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Assessment of Commercially Available and Experimental Hydrogen Electrodes

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ASSESSMENT OF COMMERCIALLY AVAILABLE AND EXPERIMENTAL HYDROGEN ELECTRODES

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SUMMARY

NASA Lewis Research Center is currently involved in advanced cell component development for nickel-hydrogen cells and batteries. Long life, high energy density, improved performance and reliability are required for energy storage systems in future space missions. Commercially available as well as experimental hydrogen electrodes were assessed and compared to the state-of-the-art hydrogen electrode that is currently being used in the nickel-hydrogen batteries. These electrodes were evaluated by scanning electron microscopy and standard electrochemical polarization measurements. Production variables such as Teflon content and platinum catalyst loading were considered in order to assess various hydrogen electrodes with regard to the different electrode manufacturing processes.

INTRODUCTION

Advanced cell component development is being performed at NASA Lewis to achieve improved performance and life for nickel-hydrogen batteries. The state-of-the-art (SOA) hydrogen electrodes used in nickel-hydrogen cells consist of a Teflon-platinum catalyst mixture, bonded to a pure nickel photochemically etched screen substrate. The substrate is backed with a porous Teflon (Gortex) membrane which is gas permeable (ref. 1). The catalyst loading is 7±2 mg/cm^2 fuel cell grade platinum black. This electrode is manufactured under contract by Hughes Aircraft Company for the Air Force. Commercially available hydrogen electrodes and experimental hydrogen electrodes were evaluated and compared with the SOA hydrogen electrode. The commercially available hydrogen electrodes selected for study were made by Energy Research Corporation (ERC) and Life Systems, Inc. (LSI). The ERC hydrogen electrodes consisted of a Teflon-platinum catalyst mixture, (2 mg/cm^2 fuel cell grade platinum black catalyst), bonded to a nickel substrate with a porous Teflon backing. The LSI (fuel cell type) electrodes consisted of a platinum-Teflon mixture deposited on a porous gold-plated nickel screen. The catalyst loading was greater than 10 mg/cm^2. The manufacturing process and electrode properties are proprietary. Experimental hydrogen electrodes were made for NASA under contract by LSI according to Hughes specifications at various catalyst loadings (0.5 mg/cm^2-10 mg/cm^2).

CHARACTERIZATION OF HYDROGEN ELECTRODES

Hydrogen electrodes usually consist of three different materials: catalyst, Teflon and fine-meshed metal screen. They are fabricated by applying a mixture of catalyst and Teflon on a metal screen which serves as a current collector and as mechanical support for the catalyst mixture. In order to produce acceptable hydrogen electrodes on a production scale, the following

variables must be defined: Teflon content, platinum-catalyst loading and sintering temperature. Teflon is used as a binder to give the electrode a degree of hydrophobicity, which makes it possible for gaseous reactants to diffuse readily to reaction sites. Platinum black is used as the catalyst because of its high exchange current density in alkaline electrolyte. Since the catalyst layer of an electrode consists of a mixture of very small hydrophilic platinum-black particles and hydrophobic Teflon particles, their arrangement in the layer will have a great influence on the wettability characteristic of the electrode. In order for a porous gas diffusion hydrogen electrode to be effective, there must be an appropriate amount of catalyst which, after being wetted by electrolyte, provide reaction sites for the heterogeneous electrochemical reactions to take place. The Teflon-catalyst mixture must allow uniform rapid recombination of oxygen which is generated during overcharge in nickel-hydrogen batteries. Too high a Teflon content will cause the catalyst to form a discontinuous matrix, so that the catalyst particles will exist as isolated "islands." Permanent dry regions of the electrocatalyst would not be utilized because of inadequate electrolyte channels (ref. 2). This would cause very limited utilization of the hydrogen electrode which in turn would lead to a sharp decrease in electrode efficiency. Too low a Teflon content may cause "flooding" of the electrochemical active sites.

An improper sintering temperature-time profile or the use of an aged Teflon suspension in the electrode mixture can result in hydrogen electrodes which cannot adequately catalyze the electrochemical oxidation and reduction reaction.

