

NICKEL-HYDROGEN CAPACITY LOSS ON STORAGE

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Summary

A controlled experiment evaluating the capacity loss experienced by nickel electrodes stored under various conditions of temperature, hydrogen pressure, and electrolyte concentration was conducted using nickel electrodes from four different manufacturers. It was found that capacity loss varied with regard to hydrogen pressure and storage temperature, as well as with regard to electrode manufacturing processes. Impedance characteristics were monitored and found to be indicative of electrode manufacturing processes and capacity loss. Cell testing to evaluate state-of-charge effects on capacity loss were inconclusive as no loss was sustained by the cells tested in this experiment.

Introduction

Nickel-hydrogen batteries are rapidly becoming accepted for use in low-earth-orbit and geosynchronous orbit applications. With their increased use, it has become evident that the storage procedures commonly used for nickel-cadmium cells are not adequate for the nickel-hydrogen system. Frequently, cells that have been stored, under varied conditions, have exhibited a significant loss of capacity. However, much of the data available on capacity loss have been confusing and often conflicting [1 - 6]. As a result, members of the Electrochemical Technology Branch at the NASA Lewis Research Center conducted a controlled determination of the capacity loss exhibited by nickel electrodes when exposed to different storage conditions.

A comprehensive test matrix was developed to evaluate the capacity loss characteristics of nickel electrodes from four different manufacturers. Two types of tests were run: individual electrode tests, which involved flooded capacity and impedance measurements before, and after, storage under varied conditions of temperature, hydrogen pressure, and electrolyte concentration; and cell tests which primarily evaluated the effects of state of charge on storage. The electrode tests were run using electrodes from Gates Aerospace Batteries (GAB), Whittaker-Yardney (W/Y), Hughes (HAC), and Eagle-Picher-Joplin (EP). The cell tests, that were only run with Hughes electrodes, evaluated capacity loss on cells stored open circuit, shorted, and trickle charged at $C/200$ following a full charge.

The results indicate that capacity loss varies with the specific electrode manufacturing process, storage temperature, and storage pressure. In general, electrodes stored at low temperatures or low hydrogen pressures exhibited a smaller loss in capacity over the twenty-eight day storage period than did those stored at high pressure or high temperature. The capacity loss appears to correlate with the level of cobalt in the nickel electrode, with a greater capacity loss observed in electrodes with higher cobalt levels. Impedance measurements appear to correlate well with capacity loss for a given type of electrode, but do not correlate well with the capacity loss observed between electrodes fabricated by different manufacturers. There was a definite correlation between the electrode potential measured immediately following storage and the measured capacity loss. The cell storage tests indicated a temporary capacity loss in cells stored discharged in the open-circuit condition, and shorted. The cell stored on trickle charge did not exhibit a loss of capacity.

Experimental

Nickel electrode storage test procedures

Before storage flooded capacity measurements

Fifteen electrodes were obtained from each of four nickel-hydrogen cell manufacturers for the capacity-loss-on-storage test matrix. The following manufacturers supplied electrodes for this study: Eagle-Picher-Joplin, Hughes, Gates Aerospace Batteries, and Whittaker/Yardney. The characteristics of the electrodes are summarized in Table 1. The electrodes were divided, by manufacturer, into two groups of thirty each for the flooded capacity measurements. Three electrodes from each manufacturer were subjected to the same set of test and storage conditions.

The initial capacity was estimated for electrodes from each manufacturer. Where capacity differences existed between electrodes in the groups tested together, test parameters (charge and/or discharge rates) were adjusted to accommodate the subgroups of electrodes. Since electrodes of varying capacity were tested in the same series string, relative "C" rates may have varied; however, in all cases the before storage and after storage measurements were made in the same way. (The C rate will discharge the nominal electrode capacity in one hour.) Since the variable of interest was percent change in capacity, it was felt that the results would be valid and comparable.

The flooded capacity measurements were made using a nickel counter electrode and an amalgamated zinc reference electrode. 31% KOH was used for the majority of measurements. One group from each manufacturer was tested in 26% KOH for a measure of capacity retention *versus* electrolyte concentration. The initial formation charges were run at C/7.5 or C/10 for 16 h. The electrodes were discharged at the C/4 or C/5 rate. Formation cycles were run until a uniform capacity was obtained on consecutive cycles.

TABLE 1

Nickel electrode characteristics

Characteristic	Hughes	Eagle-Picher	Whittaker/ Yardney	Gates
Plaque type	Dry powder	Slurry	Slurry	Dry powder
Plaque porosity (%)	80	80	80	80
Impregnation process	Alcoholic	Aqueous	Aqueous	Aqueous
Loading level (g cm^{-3} void)	1.60	1.65	1.68	1.63
Cobalt level (mole%)	10	5	5	*
Thickness (mil)	30	30	35	31 or 37

*Proprietary information.

