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NICKEL-METAL HYDRIDE BATTERY DEVELOPMENT

FINAL TECHNICAL REPORT

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SUMMARY

Rechargeable batteries are used as the power source for a broad range of portable equipment. Key battery selection criteria typically are weight, volume, first cost, life cycle cost, and environmental impact. Rechargeable batteries are favored from a life cycle cost and environmental impact standpoint over primary batteries.

The nickel-metal hydride (Ni-MH) battery system has emerged as the battery of choice for many applications based on its superior characteristics when judged on the above criteria against other battery types. In most cases commercial Ni-MH batteries are constructed with coiled electrodes in cylindrical metal containers.

Electro Energy, Inc. (EEI) has been developing a novel, flat bipolar configuration of the Ni-MH system that offers weight, volume, and cost advantages when compared to cylindrical cells. The unique bipolar approach consists of fabricating individual flat wafer cells in conductive, carbon-filled, plastic face plates. The individual cells contain a non-conductive plastic border which is heat sealed around the perimeter to make a totally sealed unit cell. Multi-cell batteries are fabricated by stacking the individual wafer cells in such a way that the positive face of one cell contacts the negative face of the adjacent cell. The stack is then contained in an outer housing with end contacts.

The purpose of this program was to develop, evaluate, and demonstrate the capabilities of the EEI Ni-MH battery system for consumer applications. The work was directed at the development and evaluation of the compact bipolar construction for its potential advantages of high power and energy density. Experimental investigations were performed on various nickel electrode types, hydride electrode formulations, and alternate separator materials. Studies were also directed at evaluating various oxygen recombination techniques for low pressure operation during charge and overcharge.

While not fully optimized, single cells were capable of delivering 28 Wh/lb (61.8 Wh/kg) and 2.1 Wh/in³ (128 Wh/l). Good performance was obtained at discharge rates up to the half hour rate. Many of the single cells were life tested under a cycle condition of 2 h charge and 1 h discharge at a depth of approximately 66% of the nominal capacity. Cells with some of the component variables achieved life in excess of 1500 stable cycles for more than six months continuous testing to the conclusion of the program. Five-cell stacks were cycle tested up to 1200 cycles under similar conditions.

Potential commercial applications exist for this type of battery that include electric vehicles, portable electronics (i.e. cellular telephones, laptop computers, camcorders, electric drills, point-of-sale devices, etc.). Furthermore, this battery system is much more ecological than the traditional lead-acid (Pb-acid) and nickel-cadmium (Ni-Cd) batteries now used in many of these applications since its materials do not pose the toxic hazards of lead and cadmium.

The overall results demonstrated the feasibility of the wafer cell concept for consumer applications. Additional work will be required to finalize bipolar battery packages.

INTRODUCTION

Batteries serve as the power source for a broad range of electrical portable equipment. In many applications rechargeable batteries are preferred over throw-away primary batteries because they are more cost effective, conserve materials, and do not create as great a disposal problem. The selection of a battery type for a given application is driven by a trade-off of multiple requirements: safety, energy density (energy per unit weight and volume,) power density (power per unit weight and volume,) first cost, cycle life, wet life, operating temperature limits, rate capability, materials availability, materials toxicity, energy efficiency, charge retention, etc.

Despite considerable R&D efforts only two battery chemistries (Pb-acid and Ni-Cd) have achieved significant commercial success as rechargeable batteries through 1990. Both of these systems utilize toxic heavy metals, lead or cadmium. Certainly better rechargeable batteries are a well recognized need. Recently the Ni-MH system has emerged as a viable commercial product for small portable applications. Lithium rechargeable batteries are receiving considerable interest but their wide-spread commercial viability remains to be validated.

The baseline battery system for small portable appliances has been the Ni-Cd system. The desire to eliminate the use of toxic cadmium in production and in disposal and improve energy density has lead to the development of the Ni-MH system for newer applications. Present cylindrical cell-packaged batteries yield 35-50 Wh/kg and approximately 80-110 Wh/l. As the electronics are improved in portable appliances, greater emphasis will be placed on increasing battery energy density to keep battery weight and volume within manageable limits. The spiral single cell version developed for the Ni-MH system has proven to be costly and does not take full advantage of the space available in typical prismatic battery packages. A higher energy and power density battery version at lower cost is desired. The Ni-MH system has demonstrated stable life and other desirable characteristics and improvements to this system offer a low risk approach to yielding an improved battery. When all the factors are considered for portable appliances, Ni-MH is a leading system of known characteristics with room for significant improvements. This is the rationale of this program.

A solid hydride, hydrogen storage electrode is used in place of the cadmium electrode in the hydride system. This decreases battery volume and allows for low pressure operation and results in improved energy density over the Ni-Cd system.

The cell's reactions are essentially the same as gaseous Ni-H₂ cells, as follows:

The overcharge reactions for the cell are the same as for Ni-Cd and nickel-hydrogen (Ni-H₂) cells. The oxygen generated on the nickel electrode at the end of charge and overcharge reacts on the negative electrode to form water in the Ni-H₂ case and Cd(OH)₂ in the Ni-Cd case.

