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Effect of Impregnation Method on Cycle Life of the Nickel Electrode

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EFFECT OF IMPREGNATION METHOD ON CYCLE LIFE OF THE NICKEL ELECTRODE

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ABSTRACT

The nickel electrode has been identified as the life limiting component for individual pressure vessel (IPV) nickel-hydrogen cells when cycled under a low earth orbit (LEO) cycle regime at deep depths of discharge. As a part of an overall program to develop a long life nickel electrode for nickel-hydrogen cells, the effect of two different methods of electrochemical impregnation on the cycle life of the nickel electrode was investigated. One method was the Pickett (aqueous/ethanolic) process. The other was the modified Bell (aqueous) process. The plaques for both impregnation methods were made by sintering dry carbonyl nickel powder in a reducing atmosphere. The plaques contain a nickel screen substrate.

Electrodes made from both processes were cycle tested in Air Force design IPV nickel-hydrogen cells. The only factors different for this test was the method of plaque impregnation; all other factors were the same. The cells were cycled to failure under a 90 min LEO cycle regime at a deep depth of discharge (80 percent DOD). Failure for this test was defined to occur when the cell voltage degraded to 1.0 V prior to the completion of the 35 min discharge.

CONTEMPORARY PIV NICKEL-HYDROGEN CELLS (Air Force/-Hughes, Comsat) are adequate for geosynchronous orbit (GEO) applications, where not many cycles are required over the life of the storage system. However, for the demanding LEO applications, the current cycle life at deep depths of discharge (2000 to 8000 cycles) is not acceptable (1,2).* Some investigators report that this limited cycle life is mainly due to degradation of the nickel electrode (3-5).

As part of an overall program to develop a long life nickel electrode for nickel hydrogen cells, the effect of two different processes of electrochemical impregnation on the cycle life of the nickel electrode was investigated. One process was the Pickett (acqueous/alcohol) method (PM). The other was the modified Bell (aqueous) method (MBM). The electrodes from both methods were cycle tested in Air Force/-Hughes design 6 Ah IPV nickel-hydrogen boiler plate cells.

In this communication the results of cycle life testing both types of electrodes are reported.

EXPERIMENTAL

TEST FACILITY - The test facility used to cycle life test the nickel hydrogen cells is illustrated in Fig. 1. The facility design incorporates two main features: safety and versatility. Since the nickel-hydrogen cells are precharged with hydrogen and also generate hydrogen during charge, special attention was given to personnel safety. The cells were located on top of the instrumentation cabinets. There were two cells for each cabinet. Each cell was located within a cylindrical shapnel shield in case of the improbable event of an explosion or rupture of the cell pressure vessel. During a test, the cylindrical shield was purged with nitrogen to create an inert atmosphere. The nitrogen gas, and hydrogen gas if any, would be exhausted from the test laboratory through a hood located above the cells. If the exhaust fan would fail or the nitrogen purge would become interrupted, the test would be automatically terminated. A test can also be terminated on a present upper and/or lower limit of cell voltage, current pressure, and temperature.

The facility's versatility allows for testing over a wide range of cycle regimes. A geosynchronous earth orbit (GEO) cycle regime can be run in real time using a programmable timer. Various accelerated GEO and low earth orbit cycle regimes can be run using a Texas Instrument timer. The cell discharge current is controlled by an electronic load, which can be varied from 0 to 100 A. The charge current can also be varied in the same range. Test data are printed out locally using a Fluke data collector. Strip chart recorders are used to record cell voltage, current, and pressure as a continuous function of charge and discharge time for selected cycles. A maximum for twelve cells can be tested at the same time.

TEST CELL DESCRIPTION

AIR FORCE DESIGN CELL - The Air Force recirculation stack design cell is illustrated in Fig. 2. It consists of a stack of nickel electrodes, separators, hydrogen electrodes, and gas screens assembled in a non back-to-back electrode configuration. The stack is packaged in a cylindrical pressure vessel, with hemispherical end caps. This is made of Inconnel 718 and lined with zirconium oxide which serves as a wall wick. The components are shaped in a "pineapple" slice pattern. The electrodes are connected electrically in parallel. In this configuration electrodes of different types directly face each other. Hence, since a high bubble pressure asbestos separator is used, the oxygen generated at the nickel electrode on charge is directed to the hydrogen electrode of the next unit cell, where it recombines chemically to form water. The fuel cell grade asbestos separators are extended beyond the electrodes to contact the wall wick. Hence electrolyte which leaves the stack during cycling will be wicked back into the stack. The gas screens are polypropylene. The electrolyte is a 31 percent aqueous solution of potassium hydroxide.