This usually took six to seven cycles for each group of electrodes. An average formation capacity was obtained for each electrode.

Based on the formation capacity, $C/2$ charge and $C/4$ discharge cycles, with a C:D of 1.12 - 1.15, were planned for the electrode capacity measurements. However, as stated above, the grouping of electrodes of unequal capacities led to relative "C" rates varying from $C/4$ to $C/5.25$ on discharge. A total of five to six capacity determination cycles were run. An average before storage capacity was determined for each electrode.

Before storage impedance testing

Following the pre-storage capacity measurements the electrodes were left in KOH in the discharged state until impedance measurements could be made. A Princeton Applied Research 5208 Two-Phase Lock In Analyzer coupled with a Princeton Applied Research Potentiostat-Galvanostat Model 273 was used to make the impedance measurements. Impedance tests were run from 0.0007 Hz to 5.65 Hz. All electrodes were tested in the discharged state following equilibration at 0.2 V for 1 h *versus* an Hg/HgO reference electrode.

One electrode from each group of three was also measured in the charged state. The electrode was charged at approximately the $C/3$ rate for 0.5 h, then equilibrated at 0.4 V *versus* Hg/HgO for 1 h, before measuring impedance. Following the impedance measurements, the electrodes were returned to 0.2 V by discharging at rates similar to those used in the capacity measurement cycles, and equilibrated there for 1 h before storage.

Storage procedures

As testing on groups of six electrodes that were to be subjected to the same storage conditions (three from each manufacturer in the subgroup) was completed, the electrodes were installed in a vessel and put on storage stand for twenty-eight days. Storage conditions and their identifying codes are described in Table 2. Storage temperature, hydrogen pressure, and electrolyte concentration were the parameters that were varied.

TABLE 2

Nickel electrode storage conditions

H ₂ Pressure (psig)	Temperature (°C)	KOH concentration (%)	Code
500	RT	31	HPRT31
50	RT	31	MPRT31
0	RT	31	APRT31
500	RT	26	HPRT26
500	-20	31	HPLT31

All electrodes were stored in the discharged state, open circuited; in boiler plate pressure vessels, stacked on cores that approximate flight hardware. They were separated by gas screens. No mechanical pressure was exerted on the stack.

The vessels were evacuated and backfilled with hydrogen to the desired pressure. The zero psig vessels were backfilled with hydrogen then the pressure was released until the gauge read zero. The vessels were then stored under the appropriate conditions and monitored, to ensure that the desired storage conditions were maintained throughout the twenty-eight day storage period.

After storage procedures

The electrodes were removed from the vessels following twenty-eight days of storage at the specified conditions. The electrodes were placed in a solution of KOH at the proper concentration. Open circuit voltages were measured *versus* Hg/HgO as soon as possible following removal from storage. Impedance measurements were made in the discharged state at the electrode open circuit potential over the same frequency ranges as the before-storage measurements.

The electrodes were then set aside, flooded with the proper concentration KOH, until the entire group of thirty electrodes had completed storage and initial impedance evaluation at the specified conditions. The after-storage capacity measurements were made in the flooded state following the same procedures used for the initial capacity measurements. Again, five to six cycles were run and the results averaged. The average before, and after, capacities were compared in order to determine the percent. change in capacity for each electrode. Data from the groups of three were also averaged for comparison purposes.

Following the after-storage capacity measurements, impedance was measured after equilibration at 0.2 V for 1 h, as in the before-capacity measurements. After-storage measurements were not made at 0.4 V.

Nickel-hydrogen cell storage test procedures

Cell construction parameters

Representative cells were built to evaluate state of charge on storage in completed cells. Due to electrode availability and configuration, only nickel electrodes from Hughes were used for this portion of the study. Three stacks, composed of three pairs of electrodes per stack, were constructed. The standard Air Force recirculating design configuration was used. The hydrogen electrode used was of the standard Air Force design. The separator used for all three cells was a potassium titanate/poly(ethylene) blend prepared under a grant with Miami University.

Before storage impedance measurements

The cell impedances were measured following activation. Impedances were measured at the cell open circuit voltage over the range 0.0007 Hz - 5.65 Hz.

Before storage capacity determination procedure

The formation procedure used on the cells was similar to that used on the nickel electrodes. The cells were charged at $C/10$ for 16 h and discharged at the $C/4$ rate. Capacity to 1.0 V was measured. The formation cycles were repeated until a stable capacity was achieved. Four cycles were run.

