Progress in the Development of Lightweight Nickel Electrode for Aerospace Applications

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The NASA Lewis Research Center (LeRC) is currently developing nickel electrodes for nickel-hydrogen (Ni-H\textsubscript{2}) cells and batteries. These electrodes are lighter in weight and have higher specific energy than the heavy sintered state-of-the-art (SOA) nickel electrodes.

In the present approach, lightweight materials or plaques are used as conductive supports for the nickel hydroxide active material. These plaques (fiber, felt, and nickel plated plastic) are fabricated into nickel electrodes by electrochemically impregnating them with active material. Initial performance tests include capacity measurements at five discharge levels, C/2, 1.0C, 1.37C, 2.0C, and 2.74C. The electrodes that pass the initial tests are life cycle tested at 40 and 80% depths-of-discharge (DOD).

Different formulations of nickel fiber materials obtained from several manufacturers are currently being tested as possible candidates for nickel electrodes. Over 7000 cycles in life cycle testing have been accumulated at 40% DOD, using the lightweight fiber electrode, in a boiler plate Ni-H\textsubscript{2} cell with stable voltage.

As part of the Ni-H\textsubscript{2} cell technology development program at NASA LeRC, an advanced Ni-H\textsubscript{2} cell design was developed. One specific goal was to improve the specific energy of the SOA Ni-H\textsubscript{2} cell from 50 Wh/kg to 100 Wh/kg. One of the components needed to accomplish this goal was to develop a better performing and lighter weight nickel electrode which, in addition to being identified as the critical component, has also been identified as the heaviest component of the Ni-H\textsubscript{3} cell. The SOA nickel plaque is made by sintering fine nickel powder onto a wire screen at elevated temperature (1000°C) in a reducing atmosphere. This plaque has the advantage of providing a highly conductive and porous substrate for the active material but has the disadvantage of being very heavy. The nickel hydroxide active material is deposited into the pores of the plaque either by chemical or electrochemical methods.

The use of a lightweight nickel plaque in place of the heavy SOA sintered nickel plaque is expected to lead to improvements in weight and performance of the nickel electrode. After some preliminary experiments, the Fibrex\textsuperscript{1} fiber plaque from National Standard was selected as one of the most promising support candidates for the nickel hydroxide (Ni(OH)\textsubscript{2}) active material. The Fibrex material is formed by reducing and sintering fibers extruded from a mixture of

\textsuperscript{1}Trademark of National Standard Company, Niles, Michigan
nickel oxide and binding agents (1). A special type of Fibrex mat layered with carbonyl nickel and cobalt powder is currently being tested. This special type of material contains 50 parts nickel fiber, 35 parts nickel powder, and 15 parts cobalt powder. The plaques are available in different thicknesses, porosities and densities.

**EXPERIMENTAL**

**Nickel Plaques**

Porosity and thickness of nickel electrodes affect the specific energy, initial performance and cycle life of the Ni-H₂ cell. One advantage of the lightweight plaques over the SOA sintered plaque is that the lightweight plaques can easily be manufactured with much larger porosities than the SOA plaques. Fibrex fiber/powder structures are commercially available in porosities up to 98% while commercial SOA sintered nickel plaques are available in porosities of 80 to 86%.

The Fibrex plaques reported in this study are the 30 mil thick, 85% porous plaque; the 30 mil thick, 93% porous plaque; and the 80 mil thick, 90% porous plaque.

**30 mil thick, 85% porous plaques**

Preliminary tests were performed using electrodes made from 30 mil thick, 85% porosity Fibrex plaques. The calculated specific energy of a 48 Ahr Ni-H₂ cell using this Fibrex electrode (61 Wh/kg) is about 9% higher than that using the SOA electrode (56 Wh/kg) with similar thickness, porosity and loading level (1.6 g/cm³ void volume).

**30 mil thick, 93% porous plaques**

One factor affecting the specific energy of a Ni-H₂ cell is the porosity of the nickel electrode. For example, the calculated specific energy of a 48 Ahr Ni-H₂ cell increases from 56 Wh/kg to 66 Wh/kg, an 18% improvement, by replacing the nickel electrode made from an 85% porous SOA plaque with the lightweight nickel electrode made from a 93% porous Fibrex plaque, with the same thickness and loading level of 1.6 g/cm³ void volume.

**80 mil thick, 90% porous plaques**

Another approach that will result in a higher specific energy of the Ni-H₂ cell is the use of thick nickel electrodes. Utilizing fewer thick nickel electrodes will reduce the number of other components, e.g., hydrogen electrodes and separators. The calculated specific energy of a 48 Ahr Ni-H₂ cell using an 80 mil thick electrode made from a 90% porous plaque, which is loaded to 1.6 g/cm³ void volume, is 77 Wh/kg.

