NASA Technical Memorandum 102399

Characterization and Cycle Tests of Lightweight Nickel Electrodes

Doris L. Britton
Lewis Research Center
Cleveland, Ohio

Prepared for the
Electrochemical Society Meeting
Hollywood, Florida, October 16-20, 1989

NASA

(NASA-TM-102399) CHARACTERIZATION AND CYCLE TESTS OF LIGHTWEIGHT NICKEL ELECTRODES (NASA) 13 p CSCL 07D

N90-12696

Unclas
G3/25 0243246

NASA Technical Memorandum 102399

Characterization and Cycle Tests of Lightweight Nickel Electrodes

Doris L. Britton
Lewis Research Center
Cleveland, Ohio

Prepared for the
Electrochemical Society Meeting
Hollywood, Florida, October 16–20, 1989

(NASA-TM-102399) CHARACTERIZATION AND CYCLE TESTS OF LIGHTWEIGHT NICKEL ELECTRODES (NASA) 13 p CSCL 07D

N90-12696

Unclas
G3/25 0243246

CHARACTERIZATION AND CYCLE TESTS OF LIGHTWEIGHT NICKEL ELECTRODES

Doris L. Britton
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

ABSTRACT

Development of a high specific energy nickel electrode is the main goal of the lightweight nickel electrode program at NASA Lewis Research Center. The approach has been to improve the nickel electrode by continuing combined in-house and contract efforts to develope a more efficient and lighter weight electrode for the nickel-hydrogen battery. High energy nickel electrodes suffer from having shorter lives than the state-of-the-art electrode. However, these lightweight electrodes appear to be favorable for missions requiring moderate cycle lives and depth-of-discharge.

E-5153

INTRODUCTION

As part of an overall effort to advance the technology of nickel-hydrogen ($Ni-H_2$) batteries, improved nickel electrode designs have been identified. The main goal of this effort is to develop a lighter weight nickel electrode which will improve the specific energy and specific volume of the $Ni-H_2$ system for the low-Earth-orbit (LEO) cycle regime. The approach has been to affect electrode improvements through continuing combined in-house and contract efforts. The use of a lightweight nickel plaque in place of the heavy-sintered state-of-the-art (SOA) plaque is expected to lead to improvements in specific energy, weight, cost, and performance of the nickel electrode. Several commercially available plaques other than the sintered plaque have been identified as having potential as a lightweight support for the nickel hydroxide active material. These plaques are not only lighter in weight but have pore sizes comparable with that of a typical commercial sintered nickel plaque.

EXPERIMENTAL PLAQUES

One type of a lightweight plaque used in this study is the Fibrex[1] fiber mat from National Standard. The Fibrex mat has some advantages over the SOA sintered plaque. The cost and weight of the Fibrex fiber mat is substantially lower than the SOA plaque. A special type of Fibrex plaque that is layered with 50 parts nickel fiber, 35 parts nickel powder, and 15 parts cobalt powder is currently being impregnated and tested.

Various Fibrex plaques, with thicknesses ranging from 30 to 80 mil and porosities of 85 and 90% are being electrochemically impregnated with active material and tested at NASA Lewis Research Center (LeRC). Eagle-Picher in Joplin, Missouri, is currently impregnating Fibrex plaques with 40, 60, and 80 mil thicknesses and 85 and 90% porosity to a loading level of 1.8 to 2.0 gram/cm^3 void. These electrodes will be cycled in a bipolar boiler plate cell at NASA LeRC. Hughes Aircraft Co. has a contract with NASA LeRC to develope and test the same types of Fibrex electrodes. Another lightweight mat that is currently being tested at NASA LeRC is the nickel felt from Sorapec (France). Sorapec developed a new type of support with small fibers (approximately 17 microns) and two thicknesses (80 and 120 mil) both with 90% porosity.

