Development of Sintered Fiber Nickel Electrodes
For Aerospace Batteries

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ABSTRACT
The nickel electrode is the specific energy limiting component in nickel battery systems. A concerted effort is currently underway to improve NiH_2 performance while decreasing system cost. Increased performance with electrode specific energy (mAh/g) is the major goal of this effort. However, cost reduction is also an important part of the overall program, achieved by reducing the electrode weight. A lightweight, high energy density nickel electrode is being developed based on a highly porous, sintered fiber, nickel substrate. This developing technology has many applications, but is highly applicable to the military and aerospace industries.

Introduction

The aerospace industry has used the nickel-hydrogen battery system for more than 20 years developing both an extensive history and a large database. The aerospace industry demands a high degree of performance and reliability in which the nickel hydrogen battery is able to maintain. Advances in technology are constantly being made. The focus of the present work is to develop an aerospace flight qualified nickel electrode. Rapid growth in earth orbital satellite applications, including small satellites, and increasing spacecraft power system performance requirements, have created a need for improved flight qualified nickel hydrogen (NiH_2) battery technology. However, these performance improvements must not compromise the inherent safety or reliability of the NiH_2 battery. A concerted effort is currently underway to improve the NiH_2 performance while decreasing system cost. This effort involves work at the component, cell and full battery level. Component level development work includes performance enhancement and cost reduction at the basic electrode level. Increased performance, with electrode specific energy (mAh/g) as figure of merit, is the major goal of this effort. However, cost reduction is also an important part of the overall program.

Electrode Substrate Material

Eagle-Picher Ind., Inc. currently manufacture the sintered carbonyl nickel powder electrode substrate. This forms a rigid, highly porous matrix into which the nickel-hydroxide active material may be introduced. Sintered nickel powder is very strong and dimensionally stable, but it contributes adversely to the overall electrode weight. This type of electrode may account for more than 50% of the total weight in a typical aerospace nickel electrode. A lightweight substrate would greatly improve the electrode specific energy. The approach used in this development effort has been to utilize fiber based nickel electrode substrates, prepared using proprietary micro-diameter metal fiber technology. This material is superior to prior fiber substrates based on the small fiber diameter, smaller equivalent pore size and dimensional stability. Two vendors which produce such substrates are Memtec America Corp. and Ribbon Technology Corp. Due to proprietary reasons, the data will not specify to which company it refers.

The active material loading obtained typically with fiber based substrates has been relatively low. An additional problem is that the active material utilization has also been typically low. This results in an electrode with a relatively low specific energy (in terms of milliampere-hours per gram), even though the fiber is lighter in weight than sintered nickel powder.

In general, the electrochemical impregnation method deposits the nickel hydroxide active material directly into the pores of the electrode substrate from the "inside out". Nickel hydroxide is produced inside the pore structure of the electrode by the nitrate reduction process. Since the outer pores near the electrode surface are filled last with active material, the entire electrode structure is used. This technique provides for much more intimate contact between the active material, and the current collector, which results in a lower effective current density during electrode operation. The resultant electrode has lower impedance, increased rate capability, higher electrochemical utilization based on theoretical energy density and improved cycle life.

The small pore structure retains active material much better than a corresponding larger pore size material, which con-

tributes significantly to charge/discharge cycle life. As the electrode is cycled, the active material undergoes significant changes in phase, oxidation state, state of hydration, structure, crystallinity, and density. These changes in the active material cause the gradual extrusion of the active material out of the substrate and into the electrolyte/separator matrix in the cell. The smaller pore size in the electrochemically impregnated substrate and the more intimate contact between the active material and the substrate minimizes this active material extrusion loss during cycling.

Electrode Active Material Impregnation/Formation

The highly porous substrate material allows the nickel hydroxide active material to be inserted into the electrode. This work is being performed primarily for aerospace applications. Therefore, the nickel hydroxide active material insertion method primarily being investigated is a close variation of the aerospace electrochemical impregnation method.

In general, the porous electrode substrate is cathodically polarized in a bath of aqueous nickel-nitrate. The charge/discharge cycle then forms the active material, creating a working nickel electrode. The basic chemical reactions are listed in Table I. The electrochemical reactions at the catalytic electrode are similar to basic alkaline fuel cell chemistry. When the nickel electrode is charged, the nickel active material is oxidized to a higher oxidation state at the nickel electrode. This is typically shown as a charge from nickel (II) to nickel (III). The reaction at the gas electrode is essentially the alkaline electrolysis of water, in the presence of a catalyst, to produce molecular hydrogen gas. This is essentially a reduction reaction. When the electrode is discharged, the nickel active material is reduced to its original state and the hydrogen gas is oxidized to form water, producing two electrodes per molecule of gas that reacts.

