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Capacity Loss on Storage and Possible

Capacity Recovery for HST Nickel-Hydrogen Cells

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Nickel-Hydrogen Capacity Loss During Storage

- Observed in cells with Negative (Hydrogen) Precharge.
- Capacity Loss measured in cells stored for one month.
- Amount of recoverable capacity decreases with an increase in length of storage period.
- Plausible explanation is migration of Cobalt in Nickel Plate under Hydrogen pressure.
- At low potentials CoHO2 is formed from Nickel active material.
- CoHO2 will redistribute upon cycling as differences in electrode potentials are increased and held.
- Orignal lattice structure of active material is altered and cannot be regained.

Nickel-Hydrogen Capacity Loss During Storage

Negatively (Hydrogen) precharged Nickel-Hydrogen battery cells exhibit a capacity loss/fade during storage. Cells from all vendors are prone to this phenomenon. The loss of useable capacity has been observed in cells stored for short periods of time. One month of storage has caused some cells to exhibit a capacity loss. The amount of capacity lost or shifted and the ability to recover this capacity is a function of the length of storage time. The generally accepted mechanism of capacity loss is a migration of Cobalt away from the substrate in the Nickel plate; higher electrolyte concentrations seem to aid this movement. At electrode potentials less than .5 Volts, under Hydrogen pressure, $CoHO_2$ is formed from the active Nickel material. Destructive Physical Analysis of other battery cells using Nickel couples (Ni-Cd), stored with a Hydrogen pressure, have shown a migration of the Cobalt and the formation of undesirable Cobalt Hydroxides. This migration can lead to the formation of a new voltage plateau below 1.0 Volt. In most cases the lower voltage is not usable and is equivalent to a loss in capacity. Some of the lost capacity can be recovered. The generally accepted method for recovery is to cycle the cell; capacity can be regained more quickly if the difference in electrode potential is raised above 1.2 Volts and the cell is allowed to sit open circuit at 20 to 30 degrees C for several days. Cobalt will redistribute itself in the cell more rapidly by following the latter procedure. The original capacity of the cell cannot be regained after a period of storage in which the capacity fades. The lattice structure of the active material is altered and the Cobalt cannot return to its original form.

Cells

- 24 Cells left from HST Program, TM and FM Lot Cells.
- Stored approximately two years, open circuit at 30 - 40 degrees F.
- Open circuit voltage < .4 Volts.
- Cell Design:

  Air Force Design.
  Dry Sintered Nickel Electrodes, "back to back".
  Zircar Separators with wall wicking.
  Rabbit Eared, Pineapple Slice.
  Stacked on Polysulfone Core with Belleville Washer.
  27% KOH.
  Hydrogen Precharged.

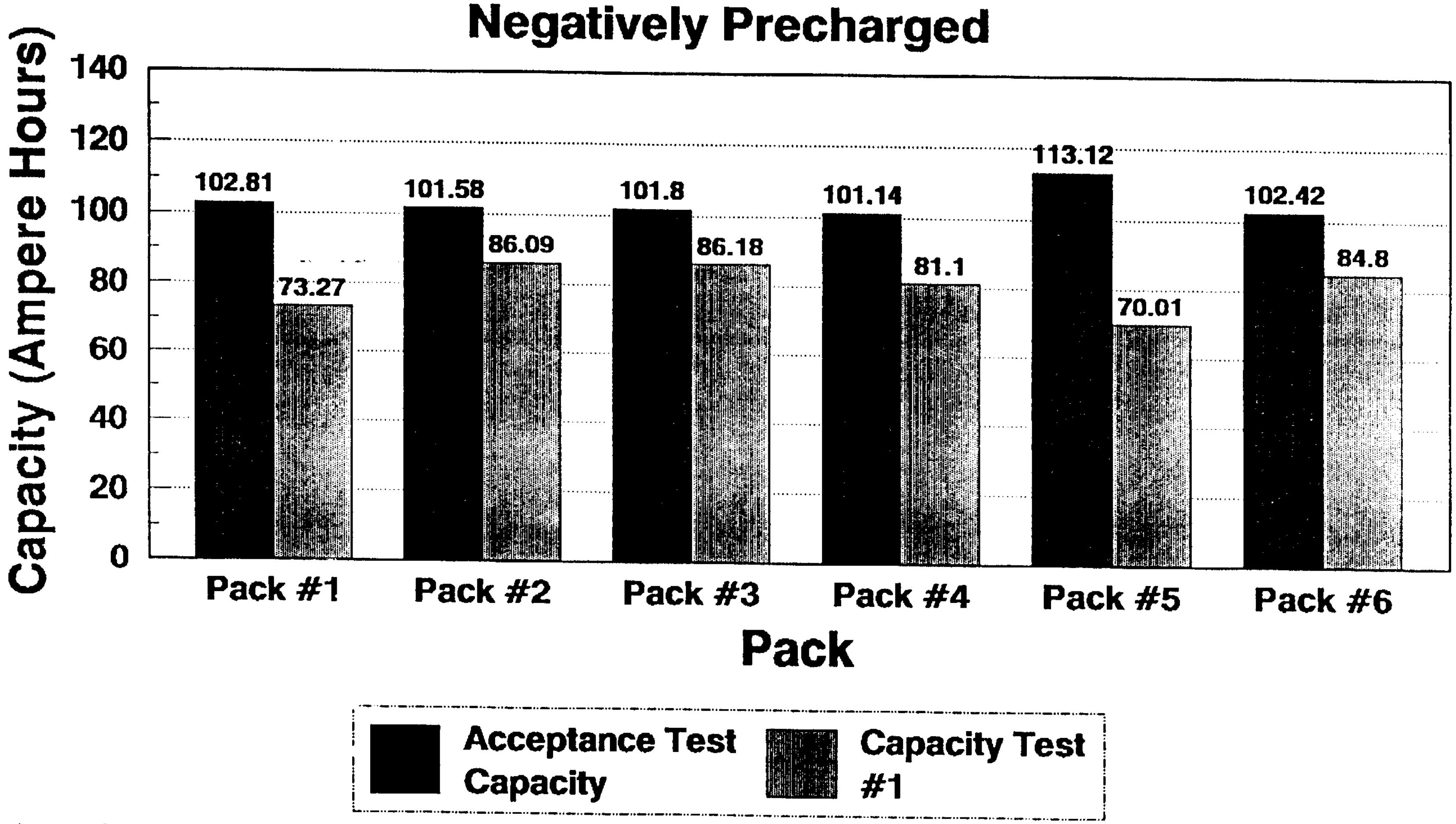
A capacity fade on storage has been observed in the negatively precharged Nickel-Hydrogen cells built during the Hubble Space Telescope program. This capacity fade was noted when residual HST cells were brought out of storage for use in other Nickel-Hydrogen test activities. Twenty four cells were removed from storage and placed in mounting sleeves in preparation for LEO cycling at moderate depths of discharge. These cells had been stored for approximately two years, open circuit in a refrigerator at 0 to 5 degrees C. The open circuit voltage of the cells was less than .4 Volts with an average of .2 Volts.