EXPERIMENTAL

Electrochemical Impregnation and Formation

The plaques are electrochemically impregnated in an aqueous bath containing 1.5M $Ni(NO_3)_2$, 0.175M $Co(NO_3)_2$, and 0.075M $NaNO_3$ made acidic to a pH of 3 by the addition of 50% nitric acid. The plaques are impregnated for various periods of time (6 to 10 hr) and current densities (50 to 78 mA/cm^2) to determine the conditions needed to obtain a loading of 1.8 to 2.0 g/cm^3 void. The impregnated plaques are formed by charging and discharging for 20 minutes each at approximately 3C rate. The formation process serves to remove impurities, which are chiefly nitrates, carried

[1]Trademark of National Standard Company, Niles, Michigan

over from the impregnation bath. The process also gives the nickel hydroxide active material electrochemical "exercise" by a repeated oxidation-reduction process which brings it to full capacity.

The theoretical capacity is determined from the weight of the active material in the electrode, calculated from the weight gained after the impregnation/formation process, using the electrochemical equivalent of 0.289 AH/g of nickel.

Cycle Life

The objective of the cycle test is to obtain life data and to identify and evaluate any trends or degradation in electrode performance. The cycling tests are continuous cycling in a low-Earth-orbit (LEO) regime of 55 minute charge and 35 minute discharge at 80% depth-of-discharge (DOD). The voltage as a function of time is plotted continuously and capacities are measure every 50 cycles during the test for the first 1000 cycles and every 500 cycles thereafter. The end of life or failure is defined as the point where the discharge voltage degrades to -0.2 V versus the Hg/HgO reference electrode.

Failure Analysis

At the end of life, the cell is disassembled and the components are visually inspected. After a thorough rinsing and drying, the nickel electrode is weighed and measured. Scanning electron micrographs and pore size distribution curves of the cycled electrode are analyzed and compared with that of the uncycled nickel electrode.

EXPERIMENTAL RESULTS

Electrochemical Impregnation and Formation

Table 1 shows the impregnation parameters and characteristics of the Fibrex and Sorapec nickel electrodes. A 9 to 14% increase in thickness was measured when loading the porous plaques at the levels shown. The electrode thickness increased as the loading level increased as reported earlier (1,2). To solve this expansion problem, a new set of Fibrex mat (e.g., Fibrex8090 in table 1) was developed by National Standard Corp. The new fiber mat was sintered twice as long as the original material to produce a stronger and expansion-free plaque. The 3% thickness expansion on the new and stronger Fibrex8090 was mainly due to surface deposition.

Cycle Life

The utilization changes of the Fibrex and Sorapec nickel electrodes against cycle life are shown in Figures 1 through 4. Approximately every 1000 cycles, capacity measurements are made by discharging to -0.2 V (versus a Hg/HgO reference electrode) at a 1.37C rate after charging for 80 minutes at a 1.1C rate. The percent utilization of the electrode is calculated by using the ratio of the measured capacity to the theoretical calculated based on the weight of the active material deposited. The initial utilization of the porous nickel electrodes made from a 90% porosity plaque (Figures 2,3, and 4) were initially lower (40 to 55%) than the less porous (Figure 1) electrode. The maximum utilization of the nickel electrodes can exceed 100% since the valence change of the nickel ions during charge and discharge can be greater than 1. The percent utilization values in this report are calculated based on a nickel ion valence change of 1.

A Fibrex electrode made from a 30-mil thick, 85% porosity plaque, as shown in Figure 1, took about 100 cycles to reach 100% utilization. At cycle 2150, this electrode reached its maximum utilization value of 121% and cycled for another 2384 cycles before it reached its end of life. Figure 2 depicts the cycle life data of a more porous Fibrex electrode made from a 30 mil thick, 90% porosity mat. It took over 1000 cycles for this electrode to reached 100% utilization and another 500 cycles to reached its maximum utilization value of 140%. This particular electrode has accumulated over 3000 cycles so far with stable voltage and capacity.