Table I. Electrochemical Reactions Experienced by the Electrodes

Water and Ion Balanced Reactions
Positive: $NiO(OH) + H_2O + e \Rightarrow Ni(OH)_2 + (OH)-$
Negative: $\frac{1}{2}H_2 + (OH)- \Rightarrow H_2O + e$
Net Reaction: $\frac{1}{2}H_2 + NiO(OH) \Rightarrow Ni(OH)_2$

Unlimited Overcharge Capability
Positive: $2(OH)- \Rightarrow 2e + \frac{1}{2}O_2 + H_2O$
Negative: $2H_2O + 2e \Rightarrow 2(OH)- + H_2$
$\frac{1}{2}O_2 + H_2 \Rightarrow H_2O$

High Cell Reversal Tolerance
Positive: $H_2O + e \Rightarrow (OH)- + \frac{1}{2}H_2$
Negative: $\frac{1}{2}H_2 + (OH)- \Rightarrow H_2O + e$

Process parameters such as temperature, current, pH, and others are precisely controlled with specific limits.

Electrochemical Impregnation Results

A number of electrodes were tested within nine separate groups.

Individual results were obtained, however, Table II shows all 80 electrodes averaged according to the category from which they belong.

The column labeled "Standard" is similar data for a standard aerospace grade electrode. The initial substrate thickness for the R&D substrate was measured using a dial micrometer. The average initial substrate thickness is indicated along with the standard deviation, which is a measure of substrate uniformity. Table III shows the calculations used for each electrode and how the information was derived.

Electrode Parameters after the Electrochemical Impregnation

The sample area is constant since there is no measurable change with the length and width of the substrate. The thickness, however, does increase during the impregnation process. This is the result of filling substrate voids with nickel-hydroxide active material. The substrate is dimensionally stable in the length and width because of the way the that the fibers are randomly oriented within the electrode during the layering process. They are essentially interwoven in interlocking layers. The substrate is much less stable in the thickness direction. Even though the substrate is sintered to provide additional strength in this direction, the forces involved in the active material changes that occur cannot completely overcome. One of the major factors effecting ultimate electrode performance is this tendency towards thickness growth. Minimizing this effect is essential, particularly for a long life aerospace application, and is one of the major goals of the current study.

As can be seen from Table II, the impregnated electrode thickness increases from 63.5% to 181.91%. This is considerably more than the corresponding increase observed in aerospace sinter powder electrodes. Growth occurs mainly during impregnation due to the addition of the nickel. Growth also occurs - although not as much - during formation as the result of active material expanding during the charge/discharge cycle. Considerable progress has been made in optimizing fiber substrate parameters to minimize growth. While excessive thickness increase is not desirable, it is not necessarily prohibitive in an electrolyte starved compressed cell stack design, such as a NiH_2 cell design. Figures 1 & 2 show

