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Energy Products

Gates Aerospace Batteries

NiMH STORAGE TEST

AND CYCLE LIFE TEST

R. Dan Dell
Glenn C. Klein
David F. Schmidt
Gates Aerospace Batteries

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NiMH STORAGE TEST AND CYCLE LIFE TEST

R. Dan Dell, G. C. Klein and D. F. Schmidt
Gates Aerospace Batteries
Gainesville, Florida

Abstract

Gates Aerospace Batteries is conducting two long term test programs to fully characterize the NiMH Cell Technology for aerospace applications. The first program analyzes the effects of long term storage upon cell performance. The second program analyzes cycle life testing and preliminary production lot testing. This paper summarizes these approaches to testing the NiMH couple and culminates with initial storage and testing recommendations.

Long term storage presents challenges to deter the adverse condition of capacity fade in NiMH cells. Elevated but stabilized pressures and elevated but stabilized end-of-charge voltages also appear to be a characteristic phenomenon of long term storage modes. However, the performance degradation is dependent upon specific characteristics of the metal-hydride alloy. To date, there is no objective evidence with which to recommend the proper method for storage and handling of NiMH Cells upon shipment from our facility. This is particularly critical due to limited data points that indicate open circuit storage at Room Temperature for 60 to 90 days will result in irrecoverable capacity loss. Accordingly a test plan was developed to determine what method of mid term to long term storage will prevent irrecoverable capacity loss. The explicit assumption is that trickle charging at some rate above the self-discharge rate will prevent the irreversible chemical changes to the negative electrode that result in the irrecoverable capacity loss. Another premise is that lower storage temperatures, typically 0 °C for aerospace customers, will impede any negative chemical reactions. Three different trickle charge rates are expected to yield a fairly flat response with respect to recoverable capacity versus baseline cells in two different modes of open circuit. Specific attributes monitored include: end-of-charge voltage, end-of-charge pressure, mid-point discharge voltage, capacity, and end-of-discharge pressure.

Cycle life testing and preliminary production lot testing continue to dominate the overall technology development effort at GAB. The Cell Life Test Program reflects continuing improvements in our baseline cell designs. Performance improvements include lower and more stable charge voltages and pressures. The continuing review of Production Lot Testing assures conformance to our design criteria and expectations. This is especially critical during this period of transferring technology from the R & D status to production.

Long Term Storage Test Program

Introduction: NiMH cells with certain alloy negatives are known to experience measurable capacity fade when stored under adverse conditions. However, there was no objective evidence with which Gates Aerospace Batteries could recommend to their customers the proper method for storage and handling of NiMH Cells upon receipt at their facility. This is particularly critical due to limited evidence that indicates that open circuit storage at Room Temperature for 60 to 90 day will result in irrecoverable capacity loss.

A Test Plan was developed to determine what method of mid term to long term storage would prevent irrecoverable capacity loss. The explicit assumption is that trickle charging at some rate above the self-discharge rate will prevent the irreversible chemical changes to the negative electrode that result in the irrecoverable capacity loss. Another assumption is that lower storage temperatures, typically 0 °C for aerospace customers, will slow down any negative chemical reactions. Finally, the general recommendation to not deplete NiMH cells below 0.5 volts explicitly prevents storage in the shorted condition as is typical with NiCd technology.

Accordingly, a test plan was devised to subject five cells to five different storage methods for a minimum of 90 days. This initial 90 day period was divided into three specific periods of 30 days. Extension of that test plan to a longer period is dependent upon those results in addition to availability of test equipment. Further iterations to that test plan both for test parameters and quantity of cells are dependent upon those results.

Test Cells: The five test cells selected for the test program are residuals from the first production lot of 47B024AM01 cells rated at 24 Amp-Hour. Initial capacity for all cells will be as tested during normal Acceptance Testing. The cells weigh 670 grams with a Specific Energy of 43.77 Whr/Kg.

Test Plan: The overall plan shown in Figure 1 is to subject three cells to three different rates of trickle charge while at 0 °C, this will determine the optimum charge rate should a trickle charge be necessary. Two additional cells to be left in open-circuit and then become the fourth and fifth test cells. The fourth cell will be fully charged, then open-circuited and placed in the same environmental chamber at 0 °C as a first baseline. The fifth cell will be depleted to 0.5 volt, then open-circuited and placed in the same environmental chamber at 0 °C as a second baseline.

The five cells were initially discharged to 0.5 volts at 23 °C upon completion of Acceptance Testing. The cells were then evacuated to a vacuum of 26 to 30 inches Hg, and the gage/valve assembly left on each cell. Cell Nos. 1, 2, and 3 were charged at 2.4 amps for 20 hours @ Room Temp and then stored at trickle charge rates of C/100, C/75 and C/50 based upon actual lot average capacity. Numerical charge rates are 250, 333 and 500 milliamps respectively. Cell No. 4 was charged at 2.4 amps for 20 hours @ Room Temp placed in open circuit and stored in the same environmental chamber at 0 °C. Cell No. 5 was placed in open circuit and stored in the same environmental chamber at 0 °C.

