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Nickel-Hydrogen Component Development

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NICKEL-HYDROGEN COMPONENT DEVELOPMENT

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SUMMARY

The NASA Lewis Research Center is currently involved in the research and development of light weight energy storage systems for future space missions. One of the systems now being studied is the nickel-hydrogen battery. This battery is designed to achieve longer life, improve performance, and higher energy densities for space applications. This paper will discuss the recent nickel-hydrogen component development. Test data from polarization measurements of the hydrogen electrode componer will be presented.

INTRODUCTION

Future NASA space missions will require long life, high power and light weight energy storage systems which are b yond the capability of existing systems. Therefore, the NASA Lewis Research Center (Lewis) is currently involved in research in the area of electrochemical energy conversion and storage for space applications. The objective of this work is to achieve improved performance, higher energy density, and longer life for electrochemical devices for space applications. One of the systems being studied is the nickel-hydrogen battery.

The Air Force has spent considerable time and money developing a workable nickel-hydrogen cell and attempting to establish a commercial supplier of components and light weight cells. In industry, COMSAT has also expended considerable effort on the nickel-hydrogen system for communication satellites. NASA Lewis is complementing this work by evaluating the cell designs and optimizing cell components to achieve improved performance and life. Advanced cell component development is necessary, particularly for low-earth orbit applications which require 5-yr life at deep depths-of-discharge. This means that most of the battery capacity is discharged and recharged in each low-earth orbit cycle, which is about 90 min. Advanced technology development work is being performed on the nickel electrode, the separator, and the hydrogen electrode.

Chemistry and Electrochemistry of Nickel Hydrogen Cells

During charge, as shown in table 1, the nickel hydroxide is converted to the more charged form of nickel hydroxide. At the hydrogen electrode, water is electrolyzed to form hydrogen during charge. During the discharge cycle, the evolved hydrogen gas is consumed by oxidation at the hydrogen electrode, the nickel electrode is discharged and electrical energy is produced.

Cell Components

A typical nickel-hydrogen cell is shown in figure 1. This is the Air Force design which is cylindrically shaped with hemispherical end caps. The pressure vessel is made of Inconel 718. The inner surface is coated with a thin layer of zirconium oxide to provide a wick to maintain proper distribution of electrolyte.

Figure 2 illustrates the individual stack assembly which consists of nickel and hydrogen electrodes, separators and a gas screen, which are shaped in a "pineapple slice" pattern. These components are supported on a central core and two rigid end plates attached to an Inconel weld ring which is subsequently welded at the cylinder dome interface. The nickel electrodes used in the nickel-hydrogen cells are made with a nickel screen substrate and a sintered carbonyl nickel powder plaque, which is electrochemically impregnated with nickel-hydroxide active material.

Acceptance of the nickel-hydrogen cell as a viable energy storage system for space application depends on its cycle life. An important factor limiting the cycle life of the nickel-hydrogen cell is degradation of the nickel electrode. Some of the modes of degradation are as follows: (1) change in pore size distribution during cycling; (2) extraction of electrolyte from the separator by the increasing number of small pores in the nickel electrode; (3) density changes of the active material during charge and discharge; and (4) active material flaking or being extruded from the electrode. Through contractual efforts with Hughes Aircraft Company, these problems are being addressed. Two types of separator material are used as state-of-the-art separators in nickel-hydrogen cells; they are asbestos and zircar (zirconium oxide felt). Separator selection is known to affect the voltage characteristics of the cell and affects the oxygen recombination rate. The rapid oxygen recombination on hydrogen electrodes is referred to as "popping" and is believed to be caused by channeling of evolved oxygen through paths available in the separator. Asbestos separators do not allow popping, but life tests have shown that cells with asbestos separators give a slightly lower end-of-discharge voltage. Zircar separators exhibit some popping effects, but give a better cell performance during long term testing. We are presently working on developing separator materials that are superior to either asbestos or zircar.

The gas screen provides stiffness and adequate gas flow. It is made of a monofilament polypropylene screen.

The hydrogen electrode used in nickel-hydrogen cells consists of a Teflon-platinum catalyst mixture bonded to a pure nickel photochemically etched foil substrate or a screen substrate. The electrode is backed with a porous Teflon (Goretex) hydrophobic membrane which is gas permeable. The nickel foil or screen substrate has good mechanical stability and acts as the current collector. This electrode has demonstrated a remarkable degree of stability with respect to electro-oxidation; however, some problems have been encountered with these electrodes. One problem is flooding, which blocks the pores of the electrode preventing the free flow of gases within the cell. Another problem is the high cost of the platinum electrocatalyst. The high cost of the platinum electrocatalyst can be decreased by reducing the catalyst loading. Hydrogen electrodes have been fabricated with various catalyst loadings. These electrodes are evaluated using polarization test data.