**Electrochemical Impregnation**

The plaques are pretreated prior to impregnation in order to eliminate any surface contaminants that were obtained during handling and storage. The pretreatment procedure used in this study is the wet oxidation cleaning treatment.
which consists of heating the wet plaque at 350° C in air for 20 minutes. The cleaned plaques are then measured, weighed, and electrochemically impregnated in an aqueous bath containing 1.5M Ni(NO₃)₂, 0.175M Co(NO₃)₂, and 0.075M NaNO₂ made acidic by the addition of 50% nitric acid (3). The bath is maintained at a constant temperature of 95-100° C and a pH of 3-4.

The plaques are impregnated for various periods of time (2 to 5 hours) and current densities (50 to 93 mA/cm²) to determine the conditions needed to obtain the optimum loading level. The plaques are impregnated in a reaction vessel which consists of a 600 ml beaker containing a 400 ml aqueous bath. The plaques are placed between two standard nickel counterelectrodes in a teflon holder.

After impregnation, the electrodes are rinsed in deionized water and are formed using the Eagle-Picher formation procedure (4). The procedure consists of eight cycles of 20 min charge and 20 min discharge at a current density of 70 mA/cm² in 26% potassium hydroxide (KOH) solution. After formation, the electrodes are thoroughly rinsed in deionized water, dried at a temperature of 60° C for 4 hr and weighed. The theoretical capacity is determined from the weight of the active material in the electrode using the electrochemical equivalent of 0.289 Ahr/g of Ni(OH)₂.

Cycle Life

Initial evaluation of the cycle life of the lightweight nickel electrodes are conducted in a half-cell configuration. To validate the performance of a Ni-H₂ cell using the lightweight electrodes, additional cycle testing is conducted using a 2- by 2-inch boilerplate cell.

Half-Cell Cycle Test

The components and configuration of the half-cell test vessel are illustrated in figures 1 through 3. Figure 1 shows the components of the test cell which consist of a 1-inch diameter lightweight nickel electrode as the cathode, a 1-inch diameter standard nickel counterelectrode as the anode, a single layer each of 1-inch diameter asbestos and polypropylene as the separator, and a mercury/mercuric oxide (Hg/HgO) as the reference electrode. These components are assembled in the test configuration, as shown in figure 2, with nickel sheets, placed at the ends of the stack, which serve as current collectors. The stack is packaged in a test cell, as shown in figure 3, and filled with an excess of 26% KOH.

The cycling tests are in a LEO regime (55 minute charge, 35 minute discharge) at 80% DOD. The voltage as a function of time is plotted continuously. Approximately every 1000 cycles, capacity measurements are made by discharging to -0.2 volts (versus a Hg/HgO reference electrode) at a 1.37C rate after charging for 80 minutes at a C rate. The percent utilization of the electrode is calculated by using the ratio of the measured capacity to the theoretically calculated capacity based on the weight of the active material deposited. End of life or failure is defined as the point where the discharge voltage degrades to -0.2 V versus a Hg/HgO electrode.
Boilerplate Cell Cycle Test

A 1.7 Ahr Ni-H$_2$ cell using Fibrex nickel electrode has been built at NASA LeRC to establish the validity of test results in boilerplate hardware. The boilerplate cell, as shown in figure 4, consists of the lightweight nickel electrode, a 19 mil thick hydrogen electrode made by Life Systems Incorporated, and three layers of 6 mil thick beater-treated asbestos separator. The gas screen, located behind the hydrogen electrode, is a 60 mil thick nickel Exmet which is compressed to 40 mil to fit into the cavity designed for the hydrogen electrode and gas screen. An electrolyte reservoir plate (ERP) is incorporated into the cell. The ERP material used is a 125 mil thick foam metal. A graphic representation of the unit cell cross section is shown in figure 5. The components are assembled in a stack. After assembly, the entire stack is vacuum-filled with 26% KOH electrolyte. The KOH is allowed to stand in the stack overnight then the excess electrolyte is drained out. The stack is contained in the pressure vessel. The test chamber is evacuated and filled with hydrogen to 3.4 atmosphere (50 psi).

The procedure used for testing the boilerplate Ni-H$_2$ cell is similar to the half-cell continuous cycle regime but at 40% DOD instead of the 80% DOD used for the half-cell testing.

Electrode Performance

The electrode performance at different cycles is measured at five discharge levels, C/2, 1.0C, 1.37C, 2.0C, and 2.74C rates. The voltage as a function of time and the capacities at each rate are recorded and compared with sintered nickel electrode and other experimental electrodes.