Subject test cells utilized in this test bed are Eagle-Picher RNH 90-3 cells remaining after completion of the Hubble Space Telescope (HST) program. There are 24 cells from three different cell builds (TM-1, FSM and FM-1) divided into six groups of four cells. Each cell has a cylindrical individual pressure vessel of 718 Inconel formed in two halves 40 mils thick providing a safety factor of four when a 1200 psi operating pressure is assumed. Cell walls are coated with zirconium oxide which in combination with zirconium oxide impregnated cloth separators provides improved electrolyte management, wall wicking and better gas flow path establishment. The cell is stacked using the "pineapple slice" system with back to back nickel oxide positive plates to reduce the number of gas diffusion screens required. The stack is built according to the following pattern on a polysulfone core attached to the weld ring: gas diffusion screen, platinum catalyst negative plate, zirconium oxide cloth separator (2 layers), two nickel oxide positive plates, zirconium oxide cloth separator (2 layers), negative platinum catalyst plate followed by a gas diffusion screen. The stack is held on the core by a Belleville washer and nut at the proper compression. The electrode tabs run down the center of the stack and exit the pressure vessel at the same end at a 45 degree angle to the centerline of the cell (rabbit ear design). The cell halves are attached to the center weld ring and the plate tabs attached to the terminal posts by electron beam welding. The cell is sealed with a formed nylon compression washer (Zytel) which acts as an insulator (terminal from case) as well as a seal. The flight cell is activated with 27% potassium hydroxide, charged in a vented condition and the fill tube pinched off and welded closed.