The critical issues of a Ni-MH battery are currently driven by the characteristics of the hydride electrode which are:

- (1) cycling stability of the hydride electrode in the cell's environment
- (2) hydride electrode's rate capability
- (3) hydrogen storage capability
- (4) cost

The recent focus to eliminate the use of cadmium for environmental reasons has resulted in the development of new stable metal hydride alloys and such batteries are now finding commercial applications. It is predicted they will replace up to half the small commercial Ni-Cd batteries now in use by the year 2000. It appears appropriate to pursue the development of an improved bipolar Ni-MH battery for consumer applications based on these developments.

Shown below is the baseline AB₅ hydride material, La-Ni₅, developed by Philips (Eindhoven) that is capable of storing hydrogen at up to a 1:1 metal-to-hydrogen ratio (six hydrogens). Also listed are its electrochemical capabilities. Figure 1 shows the Pressure Composition Isotherms (PCT) of this material. LaNi₅ material is expensive and has limited life in rechargeable batteries. When subjected to repeated cycling, oxides of lanthanum form on the surface reducing its hydrogen storage capability.

Table 1. Hydride Alloys

AB ₅ -H ₆	
LaNi ₅ -H ₆	
Mol. Wt.	438.4
g Alloy/g H	: 73
% H	: 1.37
Capacity g/Ah	: 2.72
Capacity Ah/g	: 0.367

Pressure concentration curves of MmNi_5 (---) and LaNi_5 (—) at 45°C where open circles denote absorption and closed circles desorption of hydrogen. H/M represents the ratio in the hydride of the mole fraction of hydrogen to the mole fraction of the metal.

Figure 1

To reduce costs, the lanthanum may be substituted with Misch metal (Mm), a naturally occurring mixture of rare earth metals with a typical composition as shown below:

Misch Metal:	Lanthanum	22 - 26 %
	Cerium	48 - 55 %
	Neodymium	15 - 20 %
	Praseodymium	4 - 7 %

Substitution of a portion of the nickel with cobalt, aluminum and/or manganese can stabilize the hydride by forming a protective surface oxide. These substitutions also have the effect of reducing the equilibrium hydrogen storage pressure of the hydrides. Table 2 shows the candidate hydride materials that are available from the International Battery Association. Lm abbreviates La-rich Mm. Samples 2 and 5 differ in source and performance.

Table 2. International Common Samples of MH Alloys

(1)	IBA MH No. 1	$\text{MmNi}_{3.55}\text{Co}_{0.75}\text{Mn}_{0.4}\text{Al}_{0.3}$
(2)	IBA MH No. 2	$\text{MmNi}_{3.5}\text{Co}_{0.7}\text{Al}_{0.8}$
(3)	IBA MH No. 3	LmNi alloy.
(4)	IBA MH No. 4	$\text{Ti}_{1.6}\text{V}_{2.2}\text{Zr}_{1.6}\text{Ni}_{4.2}\text{Cr}_{0.7}$
(5)	IBA MH No. 5	$\text{MmNi}_{3.5}\text{Co}_{0.7}\text{Al}_{0.8}$
(6)	IBA MH No. 6	$\text{MmNi}_{3.5}\text{Co}_{0.8}\text{Mn}_{0.4}\text{Al}_{0.3}$

With the exception of IBA #4, these materials are of the AB_5 type. Most of these materials have a hydrogen storage capacity of about 4 atoms of hydrogen per metal atom (AB_5 formula unit). Even with this limitation, these types of materials are the focus of most current efforts to commercialize the Ni-MH system.

AB_2 hydrides are also potential battery electrode materials and may have higher hydrogen storage capabilities. However, AB_2 -type hydrides tend to operate at higher pressures, lower rate and are subject to stability questions. Based on the current state-of-the-art, the AB_5 -type materials appear to be preferred for hydride batteries, and are used in most commercial cells. The efforts in this program were restricted to AB_5 -type material.

CELL DESIGN, FABRICATION AND TESTING

In addition to the emphasis on the Ni-MH system, the program was directed at the development of a novel bipolar wafer cell construction as shown in Figure 2. This type of construction was selected for its high power and energy density. Each wafer cell has one nickel and one hydride electrode similar to a bipolar stack. In a traditional bipolar construction, unlike spiral cells or prismatic cells, the cell's partition and series connection is accomplished by a common conductive bipolar plate. This offers the advantages of more compact packaging, higher active weight-to-inert weight, lower internal resistance, uniform operating current density and lighter weight multi-cell packaging.

Figure 2. Wafer Cell Concept for Bipolar Battery

The classic bipolar packaging approach generally suffers from problems of intercell electrolyte leakage, external leakage, and thermal instability. The use of bipolar packaging for gaseous hydrogen cells is not very attractive since it requires hydrogen storage space. Attempts at constructing Ni-Cd bipolar batteries have not been very successful due to leakage and thermal problems. The metal-hydride system has the potential of reducing the thermal problems because the irreversible heat of reaction is distributed differently over the charge and discharge. Cadmium short circuits are not a problem and the leakage problem can be reduced by operating at low pressure.

