cell stack and the bottom of the cell to the cold plate.

This way is convenient, simple, and simulate the actual mounting state and heat flow of satellite battery.
Schematic of the equipment

- Computer
  * Charge and Discharge control
  * Data Storage

- Pen Recorder
  * Output of temperature data

- Circulating Pump of constant temp.

- Voltage meter

- Computer
  * Heat Sensor data storage

- GP-IB
There is some heat leak from styrene BOX.

To evaluate this leak, we use the dummy cell which has 35Ah cell case, and in it, the heater is tied around the electrode plate.

Using this dummy cell, we calibrate the measurement value of heat sensor to real generated heat.
Result of Dummy Cell Test

Ni-MH Heat Flow / コッセイセル 2

Dummy Cell Voltage

Output of Heat Sensor

MONITOR TIME (HI)
We got result that measurement value is linear to output of heater, and proportional constant is about 0.8(sensor/heater).

The response time that output reaches steady heat rate is about two hours.

Therefore output heat of cell does not always indicate instantaneous heat rate.
Specimen: 35Ah Ni–Cd and Ni–MH cell (SANYO)
Cold Plate Temperature: 10° Centigrade

We chose the test condition to simulate the Low Earth Orbit Cycling which may be used by OICETS.

### Cycling Test Condition

<table>
<thead>
<tr>
<th></th>
<th>Condition 1</th>
<th>Condition 2</th>
<th>Condition 3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Charge</strong></td>
<td>C/3 (11.67A)</td>
<td>C/3 (11.67A)</td>
<td>C/3 (11.6A)</td>
</tr>
<tr>
<td></td>
<td>31.5 min.</td>
<td>47.5 min.</td>
<td>19.0 min.</td>
</tr>
<tr>
<td><strong>Trickle Charge</strong></td>
<td>C/50 (0.7A)</td>
<td>C/50 (0.7A)</td>
<td>C/50 (0.7A)</td>
</tr>
<tr>
<td></td>
<td>28.5 min.</td>
<td>12.5 min.</td>
<td>41.0 min.</td>
</tr>
<tr>
<td><strong>Discharge</strong></td>
<td>C/3 (11.67A)</td>
<td>C/2 (17.5A)</td>
<td>C/5 (0.7A)</td>
</tr>
<tr>
<td></td>
<td>30.0 min.</td>
<td>30.0 min.</td>
<td>30.0 min.</td>
</tr>
<tr>
<td><strong>DOD</strong></td>
<td>17%</td>
<td>25%</td>
<td>10%</td>
</tr>
</tbody>
</table>
Result of Cycling Condition 1 (DOD17%)

Ni-Cd, Ni-MH cell

Temperature = 10°C Centigrade

TEST(1), 10~12 cyc

Cell Voltage

Output of heat sensor

Heat rate (W)

Ni-Cd

Ni-MH
Result of Cycling Condition 2 (DOD25%)

Ni-Cd, Ni-MH

Temperature = 10°C Centigrade  TEST(2), 10-12 cyc

Cell Voltage

Output of heat sensor

Ni-Cd
Ni-MH

Heat rate (W)

TEST TIME (H)
Ni-Cd, Ni-MH%

Temperature = 10° Centigrade

Cell Voltage

TEST (3), 10~12cyc

Ni-Cd
Ni-MH

Output of heat sensor

Heat rate (W)
Findings (Cycling test)

Cycling Test

- Concerning the width between min. and max. of heat flow, Ni–MH is bigger than Ni–Cd at DOD 10%, and smaller at DOD 25% and 17%.
- Cell heat became large as DOD is deeper.
- Amplitude and variation of cell heat is different between Ni–MH and Ni–Cd cell but heat average is almost same.
- Ni–MH heat characteristic of charge and discharge seems different from Ni–Cd.
Test Condition (various charge and discharge)

- Heat characteristic at cycling test indicate heat average due to the response time.
- To evaluate the detail characteristics under different charge and discharge rate, we chose the condition as follows,