Useable Capacity Fading

EPI RNH 90-3

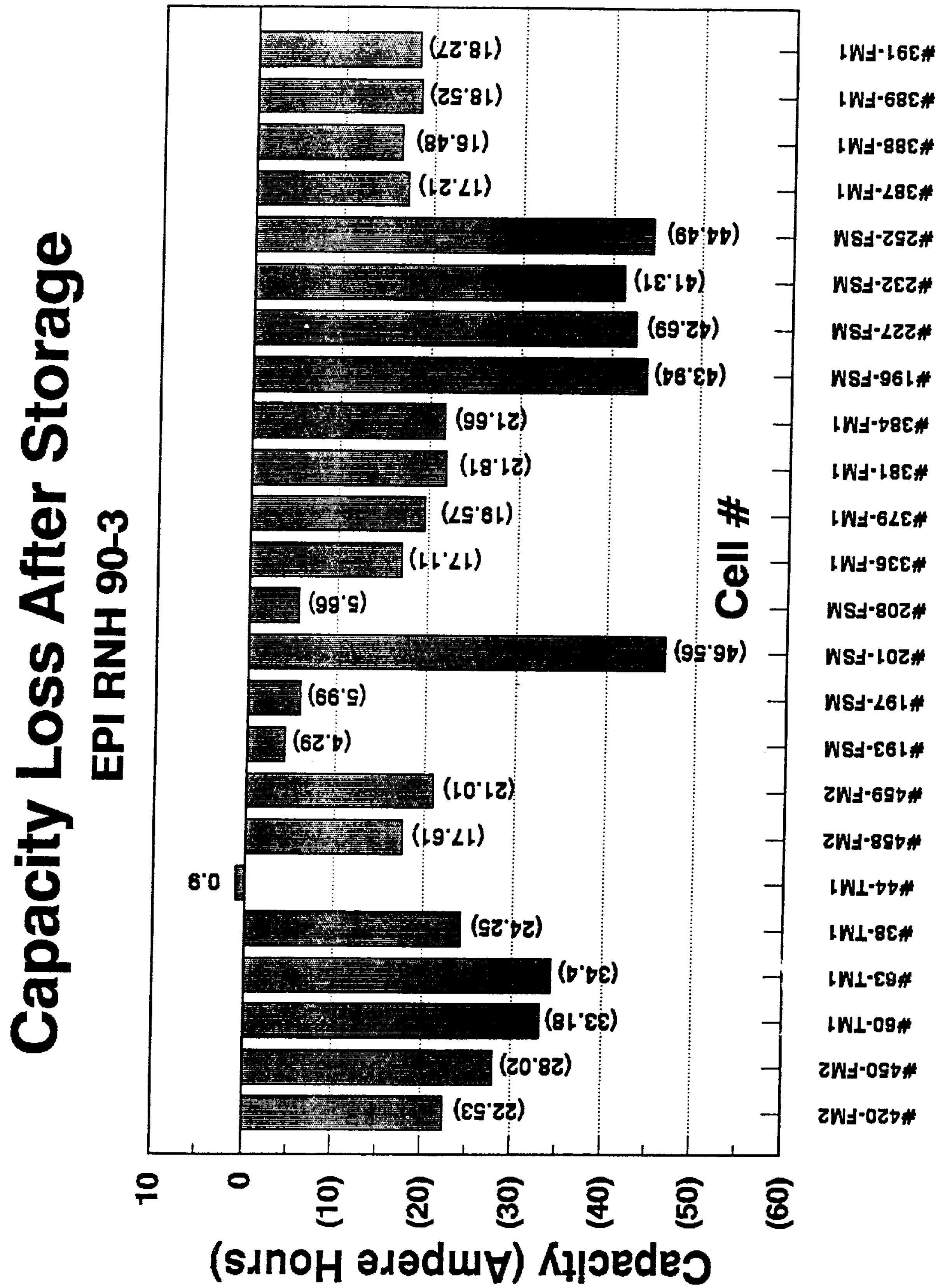
Negatively Precharged



Acceptance Test Capacity, June 1989 – 1.2 Volts.
First Capacity Test, June 1991 – 1.0 Volts.

After installation in the test bed a baseline charge and capacity test was run on the packs to measure the amount of capacity that had been lost during storage. A baseline charge consists of a 160% charge based on the nameplate capacity rating. This charge is accomplished in a 24 hour period at 9.3 amperes for 10 hours and 4 amperes for 14 hours. An hour is allowed for gas recombination and thermal stabilization and a discharge at C/6 (15 amperes) is run to an average cell voltage of 1.0 volt. The ambient temperature was fixed at a constant 0 degrees C during this time. The measured capacity could then be compared to the capacity measured during acceptance testing of the cells. The acceptance test capacity was measured to 1.2 volts while the later tests measure capacity to 1.0 volt. The amount of capacity between 1.2 and 1.0 volts is very small.

It is interesting to note the differences in the amounts of capacity lost. Pack #3 and pack #5 are both composed of flight spare module cells; pack #5 with the highest initial capacity, showed the largest loss while pack #3 with near the lowest capacity retained the most capacity after storage. Pack #5 cells were activated with 31% KOH while pack #3 had three cells activated with 27% KOH and one cell activated with 31% KOH. Packs #4 and #6 contain flight module 1 cells activated with 27% KOH. These two packs show good matching and provide independent data points.



Capacity Loss After Storage
EPI RNH 90-3
Capacity (Ampere Hours)
10
0
(10)
(20)
(30)
(40)
(50)
(60)
Cell #
#420-FM2 (22.53)
#450-FM2 (28.02)
#60-TM1 (33.18)
#63-TM1 (34.4)
#38-TM1 (24.25)
#44-TM1 0.8
#458-FM2 (17.61)
#459-FM2 (21.01)
#193-FSM (4.29)
#197-FSM (5.99)
#201-FSM (46.56)
#208-FSM (5.66)
#336-FM1 (17.11)
#379-FM1 (19.57)
#381-FM1 (21.81)
#384-FM1 (21.66)
#196-FSM (43.84)
#227-FSM (42.69)
#232-FSM (41.31)
#252-FSM (44.49)
#387-FM1 (17.21)
#388-FM1 (16.48)
#389-FM1 (18.52)
#391-FM1 (18.27)

Looking at the cells on an individual basis, it is easy to pick the five cells activated with 31% KOH, they show the highest capacity loss during storage. The other three cells in this test from the same manufacturing build lot were activated with 26% KOH and show the least capacity loss during storage. This data indicates that higher electrolyte concentrations during storage greatly increase the undesirable reactions leading to capacity fading. Packs #4 and #6 show the same range of loss.