Data Collection: The data collected in this test included response voltage and pressure on a daily basis. Each 30 days the five cells are removed and discharged at 12.0 amps to 0.9 volts. The cells are then subjected to three Room Temperature Verification Capacity Cycles per the standard acceptance testing to determine if capacity loss has occurred. The cells are charged at 2.4 amps for 20 hours before returning to their respective Trickle Charge. It was initially expected that 3 or 4 of these 30 day cycles can be performed with currently available resources.

Expected Results: The three different trickle charge rates are expected to yield a fairly flat response with respect to recoverable capacity. Cell No. 4 stored in fully charged open-circuit is expected to not yield a measurable capacity fade. Cell No. 5 stored in depleted open-circuit is expected to yield a measurable capacity fade, or irrecoverable capacity. These results will be compared with a previous test wherein a single 7 AH cell was stored in open-circuited condition at Room Temperature for 90 days. Specific attributes to be monitored include: end-of-charge voltage

[EOCV], end-of-charge pressure [EOCP], mid-point discharge voltage, capacity, and EODP.

Specific attributes to be analyzed include:

1. Stability of voltages and pressures for the three cells at different trickle charge rates,

2. Stability of voltages and pressures for all cells during the charge portion of the Capacity Verification Cycles following each 30 day storage period; and,

3. Stability of capacities and end-of-discharge pressures for all cells during the discharge portion of the Capacity Verification Cycles following each 30 day storage period.

<u>Test Results</u>: Test Results are summarized in Tables 1 and 2, and are graphically displayed thereafter in Figures 2 to 7. The key to Cell Condition as noted in Tables 1 and 2 is as follows:

0.250A T/C indicates a fully charged cell and trickle charge rate of 0.25 amps during storage;
0.333A T/C indicates a fully charged cell and cell trickle charge rate of 0.25 amps during storage;
0.500A T/C indicates a fully charged cell and cell trickle charge rate of 0.25 amps during storage;
C & O/C indicates a cell that was fully charged and stored in open-circuit; and,
D & O/C indicates a cell that was depleted and stored in open-circuit.

The Ave. Volt. [average pressure] at Day 1 to 3 and at Day 28 to 30 was used to remove any perturbations from a single day. The average pressure was treated similarly. EOCV and EOCP are common abbreviations for end-of-charge voltage and pressure. However, the abbreviation EODP for end-of-discharge pressure has more significance with nickel-metal hydride technology. This is due to residual partial pressures from deterioration of the hydride alloy that may tend to inflate this EODP and thus become a strong indicator of cell deterioration and failure.

Thus, Table 1 becomes the simple summary of performance readings over three periods of thirty days. Table 2 provides the first indication of performance characterization and stability. This data is plotted on Figures 2 to 7 and forms the basis of the following discussion of test results:

End-of-Charge Pressures (see Figure 2) appear consistent for all cells at this point as was expected. These pressures remain fairly constant with increasing number of 30 day cycles. These pressures are somewhat elevated, but otherwise appear unremarkable.

End-of-Charge Voltages (see Figure 3) appear both consistent and constant for all cells with increasing number of 30 day cycles.

End-of-Discharge Pressures (see Figure 4) appear consistent for all cells at this point as was expected. The slight rise and fall with increasing number of 30 day cycles is a test artifact that appears to affect all cells equally.

Capacity (see Figure 5) appears fairly consistent except for Cell Nos. 3 and 5. Certainly, some test artifact appears to have affected those two cells. It is too early to determine from this single indicator whether capacity degradation is occurring on Cell No. 5. Cell No. 3 does appear to be experiencing some continuing capacity growth as confirmed by the mild overcharging indicated in Figure 7.

Voltage Change (see Figure 6) of -360 mV for Cell No. 5 appears to be a test artifact. From Table 1, the cell voltage at the end of the second 30 day period is significantly out-of-family for inexplicable reasons.

Voltage Change over multiple 30 day periods for cells undergoing three different trickle charge rates appears to be independent of their respective charge rates.

Pressure Change (see Figure 7) over multiple 30 day periods appears independent of the initial state-of-charge for those cells in open-circuit.

Pressure Change for multiple 30 day periods appears somewhat inconsistent as regards the trickle charge rate of 0.33 amps in that it would be expected to lie between the response curves for the 0.25 amp and 0.50 amp charge rates. However, Cell No. 2 at 0.33 amp trickle charge rate appears to have a tapering-off of pressure response. Whereas Cell No. 3 at 0.50 amps is still experiencing some mild overcharging during the 30 day period.

