Progress in the Development of Lightweight Nickel Electrode for Nickel-Hydrogen Cell

Doris L. Britton
Glenn Research Center, Cleveland, Ohio

September 1999
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This report is a formal draft or working paper, intended to solicit comments and ideas from a technical peer group.

This report contains preliminary findings, subject to revision as analysis proceeds.

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ABSTRACT

Development of a high specific energy battery is one of the objectives of the lightweight nickel-hydrogen (Ni-H₂) program at the NASA Glenn Research Center. The approach has been to improve the nickel electrode by continuing combined in-house and contract efforts to develop a lighter weight electrode for the nickel-hydrogen cell. Small fiber diameter nickel plaques are used as conductive supports for the nickel hydroxide active material. These plaques are commercial products and have an advantage of increased surface area available for the deposition of active material. Initial tests include activation and capacity measurements at five different discharge levels, C/2, 1.0C, 1.37C, 2.0C, and 2.74C. The electrodes are life cycle tested using a half-cell configuration at 40 and 80% depths-of-discharge (DOD) in a low-Earth-orbit regime. The electrodes that pass the initial tests are life cycle-tested in a boilerplate nickel-hydrogen cell before flightweight designs are built and tested.

INTRODUCTION

Future NASA missions will require long life, high power, and light weight energy storage systems which are beyond the capability of existing systems. NASA Glenn Research Center (NASA GRC) is currently involved in research in the area of electrochemical energy conversion and storage for space and terrestrial applications. The objective of this work is to achieve improved performance, higher specific energy, and longer life for electrochemical devices for space and terrestrial applications. One of the systems being studied is the nickel-hydrogen (Ni-H₂) battery. The Ni-H₂ battery technology has progressed rapidly in recent years as a result of advanced designs and improved components. The Ni-H₂ technology group at the NASA GRC has been working in the areas of the Individual Pressure Vessel (IPV), Common Pressure Vessel (CPV), as well as the bipolar system. One of the objectives of this program is reducing the weight of the components of the Ni-H₂ system. To achieve this objective, extensive efforts are being made at NASA GRC to improve the components of the system both in-house and on contract.

NICKEL FIBER PLAQUES

Several factors affect the specific energy of a Ni-H₂ cell. One is the porosity of the nickel electrode. The specific energy of a Ni-H₂ cell will increase by replacing the SOA sintered nickel electrode with the highly porous lightweight nickel fiber electrode. One advantage of the lightweight nickel plaques over the SOA sintered plaque is that the lightweight plaques can be easily manufactured with much larger pore sizes than the SOA plaques. Commercial SOA sintered nickel plaques are available in porosities of 80 to 86%, while the lightweight nickel fibers are commercially available in porosities up to 98%. Another limiting factor that will improve the specific energy of the Ni-H₂ cell is the nickel fiber size. Earlier Fibrex fiber plaque from National Standard (1), with fiber diameters between 22 and 25 µm have a common feature of exhibiting a low initial utilization. Using smaller diameter nickel fiber materials can reduce this problem. The advantages of using these small nickel fibers are the significant increase in surface area available for deposition of active material and the improvement in the electrochemical accessibility to the active material. Another approach that will result in a higher specific energy of a Ni-H₂ cell is to use thick nickel electrodes. Utilizing fewer thick nickel electrodes will reduce the number of other components, e.g., hydrogen electrodes and separators thus reducing the weight of the cell.
Several commercially available small fiber nickel materials were evaluated and tested in-house. After several preliminary experiments, four nickel fiber plaques were selected as promising support candidate for the nickel hydroxide active material. Preliminary results of the top three of the four promising substrates, from MicroMetal Fiber Corporation (formerly Ribbon Technology Corporation), from Memtec America Corporation, and Auburn University, are reported earlier (1,2). A new and improved nickel fiber substrate, developed and manufactured by Bekaert Fibre Technologies, was evaluated and tested at NASA GRC. This new substrate was manufactured for battery, fuel cell, and capacitor substrates and has been developed for electrode manufacturing processes. The substrate was manufactured by a proprietary wire bundle drawing process that produces the nickel fibers themselves. These fibers are drawn to a fiber diameter selected for optimum substrate performance. A novel formation process, which was developed over a period of years, is utilized to form the substrate precursor. The Bekaert nickel substrates are available in different fiber diameters (2 to 8 μm), thicknesses (30 to 80 mils) and porosities (85 to 95%). Results of the test using this nickel fiber will be discussed in this report.