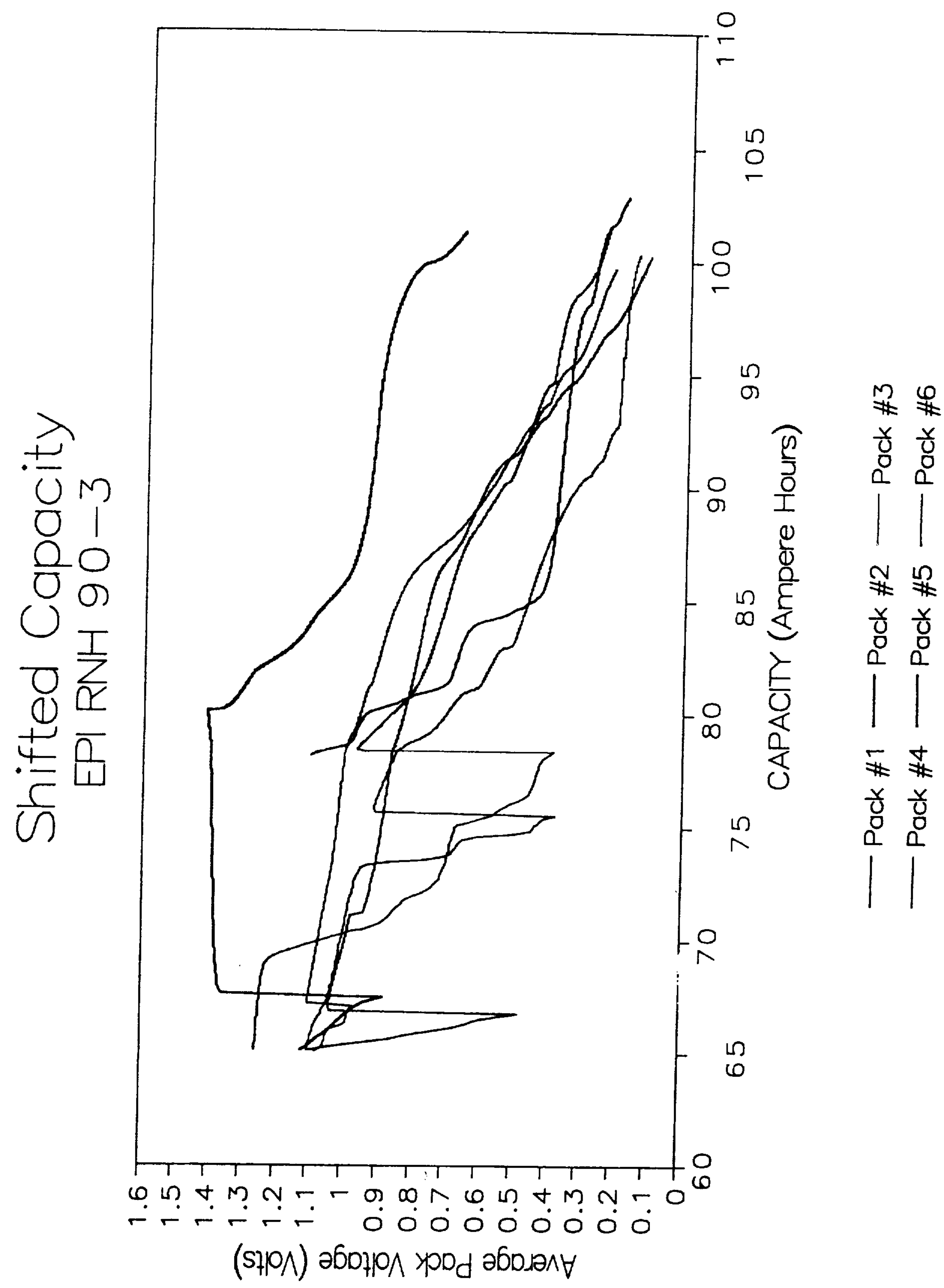
One cell in the group did not show a capacity loss; it delivered the same capacity as measured before storage. This cell belonged to the test module lot of cells and probably had a neutral or positive precharge.

CAPACITY SUMMARY EPI RNH 90−3 (HST CELL)

Capacity Test #1, June 12, 1991, After baseline charge.