NICKEL ELECTRODES - Each nickel electrode consisted of a sintered nickel powder plaque containing a nickel screen substrate which was electrochemically impregnated with nickel hydroxide active material. Two different methods of impregnation were used. One method was the Picket (aqueous/ethanolic) method (6). These electrodes were made by Eagle Picher at the

*Numbers in parenthesis designate References at end of paper.

Colorado Springs facility. The other method was the modified Bell (aqueous) method (7). These electrodes were made by Eagle Picher at the Joplin facility. The same active material loading level (1.55 g/cm^3 void volume) was used for both impregnation methods. All plaques, for both electrode types, were made by the same process at the Eagle Picher Colorado Springs facility. This process consisted of sintering dry carbonyl nickel powder (INCO 287) in a reducing atmosphere. The plaques contained a nickel screen substrate. The plaque porosity was 84±1 percent. The average pore size was 12 to 13 μm. The thickness was about 30 mils. These are the standard Colorado Springs facility plaques.

MEASUREMENTS AND PROCEDURE

For this experiment the quantities measured for each cell at the end of charge and discharge, and their accuracies were: current (±0.3 percent), voltage (±0.5 percent), pressure (±1 percent), temperature (±1 °C limit of error), and charge and discharge ampere-hours capacity (±0.5 percent). Charge-to-discharge ampere-hour ratio was calculated. Cell current, voltage, and pressure were recorded continuously as a function of time, for selected cycles, on a strip chart recorder.

Cell charge and discharge currents were measured across a shunt, using an integrating digital voltmeter. Cell voltage was also measured using an integrating digital voltmeter. Cell pressure was measured using a conventional pressure transducer. Temperature was measured using an iron-constant thermocouple located on the center of the outside pressure vessel wall. Charge and discharge ampere-hours were measured using a conventional ampere-hour meter. Charge-to-discharge ratio (ampere-hours into cell on charge to ampere-hours out on discharge) was calculated from the ampere-hour measurements.

The two different types of electrodes were cycled in 6 Ah capacity IPV Ni-H_2 boiler plate cells to failure. The cycle regime was a LEO regime. The depth-of-discharge was 80 percent of name plate capacity. For this test cell failure was defined to occur, when the discharge voltage degraded to 1.0 V during the course of a constant current 35 min discharge at the 1.37 C rate. For the first test cycle, the cells were charged for 18 hr at a C/10 rate (0.6 A) followed by discharge at the 1.37 C rate for 35 min. Then the normal LEO charge/discharge regime was initiated which consisted of charging the cells at about a constant 0.96 C rate (5.75 A) for 55 min immediately followed by discharge at a constant 1.37 C rate (8.2 A) for 35 min. The charge-to-discharge ratio was set at 1.10.

RESULTS AND DISCUSSION

Results of the cycle life test for cells using the modified Bell method (MBM) electrodes and for cells using the Pickett method (PM) electrodes are summarized in Table I. The best MBM electrode cell failed at cycle 6 706. The best PM electrode cell failed at cycle 8 630. A profile of end of discharge voltages versus cycle for these cells is shown in Fig. 3.

The maximum, minimum, and average cycle life at failure for cells using electrodes of each type is shown in Fig. 4. On the average the MBM electrode cells failed at cycle 6 585. The PM electrode cells failed at cycle 8 602. The difference between the average cycle to failure appears to be significant; indicating a difference between the two plaque impregnation methods. However, additional testing should be conducted to verify this result as it is based on a limited data base. For both electrode types the cycle life is not adequate for most LEO applications, which require a cycle life of 30 000 cycles (5 yr) or greater. The work also suggests that additional development of the nickel electrode is required.