ELECTROCHEMICAL IMPREGNATION

The substrates 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 (3), which consists of heating the wet substrate at 350°C in air for 20 minutes. The cleaned substrates 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 NaNNO₂ made acidic by the addition of 50% nitric acid. The bath is maintained at a constant temperature of 95-100°C and a pH of 3-4. The substrates are electrochemically 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 substrates are impregnated in a reaction vessel, which consists of a 600-ml beaker containing a 400-ml aqueous bath. The substrates are placed between two standard nickel counterelectrodes in a Teflon holder.

After impregnation, the impregnated substrates are formed by charging and discharging for 20 min at approximately the 3C rate. The formation process serves to remove impurities, which are chiefly nitrates, carried over from the impregnation bath.

The in-house evaluation and testing work in the past year has been involved mainly with the new nickel fiber substrates from Bekaert Fibre Technology. Table 1 summarizes the electrochemical impregnation and initial cycle testing of these electrodes. A substrate thickness of 45 to 50 mils was used in this evaluation. The sample physical size was 25 square centimeters.

Loading levels of anywhere from 1.38 to 2.04 g/cm³ void were obtained during the electrochemical impregnation procedure. The loading level is calculated based on the expanded thickness, porosity, substrate weight, and the difference between the substrate weight and the final weight after formation.

The thickness of these electrodes increased anywhere from 24 to 31% during impregnation. This is considerably more than the corresponding increase observed in standard sintered powder electrodes. This increase in thickness is a major factor affecting ultimate electrode performance. Minimizing this effect is essential for a long life space application. Considerable progress is currently being made in optimizing fiber substrate parameters as well as impregnation process to minimize this growth.

<table>
<thead>
<tr>
<th>Nickel Electrodes</th>
<th>D1</th>
<th>D2</th>
<th>D3</th>
<th>D4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loading level, g/cm³ void</td>
<td>1.38</td>
<td>1.68</td>
<td>1.9</td>
<td>2.04</td>
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<tr>
<td>Expansion, %</td>
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<td>25</td>
<td>24</td>
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<td>Initial utilization, %</td>
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<td>99</td>
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<td>Maximum utilization, %</td>
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<td>104</td>
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<tr>
<td>Specific energy, mAh/g</td>
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<td>222</td>
<td>209</td>
<td>215</td>
</tr>
<tr>
<td>Volumetric energy, mAh/cm³</td>
<td>421</td>
<td>505</td>
<td>558</td>
<td>564</td>
</tr>
</tbody>
</table>

Table 1. Electrochemical and Cycle Life Data of the Nickel Electrodes.

The utilization data is the ratio of the actual capacity to the theoretical capacity, expressed as a percentage. The actual capacity, in milliampere-hours (mAh), is determined by charging, in KOH, at a constant C rate for 80 minutes, followed immediately by discharging at constant 1.37V rate to an end voltage of -0.2 V against a Hg/HgO reference electrode. The theoretical capacity is calculated from the finished active material weight in grams multiplied by the theoretical energy density of nickel hydroxide of 0.289 Ah/g. The Bekaert nickel electrode obtained initial utilization of anywhere from 94% to 107%, as seen in table 1. Earlier lightweight nickel electrodes with larger fiber diameter have a common feature of low initial utilization (1,2). This shortcoming has been essentially solved by the use of the new and improved nickel fiber electrodes from Bekaert. Higher and longer sintering temperatures and time than the earlier experimental substrates were used in developing these Bekaert nickel fibers.

The nickel-hydroxide active material has a theoretical specific energy of 289 mAh/g. A typical state-of-the-art sintered nickel powder electrode has a theoretical specific energy of 120 mAh/g. By comparison, the lightweight nickel fiber electrodes are up to 222 mAh/g. An 85% increase in specific energy is a significant value in overall specific energy at the cell and battery level.
CYCLE LIFE

Initial evaluation of the cycle life of the lightweight nickel electrodes is conducted in a half-cell configuration. The cell consists of a stack containing a Bekaert nickel fiber electrode as the cathode, a standard Eagle-Picher heavy sintered nickel electrode as the anode, a mercury/mercuric oxide (Hg/HgO) as the reference electrode, and a polypropylene as the separator. The stack is packaged in a 1-liter beaker filled with an excess of 26% potassium hydroxide (KOH).