Pac #	Cell #	Lot	Serial #	Begin Pressure	Ending Pressure	Begin Voltage	Ahrs Cap to 1.0 V	Psi/Ahr
1	1	FM2	420	1126.24	538.28	1.407	78.3	7.51
	2	FM2	450	1297.7	513.6	1.41	75.27	10.42
	3	TM1	60	1069.82	410.35	1.406	69.52	9.49
	4	TM1	63	1139.43	449.91	1.407	70	9.85
2	1	TM1	38	1142.25	240.4	1.407	77.25	11.67
	2	TM1	44	978.1	11.16	1.396	102.8	9.41
	3	FM2	458	1223.57	441	1.412	84.1	9.31
	4	FM2	459	1058.99	357.2	1.41	80.2	8.75
3	1	FSM	193	1208.38	319.4	1.411	93.1	9.55
	2	FSM	197	1276.76	435.6	1.411	92.4	9.10
	3	FSM	201	1268.72	603.98	1.416	67.9	9.79
	4	FSM	208	1032.92	200.2	1.411	91.31	9.12
4	1	FM1	336	1054.24	322.7	1.41	82.1	8.91
	2	FM1	379	1103.08	345.5	1.411	82.1	9.23
	3	FM1	381	1115.41	392.7	1.412	79.4	9.10
	4	FM1	384	1150.47	387	1.411	80.8	9.45
5	1	FSM	196	1184.19	512.13	1.413	69.52	9.67
	2	FSM	227	1083.53	462.89	1.419	70.98	8.74
	3	FSM	232	1139.49	480.81	1.417	70.98	9.28
	4	FSM	252	1407.79	755.97	1.42	68.55	9.51
6	1	FM1	387	1142.51	331.2	1.412	85.5	9.49
	2	FM1	388	1111.73	305.1	1.409	85.4	9.45
	3	FM1	389	1212.22	418.3	1.413	84.4	9.41
	4	FM1	391	1108.53	333	1.411	83.9	9.24

During activation an attempt was made to achieve a neutral or slightly negative precharge. The activation procedure and the variance allowed on the test module cells could have produced a cell with positive precharge. End of discharge pressures for test module 1 cells indicate that this may have happened. Strain gauges were added to these cells after they were sealed and they subsequently were not able to be individually calibrated. Absolute pressure cannot be discerned; although, these pressures should not be greatly misleading, pressure deltas are correct. The performance of the cell with apparent positive precharge indicates that positively precharged cells are better able tolerate storage periods without degraded performance.