In this paper, experimental results of the polarization measurements and future electrode development work for the hydrogen electrodes will be presented and discussed.

Experimental

The polarization test described in this paper is designed to provide an indication that the hydrogen electrodes were properly made and handled before cycle testing. The polarization, or overvoltage (i.e., the change in voltage from the equilibrium voltage when current flows through an electrode) at currents below the mass transfer limiting current (point where the rate of access of hydrogen to the catalyst becomes the limiting factor), is a measure of how effective the electrode catalyst structure is in promoting the reaction:

$$H_2O + \overline{e} \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} O\overline{H} + 1/2\ H_2.$$
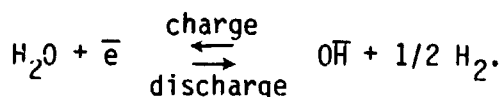
The hydrogen electrodes are affected by electrode flooding (a gradual or sudden increase in the volume of electrolyte in an electrode) which reduces the necessary hydrogen transfer to and from the electrodes. Flooded electrodes show higher polarizations than those that have not been flooded. Polarization of the hydrogen electrodes is measured before and after cycling.

Sample Preparation

All of the hydrogen electrodes were prewashed with 50-percent ethanol and 50-percent trichloroethylene before testing.

A rectangular sample measuring 1.0 x 1.2 cm was cut from the electrode, leaving the white Goretex membrane on the sample. A line was lightly cut into the backing so that a 1.0 x 1.0 cm^2 area was outlined. The 0.2 x 1.0 cm strip of membrane was carefully peeled off from the sample to expose the platinum black and the screen. A 6-in. length of nickel wire was spot welded to the exposed screen of the sample. The wire was bent 90° where it joined the sample, so that the plane of the sample is perpendicular to the nickel wire with the membrane side up. The test apparatus is shown in figure 3.

Test Procedure (refs. 1 and 2)

1. The working and the reference electrodes are floated on the surface of the KOH solution such that rising oxygen bubbles from the nickel counter electrode make minimal or no contact with them. Before taking any measurements, the test cell is purged with nitrogen for at least 5 min, then with hydrogen at a rate of 10 bubbles per second until the voltage reading is near zero.

2. Before applying current to the cell, the hydrogen rate is reduced to 2 to 4 bubbles per second.

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3. Current is passed between the working and counter electrode, and the voltage of the working electrode is compared to the voltage of the reference electrode, which has no current passing through it. Polarizations are measured at 5 to 50 mA for oxidation and reduction.

4. When the polarization measurements are completed, the apparatus is flushed with nitrogen before removing the cap of the test cell.

RESULTS

The hydrogen electrodes which were tested were manufactured by Hughes Aircraft Company and Life Systems, Inc. (LSI). LSI hydrogen electrodes were made according to Hughes' specifications. The polarization test results are shown in Table 2. The standard loading for the hydrogen electrode used in the Air Force nickel-hydrogen cell design is from 8 to 10 mg/cm^2. Table 2 compares the polarization characteristics of an electrode with a catalyst loading of 7 mg/cm^2 with an electrode having a loading of 10 mg/cm^2. (For cost-effectiveness the desired platinum loading is 0.6 mg/cm^2.) Under contract, LSI has fabricated hydrogen electrodes at loadings from 10.0 to 0.6 mg/cm^2. The polarization test results are shown in Table 3. The electrode which was fabricated at 0.6 mg/cm^2 showed much higher polarization than the electrode fabricated at 10.0 mg/cm^2.

CONCLUSION

In order to fabricate a hydrogen electrode that is similar to the present state-of-the-art hydrogen electrode with a reduction in catalyst loading, it can be concluded that the structure of the hydrogen electrode has to be optimized regarding the characteristics of the catalyst and the Teflon content (ref. (3). Too low a Teflon content may cause "flooding" of the active sites and an increase in liquid phase diffusion losses. Too high a Teflon content can cause permanent dry regions of the electrocatalyst which will then not be utilized. It is important to have a proper distribution of catalyst and Teflon so as to establish a three dimensional network with microporous regions of hydrophobic teflon phase for efficient gas diffusion and a continuous phase of wettable electrocatalyst with just a thin electrolyte film which will maintain the electrochemical reaction for the required current densities and voltages. Future research will be directed toward further optimization of the hydrogen electrode.