Pore Size Distribution

Pore distribution and porosity of new and cycled nickel electrodes are measured using the mercury intrusion porosimeter method.

RESULTS AND DISCUSSION

Three types of Fibrex nickel plaques were investigated. The first type was the 30 mil thick, 85% porous plaque used for the half-cell cycle testing. The second type was the 30 mil thick, 93% porous plaque also used for half-cell cycle testing. The third and last type was the 80 mil thick, 90% porous plaque used for boilerplate cell cycle testing.

30 mil thick, 85% porous plaques

The cycle life data of a lightweight nickel electrode made from a 30 mil thick, 85% porous Fibrex plaque is shown in figure 6. For comparison, the cycle life data of a SOA nickel electrode made from a 30 mil thick, 85% porous SOA sintered plaque from Eagle-Picher Industries (Colorado Spring, Colorado) is shown in figure 7. Both plaques were loaded at NASA LeRC to 1.6 g/cm$^3$ void volume. The maximum utilization of the nickel electrode can exceed 100% since the valence change of the nickel ions during charge and discharge can be greater than one and the percent utilization values in this report are calculated based on a nickel
ion valence change of one. The initial utilization of the Fibrex and SOA electrodes are 75 and 102% respectively. The Fibrex electrode shows a region of increasing utilization during the initial 150 cycles followed by a relatively constant plateau region. A gradual performance decrease is then observed as the number of cycles is further increased.

The Fibrex nickel electrode reached its maximum utilization after about 2100 cycles and continued to cycle for a total of 4534 cycles before it reached its end of life as shown in figure 6. The capacity of this electrode had decreased by 30% at the end of the cycle test. The thickness of the electrode measured after the cycle life test showed an increase of about 8% over the initial electrode thickness measured after the impregnation and formation procedures.

On the other hand, the SOA electrode reached its maximum utilization at cycle 500, as shown in figure 7. At the end of the cycle test (about 4500 cycles), the capacity of the SOA electrode decreased by 35% with an electrode expansion of about 10%.

Figures 8 and 9 show the utilization data of the Fibrex and SOA nickel electrodes at the different discharge rates. The results indicate that as the electrodes cycle, the utilization decreased at the high discharge rate. The initial measurement of the Fibrex electrode utilization (figure 8) is about 3% smaller at the 2.74C discharge rate than at the C/2 rate. After 3000 cycles, the utilization at the 2.74C discharge rate is 20% less than at the C/2 rate. At the low discharge rate of C/2 though, the utilization after 3000 cycles is about the same as the initial data.

The utilization curves of the SOA electrode, as shown in figure 9, shows the capacity of the cycled electrode (4520 cycles) at the very low discharge rate as similar to the initial cycle. A decrease in utilization is also exhibited at the higher rates.

The discharge voltage versus time of the Fibrex and SOA electrodes are shown in figure 10. The Fibrex electrode has an advantage over the SOA nickel electrode of a higher voltage profile. This gives a better power output (watt-hour) for the cell.

Lightweight Fibrex nickel electrode exhibits a low initial utilization which gradually increases during cycling. This phenomenon may be attributed to the large pore size of the electrode. Besides having larger pore size, the lightweight electrode also has a wider range of pore diameters and a more irregular pore shape than the SOA electrode. Figure 11 shows the pore size distribution curves of the Fibrex electrode made from a 30 mil thick, 85% porous plaque. Cycling of the Fibrex nickel electrode increases the total pore volume which is probably due to the expansion of the electrodes. The pore size distribution of the electrode shows distinct multiple peak profiles from 0.01 to 100 μm as opposed to the minimal peak profile of the SOA nickel electrode as shown in figure 12 (5). There is a definite shift in the average pore size and distribution of the cycled SOA electrode toward smaller pores. The peaks at 0.7 and 2 μm and in the range greater than 7 μm decrease while the peak at 0.01 μm increases in size and slightly shifts to the right. The shift to smaller pores and increase in volume requirements of the SOA electrode result in the electrode having a greater affinity for electrolyte. This effect can dry the separator and will lead to a high separator resistance. In addition to a two-fold increase in
volume of the micropores of the cycled Fibrex electrode (figure 11), the volume of the larger pores (over 9 \( \mu \)m) increases 2 to 4 times.

More data is needed to correlate the resulting pore size distribution of these lightweight electrodes with the electrolyte management in the Ni-H\(_2\) cell.