Hydrogen electrodes are affected by electrode flooding, which reduces the necessary hydrogen transfer to and from the active sites on the electrode. Flooded electrodes show a higher polarization than those that are not flooded. While investigating the cause of flooding, it was found that a substantial residue of Triton X-100 (wetting agent) was left in these electrodes after sintering.

This paper will discuss the results of an assessment of commercially available and experimental hydrogen electrodes for nickel-hydrogen batteries. These electrodes were evaluated by scanning electron microscopy and standard electrochemical polarization measurements. Production variables such as Teflon content and platinum catalyst loading were considered in order to assess various hydrogen electrodes with regard to the different electrode manufacturing processes. Sintering temperatures were not considered since this information was proprietary.

EXPERIMENTAL

Hydrogen electrodes obtained from commercial suppliers along with the SOA hydrogen electrode were evaluated by scanning electron microscopy and polarization measurements.

A. Scanning Electron Microscopy - The scanning electron microscopy technique was used to investigate the detailed structure of Teflon and catalyst with respect to various electrode manufacturing processes. This technique provided information on the size, shape, and microstructure of the catalyst-Teflon mixture and on the arrangement and distribution of catalyst aggregates. Photomicrographs were taken with an Amray 1200B Scanning Electron Microscope

(SEM). Samples were coated with a Polaron E5100 "Cool" Sputter Coater. After the samples were coated they were placed into the vacuum chamber of the scanning electron microscope. Photomicrographs were taken of the catalyst side and the Teflon backing of each hydrogen electrode at magnification ranges of 50-1KX.

B. Polarization Measurements - Standard electrochemical measurements were made using the "floating half cell" method (ref. 3).

SAMPLE PREPARATION

A rectangular sample measuring 1.0 by 1.2 cm was cut from the electrode, leaving the white Gortex membrane on the sample. A 0.2 by 1.0 cm strip of membrane was carefully peeled off from the sample to expose the platinum black and the screen. A 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 was perpendicular to the nickel wire with the membrane side up. The test apparatus is shown in figure 1.

TEST PROCEDURE

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

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

3. Current was passed between the working and counter electrode, and the voltage of the working electrode was measured with respect to the hydrogen Pt/Au reference electrode. Polarization measurements were made from 5 to 50 mA for both the anodic and cathodic reaction.

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

RESULTS AND DISCUSSION

Commercially available and experimental hydrogen electrodes were examined with an Amray 1200B Scanning Electron Microscope (SEM). Figure 2 shows SEM photomicrographs of three hydrogen electrodes with similar platinum catalyst loadings. These electrodes were fabricated using different electrode manufacturing processes. The Hughes SOA hydrogen electrode showed a relatively uniform cluster of catalyst-Teflon mixture, LSI experimental and LSI fuel cell type electrodes showed a series of void channels between the platinum-Teflon mixture throughout the surface of the electrode. Figure 3 shows SEM photomicrographs of hydrogen electrodes manufactured at reduced catalyst loadings. The LSI experimental hydrogen electrode with a loading of 0.6 mg/cm^2 showed the platinum-Teflon mixture being randomly distributed with most of the nickel screen substrate being exposed. The LSI experimental electrode with a catalyst

loading of 2 mg/cm^2 also indicated a nonuniform distribution of catalyst mixture but of less intensity. The ERC commercial hydrogen electrode also had a catalyst loading of 2 mg/cm^2. The Teflon-catalyst mixture of this electrode consists of a series of long channels. The electrode structure is very uniform. The SEM photomicrographs clearly indicate that each electrode's morphological structure differs depending upon the manner in which the Teflon-platinum catalyst mixture was applied to the substrate material. The difference may be caused by variations in Teflon content and sintering temperatures.

Standard polarization measurements were made in order to determine how effective the catalyst structure was in promoting the required electrochemical reaction. Figure 4 shows anodic and cathodic polarization plots of various hydrogen electrodes. LSI (fuel cell type) electrodes showed lower polarization than any of the other electrodes tested. Figure 5 shows polarization plots of electrodes that were fabricated at a reduced catalyst loading. The LSI experimental (0.6 and 2 mg/cm^2) electrodes anodic polarization measurement showed a significant increase in voltage. This indicated that these electrodes were not as reversible. The high polarization measurements may be attributed to the fact that the Teflon-catalyst mixture was not uniformly dispersed as shown in the SEM photomicrographs in figure 3. The ERC commercial hydrogen electrode, which had a more uniform catalyst distribution, showed a more reversible anodic and cathodic polarization measurement.