The initial cycle life data of the Fibrex electrode made from the new expansion-free, 80 mil thick, 90% porosity fiber mat is shown in Figure 3. With over 500 cycles to date, this electrode is showing a trend similar to the thinner (30 mil) electrode with the same porosity. This thick expansion-free Fibrex electrode continues to cycle with stable voltage and increasing utilization.

Figure 4 shows the cycle life data of the Sorapec nickel electrode made from an 80 mil thick, 90% porosity nickel felt. The Sorapec electrode has an advantage over the Fibrex electrode with similar properties (80 mil thick, 90% porosity) of a higher utilization during the first 300 cycles. However, the Sorapec electrode did not reach 100% of its utilization and its capacity decreased rapidly early in life.

Failure Analysis

Figures 5 and 6 depict the performance of the Fibrex and Sorapec electrodes at the different discharge rates and cycles. The initial utilization of the electrodes was dependent upon the discharge rate and showed slightly lower values at the higher rate. The utilization of the Fibrex electrode made from a 30-mil thick, 85% porosity mat at the 2.74C rate is 30% less at the end of life than its initial value as shown in Figure 5. In the case of the Sorapec electrode (Figure 6), the utilization decreased severely as the discharge rate increased. However, at the lower rate (C/2), the utilization of both the Fibrex and Sorapec electrodes did not decrease. This suggests that the failure of the electrodes is due to the loss of high rate discharge capacity rather than the loss in total electrode capacity.

The thickness of the cycled electrodes increased with cycling. The thickness of the cycled Sorapec electrode increased by about 16% from the initial electrode thickness (over and above the increased thickness after the impregnation process). This significant increase in thickness of the Sorapec electrode may have caused the extrusion of some active material out of the electrode. This extrusion, in turn, caused the Sorapec electrode to loss a substantial amount of weight (about 18%). From the observations made, it can be said that the poor high rate performance and short life of the Sorapec electrode are due to the electrode expansion and weight lost.

After cycling for 4534 cycles, the Fibrex electrode expanded about 6% and showed a weight loss of approximately 8%. For comparison, the thickness of the SOA sintered electrode expanded about 10% after 4500 cycles (3). Figures 7 through 9 show the progression of pore size distribution with cycling for the nickel electrodes. Cycling the electrodes to failure resulted in a change of the total pore volume and distribution. The peak of the cycled Sorapec electrode at the 0.015 μm, as shown in Figure 7, shifted slightly to the right and increased in size. The peaks in the range of 0.02 to 0.05 μm and the broad distribution of 0.25 to 7 μm increased in size with the latter shifting to the right. This increase in volume and the shift to larger pores of the Sorapec electrode are caused by the expansion and active material extruding out of the pores of the electrode.

Figure 8 shows the pore size distribution of the Fibrex electrode. The distribution shows a distinct multiple peak profile from 0.01 to 10 μm as opposed to the minimal peak profile of the SOA electrode (Figure 9) across the same region (4). There was a definite shift in the average pore size and distribution of the cycled SOA electrode toward smaller pore which could result in the electrode having a greater affinity for electrolyte. This effect can result in drying of the separator which will lead to a high separator resistance. This traditional increase in small pores of the cycled SOA electrode was not found in either the Fibrex and Sorapec electrodes. In addition to an increase in volume of the micropores of the cycled Fibrex and Sorapec electrodes, the volume of the larger pores also increased by a factor of 2 to 4. The pore size distribution of the cycled Fibrex and Sorapec electrodes should not result in the electrodes competing with the separators for electrolyte because of their bimodal pore size distribution.

CONCLUSION

Fabrication and life cycle testing of lightweight nickel electrode using fiber plaques have demonstrated the feasibility of developing an improved and higher energy density nickel electrode.

The initial problem of thickness expansion during impregnation of Fibrex fiber mats has been resolved by increasing the sintering time of the fiber mats.