LEO Cycle Life Test Program

Cycle life testing under LEO conditions and limited cell production has dominated GAB's in house development program for more than two years. The life test program, involving a host of different cell designs continues to confirm the selection of the first generation cell design earlier this year. This portion of the paper continues to update the battery community of the cycle life performance of the first generation cells, compared to a) early cells put on test 2 years ago, and b) some recent cell designs that show some rather interesting and different performance characteristics.

A first generation cell design was selected out of the many cell designs that have been subjected to a LEO life test cycle of 50% DOD and 23 °C.

Figure 8 shows a tabulation of the (55) cells in the GAB test program of engineering model cells. Twenty-five (25) cells are continuing the life test as of this Battery Workshop.

Additional cells can be added to the program on a periodic basis in order to validate new design parameters as required. Cell test data, predominately LEO life cycle testing, has been reported at various customer meetings, previous NASA Battery Workshops, the AF Space Power Workshop, and in GAB's NiMH Product Information binder. The latter document is presently in the hands of about 150 customers worldwide.

The cells built for the test program have involved a great number of design variables such as positive electrode types and impregnation, AB_2 and AB_5 negative electrodes, electrode processing and treatments, and at least 6 different separators. Each group of cells shown in Figure 8 contains one or two cells built with the same design variable.

Life cycling for all cells in the table was performed in a 90 minute LEO simulation regime of 35 minutes discharge and 55 minutes charge using an integrator controlled cycler. Each cell is monitored using a FLUKE scanning multimeter interfaced to a PC based data collection system. Cell pressures are monitored by direct reading of gauges (Ashcroft A1S1) attached to the cells. Pressure data is manually entered into the correct data file. The specific test conditions are shown on Figure 8.

All cells were cycled at 50% DOD (nameplate) and room temperature, nominally at 23 °C. A 50% DOD level has been shown in previous testing of NiCd and NiH_2 cells to be sufficiently robust to develop meaningful performance data within a reasonable period of time. The conditions of test were held constant throughout the cells development program so that changes in performance could be meaningfully measured.

The data from three cell designs groups are presented graphically in Figure 9. The first cell group , which we will call "early cells" is the 6 Ahr (AP6:1-6) cell design put on test in October 1991. The last cell of this group, #5, was terminated after 6600 cycles in November 1992.

The second set of data represents GAB's First Generation Cell Design. Cells AP7: #8 and #9 are performing well after 7800 cycles. It is estimated that this group of cells will make 10,000 cycles or more before the EODV drops below 1.0 volt, and cell pressure will still be at a tolerable level.

A third cell design designated AP7:#16 is a more recent design that differs in voltage and pressure characteristics from either the Early or First Generation cell designs and is now up to about 3400 cycles. Pressures are much lower, EOCV is lower but rising at a faster rate, and the EODV is dropping rapidly and may stabilize.

Thus far the First Generation Cell Design still remains an excellent choice. Its voltage and pressure characteristics are relatively stable under such a robust test regime and it is continuing on cycle life at this time. With over 7800 cycles, while AP7: #16 provides the lowest pressure, stabilization of the EODV is still uncertain.

The internal design components of the cell designs being discussed are not being disclosed at this time in view of license agreements, competitive pressures, and GAB ownership interests that could have an impact on future sales and profits.

In order to further establish the performance capability of the NiMH chemistry, GAB has committed an additional 10 cells, of the same first generation cell design, to a matrix LEO cell program. Furthermore, some of our customers have also agreed to perform life tests at their facilities on an additional 38 cells. All the cells are based on the same First Generation cell design.

This matrix test program, in time, will further establish the capability of the GAB NiMH design in the Battery Community.