It should be noted that the results reported here are for a deep depth of discharge (80 percent). For a shallower DOD (40 percent), the LEO cycle life is projected to be about 34 000 cycles based on the model that cycle life double when DOD is reduced from 80 to 60 percent and from 60 to 40 percent.

Post cycle teardown and failure analyses of the MBM electrode cells indicate that the components had adequate electrolyte (visual inspection). There was also free electrolyte at the bottom of the pressure vessel. The MBM nickel electrodes on the average increased about 36 percent in thickness compared to similar uncycled electrodes. For a representative MBM electrode cell the pre- and post-cycle ampere-hour capacity as a function of discharge rate is shown in Fig. 5. The capacity decreased at an increased discharge rate. The difference in the initial capacity between the discharge rates of 0.5 and 2.74 C was 13 percent. After the cycle life test the differences in the capacity between these discharge rates was 33 percent. At the low discharge rate (0.5 C) the cell capacity after cycling was unchanged from the initial capacity. At the high discharge rate (2.74 C) the cell capacity after cycling was 23 percent lower. Loss of capacity at the 1.37 C discharge rate was confirmed by flooded nickel electrode beaker test capacity measurements. This data indicate that the main failure mode of a nickel-hydrogen cell is due to a loss of high rate discharge capability of the nickel electrode rather than an absolute loss of the electrode capacity. This result is in agreement with data published by Dr. Hung Sup Lim of Hughes Research Laboratories (8). Dr. Lim also proposed a failure model to explain this gradual loss of high rate discharge capability as the electrodes age due to cycling (8).

The main failure mechanism as suggested by Lim was caused by expansion of active material due to cycling. The expansion forced the active material to redistribute within the nickel plaque. This redistribution caused an incomplete discharge of the active material at a high discharge rate. This suggests that control of the active material expansion rate is the most important factor in extending the cycle life of the nickel electrode. A possible method of accomplishing this is to change the electrolyte composition. A reduction of KOH electrolyte concentration from 31 percent (used in SOA) to 26 percent increased the cycle life of IPV Ni-H_2 cells by greater than three times in a continuing test sponsored by the NASA Lewis Research Center at Hughes Research (9).

Post test cycle teardown and failure analyses of the PM electrode cells indicate that the components had adequate electrolyte (visual inspection). However, there was no extra electrolyte at the bottom of the pressure vessel. The nickel electrodes, on the average increased in thickness 51 percent compared to similar uncycled electrodes. For a representative PM electrode cell the pre and post cycle ampere-hour capacity as a function of discharge rate is shown in Fig. 6. There was a decrease in the available capacity at the higher rates of discharge. The difference in the initial capacity between the discharge rates of 0.5 and 2.74 C was 10 percent. After the cycle life test, the difference in capacities between these discharge rates was 18 percent.

At the low discharge rate (0.5 C) the post cycle cell capacity was 4.7 percent lower. At the higher discharge rate (2.74 C) the post cycle cell capacity was 14.3 percent lower. This data indicates, as was the case with the MBM electrode cells that the main failure mode of the nickel-hydrogen cell is due to a loss of high rate discharge capability of the nickel electrode rather than an absolute loss of electrode capacity. The same failure model is advanced for the PM electrodes as for the MBM electrodes.

CONCLUDING REMARKS

The effect of two different methods of electrochemical impregnation of dry sinter nickel plaques, on the cycle life of the nickel electrodes was investigated. One method was the modified Bell process and the other was the Pickett process. Electrodes made from both processes were cycled to failure under a LEO cycle regime in Air Force/Hughes design IPV nickel-hydrogen boiler plate cells. On the average the Pickett process electrode cells took about 2000 cycles longer to fail than the modified Bell process electrode cells. However, for both electrode types, the LEO cycle regime at deep depths of discharge is inadequate for most LEO applications. These results confirm that further development of the nickel electrode is required. The main failure mode for the nickel-hydrogen cells, using either type of electrode, is due to a loss of high rate discharge capacity of the nickel electrode rather than an absolute loss of electrode capacity.