Table II A Listing of the Average of All 80 Electrodes Used in the Study

|	STANDARD	Group A				Group B				
	AVGS	1 AVGS	2 AVGS	3 AVGS	4 AVGS	1 AVGS	2 AVGS	3 AVGS	4 AVGS	5 AVGS
Approximate size (in²)	7.900	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000
Substrate Weight (g)	8.610	1.599	1.782	2.254	2.337	2.295	2.371	3.056	3.242	3.221
Raw Weight with Tab (g)		6.950	6.768	7.269	7.670	7.739	7.858	8.550	8.923	8.538
Initial Thickness Average (in)	0.030	0.045	0.050	0.059	0.061	0.044	0.047	0.053	0.062	0.066
Initial (thickness) Porosity (%)	80.000	93.958	93.883	93.490	93.441	90.988	91.249	89.810	91.010	91.605
Initial Volume (cc)	3.880	2.975	3.278	3.894	4.016	2.870	3.050	3.446	4.052	4.311
Initial Void Volume (ccvv)	2.940	2.795	3.078	3.641	3.754	2.612	2.784	3.102	3.687	3.949
Number of Impregnation Cycles	2	2	2	2	2	2	2	2	2	2
Final Thick Average (in)	0.031	0.076	0.080	0.104	0.094	0.088	0.088	0.090	0.106	0.117
Final (thickness) Porosity (%)	80.000	96.372	96.147	96.263	95.697	95.454	95.284	93.908	94.742	95.174
Final Volume (cc)		4.984	5.221	6.798	6.136	5.773	5.784	5.919	6.949	7.663
Final Void Volume (ccvv)	3.050	4.805	5.021	6.544	5.873	5.515	5.525	5.575	6.585	7.301
Final Weight (g)	13.640	11.072	12.074	16.150	12.217	15.314	12.307	9.109	17.282	18.090
Finished Raw Weight (g)		5.721	7.088	11.135	6.884	9.869	6.820	14.603	11.602	12.773
Finished Pick-up (g)	5.030	4.122	5.306	8.881	6.915	7.575	6.885	6.053	8.359	9.551
Total Thick Increase (in)	0.001	27.791	33.855	42.311	33.930	79.407	69.868	55.141	39.988	62.588
Total Thick Increase (%)	5.880	63.569	68.040	71.412	56.111	181.910	149.097	109.629	65.195	94.980
Final (thickness) Load (g/ccvv)	1.650	0.851	1.048	1.359	1.163	1.377	1.245	1.091	1.271	1.306
Flood Capacity* (Ah)	1.740	0.737	1.159	1.780	1.330	1.719	1.685	1.630	1.653	2.021
Theoretical Capacity (Ah)	1.450	1.191	1.533	2.567	1.998	2.189	1.990	1.749	2.416	2.760
Utilization (%)	120.000	61.411	76.634	70.260	67.739	79.206	86.231	93.629	68.450	75.519
mAh/in²		184.286	290.079	444.893	332.921	429.643	421.587	408.190	413.214	505.714
Ah/in³		2.404	3.621	4.304	3.529	4.906	4.825	4.521	3.908	4.421
mAh/cm²		28.564	44.962	68.959	51.603	66.595	65.346	63.270	64.048	78.386
mAh/cm³		146.687	220.937	262.608	215.337	299.313	294.406	275.850	238.409	269.743
Active mass (%)	36.870	71.466	74.056	79.596	73.916	76.528	73.835	65.521	72.060	74.311
Inactive mass (%)	63.130	14.543	19.496	14.003	20.545	15.024	20.571	25.885	18.751	21.601
Specific Energy (mAh/g)	127.850	127.029	163.517	161.061	144.171	174.928	183.065	176.605	142.469	160.941

Table III A Listing Of The Mathematical Formulas Used

	SAMPLE
	0.06
Approximate size (in²)	9
Substrate Weight (g)	3.63
Raw Weight with Tab (g)	9.2101
Initial Thickness Average (in)	AVERAGE OF THICKNESS
Initial (thickness) Porosity (%)	100*INITIAL VOID VOLUME/INITIAL VOLUME
Initial Volume (cc)	APPROXIMATE SIZE*INITIAL THICKNESS AVERAGE*16.39
Initial Void Volume (ccvv)	(INITIAL VOLUME)-(SUBSTRATE WEIGHT/8.9)
Number of Impregnation Cycles	2
Final Thick Average (in)	AVERAGE OF THICKNESS
Final (thickness) Porosity (%)	100*FINAL VOID VOLUME/FINAL VOLUME
Final Volume (cc)	APPROXIMATE SIZE*FINAL THICKNESS AVERAGE*16.39
Final Void Volume (ccvv)	(FINAL VOLUME)-(SUBSTRATE WEIGHT/8.9)
Final Weight (g)	22.4668
Finished Raw Weight (g)	SUBSTRATE WEIGHT+GREEN WEIGHT
Finished Pick-up (g)	FINAL WEIGHT-RAW WEIGHT WITH TAB
Final (thickness) Load (g/ccvv)	FINISHED PICKUP/FINAL VOID VOLUME
Flood Capacity* (Ah)	3.1177
Theoretical Capacity (Ah)	FINISHED PICKUP*0.289
Utilization (%)	100*FLOOD CAPACITY/THEORETICAL CAPACITY
mAh/in²	1000*FLOOD CAPACITY/APPROXIMATE SIZE
Ah/in³	FLOOD CAPACITY/(APPROXIMATE SIZE*FINAL THICKNESS AVERAGE)
mAh/cm²	1000*FLOOD CAPACITY/(APPROXIMATE SIZE*2.54*2.54)
mAh/cm³	1000*FLOOD CAPACITY/ (APPROXIMATE SIZE*16.39*FINAL THICKNESS AVERAGE)
Active mass (%)	100*FINISHED PICKUP/FINISHED RAW WEIGHT
Inactive mass (%)	100*SUBSTRATE WEIGHT/FINAL WEIGHT
Specific Energy (mAh/g)	1000*FLOOD CAPACITY/FINISHED RAW WEIGHT

the percentage of weight and thickness gained and lost. This shows the greatest thickness occurring at the final formation and the most weight at the last impregnation.