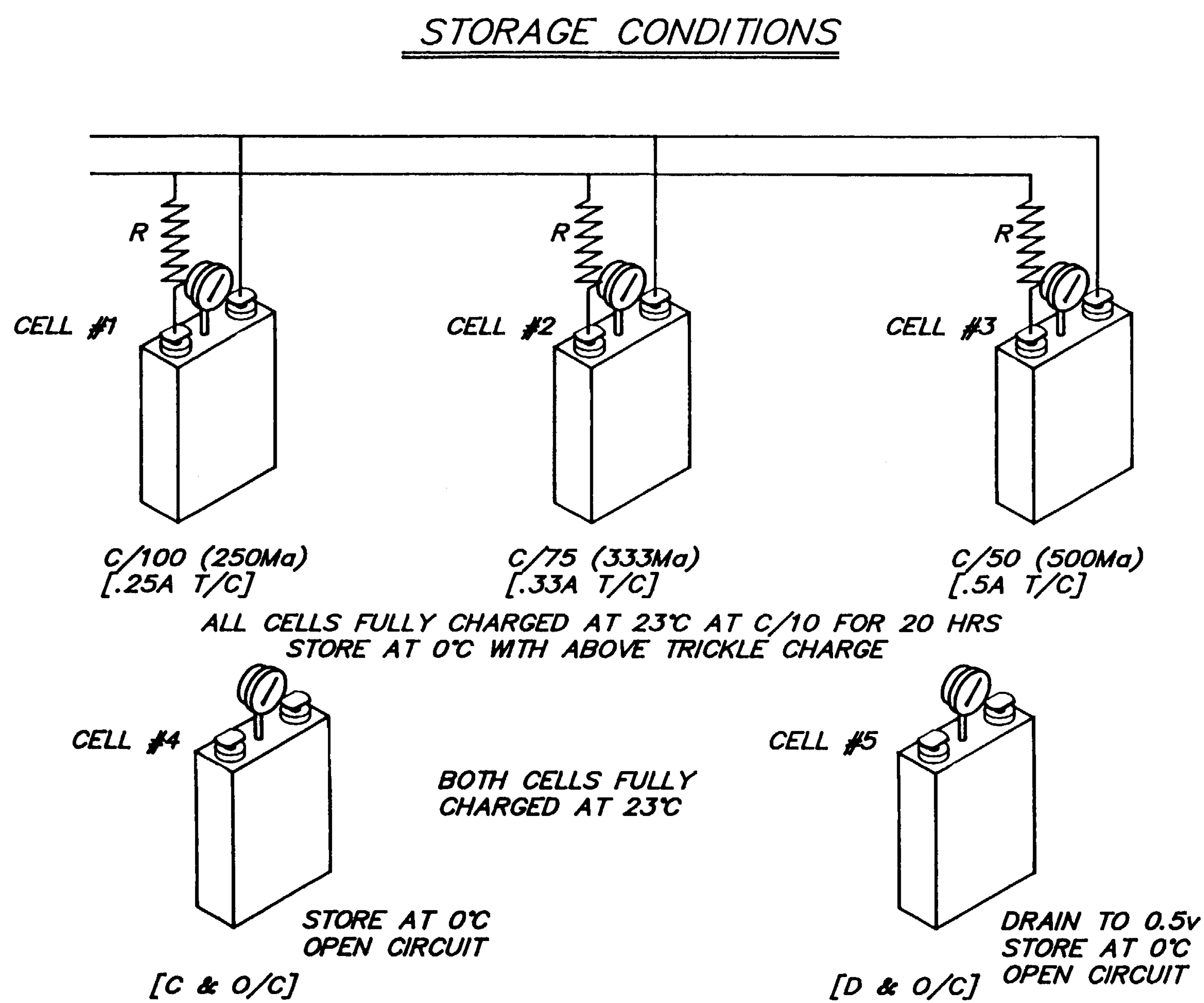
Summary and Conclusions

1. The Long Term Storage Test Program, as originally defined, produced expected results after 3 months. The estimates for the three Trickle Charge rates did show initially to be the probable limits to be used at 0 °C.

2. The true effect of open-circuit storage remains indeterminate during this initial phase of the Long Term Storage Test Program. This is because the state-of-charge is necessarily reset every 30 days by default. Accordingly, since test space is now still available, this test will now be continued uninterrupted for a six month period.

3. GAB has demonstrated LEO life performance to 7800 cycles at 50% DOD and 23 °C. The improvements in cell design have esentially eliminated high pressure as a mode of failure.

Figure 1



STORAGE CONDITIONS
R
R
R
CELL #1
CELL #2
CELL #3
C/100 (250Ma)
[.25A T/C]
C/75 (333Ma)
[.33A T/C]
C/50 (500Ma)
[.5A T/C]
ALL CELLS FULLY CHARGED AT 23°C AT C/10 FOR 20 HRS
STORE AT 0°C WITH ABOVE TRICKLE CHARGE
CELL #4
CELL #5
BOTH CELLS FULLY
CHARGED AT 23°C
STORE AT 0°C
OPEN CIRCUIT
[C & O/C]
DRAIN TO 0.5v
STORE AT 0°C
OPEN CIRCUIT
[D & O/C]

TABLE 1: Summary of Raw Data

Cell & Condition	30 Day Storage [First Period] Ave. Volt. [day 1-3] (volts)	Ave. Volt. [day 28-30] (volts)	Voltage Change (mV)	Ave. Press. [day 1-3] (PSIA)	Ave. Press. [day 28-30] (PSIA)	Pressure Change (PSIA)	Capacity Verification Cycles [3rd Cycle] Capacity (AH)	EODP (PSIA)	EOCV (volts)	EOCP (PSIA)
1: 0.25A T/C	1.459	1.457	-2	0	2	2	25.95	10	1.460	45
2: 0.33A T/C	1.466	1.465	-1	22	19	-3	25.99	9	1.459	62
3: 0.50A T/C	1.473	1.468	-5	32	22	-10	25.56	8	1.457	64
4: C & O/C	1.303	1.201	-102	12	12	0	25.95	8	1.456	54
5: D & O/C	1.143	1.110	-33	13	13	0	25.30	8	1.459	65