The plaque porosity appears to affect the increasing utilization during cycling. The electrodes made of a higher porosity (90%) material took longer for the utilization to reach its maximum value. Further study will determine whether improvement in the initial utilization at the high rate is possible.

Preliminary measurements on the cycled nickel electrode indicate expansion of the active material contributed to the short life and poor performance of the thick Sorapec electrode. This electrode expansion also caused an increase in total pore volume of the cycled nickel electrodes.

The expansion of the Fibrex electrode after cycling was about 40% less than the SOA nickel electrodes. The expansion in the SOA electrodes results in poor electrolyte distribution in the Ni-H_2 cell which has been considered to be one of the major failure modes of the cell. The bimodal distribution of the cycled Fibrex electrode should reduce this problem.

The major performance change of the Fibrex and Sorapec electrodes during cycling is the decrease of the high rate discharge capability rather than the decrease in the total capacity.

DISCUSSION

A computer program was developed at NASA LeRC (5) to calculate the weight and specific energy of a nickel electrode. This program, using fiber and felt plaques, varies parameters such as the active material loading level, plaque porosity and thickness, and the utilization of the electrode. The specific energy of the electrode depends on the thickness and porosity of the nickel plaque as well as on the active material loading level as shown Table 2. An improvement of as much as 60% in specific energy is possible by using porous and/or thicker lightweight plaques with increased loading level and utilization.

Improving performance and cycle life as well as increasing the specific energy of the system are the drivers of the technology development program at NASA LeRC. Our means of achieving these goals are by developing lightweight, longer life, lower cost, and high performance nickel electrodes.

REFERENCES

1. Britton, D. L.: Performance of Lightweight Nickel Electrodes. Proceeding of the 33rd International Power Sources Symposium, pp. 467-475 June 13-16, 1988. NASA TM 100958, 1988.

2. Britton, D. L.: Lightweight Fibrous Nickel Electrodes for Nickel-Hydrogen Batteries. Proceedings of the Fourth Annual Battery Conference on Applications and Advances. January 17-19, 1989, California State University - Long Beach, Long Beach, CA. NASA TM 101997, 1989.

3. Lim, H.S.; and Verzwyvelt, S.A.: Long Life Nickel Electrodes for a Nickel-Hydrogen Cell Cycle Life Tests. NASA CR-174815, 1985.

4. Thaller, L.H.; Manzo, M.A.; and Gonzales-Sanabria, O.D.: Design Principles for Nickel-Hydrogen Cells and Batteries. NASA TM-87037, 1985.

5. Collaboration with Michelle Manzo, NASA Lewis Research Center, Cleveland, Ohio.

TABLE 1. - CHARACTERISTICS OF IMPREGNATED FIBREX AND SORAPEC SUBSTRATES

ELECTRODE	PLAQUE POROSITY (%)	PLAQUE THICKNESS (mil)	THICKNESS EXPANSION (%)	LOADING LEVEL (g/cc void)	INITIAL UTILIZATION (%)
Fibrex3085	85	30	14	1.7	75
Fibrex3090	90	30	9	1.8	43
Fibrex8090*	90	80	3	1.8	47
Sorapec2	90	80	11	1.7	56

*stronger plaque

TABLE 2. - SPECIFIC ENERGY OF A 50 AH IPV NICKEL-HYDROGEN CELL USING NICKEL ELECTRODES WITH DIFFERENT THICKNESSES, POROSITIES, AND LOADING LEVELS