CONCLUSION

Commercially available and experimental hydrogen electrodes have been assessed and evaluated. Only electrodes manufactured at catalyst loadings greater than 10 mg/cm^2 gave slightly lower polarization measurements when compared to the SOA hydrogen electrode. For electrodes manufactured at reduced catalyst loadings, the morphological structure of the hydrogen electrode must be optimized to best utilize the characteristics of the catalyst-Teflon mixture for optimum electrochemical activity. Electrode manufacturing processes must be better defined to produce hydrogen electrodes that are comparable to the SOA for improved performance and reliability.

REFERENCES

1. Charleston, J. A.: Nickel-Hydrogen Component Development. NASA TM-83487, 1983.

2. Lee, M.C.: Transport Processes in Teflon-Bonded Fuel Cell Electrodes. University of Microfilm International, Ann Arbor, Michigan, 1976.

3. Giner, J.; and Smith, S.: A Simple Method for Measuring the Polarization of Hydrophobic Gas Diffusion Electrodes. Electrochem. Technol., 5(1-2):59-61, Jan.-Feb. 1967.

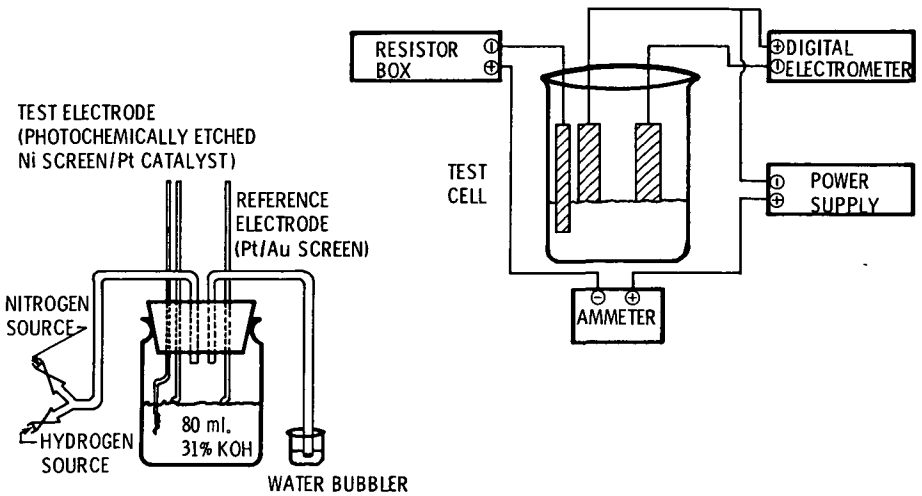

Figure 1. - Polarization test cell and polarization test schematic diagram.

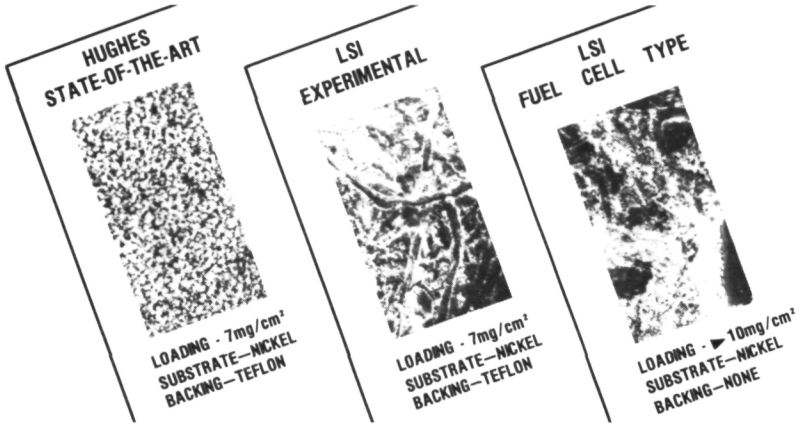

Figure 2. - SEM photomicrographs of commercially available and experimental hydrogen electrodes.