The pre-storage capacity was determined at the $C/2$ charge rate with a 10% overcharge and a $C/4$ discharge to 1.0 and 0.1 V. Nine pre-storage capacity determination cycles were run.

The impedance measurements were repeated before storing the cells. The measurements were made at open circuit following the discharge to 0.1 V at $C/10$. They were made over the same frequency range as the before-formation measurements.

Storage procedures

The storage procedures and conditions for the cells are summarized below. Cell 1 was discharged at the $C/4$ rate to 1.0 V then discharged at $C/10$ to 0.1 V. The cell was then stored at room temperature in the open circuit state for twenty-eight days. Cell 2 was discharged under conditions similar to those used for cell 1, then stored at room temperature, shorted through a $1\ \Omega$ resistor for twenty-eight days. Before storage, cell 3 was charged at the $C/2$ rate with a 10% overcharge. The cell was then trickle charged at $C/200$ for the twenty-eight day storage period. In order to emphasize any pressure effects, all cells were stored at room temperature and at 500 psi hydrogen.

After storage procedures

Following storage for twenty-eight days, the cells were charged and discharged as in the pre-storage capacity measurements. The cells were charged at $C/2$ with a 10% overcharge, and discharged at $C/4$ to 1.0 and 0.1 V. A number of cycles were run and capacity trends were monitored. Impedance tests were repeated following the after-storage capacity measurements.

Results and discussion

Nickel electrode storage tests

Capacity loss measurements

The capacity loss suffered as a result of storage at the various conditions is summarized in Figs. 1 and 2. Figure 1 compares capacity loss as a function of storage conditions for each of the electrode manufacturers. In general, electrodes stored in 31% KOH, at 500 psi, and room temperature experienced the greatest loss in capacity. This was consistent for all four manufacturers. Storage at -20°C helped to minimize the capacity loss, even at hydrogen pressures of 500 psi. The low temperature storage resulted in a 0.6 - 13% decrease in capacity loss with other storage parameters remaining constant. Similar reductions, 4 - 13%, were achieved by reducing the storage pressure from 500 psi to 50 psi. No additional reduction in capacity loss was achieved by reducing the storage pressure to ambient conditions. Electrolyte concentration appeared to have a minimal impact on capacity loss with storage in the presence of hydrogen.

Figure 2 compares the capacity loss as a function of electrode manufacturer for each of the storage conditions. Nickel electrodes from Hughes exhibited the greatest capacity loss for all storage conditions. This may be a result of the impregnation method or the concentration of cobalt in the

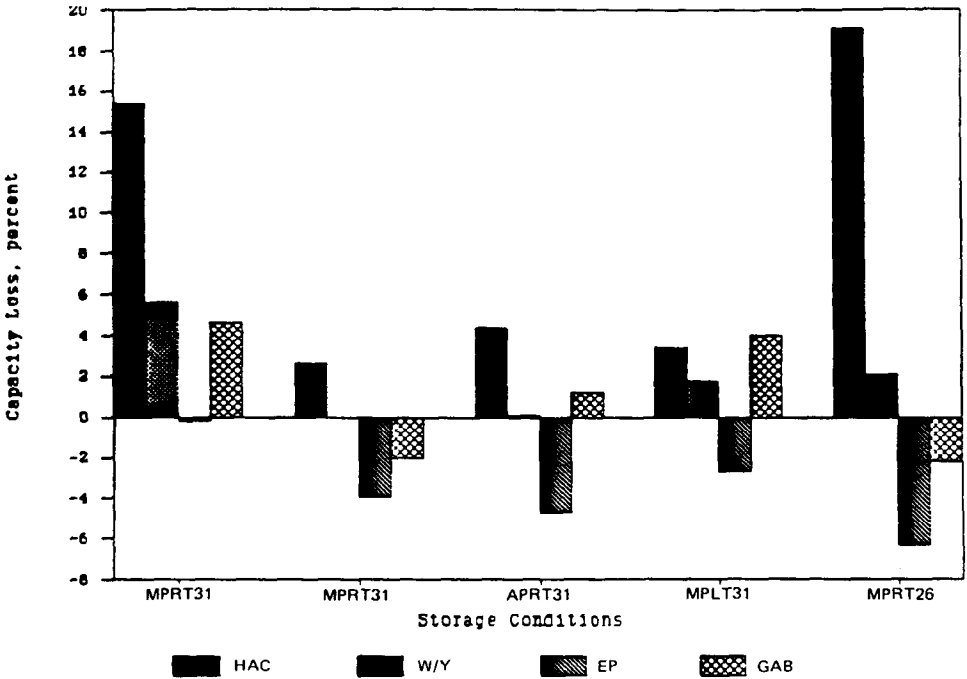


Fig. 1. Capacity loss vs. storage conditions for nickel electrodes from various manufacturers.