Electrode	Thickness (mil)	Porosity (%)	Utilization (%)	Loading Level (g/cc void)	Specific Energy (Wh/kg)	Relative Specific Energy
SOA	30	80.3	107.3	1.6	61.269	1.00
Fibrex	30	85	120	1.6	70.475	1.15
	30	85	120	1.8	73.215	1.20
	30	85	120	2.0	76.527	1.25
	30	90	130	1.6	79.750	1.30
	30	90	130	1.8	83.060	1.36
	30	90	130	2.0	87.137	1.42
	80	85	90	1.6	63.294	1.03
	80	85	90	1.8	66.777	1.09
	80	85	90	2.0	71.183	1.16
	80	85	120	1.8	80.140	1.31
	80	90	90	1.6	69.746	1.14
	80	90	90	1.8	76.840	1.25
	80	90	90	2.0	74.649	1.22
	80	90	120	1.8	83.999	1.37
	40	90	120	1.6	78.277	1.28
	40	90	120	1.8	82.565	1.35
	40	90	120	2.0	85.353	1.39
	60	90	100	1.6	73.536	1.20
	60	90	100	1.8	76.463	1.25
	60	90	100	2.0	80.161	1.31
Sorapec	80	90	90	1.6	80.164	1.31
	80	90	90	1.8	87.111	1.42
	80	90	90	2.0	84.306	1.38
	80	90	120	1.8	94.432	1.54
	120	90	90	1.6	80.044	1.31
	120	90	90	1.8	86.220	1.41
	120	90	90	2.0	94.854	1.55
	120	90	120	1.8	97.133	1.59
	40	90	120	1.6	87.680	1.43
	40	90	120	1.8	91.692	1.50
	40	90	120	2.0	94.162	1.54
	40	90	90	1.8	79.951	1.30

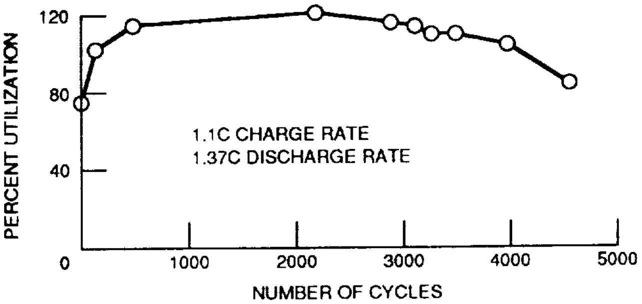

Figure 1. - Utilization versus number of cycles of Fibrex nickel electrode made from a 30 mil thick, 85 percent porosity fiber mat.

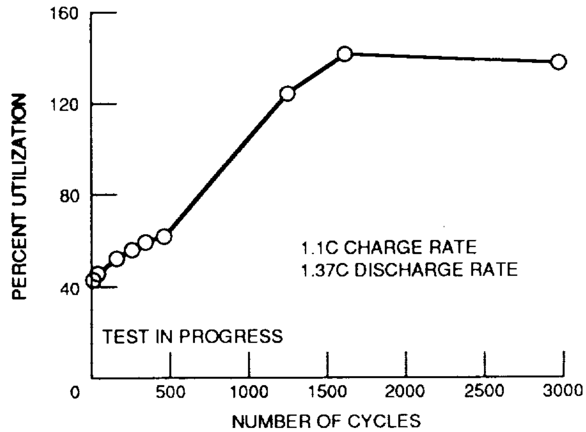

Figure 2. - Utilization versus number of cycles of Fibrex nickel electrode made from a 30 mil thick, 90 percent porosity fiber mat.

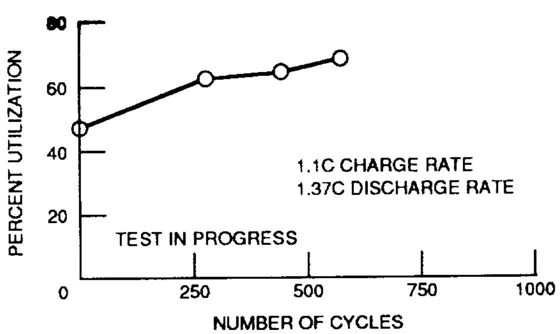

Figure 3. - Utilization versus number of cycles of Fibrex nickel electrode made from an 80 mil thick, 90 percent porosity fiber mat.