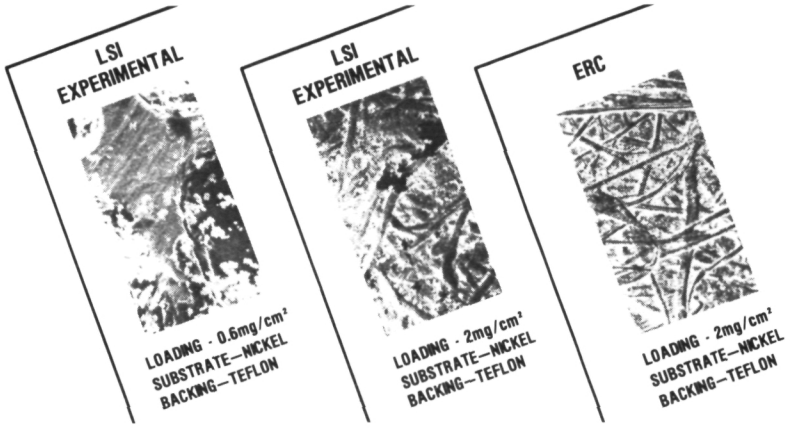

Figure 3. - SEM photomicrographs of commercially available and experimental hydrogen electrodes at reduced catalyst loadings.

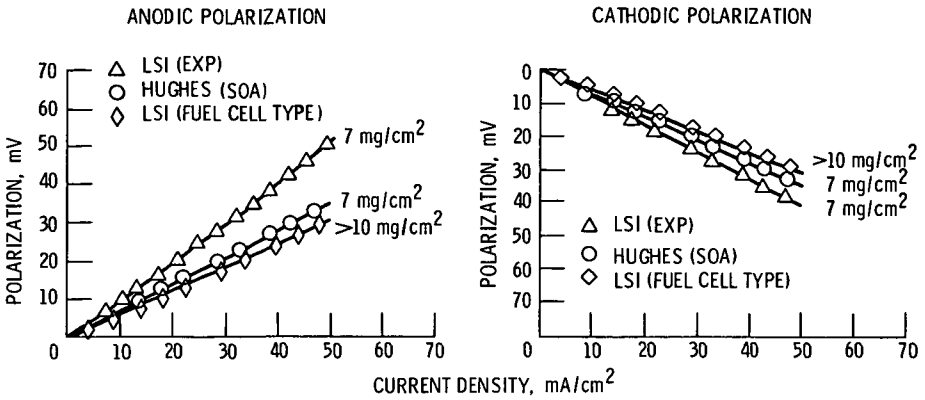

Figure 4. - Polarization of commercially available and experimental hydrogen electrodes.

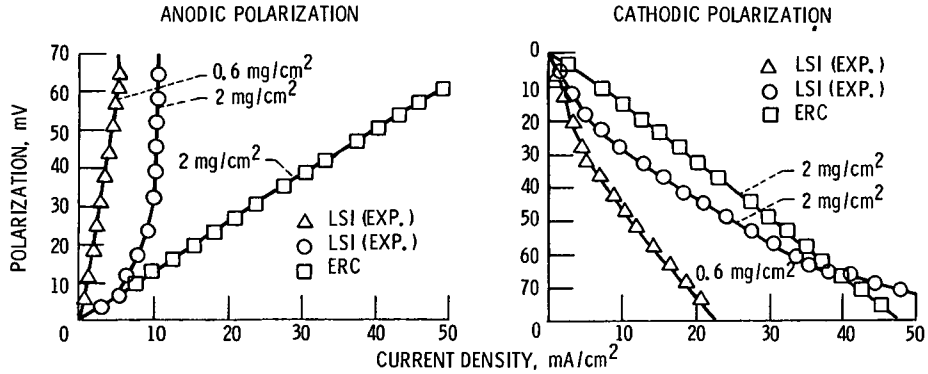

Figure 5. - Anodic and cathodic polarization as a function of Pt catalyst loading.

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15. Supplementary Notes

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