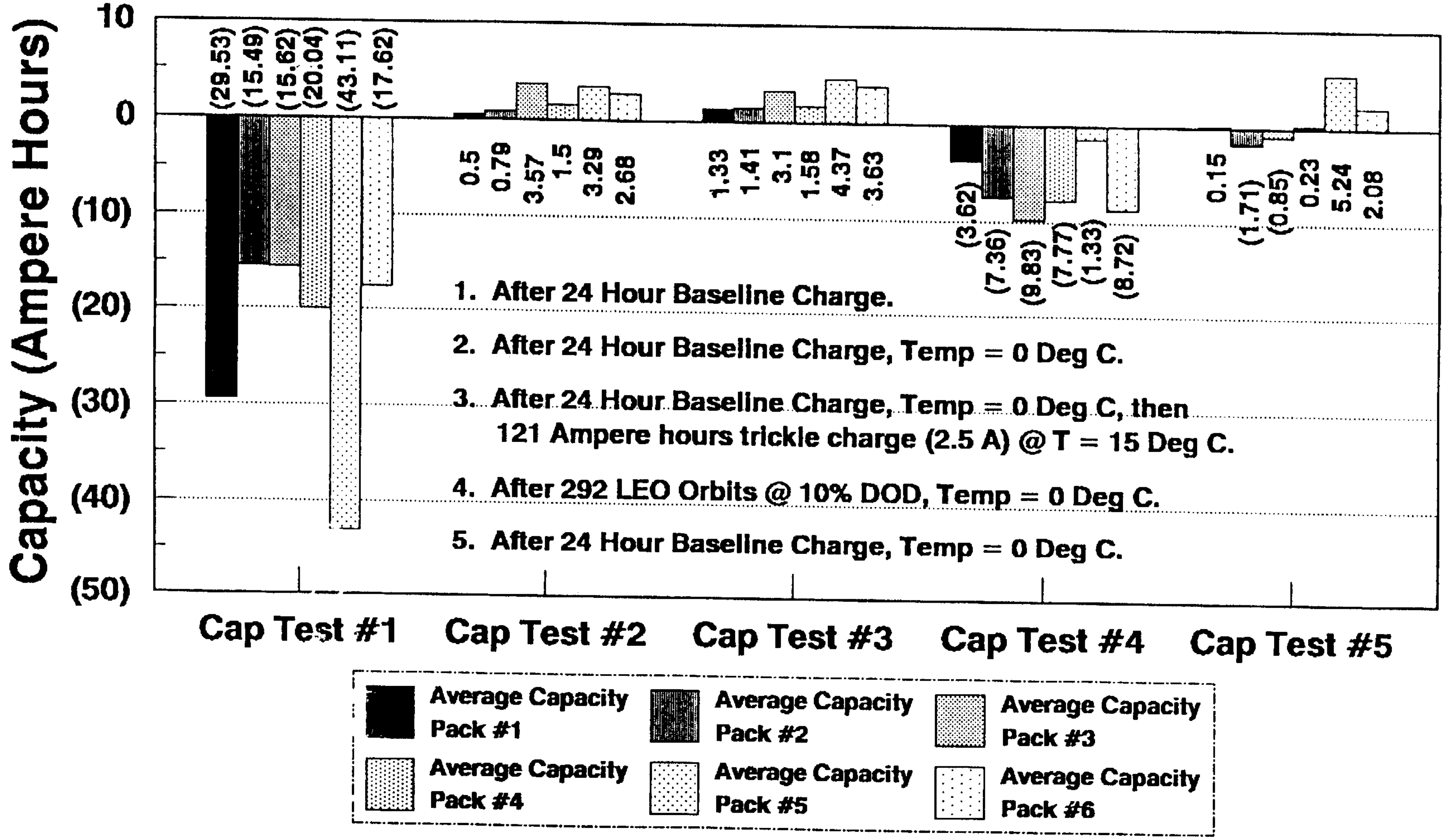


Shifted Capacity
EPI RNH 90—3
Average Pack Voltage (Volts)
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
60
65
70
75
80
85
90
95
100
105
110
CAPACITY (Ampere Hours)
Pack #1
Pack #2
Pack #3
Pack #4
Pack #5
Pack #6

This graph is an attempt to ascertain a shift in capacity to a lower voltage plateau. The graph shows the average cell voltage at the end of the first capacity test as the pack entered reconditioning. The C/6 load was maintained as long as possible until all cells were below 1.0 volts before reconditioning. Packs #4 and #5 and possibly #1 exhibit a shifted (lower) voltage plateau; this plateau does not extend to the original capacity. Pack #6 should have behaved as #4. With the other packs we cannot tell if a shift in capacity has occurred.

Attempts to Recover Capacity

EPI RNH 90-3



Acceptance Test Capacity, June 1989 – 1.2 Volts.
Other Capacity Tests, – 1.0 Volts.

After the first capacity test a second baseline charge and capacity test were performed to check the validity of the first test. The results of the second test verified the first test. At this point, it was recognized that the HST spare battery module (FM1), stored similarly, probably had the same kind of loss in useable capacity. Several procedures followed in an effort to demonstrate the ability of the cells to recover enough capacity to meet the requirements of the HST specification.

The third capacity test occurred after a baseline charge and extensive overcharge. At 0' C the cells received a 24 hour baseline charge and 121 ampere hours trickle charge at 2.5 amperes rate; the temperature was raised to 15' C during the period of trickle charge. It was hoped that by increasing the electrode potential difference to more than 1.2 volts and maintaining the difference at an elevated temperature, the Cobalt would redistribute. The results were not encouraging. It seems that the gas recombination during overcharge precluded the movement.

LEO cycling is thought by many people to be an effective way of recovering faded capacity; subsequently, 292 LEO orbits at 10% DOD were run. The forth capacity test was ran after the LEO cycles and the fifth test after a baseline charge. Capacity recovered was still not at an acceptable level. The beneficial effects of LEO cycling are magnified as the DOD increases; the 292 orbits at 10% DOD had no appreciable effect. Cycling at a deeper DOD was not immediately attempted. A relatively quick method for regaining lost capacity was desired.

EPI

Capacity Recovery Procedure

Cool Cells to 0 Deg C.

Perform Baseline Charge:

- 160% Overcharge in a 24 hour Period.
- Charge 10 Hours at 9.3 Amperes.
- Charge 14 Hours at 4 Amperes.

Raise Temp to 25 Deg C.

Allow Cells to stand open circuit for 10 - 14 days.

Lower Cell Temp to Deg C.

Discharge cell at C/6 to 1.0 V/Cell.

- Discharge at 15 Amperes.

Recondition Cell to > .1 V with resistor.

Perform Baseline Charge.