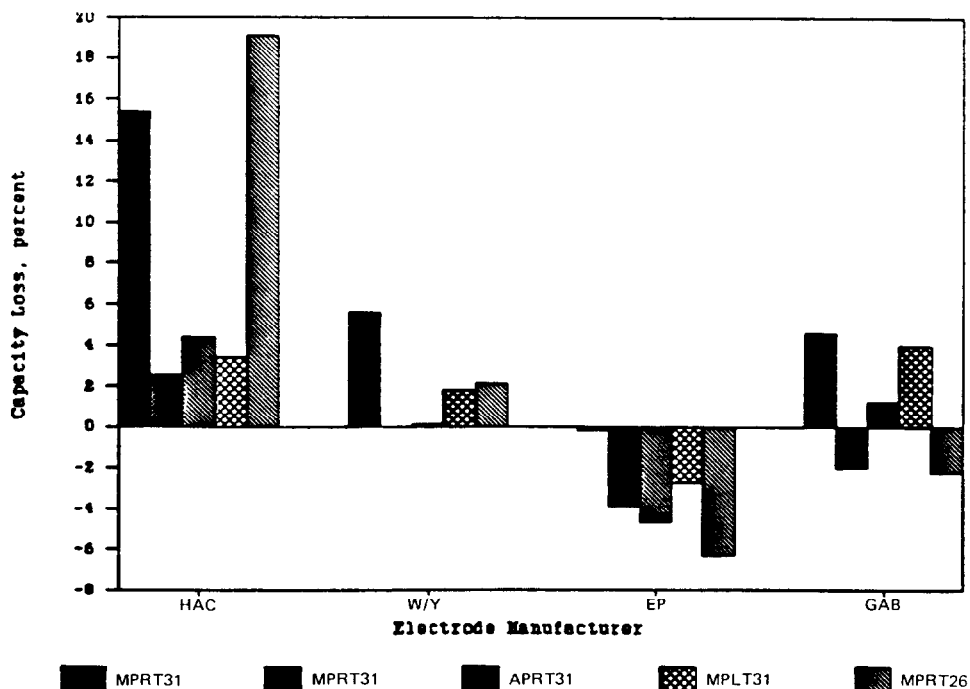


Fig. 2. Capacity loss vs. nickel electrode manufacturer for various storage conditions.

electrodes. Hughes is the only one of the manufacturers whose electrodes were tested that uses an alcoholic impregnation process; all others use aqueous methods. The Hughes electrodes also have the highest cobalt level of those tested (Table 1). It has been postulated that cobalt segregation in reducing environments may be responsible for performance changes in nickel electrodes [7]. Thus, cobalt levels may affect the capacity loss characteristics as well. In order to evaluate the effects of cobalt concentration, electrodes impregnated by the same process have been prepared with 5% and 10% cobalt levels for impedance testing and capacity-loss-on-storage evaluation.

In general, the capacity loss experienced by electrodes from the manufacturers other than Hughes was minimal; less than 5%. In fact, the Eagle-Picher electrodes experienced a slight increase in capacity measured after storage compared with that measured before storage.

Impedance measurements

Electrodes from each manufacturer exhibited characteristic impedance behavior when measured in 31% KOH, at 0.2 V versus Hg/HgO as shown in Fig. 3. However, when measured at 0.4 V versus Hg/HgO, the impedance spectra were similar for all four types of electrodes and could not be differentiated. It appears that the diffusion resistance increases abruptly as the electrode voltage decreases [8]. This, in turn, affects the kinetic resistance