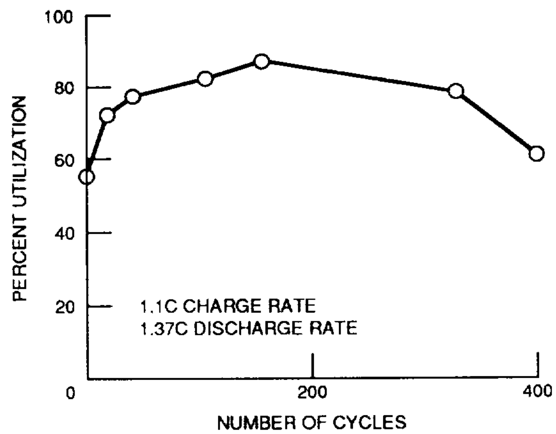

Figure 4. - Utilization versus number of cycles of Sorapec nickel electrode made from an 80 mil thick, 90 percent porosity nickel felt.

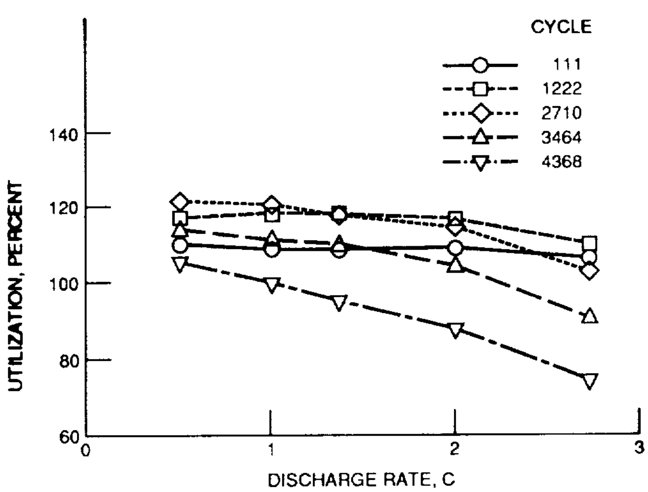

Figure 5. - Performance of Fibrex nickel electrode made from a 30 mil thick, 85 percent porosity fiber mat.

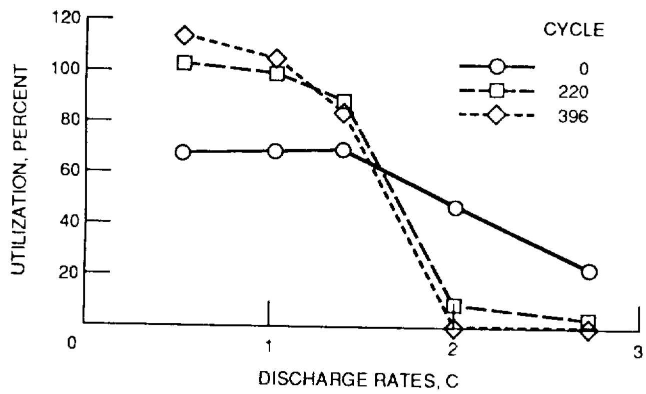

Figure 6. - Performance of Sorapec nickel electrode made from an 80 mil thick, 90 percent porosity nickel felt.

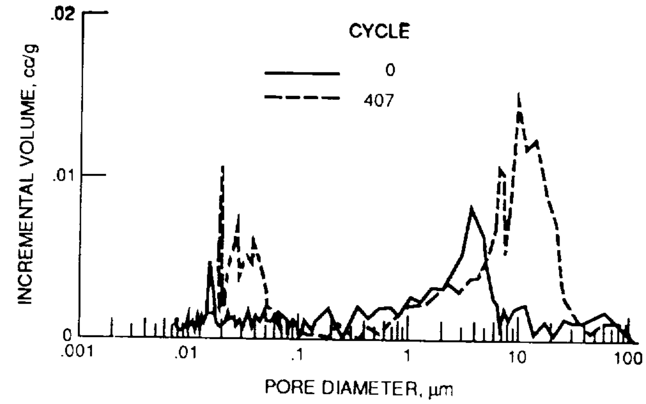

Figure 7. - Pore size distribution curves of new and cycled Sorapec nickel electrode (80 mil, 90 percent porosity).