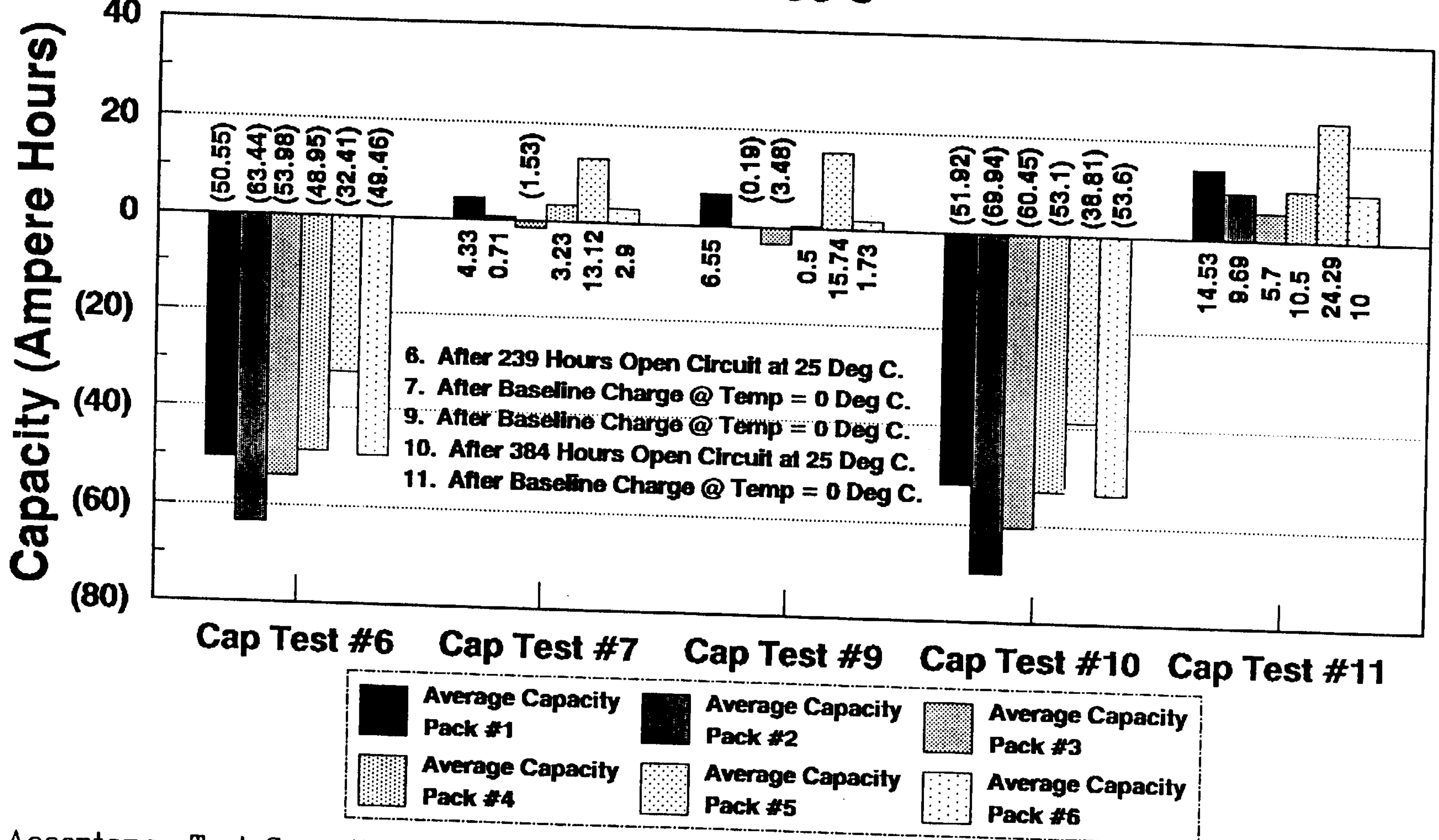
Allow Cells to Stand Open Circuit for 1 Hour.

Discharge cell at C/6 to 1.0 V/Cell.

The cell manufacturer recommended a capacity recovery procedure that elevated the electrode difference of the cell to a high level and allowed the cell to self discharge at room temperature for 10 to 14 days. The manufacturer's suggested procedure was then employed. A capacity test and reconditioning were run after the period of self discharge. A baseline charge and capacity test were then run to measure the effectiveness of the capacity recovery technique.