REFERENCES

1. Giner, J.; and Smith, S., Jan.-Feb. 1967. "A simple method for measuring the polarization of hydrophobic gas diffusion electrodes," Electrochem. Technol. 5(1-2):59-61.

2. Giner, J.; Parry, J. M.; Smith, S.; and Turchan, M., Dec. 1969. "Methods for characterizing the structure and electrochemical behavior of Teflon-bonded Pt electrodes," J. Electrochem. Soc. 116(12): 1692-1696.

3. Giner, J.; and Hunter, C., Aug. 1969, "The mechanism of operation of the Teflon-bonded gas diffusion electrode: a mathematical model," J. Electrochem. Soc. 116(8): 1124-1130.

Table 1. - CHEMISTRY AND ELECTROCHEMISTRY OF Ni-H$_2$ Cells

Charge - Discharge:	
$Ni(OH)_2 + O\overline{H} \rightleftharpoons NiOOH_2 + H_2O + \overline{e}$	- Nickel electrode
$H_2O + \overline{e} \rightleftharpoons 1/2\ H_2 + O\overline{H}$	- Hydrogen electrode
$Ni(OH)_2 \longrightarrow NiOOH + 1/2\ H_2$	- Overall cell reaction
Overcharge:	
$2O\overline{H} \longrightarrow 1/2\ O_2 + H_2O + 2\overline{e}$	- Nickel electrode
$2H_2O + 2\overline{e} \longrightarrow H_2 + 2O\overline{H}$	- Hydrogen electrode
$H_2O \longrightarrow H_2 + 1/2\ O_2$	- Overall net reaction
$H_2 + 1/2\ O_2 \longrightarrow H_2O$	- Resultant chemical recombination

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TABLE 2. – POLARIZATION OF HUGHES AND LSI ELECTRODES[a]

Electrode	Current density, mA/cm²	Polarization	
		RED, mV	OXY, mV
Hughes 7 mg/cm² (25 percent teflon)	0	-0.0	+0.7
	5	-4.2	+3.7
	10	-7.8	+6.7
	25	-17.1	+17.0
	35	-24.6	+?4.2
	50	-35.0	+35.0
LSI 10 mg/cm² (25 percent teflon)	0	-0.0	+0.1
	5	-7.2	+7.5
	10	-14.6	+16.3
	25	-35.6	+43.9
	35	-50.4	+63.8
	50	-71.1	+94.3

[a]All electrodes are presoaked in 31 percent KOH for 24 hours.

TABLE 3. - POLARIZATION OF LSI ELECTRODES AT DIFFERENT LOADINGS[a]

Platinum loading, mg/cm²	Current density, mA/cm²	Polarization	
		RED, mV	OXY, mV
1.0 mg/cm² (25 percent teflon)	5	-7.2	+7.7
	10	-14.7	+16.5
	25	-36.0	+42.8
	35	-50.7	+62.6
	50	-74.0	+93.0
0.6 mg/cm² (25 percent teflon)	5	-31.4	+59.7
	10	-46.8	+159.0
	25	-85.9	+169.8
	35	-115.9	+176.4
	50	--	--

[a]All electrodes are presoaked in 31 percent KOH for 24 hours.
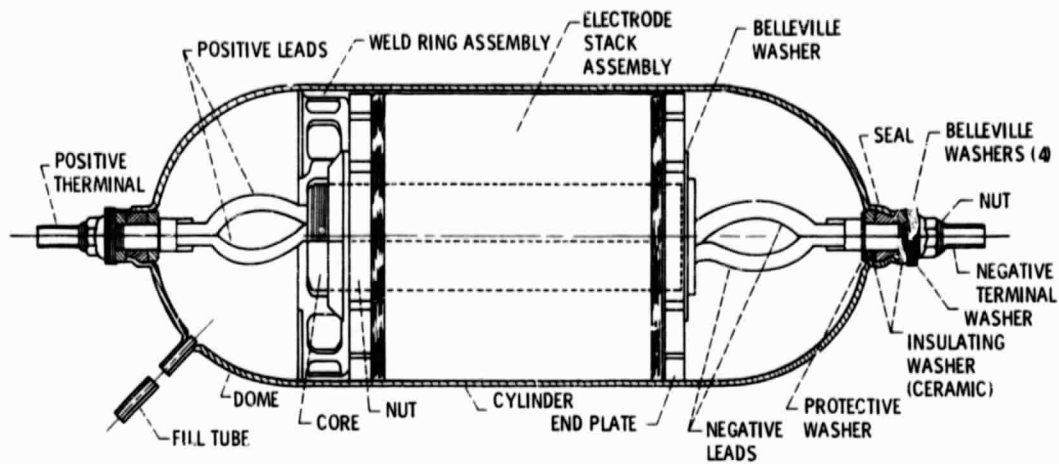
Figure 1. - 50A-hr nickel hydrogen cell.