Cell & Condition	30 Day Storage [Second Period] Ave. Volt. [day 1-3] (volts)	Ave. Volt. [day 28-30] (volts)	Voltage Change (mV)	Ave. Press. [day 1-3] (PSIA)	Ave. Press. [day 28-30] (PSIA)	Pressure Change (PSIA)	Capacity Verification Cycles [3rd Cycle] Capacity (AH)	EODP (PSIA)	EOCV (volts)	EOCP (PSIA)
1: 0.25A T/C	1.413	1.454	41	5	3	-2	26.18	7	1.461	60
2: 0.33A T/C	1.428	1.459	31	1	16	15	26.27	6	1.461	61
3: 0.50A T/C	1.441	1.467	26	19	20	1	26.45	8	1.460	51
4: C & O/C	1.272	1.247	-25	8	9	1	26.17	6	1.463	48
5: D & O/C	1.168	0.808	-360	9	9	0	25.87	3	1.466	76

Cell & Condition	30 Day Storage [Third Period] Ave. Volt. [day 1-3] (volts)	Ave. Volt. [day 28-30] (volts)	Voltage Change (mV)	Ave. Press. [day 1-3] (PSIA)	Ave. Press. [day 28-30] (PSIA)	Pressure Change (PSIA)	Capacity Verification Cycles [3rd Cycle] Capacity (AH)	EODP (PSIA)	EOCV (volts)	EOCP (PSIA)
1: 0.25A T/C	1.405	1.447	42	1	1	0	25.85	6	1.459	72
2: 0.33A T/C	1.454	1.448	-6	19	16	-3	25.97	6	1.458	73
3: 0.50A T/C	1.464	1.459	-5	25	20	-5	26.30	6	1.458	62
4: C & O/C	1.272	1.226	-46	8	8	0	25.90	5	1.461	64
5: D & O/C	1.202	1.150	-52	7	7	0	25.15	3	1.465	92

TABLE 2: Performance Characterization and Stability

Performance Characterization

[As a function of multiple 30 day periods]

Cell & Condition	Capacity [AH]			
	ATP	Period 1	Period 2	Period 3
1: 0.25A T/C	25.80	25.95	26.18	25.85
2: 0.33A T/C	25.72	25.99	26.27	25.97
3: 0.50A T/C	25.92	25.56	26.45	26.30
4: C & O/C	25.93	25.95	26.17	25.90
5: D & O/C	25.90	25.30	25.87	25.15

Cell & Condition	End-of-Discharge Pressure [PSIA]			
	ATP	Period 1	Period 2	Period 3
1: 0.25A T/C	3	10	7	6
2: 0.33A T/C	2	9	6	6
3: 0.50A T/C	1	8	8	6
4: C & O/C	4	8	6	5
5: D & O/C	4	8	3	3

Cell & Condition	End-of-Charge Voltage			
	ATP	Period 1	Period 2	Period 3
1: 0.25A T/C	1.457	1.460	1.461	1.459
2: 0.33A T/C	1.457	1.459	1.461	1.458
3: 0.50A T/C	1.458	1.457	1.460	1.458
4: C & O/C	1.454	1.456	1.463	1.461
5: D & O/C	1.458	1.459	1.466	1.465

Cell & Condition	End-of-Charge Pressure [PSIA]			
	ATP	Period 1	Period 2	Period 3
1: 0.25A T/C	78	45	60	72
2: 0.33A T/C	81	62	61	73
3: 0.50A T/C	82	64	51	62
4: C & O/C	57	54	48	64
5: D & O/C	75	65	76	92

Stability of Performance

[During multiple 30 day periods]

Cell & Condition	Voltage Change [mV]		
	Period 1	Period 2	Period 3
1: 0.25A T/C	-2	41	42
2: 0.33A T/C	-1	31	-6
3: 0.50A T/C	-5	26	-5
4: C & O/C	-102	-25	-46
5: D & O/C	-33	-360	-52

Cell & Condition	Pressure Change [PSIA]		
	Period 1	Period 2	Period 3
1: 0.25A T/C	2	-2	-4
2: 0.33A T/C	-3	15	18
3: 0.50A T/C	-10	1	11
4: C & O/C	0	1	1
5: D & O/C	0	0	0