The electrode flooded capacity is determined by cycling in KOH. The electrode is charged at a constant C/2 rate until 150% overcharge is reached. The electrode is then discharged at constant current at the C/2 rate and the time measured relative to an end voltage (typically -1.7VDC verses the nickel counter electrode). The electrical capacity is then expressed in milliampere-hours. The electrode theoretical capacity is calculated from the finished active material weight in grams multiplied by 0.289 Ah/g. which is the theoretical energy density of the nickel-hydroxide electrochemical reaction, based on a one electron reaction (Ni++/Ni+++). State-of-the-art aerospace electrodes manufactured by Eagle-Picher typically yield about 120% of theoretical capacity under these

test conditions. This attests to the efficiency of the electrochemical impregnation process. Low utilization has typically been one of the major disadvantages of fiber substrates in the past (along with excessive active material bleeding and the thickness growth). The utilization problem has been essentially solved during the development phase of this program.

Active material weight is typically lost during the formation process due to simple extrusion and expulsion through vigorous gas). Also, any surface loading is easily lost during this step. In some respect, the measure of weight loss during formation is indicative of the efficiency of the impregnation step. A lower weight loss in formation indicates that the active material is more tightly held in the substrate pores and is not easily lost during electrical cycling in KOH. The active material weight loss during formation (expressed as a
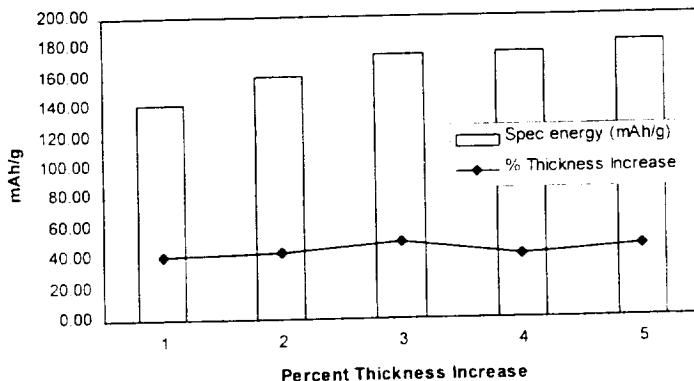
ELECTRODE A
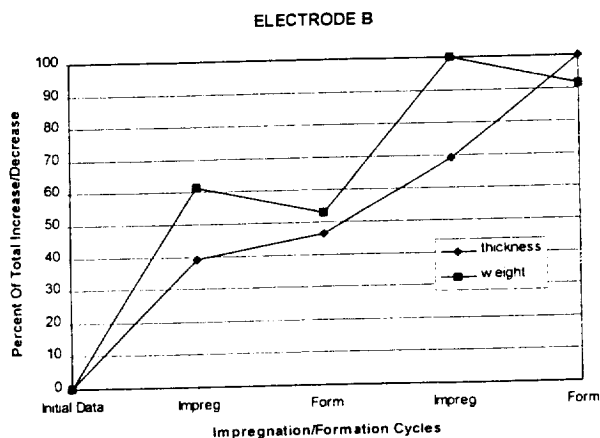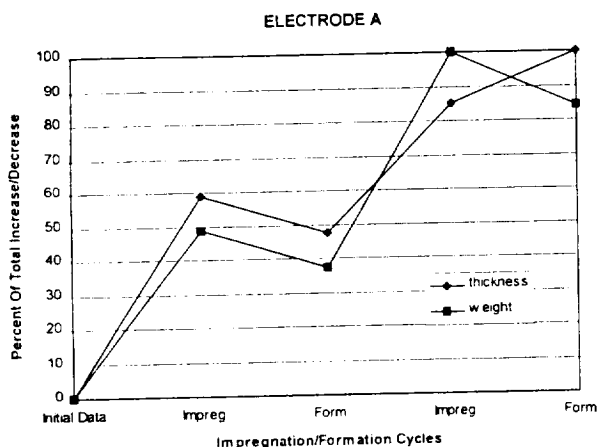
ELECTRODE B

Figures 1 and 2
Electrode A is the electrode with the lowest specific energy. Electrode B has the highest specific energy.