<table>
<thead>
<tr>
<th>160% Full Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Discharge</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

C/3,C/5,C/8 charge and C/2,C/3,C/5 discharge

<table>
<thead>
<tr>
<th></th>
<th>Condition 1</th>
<th>Condition 2</th>
<th>Condition 3</th>
<th>Condition 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge</td>
<td>C/5 (7.0A)</td>
<td>C/5 (7.0A)</td>
<td>C/8 (4.4A)</td>
<td>C/3 (11.7A)</td>
</tr>
<tr>
<td></td>
<td>6 hours</td>
<td>6 hours</td>
<td>9.6 hours</td>
<td>3 hours</td>
</tr>
<tr>
<td>Discharge</td>
<td>C/3 (11.67A)</td>
<td>C/5 (7.0A)</td>
<td>C/2 (17.5A)</td>
<td>C/2 (17.5A)</td>
</tr>
<tr>
<td></td>
<td>1 Volt cut</td>
<td>1 Volt cut</td>
<td>1 Volt cut</td>
<td>1 Volt cut</td>
</tr>
</tbody>
</table>

There is cell open state for two hours between charge and discharge.
Result of 160% Full Charge

Ni-Cd, Ni-MH%  Temperature = 10°Centigrade  0.1C 160%CHG

Cell Voltage

Output of heat sensor

Heat rate (W)

TEST TIME (H)
Findings (160% Full charge test)

160% Full charge Test

Heat flow during over charge state is almost same (5W) between Ni-Cd cell and Ni-MH cell, and this value is as same as that all of charge power became heat.
C/5 charge and C/5 discharge (Condition 2)

Ni-MH, Ni-Cd

Cell Voltage

Heat Sensor

Voltage (V)

Heat Sensor (mV)

TEST TIME (H)

1994 NASA Aerospace Battery Workshop

Advanced Technologies Session
C/3 charge and C/2 discharge (Condition 4)

- **Ni-MH, Ni-Cd**
- **Cell Voltage**
- **Heat Sensor**

![Graph showing cell voltage and heat sensor over test time for Ni-MH and Ni-Cd batteries.](image-url)
Findings (various charge and discharge)

C/2, C/3, C/5 discharge and C/3, C/5, C/8 charge test

- Cell heat of Ni-MH during effective charging time is larger than Ni-Cd cell at any discharge ratio.
- Cell heat of Ni-MH becomes large according to charge rate, but cell heat of Ni-Cd is almost 0 W at any charge rate.
- In the case of discharging time, cell heat of two kind of cell is almost same.
Summary

Cycling test
Average of heat is almost same between Ni–MH and Ni–Cd cell.
Amplitude of heat is different between Ni–MH and Ni–Cd cell.

C/3, C/5, C/8 charge test
Cell heat of Ni–MH is bigger than Ni–Cd at any charge rate.

C/2, C/3, C/5 discharge test
Cell heat of Ni–MH is almost same as Ni–Cd at any discharge rate.

Concerning the amplitude difference at cycling test
The heat of Ni–Cd cell at charge is lower than Ni–MH and cell heat at discharge is same, so at cycling condition, amplitude of Ni–Cd cell heat becomes larger than Ni–MH. This explain the result at cycling (except DOD 10%).
Summary and Future work (2/2)

Concerning the same heat average at cycling test

From the result of charge and discharge test, cell heat of Ni–MH was exothermic during charge, and in addition, discharge heat is same as Ni–Cd. This suggest that the heat average becomes more than Ni–Cd cell, but result at cycling test shown same level. Two kind of test result is not compatible.

To evaluate these result more detail, we must do quantitative analysis like computer simulation of cycling test using the result of charge and discharge test.

Future work

• For quantitative analysis, we need more measurement data.
• Simulation of Ni–MH thermal property by use of dummy cell.
• Computer simulation in the same parameter as test condition.