During the 3rd Cycle of Capacity Verification

Figure 2: End-of-Charge Pressure

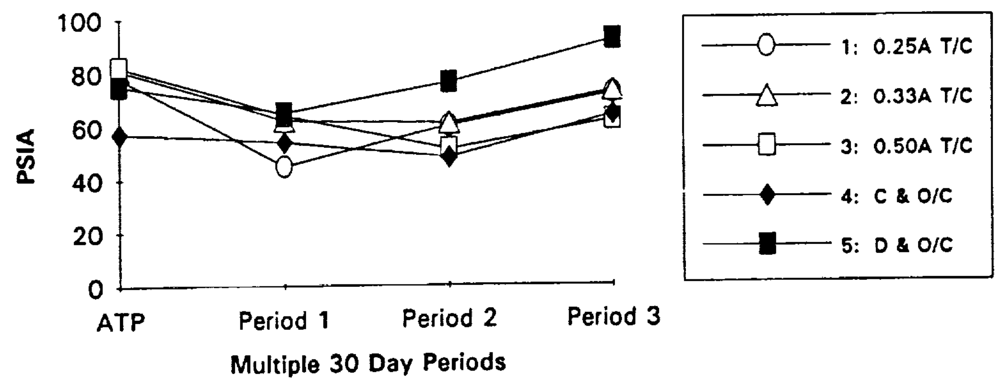


Figure 3: End-of-Charge Voltage

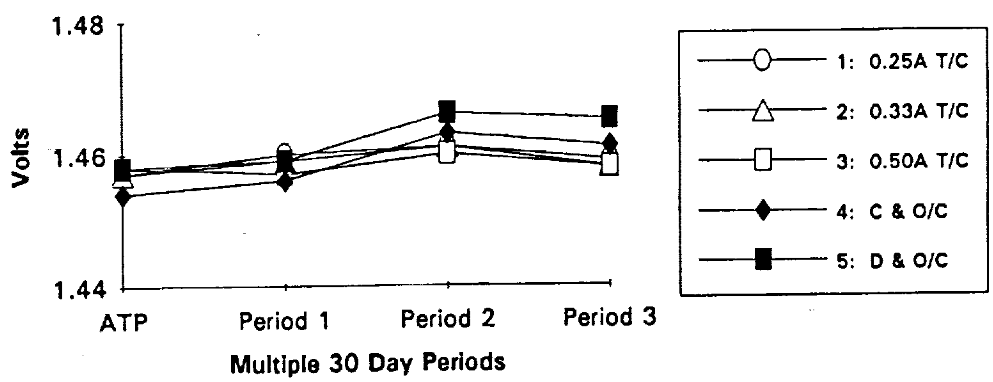
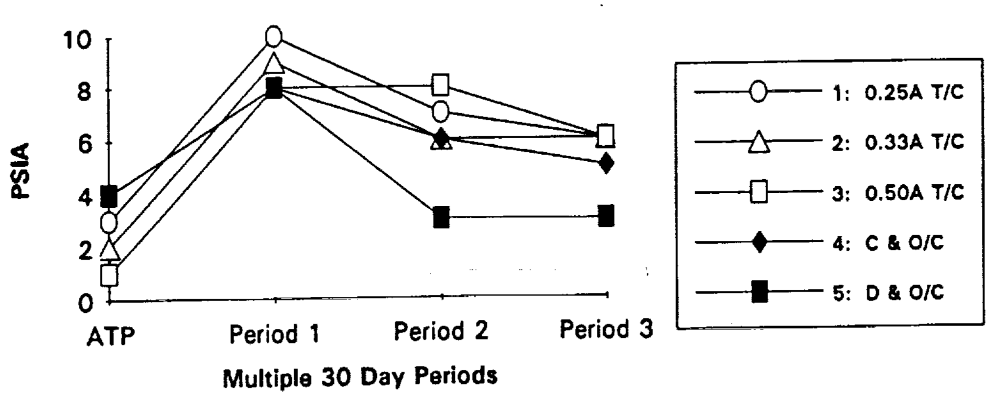
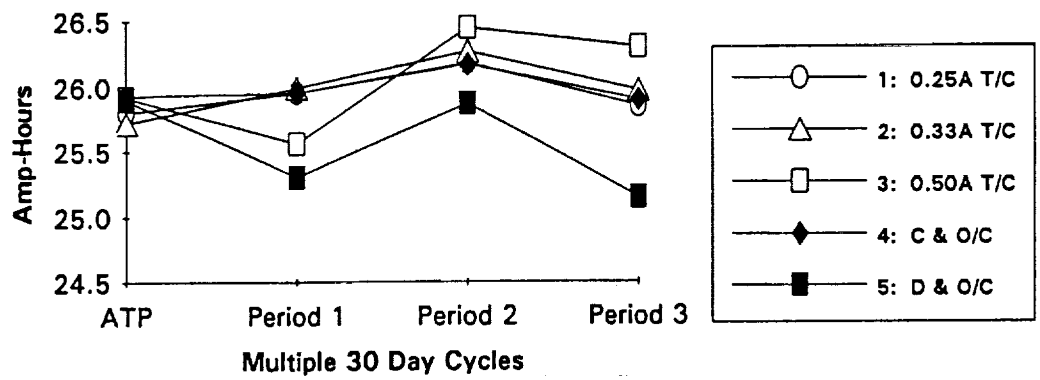