30 mil thick, 93% porosity plaques

A Fibrex nickel plaque, with 30 mil thick and 93 percent porosity, was loaded with active material to 1.8 g/cm\(^3\) void volume. The cycle life data is shown in figure 13. Over 5800 cycles had been attained at 80% DOD by this porous Fibrex nickel electrode. This electrode has the longest cycle life, at 80% DOD, of any of the lightweight nickel electrode developed in-house. The utilization of the electrode reached its maximum value after 1500 cycles, followed by a relatively constant plateau region to 5000 cycles at which point a decrease in utilization was observed. The life cycle testing was terminated due to a voltage decline. Figure 14 shows the utilization of the 30 mil thick, 93% porous Fibrex electrode at the different discharge rates. The results indicated a low utilization at the beginning of the cycle life test. A drastic increase in the utilization was observed after 3800 cycles.

The pore size distribution of the new and cycled Fibrex electrode made from a 30 mil thick, 93% porous plaque is plotted in Figure 15. Cycling of the electrode changed the total pore volume and distribution. Again, the pore size distributions of the electrode show distinct multiple peak profiles from 0.003 to 100 \( \mu \)m. There are pronounced increases in volume between 0.01 to 0.1\( \mu \)m and 2 to 50 \( \mu \)m with cycling.

80 mil thick, 90% porosity plaque

The boilerplate Ni-H\(_2\) cell cycle test data, at 40% DOD, of the lightweight nickel electrode made from an 80 mil thick, 90% porous Fibrex plaque is shown in figure 16. Figure 17 shows the cell voltage characteristics during the charge and discharge cycles. Over 7000 cycles have already been achieved without a drastic decrease in performance as shown in figure 18. The end-of-discharge voltage (EODV) remained almost constant for the first 4000 cycles and gradually decreased on further cycling. After 7000 cycles, the EODV had decreased to 1.1 volts. The end-of-charge voltage (EOCV) remained stable at 1.54 volts. The cycle testing of this cell will be continued until failure. A post-test cell teardown and failure analysis will be conducted to evaluate the cause for failure.

CONCLUSION

Fabrication and life cycle testing of lightweight fiber nickel electrodes have demonstrated the feasibility of an improved nickel electrode. These studies indicate a 37% improvement in specific energy for the Ni-H\(_2\) cell using Fibrex nickel electrode over SOA electrode.

Using lightweight, thick and highly porous nickel electrodes is expected to also improve the specific energy of the Ni-H\(_2\) cell. A greater improvement is also possible by increasing the loading level to over 1.6 g/cm\(^3\) void volume. However, thicker and/or heavily loaded SOA sintered electrodes results in premature electrode failure due to swelling on long cycling which leads to shorter life
Research directed at achieving the required active material utilization and long cycle life in the highly porous, heavily loaded and/or thick fibrous nickel electrodes will be actively pursued.

REFERENCES


Figure 1.—Components of the test cell.

Figure 2.—Components of the assembled cell in a test configuration.

Figure 3.—Test cell with 26 percent KOH electrolyte.
Figure 4.—Components of the nickel-hydrogen boilerplate cell.

Figure 5.—Cross sectional unit of the nickel-hydrogen boilerplate cell.
Figure 6.—Utilization versus number of cycles of a Fibrex nickel electrode made from a 30 mil thick, 85 percent porous plaque (1.6 g/cc void loading).

Figure 7.—Utilization versus number of cycles of a SOA nickel electrode made from a 30 mil thick, 85 percent porous plaque (1.6 g/cc void loading).
Figure 8.—Performance of a Fibrex nickel electrode made from a 30 mil thick, 85 percent porous plaque.
Figure 9.—Performance of the SOA nickel electrode.

Figure 10.—Discharge voltage versus time of Fibrex and SOA nickel electrodes made from 30 mil thick, 85 percent porous plaques.
Figure 11.—Pore size distribution curves of new and cycled Fibrex electrode made from a 30 mil thick, 85 percent porous plaque.

Figure 12.—Pore size distribution curves of new and cycled SOA electrode made from a 30 mil thick, 85 percent porous plaque.
Figure 13.—Utilization versus number of cycles of a Fibrex nickel electrode made from a 30 mil thick, 93 percent porous plaque (1.8 g/cc void loading).

Figure 14.—Performance of a Fibrex nickel electrode made from a 30 mil thick, 93 percent porous plaque.
Figure 15.—Pore size distribution curves of new and cycled Fibrex electrode made from a 30 mil thick, 93 percent porous plaque.

Figure 16.—Utilization versus number of cycles of a nickel-hydrogen boilerplate cell using Fibrex nickel electrode (80 mil thick, 90 percent porous).
Figure 17.—Evolution of nickel-hydrogen cell voltage during the cycle life test. (Fibrex nickel electrode, 80 mil thick, 90 percent porous).
Figure 1.—End of charge and discharge voltages versus number of cycles at 40 percent DOD for nickel-hydrogen cell using Fibrex nickel electrode.
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