Attempts to Recover Capacity

EPI RNH 90-3



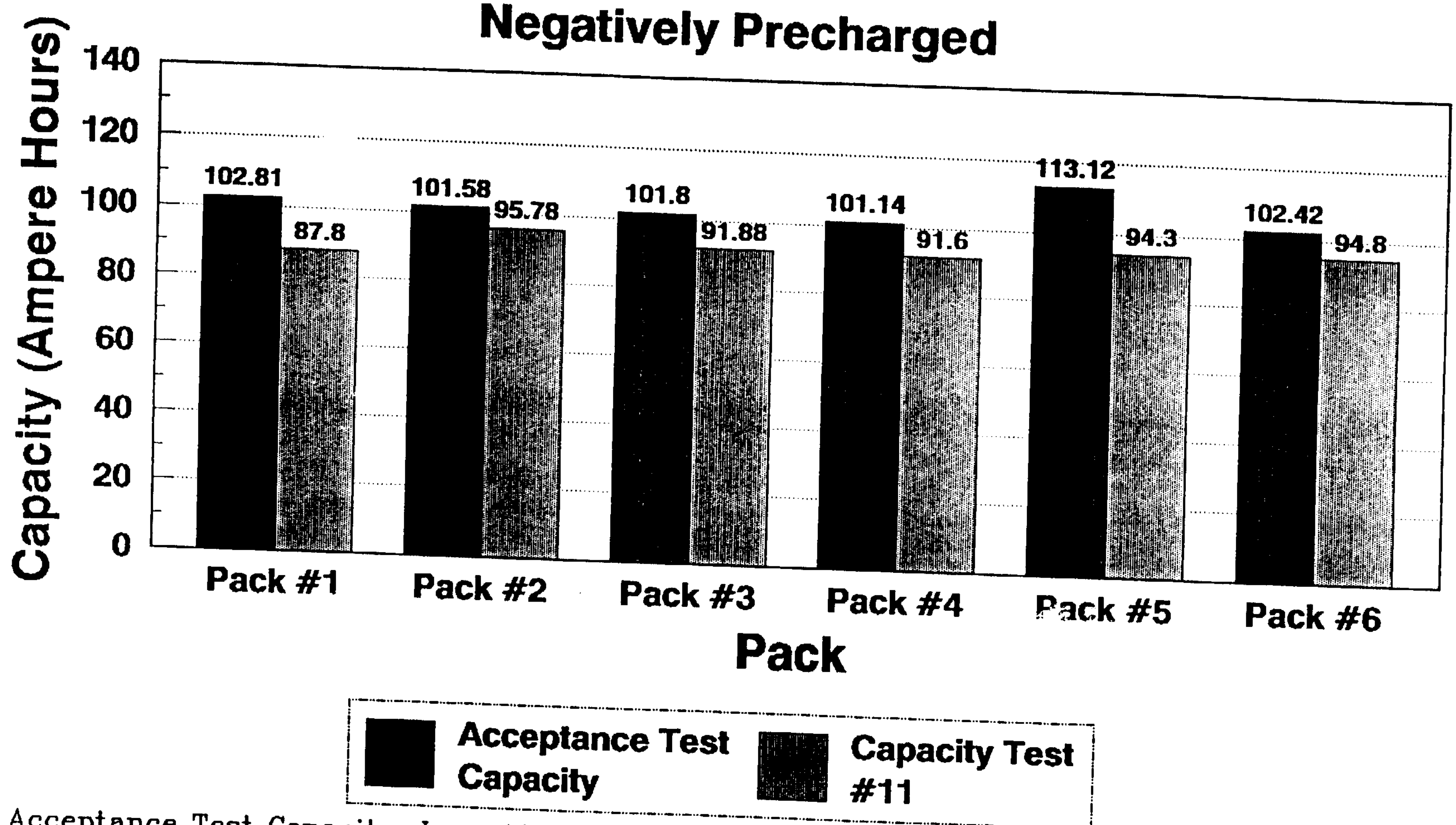
Acceptance Test Capacity, June 1989 – 1.2 Volts.
Other Capacity Tests, – 1.0 Volts.

Capacity test #6 was after the 239 hour open circuit stand. Capacity test #7 measured the capacity gain related to the charged open circuit stand at room temperature. The measured capacities showed a definite improvement when compared to capacity test #5. After capacity test #7 the packs were LEO cycled at moderate DOD's for two hundred orbits. Packs #1, #2, #3 and #4 cycled at 22% DOD while packs #5 and #6 cycled at 33% DOD. Capacity test #8 was interrupted by a power outage and data was lost. Capacity test #9 measured the effect of the LEO orbits; the LEO orbits did not significantly increase the measured capacity. The manufacturer's recovery procedure was run again with the open circuit stand time increased to 384 hours. Capacity test #11 showed the most dramatic increase in recovered capacity. Sufficient capacity had been regained to meet the requirements of the HST specification.

Useable Capacity Fading

EPI RNH 90-3

Negatively Precharged



Acceptance Test Capacity, June 1989 – 1.2 Volts.
Eleventh Capacity Test, Sept 1991 – 1.0 Volts.

After the 11th capacity test, the cells were still 8 to 10 percent degraded in capacity. The capacity will continue to increase slightly with LEO cycling at the moderate DOD's. The effect of the higher concentration of electrolyte (pack #5, 31%) after storage is negligible; the pack with 27% KOH lost much less capacity during storage and showed only slightly less capacity than the pack with 31% KOH. Pack #4 and #6, from the same lot of cells showed capacity recoveries of 10.5 and 10 ampere hours respectively.

Summary

Capacity Fading Of Negatively Precharged Nickel-Hydrogen Cells can be reversed.

Capacity can be recovered through cycling.

Recovery can be accelerated by elevating temp and keeping electrode potential difference high.

Original capacity is lost; the lattice structure of the plate is altered.

If possible, Use Positively Precharged Cells.

In summary, negatively precharged Nickel-Hydrogen cells will experience a useable capacity loss during extended open circuit storage periods. Some of the lost capacity can be recovered through cycling. Capacity recovery through cycling can be enhanced by cycling at high DOD's. The most timely procedure for recovering the faded capacity is to charge the cell fully and allow the cell to sit open circuit at room temperature. This procedure seems to be effective in part because of the enlarged structure of the active material. The compounds that formed during storage at the low electrode potentials can more easily dissolve and redistribute. All of the original capacity cannot be recovered because the lattice structure of the active material is irreversibly altered during storage. The recommendation is to use positively precharged cells activated with 26% KOH if possible. In aerospace applications the benefits of negative precharge are offset by the possibility of delays and storage periods.

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The subjects covered included nickel-cadmium, nickel-hydrogen, silver zinc, and lithium based technologies, as well as advanced technologies including nickel-metal hydride and sodium-sulfur.

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