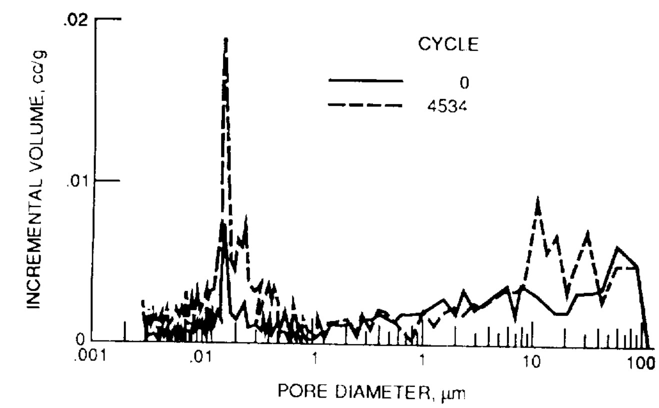

Figure 8. - Pore size distribution curves of new and cycled Fibrex nickel electrode (30 mil, 85 percent porosity).

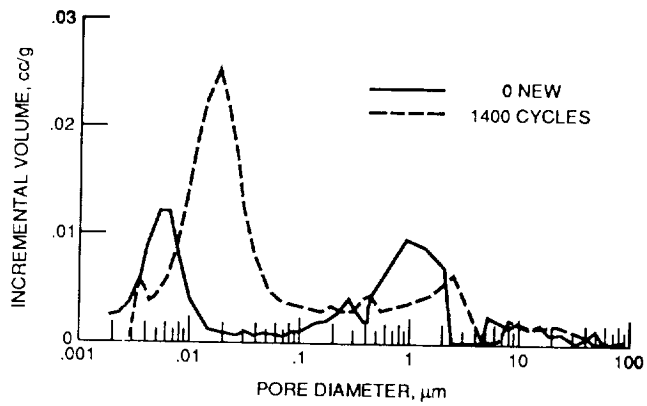

Figure 9. - Pore size distribution curves of new and cycled SOA sintered nickel electrode.

NASA
National Aeronautics and Space Administration

Report Documentation Page

1. Report No. NASA TM-102399	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle Characterization and Cycle Tests of Lightweight Nickel Electrodes		5. Report Date
		6. Performing Organization Code
7. Author(s) Doris L. Britton		8. Performing Organization Report No. E-5153
		10. Work Unit No. 506-41-21
9. Performing Organization Name and Address National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135-3191		11. Contract or Grant No.
		13. Type of Report and Period Covered Technical Memorandum
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546-0001		14. Sponsoring Agency Code

15. Supplementary Notes

Prepared for the Electrochemical Society Meeting, Hollywood, Florida, October 16-20,1989.

16. Abstract

Development of a high specific energy nickel electrode is the main goal of the lightweight nickel electrode program at NASA Lewis Research Center. The approach has been to improve the nickel electrode by continuing combined in-house and contract efforts to develop a more efficient and lighter weight electrode for the nickel-hydrogen battery. High energy nickel electrodes suffer from having shorter lives than state-of-the-art electrode. However, these lightweight electrodes appear to be favorable for missions requiring moderate cycle lives and depth-of-discharge.

17. Key Words (Suggested by Author(s)) Lightweight High Energy Nickel Impregnation	18. Distribution Statement Unclassified – Unlimited Subject Category 25

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No of pages 12	22. Price* A03

NASA FORM 1626 OCT 86

*For sale by the National Technical Information Service, Springfield, Virginia 22161