Group A - Comparing mAh/g to Thickness Increase
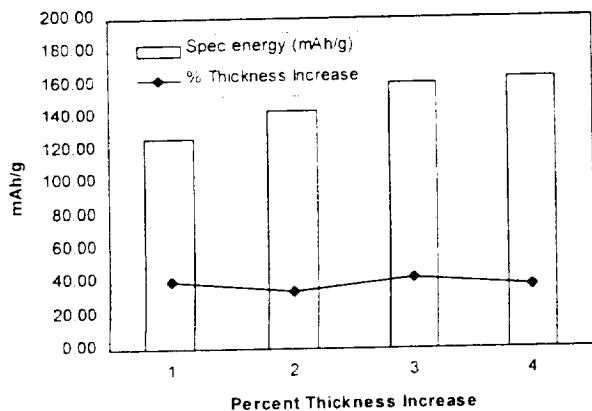
Group B - Comparing mAh/g to Thickness Increase

Figures 3 and 4
Comparing the specific energy to the % thickness increase.

percentage of the impregnated pick-up) varies from 5.823% to 12.055%.

The final active material loading (grams of active material per cubic centimeter of electrode void volume) is calculated from the difference in the substrate weight and the final weight after formation. The actual grams of active material loaded into the substrate can be very accurately determined on an analytical balance. Finished loading ranged from 0.851 g/ccvv to 1.377 g/ccvv. Electrode specific energy is the energy storage capacity per weight of the electrode and is figured by watt-hours per gram (converted to mAh g). Specific energy ranges from 127.029 mAh/g to 183.065 mAh/g. In

general, one group has higher specific energy, utilization, and flooded capacity, but also have higher thickness swelling.

In general, the single biggest disadvantage of the nickel electrode can be conveniently expressed in terms of the ratio of active material in the electrode to inactive material in the electrode. In a state-of-the-art sintered nickel powder aerospace electrode, about 63% of the total weight of the nickel electrode is electrochemically inactive. This weight is comprised of the sintered nickel powder substrate and the nickel wire mesh current collector. These components provide no energy storage capacity in the electrode. Correspondingly.

only 37% of the electrode weight is electrochemically active material. This is the reason that although the active material has a theoretical energy density of 289 mAh/g, the nickel electrode is much lower e.g. 120mAh/g, which is about 42% of theoretical. By comparison, fiber nickel electrodes are up to 60% active mass. This corresponds to an electrode specific energy of 180 mAh/g of the theoretical specific energy of pure nickel active material. An increase of specific energy from 120 to 180 mAh/g, 42% to 62% of theoretical, makes a very significant increase in overall specific energy at the full cell and battery level. The fiber based electrode, therefore, has the potential of significantly increasing the specific energy of the nickel hydrogen cell.

Conclusions

Most of the specific work done was primarily directed towards aerospace nickel hydrogen batteries. However, the nickel electrode technology developed is usable in a wide range of applications. Optimized electrode substrate microstructure, micro-fiber diameters and small equivalent pore size have greatly improved the fiber electrode substrate. The electrochemical impregnation process allows more efficient active material loading into the substrate and yields higher active material utilization. Specific energy was increased and overall weight was decreased, both being the major goals of this project. Electrodes yielding up to 180 milliamphere-hours per gram, with high utilization, have been prepared on a laboratory scale. Scale-up to full flight weight nickel hydrogen cells is underway.

There is a considerable amount of literature available on the nickel electrode in general. Several papers have been published on fiber type nickel electrodes specifically (1-5). Eagle-Picher has done substantial work in the past on fiber nickel electrodes (5-7) and in conjunction with specific battery Research and Development programs (8).

REFERENCES

1. Kohler, D.A., et.al., *Metal-Carbon Composite Electrodes From Fiber Precursors*, 24th IECEC, 1989. p.1441.

2. D.L. Britton, *Characterization and Cycle Tests of Lightweight Nickel Electrodes*, ECS Proceedings Volume 90-4, 1990.

3. W. Taucher, et.al., *Development of Lightweight Nickel Electrodes for Zinc/Nickel Oxide Batteries*, 186th ECS Meeting, 1994.

4. R. Rouget, et.al., *Connection of the Charge Efficiency and Self-Discharge of the Fibrous Electrode With the Structure of the Support*, ESC Proceedings Volume 90-4, 1990.

5. M.J. Vanderpool, et.al., *Development of the Fiber-Based Nickel Hydroxide Electrodes for Nickel-Iron Batteries*, ECS Proceedings Volume 90-4, 1990.

6. D.K. Coates, et.al., *Advances in Lightweight Nickel ElectrodeTechnology*, Space Electrochemical Research and Technology, NASA Lewis, 1988.

7. J.M. Francisco, et.al., *High Energy Density Microfiber Based Nickel Electrode for Aerospace Batteries*, 11th Annual Battery Conference, 1996.

8. D. Coates, et.al., *Advanced Dependent Pressure Vessel (DPV) Nickel Hydrogen Spacecraft Battery Design*, 19th International Power Sources Symposium, 1995.