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Table I - Summary of Cycle Life Test Results

Cell	Cell design	Nickel electrode		Cycle regime	DOD, percent	Cycle at failure	Type failure
		Plaque	Impregnation method				
1	Air force/ Hughes	Sintered dry nickel powder (Eagle Picher, Colorado Springs)	Pickett (Eagle Picher, Colorado Springs)	LEO	80	8574	Degradation of capacity, and V_{EOD} to 1.0 V, no electrical shorts
2			Pickett (Eagle Picher, Colorado Springs)			8630	
3			Modified Bell (Eagle Picher, Joplin)			6706	
4						6699	
5						6350	

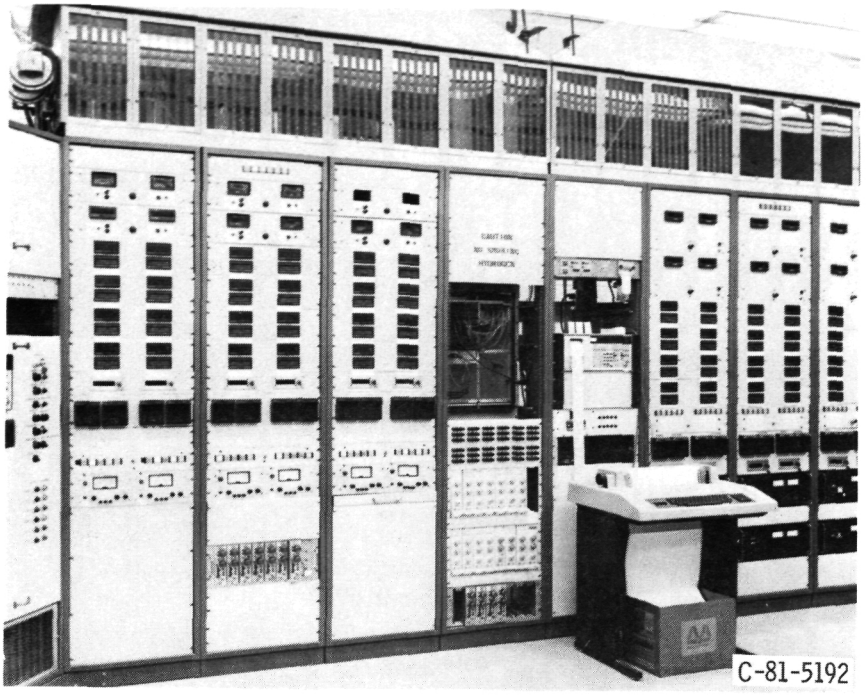

Figure 1. - Nickel-hydrogen cell test facility.

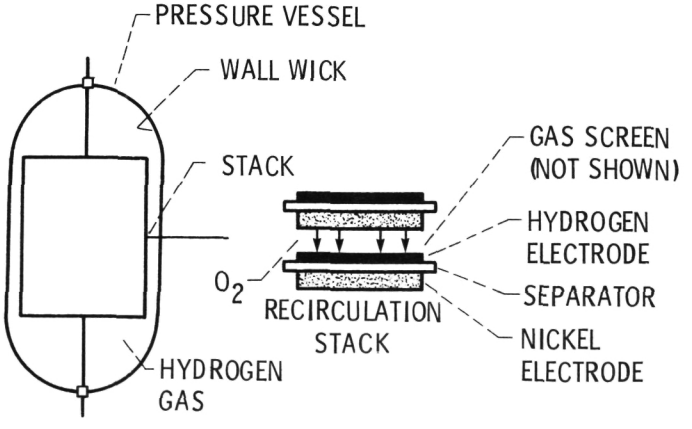

Figure 2. - Illustration of Air Force/Hughes design individual pressure vessel nickel-hydrogen cell.

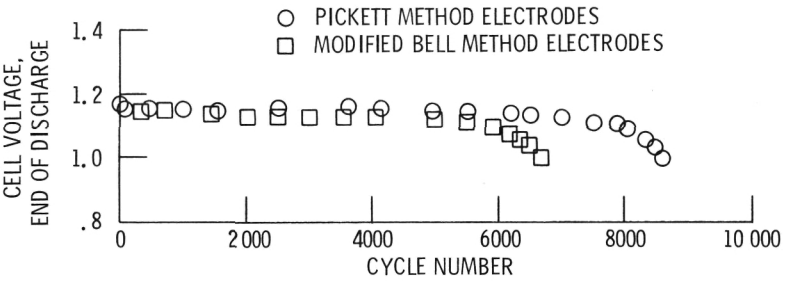

Figure 3. - Effect of cycling on end of discharge voltage of best cell.