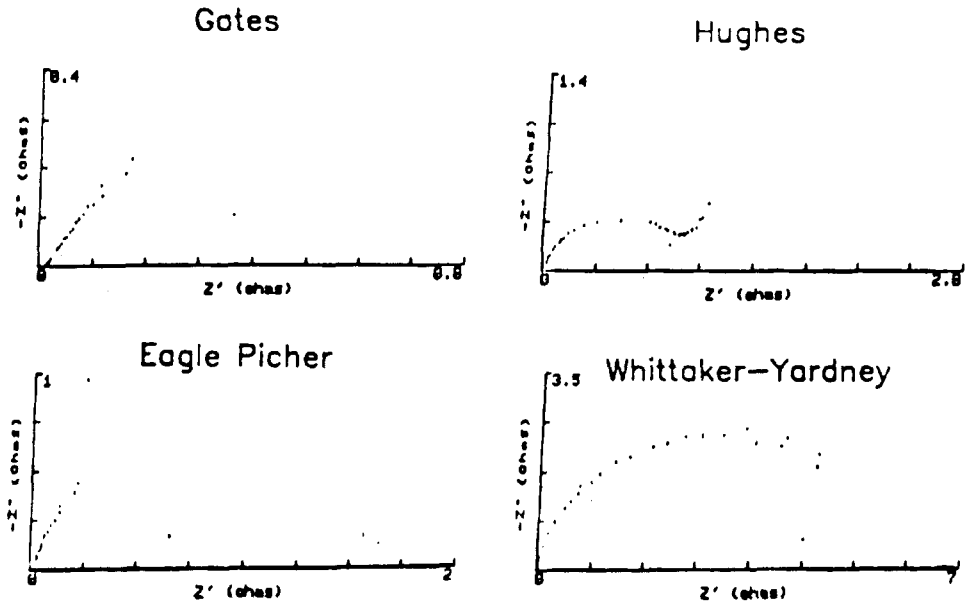


Fig. 3. Representative impedance curves for nickel electrodes from the various manufacturers. Impedance measured at 0.2 V vs. Hg/HgO.

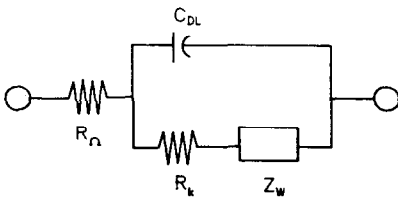


Fig. 4. Electrode model used for impedance of nickel electrodes in storage studies.

term. The point at which, and the extent to which, the diffusion resistance increases appears to vary with manufacturing process as well as previous cycle history.

The electrode model used for the impedance studies is shown in Fig. 4. The impedance values that were compared for the various electrodes are for what is generally referred to as kinetic resistance, R_k . The kinetic resistance is a measure of the resistance to electron transfer. The ohmic resistance is not a valid parameter for the electrode tests as the measurements were made in the flooded state and, as such, the ohmic resistance becomes a measure of the resistance of the electrolyte to the reference electrode. Since impedance was measured before storing the electrodes, the 'pre-storage' measurements on all electrodes, with the exception of those tested in 26% KOH, were made at the same conditions for all electrodes, *i.e.*, room temperature and 31% KOH. The initial, pre-storage kinetic resistance measurements generally

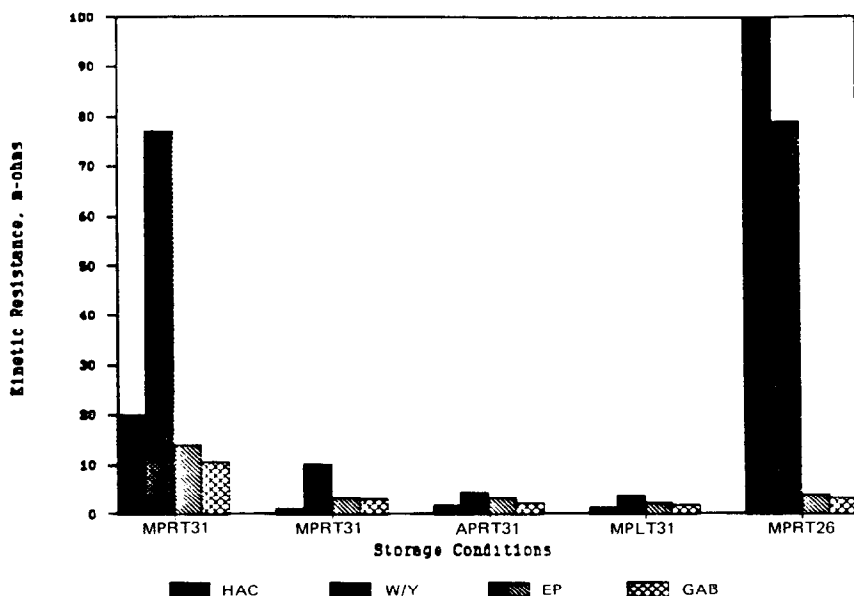


Fig. 5. After storage impedance (R_k) vs. storage conditions for nickel electrodes from various manufacturers.

ranged between 0.5 and 2 m Ω . The post-storage impedance values are shown as a function of storage conditions and electrode manufacturer in Figs. 5 and 6. There was no direct correlation between the changes in R_k as a function of storage conditions or electrode manufacturer. The impedance values seem to correlate with the capacity loss observed within a group, but not between groups. Electrodes that experienced a capacity loss after storage also exhibited changes to the impedance spectra, while those with no capacity loss did not (Fig. 7).