Figure 2. - Stack assembly.

TEST ELECTRODE
(PHOTOCHEMICALLY ETCHED
Ni SCREEN/Pt CATALYST)

COUNTER
ELECTRODE
(NI WIRE)

REFERENCE ELECTRODE
(Pt/Au SCREEN)

NITROGEN
SOURCE

HYDROGEN
SOURCE

80 ml. 31 % KOH

WATER BUBBLER
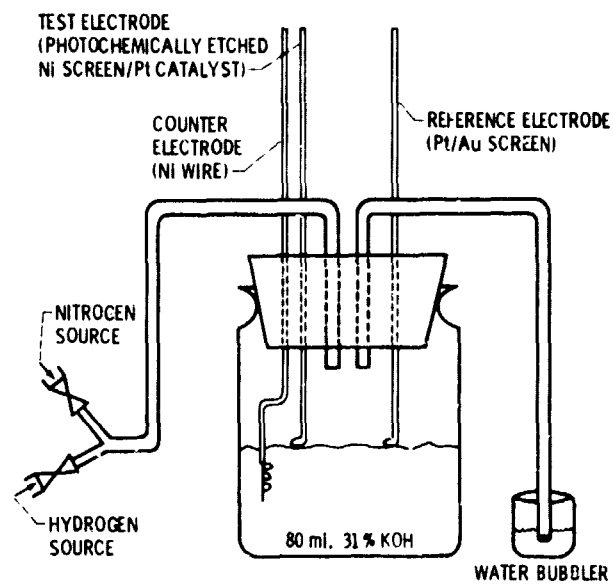
(a) Polarization test cell.

Figure 3.

RESISTOR BOX

DIGITAL
ELECTROMETER

TEST
CELL

POWER
SUPPLY

AMMETER
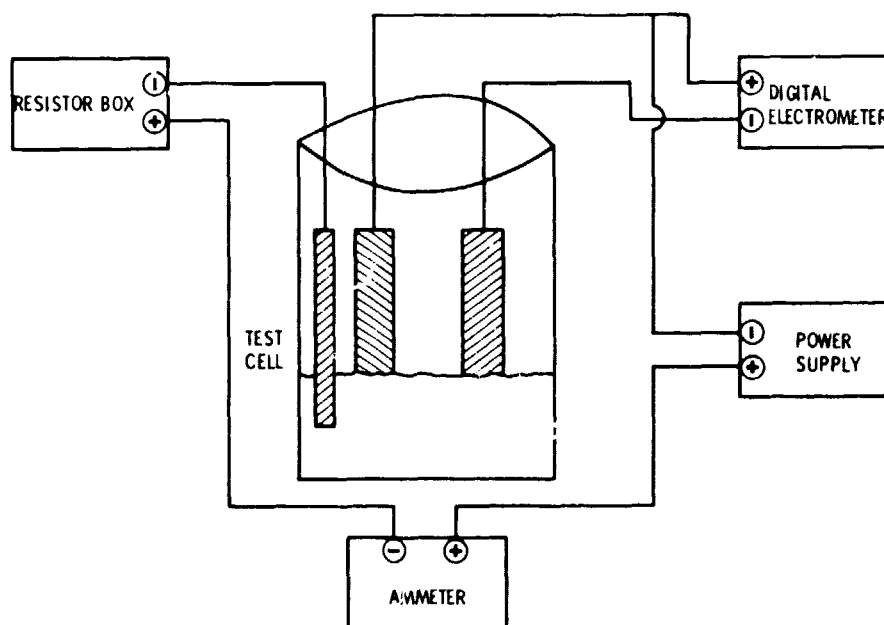
(b) Polarization test schematic diagram.

Figure 3. – Concluded.