Figure 4: End-of-Discharge Pressure

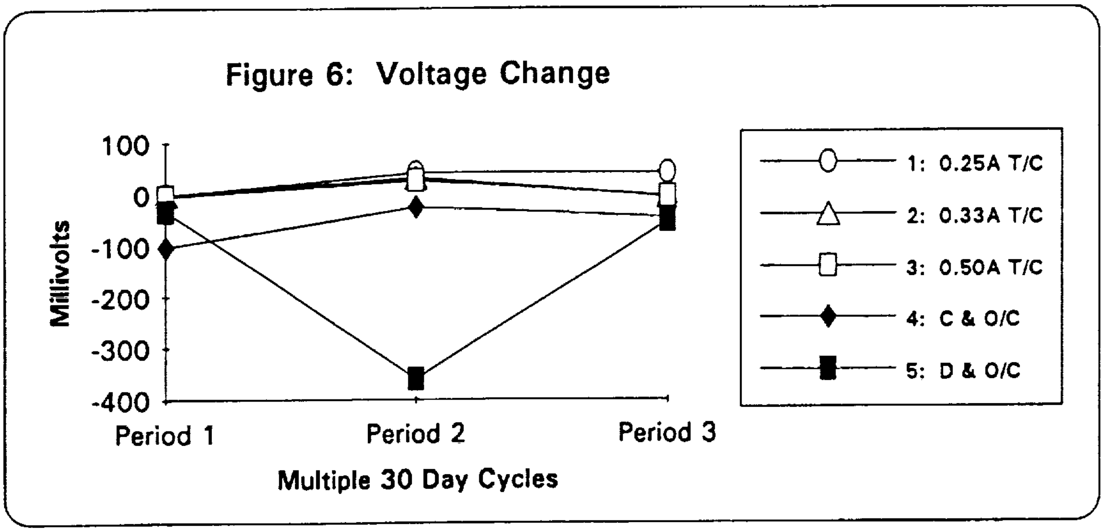


During the 3rd Cycle of Capacity Verification

Figure 5: Capacity



During the 30 Day Storage Periods



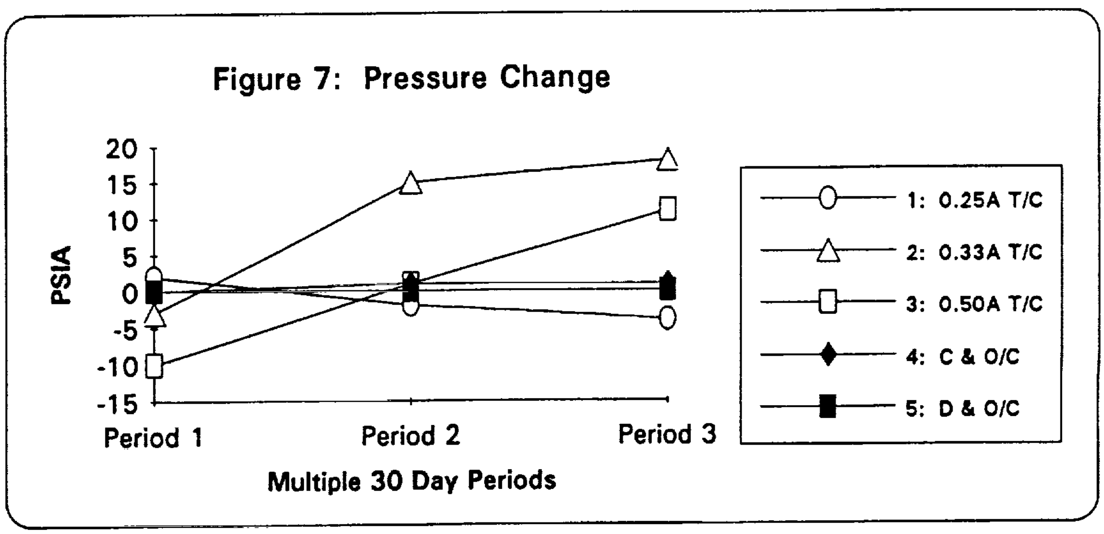


Figure 8

NiMH
CYCLE LIFE PERFORMANCE SUMMARY

(Engineering Model Cells)

Data as of 11/9/93

Cell Rating	Test Group	Temp Deg C	% DOD	# Cells in Test	Maximum Cycles Completed	Cell-cycles	Status
6 Ahr	AP6:1-6	25	50	0(6)	6656	27406	Complete
22 Ahr	AP22:1-2	25	50	0(2)	4236	8472	Complete
22 Ahr	AP22:4	25	50	0(1)	1961	1961	Complete
8 Ahr	AP8:1-12	25	50	0(12)	2206	24600	Complete
7 Ahr	AP7:1-9	25	50	2(9)*	7800	48397	In Test
7 Ahr	AP7:10-21	25	50	9(11)	3400	34600	In Test
7 Ahr	AP7:22-35	25	50	14(14)	2562	35868	In Test
		Total # of Cells		25(55)		181304	

Cells remaining on test.