The measurement of cell voltage upon removal from storage seemed to correlate very well with the capacity loss measured in the electrode tests. The Hughes electrodes stored at 500 psi and room temperature lost 15% - 18% of their initial capacity. They were also the only electrodes to have a negative voltage *versus* Hg/HgO immediately following storage. In general, the lower the electrode voltage upon removal from storage, the greater the capacity loss. Table 3 shows the electrode voltage *versus* Hg/HgO upon removal from storage for each of the manufacturers at the various storage conditions. The voltage upon removal is an indicator of the amount of active material reduction that has taken place in the nickel electrode. The impedance then follows from the voltage change. In general, the lower the voltage, the higher the electrode impedance.

Cell tests

The capacity to 1.0 and 0.1 V *versus* cycles for the cell storage tests are shown in Figs. 8 - 10. The results for the cell stored discharged/open

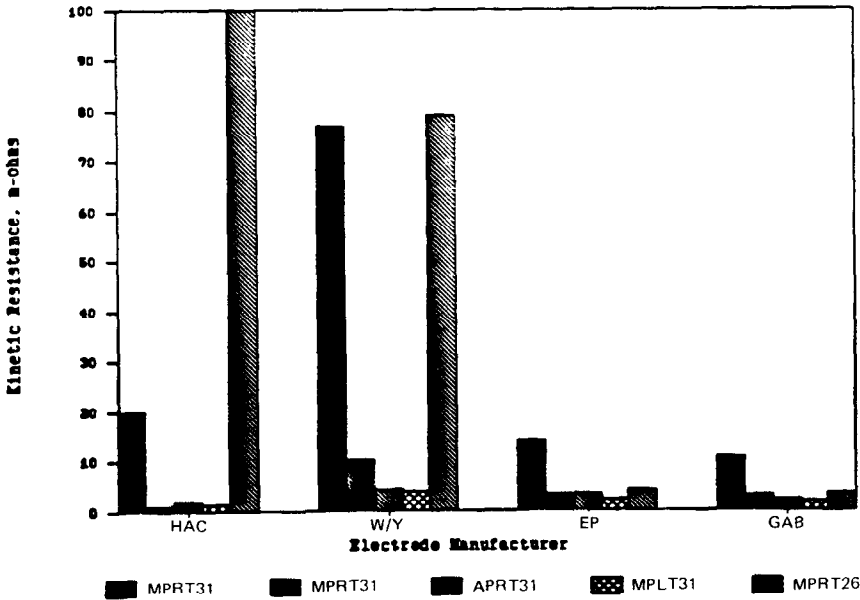
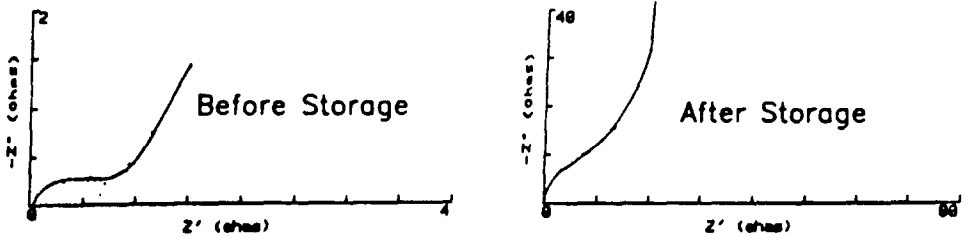


Fig. 6. After storage impedance (R_k) vs. nickel electrode manufacturer for various storage conditions.

Electrode Stored at Ambient Pressure, Room Temperature



Electrode Stored at 500 psi, Room Temperature

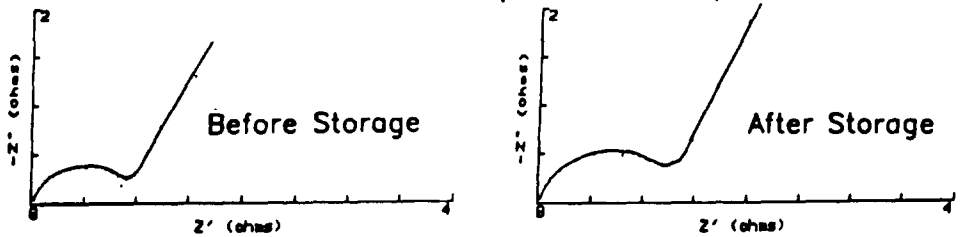


Fig. 7. Impedance spectra of nickel electrode exhibiting capacity loss after storage (above) compared with impedance spectra of nickel electrode that did not exhibit capacity loss (below).