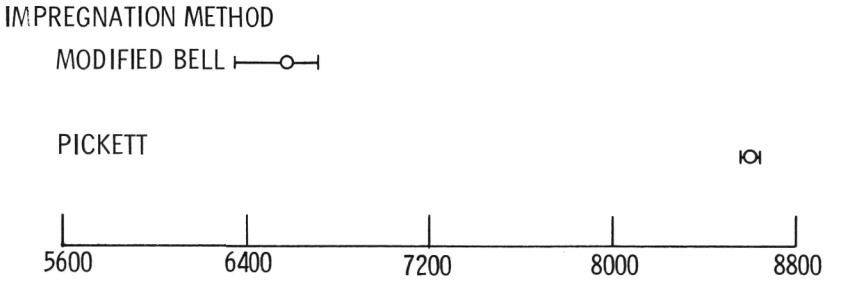

Figure 4. - Maximum, minimum and average cycle life at failure for nickel plaque impregnation methods.

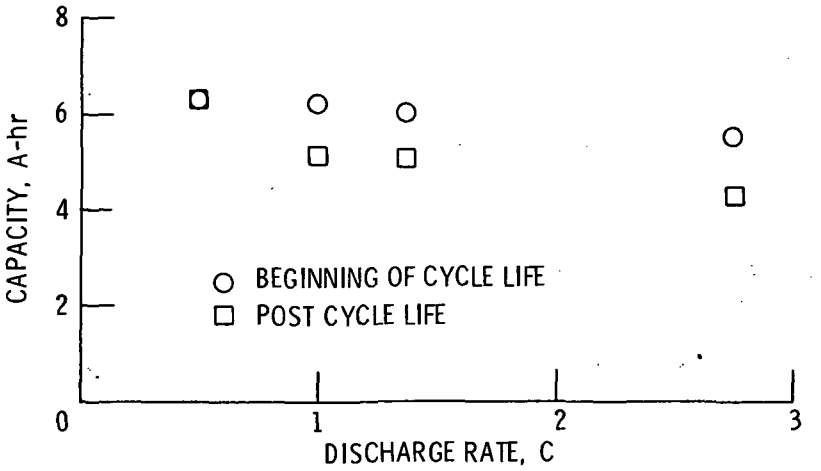

Figure 5. - Beginning of life and post cycle life capacity versus discharge rate for a representative cell using Modified Bell Electrodes.

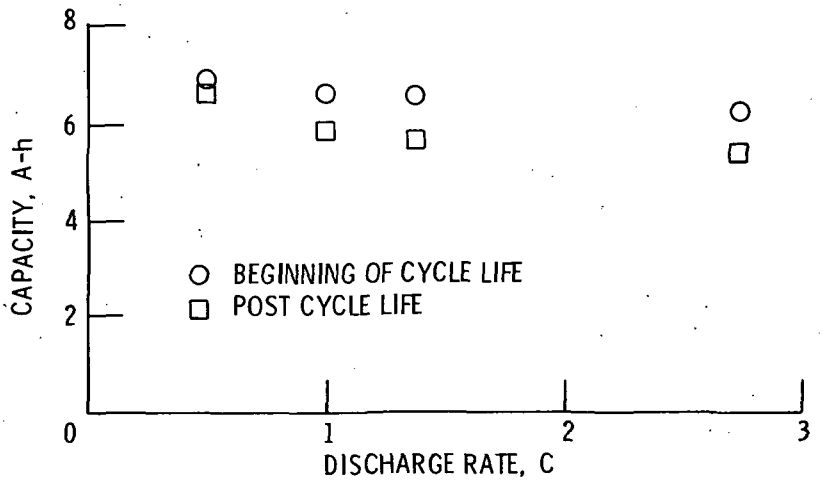

Figure 6. - Beginning of life and post cycle life capacity versus discharge rate for a representative cell using Pickett Process Electrodes.

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15. Supplementary Notes

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16. Abstract

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