Original # of cells on test

Total number of Cell-Cycles

Test Conditions:

- --Charge at C/2 Rate for 60 Minutes
- --Discharge at C Rate for 30 Minutes
- --C/D Ratio = 1.05 except in test group AP7:21-35 where some are at 1.03

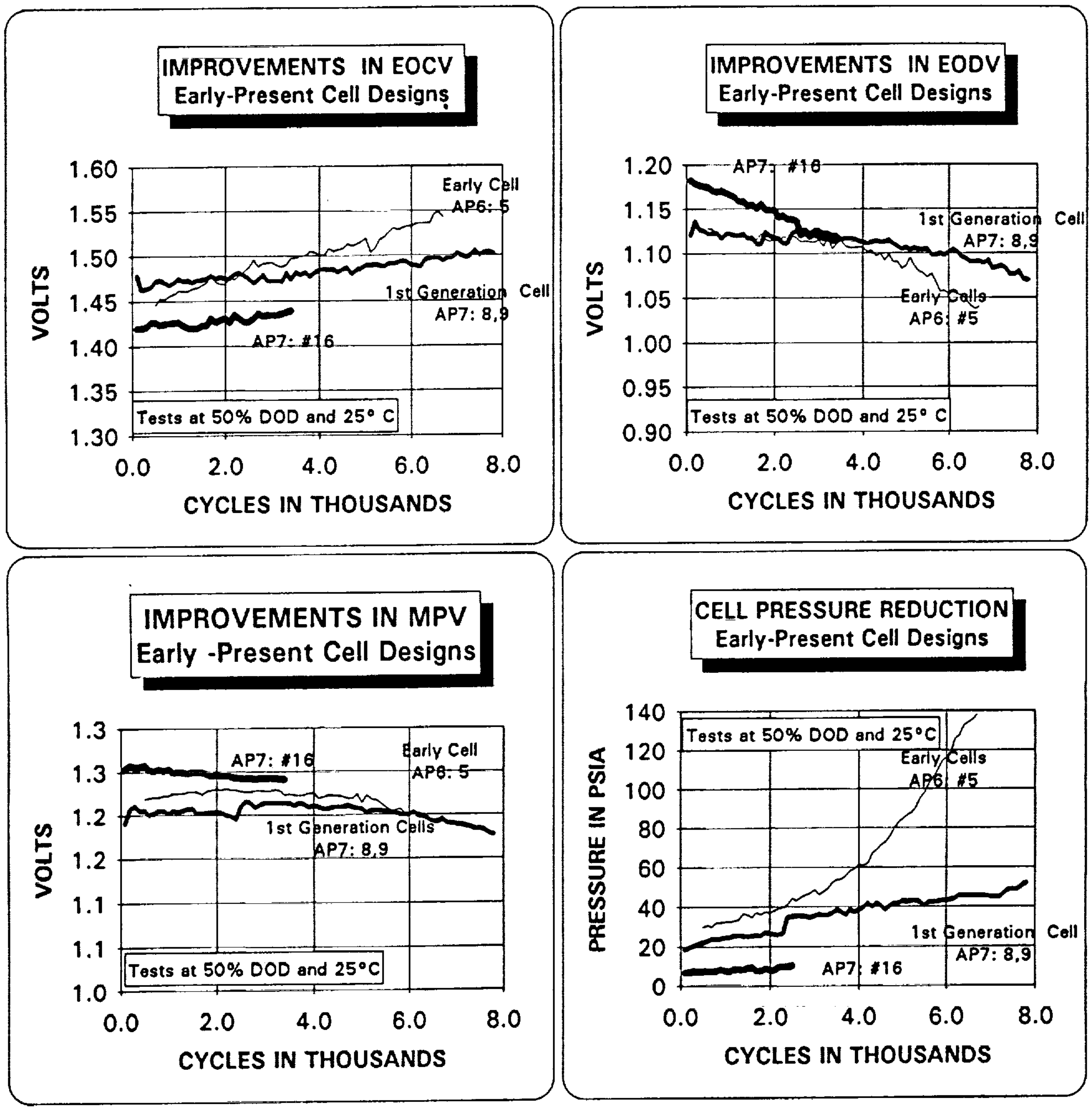
* 1st Generation cell design represented by #8 and #9 cells still on test.

Cell Design:

- --All cells are prismatic construction similiar to NiCd.
- --Each cell test group may be composed of several design variations, i.e. separator types, chemical and ED impregnation, processing additives, loadings, alloys, N/P ratio, etc.

Figure 9

COMPARISON OF EARLY TO PRESENT CELLS



Note: Electrolyte adjustment made at approx. 2400 cycles on 1st Generation Cells.