TABLE 3

Nickel electrode voltages after storage (measured vs. Hg/HgO)

Storage condition	Electrode manufacturer			
	Hughes	Eagle-Picher	Whittaker/ Yardney	Gates
HPRT31	-0.765	0.173	0.032	0.170
MPRT31	0.186	0.198	0.191	0.200
APRT31	0.212	0.240	0.216	0.244
HPLT31	0.199	0.230	0.221	0.233
HPRT26	-0.365	0.216	0.073	0.216

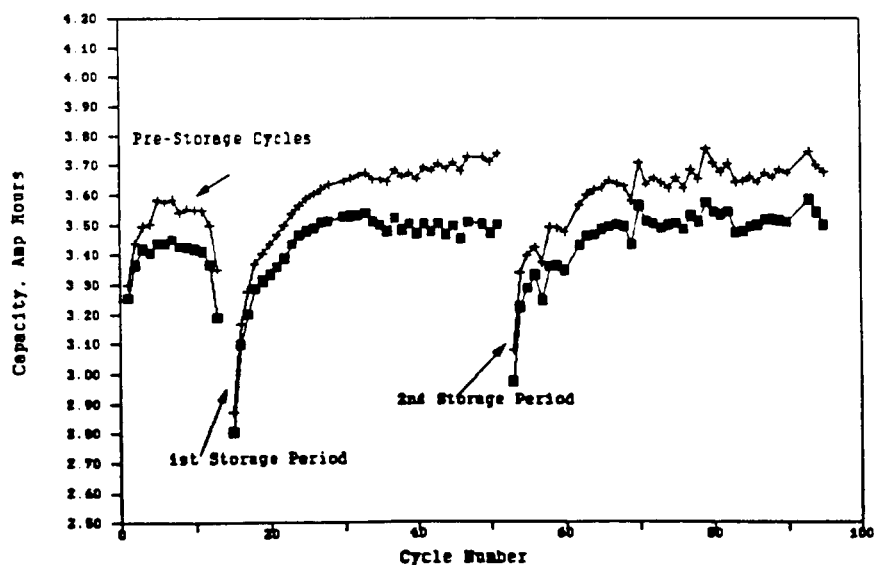


Fig. 8. Capacity vs. cycles for nickel-hydrogen cell stored discharged in the open circuit state. ■, AN to 1.0 V; +, AN to 0.1 V.

circuit and the cell stored in the shorted condition are similar. In both cases the cells exhibited a capacity loss of 17 - 18% when comparing the cycles immediately prior to, and after, storage. This capacity loss was in the same range as that seen for Hughes' electrodes stored under similar pressure and temperature conditions in the electrode portion of this study. The electrode stored at 500 psi and room temperature experienced an average 15% loss in capacity over the twenty-eight day storage period. However, the capacity loss experienced by the cells was recovered within eight cycles, as shown in Figs. 8 and 9. This does not agree with the electrode studies, that showed, essentially, no increase in capacity during the after-storage cycling. The

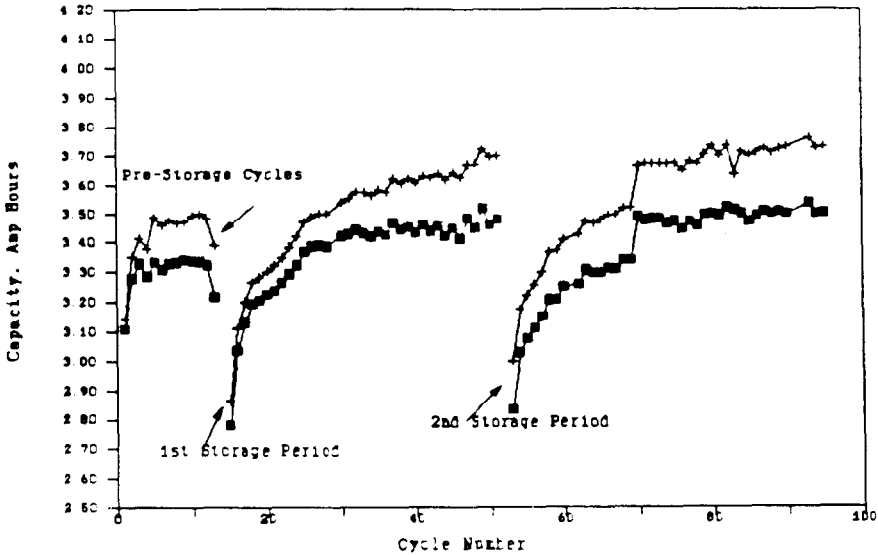


Fig. 9. Capacity *vs.* cycles for nickel-hydrogen cell stored discharged, shorted. ■, AN to 1.0 V; +, AN to 0.1 V.

storage test was repeated on the same cells and similar results were obtained the second time around.