The electrodes are life cycle tested using a low-Earth-orbit regime at 80% depth of discharge (DOD) which consists of a 55-minute charge at the C rate followed by a 35-minute discharge at the 1.37 C rate (C is the capacity of the cell in ampere-hour). Failure of the electrode is defined as the point where the discharge voltage degrades to -0.2 V against the Hg/Hg0 reference electrode during the 35-minute discharge. After the end of life, the cell is disassembled and the components are visually inspected. Performance testing of the electrode at different discharge rates is conducted before and after the life cycle test. After a thorough rinsing and drying, the nickel electrode is weighed and the thickness measured.

Figure 1 shows the comparison in the utilization as a function of cycles of the nickel fiber electrodes with different loading levels. The initial utilization of these new and improved small-diameter fiber electrodes is about 40% higher than the earlier large-diameter fiber electrodes. The performance of the electrode with the heaviest loading level (2.04 g/cm³ void) is lower than the other three electrodes. Electrodes loaded to 1.68 g/cm³ void and 1.90 g/cm³ void cycled for 1274 and 1974 respectively before they reached their end of life, which is mainly due to voltage degradation. Thicknesses of both electrodes doubled at the end of cycling. Both electrodes reached maximum utilization values of 114%, which is equivalent to a specific energy of 211 mAH/g for the 1.68-loaded electrode and 209 mAH/g for the 1.90-loaded electrode.

To date, the least loaded electrode (1.38 g/cm³ void) and the heaviest loaded electrode (2.04 g/cm³ void) have over 1400 cycles (112% utilization) and 2200 cycles (95% utilization) respectively.

ELECTRODE PERFORMANCE

Performance testing of new and cycled electrodes is accomplished by capacity measurements at various discharge rates (0.5, 1.0, 1.37, 2.74 C) after charging at a C rate for 80 minutes. Figure 2 shows results of this testing. The utilization of the heavier-loaded electrodes (1.90 and 2.04-g/cm³ void) exhibit lower values at the higher rates. This dependency is not as drastic with the lighter-loaded electrodes (1.38 and 1.68 g/cm³ void).

Figure 2. Nickel fiber electrode utilization as a function of discharge rates.

Since the 1.68 and 1.90-loaded electrodes reached their ends of life, as mentioned above, the comparison of the performance of these electrodes, new and cycled, at different discharge rates is represented in figure 3. In general, these nickel fiber electrode demonstrated better performance after being cycled. The utilization values of the new 1.68-loaded electrode at the different discharge rates are very similar. The values increased after the electrode has been cycled over 2000 cycles with a larger difference in the lower rates. In the case of the 1.90-loaded electrode, the utilization at the higher rate (1.37 C) is about 34% lower than the lower rate (C/2) for both the new and cycled electrode. An almost parallel increase in utilization values of 11% is also shown for all discharge rates after cycling for the 1.90-loaded electrode.

Figure 1. Utilization as a function of cycles.
CONCLUSION

Improving performance and cycle life as well as increasing the specific energy of the Ni-H<sub>2</sub> system are the main thrust of the technology program at NASA GRC. One of the ways of achieving these goals is by developing lightweight nickel electrodes.

Initial problems associated with lightweight plaques, such as low loading levels and low initial utilization, have been solved by the use of small diameter nickel fibers and altering substrate manufacturing process. The use of these nickel fibers results in a significant increase in the surface area available for deposition of active material without a significant reduction in void volume. Superior performance of these nickel fiber electrodes has been demonstrated.

The issue of expansion during impregnation and cycling, resulting in premature electrode failure, needs to be investigated. Nickel fiber substrates with different properties are currently being evaluated in-house.

ACKNOWLEDGMENTS

Jack Toon of Tritechnology Group of Bekaert Fibre Technologies is instrumental in providing us with the nickel fiber substrates.

REFERENCES

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