The cell stored charged then trickle charged at $C/200$ for twenty-eight days showed no degradation in capacity due to storage. A plot of the capacity obtained *versus* cycles for cell 3 is shown in Fig. 10. It should be noted that the difference between the capacity to 1.0 V and the capacity to 0.1 V increased after the storage period. The capacity to 1.0 V remained constant while the total cell capacity increased.

The cell tests showed no indication of irrecoverable capacity loss as a result of storage for any of the conditions tested. Capacity recovery which occurs within twenty cycles of storage is not considered a problem.

Comparison of impedance measurements made before, and after, storage was inconclusive. There was a great deal of scatter in the data and the absence of a reference electrode complicated the measurements.

Conclusions and recommendations

Capacity loss appears to be related to the hydrogen pressure in the vessel. Low temperatures ($-20\text{ }^{\circ}\text{C}$) seem to negate the effects of the high pressure. KOH concentration has minimal effect on capacity loss. Nickel electrodes from Hughes showed the highest capacity loss. This may be related to the impregnation process and/or cobalt levels in the electrodes. The storage tests run to evaluate the effect of state-of-charge on storage

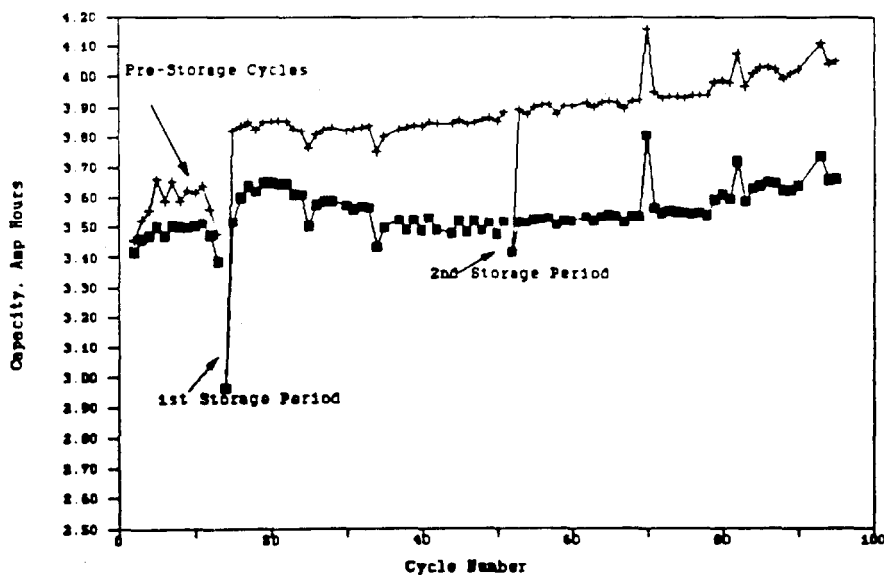


Fig. 10. Capacity vs. cycles for nickel-hydrogen cell stored on trickle charge at $C/200$. ■, AN to 1.0 V; +, AN to 0.1 V.

showed, essentially, no capacity loss for any of the conditions of storage evaluated.

The capacity loss on storage study provided much valuable information relating to the interactions of temperature, pressure, and electrolyte concentration with nickel electrodes from various manufacturers. However, in some cases, conflicting results were produced, specifically in the correlation of the electrode data with the cell storage data. As mentioned above, areas requiring further study have been identified and are being pursued. Impedance work is continuing and, as a greater understanding of the data is achieved, further correlations may be made and a deeper understanding gained from the present study.

Acknowledgements

The work described in this paper represents a group effort. The following individuals were involved in completing the study: Olga Gonzalez-Sanabria and John Smithrick developed the test matrix used to evaluate electrodes from the various manufacturers. John Smithrick coordinated efforts with the manufacturers and obtained the electrodes necessary to perform the work. Michelle Manzo planned, scheduled, and coordinated the overall test scheme, set up the flooded capacity measurement apparatus, and monitored the storage of the electrodes. Jeffrey Brewer, Doris Britton, and Olga Gonzalez-Sanabria were responsible for running the flooded capacity test measure-

ments before, and after, electrode storage. Randall Gahn wired the data acquisition system for capacity loss measurements, prepared pressure vessels for both the cell tests and electrode storage tests, and built and tested the cells for the state-of-charge storage evaluation testing. Margaret Reid provided all the impedance measurements on both the electrodes and cells. Jo Ann Charleston organized and plotted the results. Patricia O'Donnell and Lawrence Thaller served as advisors to the effort.

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