The attractive features of the bipolar concept are well recognized, but despite a number of efforts, it has not achieved commercial success in rechargeable batteries (note the Polaroid flat pack primary battery.) The major barriers to success have been (1) the availability of a stable, conductive, sealable bipolar material, and (2) achievement of acceptable contact resistance between materials.

The EEI wafer cell design has the attractive features of the classic bipolar system. It utilizes a complete individual cell assembly that can be sealed independently, pre-tested and repaired or replaced, if required, prior to battery assembly. A multi-cell battery will require end plates and containment. This was, therefore, the approach pursued in the program.

In the course of the program over 100 single cells were constructed for test and evaluation. Each cell contained one positive and one negative electrode. The electrodes in most of the cells were 7.6 cm x 7.6 cm (3" x 3") square. It was concluded that a heat sealed conductive carbon-filled plastic envelope is the preferred construction technique for the wafer cell design based on sealing trials. The cells contained a peripheral plastic frame that was heat sealed around the perimeter to serve as an edge seal. This prevented electric contact of the conductive cell faces.

Conventional hydride alloys were received as granular particles ranging in particle size from 1/8"-1/4". The materials were placed in a sealed pressure container and cycled with dry hydrogen gas to pulverize the alloys. Typically five cycles, up to 100-200 psi, were needed. The absorption of the hydrogen by the hydride alloys resulted in an expansion of the material which fractures it into a fine powder (decrepitation). The powder was then mixed with a plastic binder and additives and fabricated into sheets by a proprietary process.

Figure 3 shows the PCT curves of the hydride alloy used for most of the cells. Figure 4 shows the PCT curves of an improved material that has increased hydrogen storage capability evaluated in the latter stages of the program.

All the cells contained 30% KOH and 1% lithium hydroxide as the electrolyte.

Figure 3. PCT Curves of Sample #4661 Measured at 25, 45 and 100°C

Figure 4. PCT Curves of Sample #6453 Measured at 25, 50 and 100°C

Many of the cells were tested in a vented, flooded condition. Individual cells were held in compression by acrylic end plates and tie rods with nickel foil on the cell faces serving as the cell contacts.

The major component variables evaluated in these cells consisted of:

1. Sintered nickel electrodes supplied by Eagle Picher.
2. Plastic bonded nickel electrodes fabricated at EEI by a proprietary process. These electrodes were fabricated with nickel hydroxide, cobalt monoxide or cobalt hydroxide, graphite or other conductive additives, and a plastic binder.
3. Pasted nickel foam electrodes fabricated at EEI. The foam nickel was supplied by Eltech Corporation. The foam was pasted with a mix of nickel hydroxide, cobalt oxide or cobalt monoxide and a binder.
4. The separator material in the cells consisted of non-woven nylon (pellon) or teflon-bonded potassium titanate obtained from Energy Research Corporation.
5. The hydride materials utilized in the cells consisted of the materials similar to the International Common Samples prepared by Rhone-Poulenc.

FINDINGS AND RESULTS

The cells are initially subjected to activation and characterization testing. Selected cells were placed on cycle test based on their activation performance. Figure 5 shows a typical family of discharges over a current range from 0.5 A to 5.8 A. Promising cells were life tested on a rapid cycle to accelerate testing. This rapid cycle test consisted of a 1 h discharge at 1 A to remove 1 Ah of capacity and a recharge at 0.55 A for 2 h. The test represented a depth of 67% of the cell's nominal 1.5 Ah capacity.

Figure 6 shows life test results obtained at the single cell level on typically good cells on the rapid test cycle. Figure 7 shows life results on a 5-cell stack. Since this stack had an earlier version nickel electrode than the single cell test, the results show a slight voltage decay. A 5-cell stack made with the latest nickel electrode would be expected to have a superior voltage decay characteristic.

Limited testing was done on charge retention. Figure 8 shows the initial discharge voltage of the cell when discharged immediately after recharge. The lower portion shows the discharge after 7 days of stand. This represented a capacity loss of about 10 percent.

The weight of the cells ranged somewhat as a function of the components utilized. Figure 9 shows a typical weight breakdown of the 3" x 3" active electrode cell that had a nominal capacity of 1.5 Ah. This results in an energy density of 28 Wh/lb and 2.1 Wh/in³. There was not a major attempt at optimizing the weight of all the sub-elements since material characterization was the main concern. It is estimated that by optimizing the individual components a 20% increase in energy density could be readily achieved.

Figure 5. Single Wafer Cell Discharge Rate Performance

1A 1hr Discharge, 550mA 2hr Charge

— Apr27'94	— May23'94	— Jun18'94
— Jul20'94	— Aug15'94	— Sep10'94

**Figure 6. Plastic Bonded, Nickel Electrode, Life Test
Single Vented Wafer Cell 3" x 3" Electrodes
1.5 Ah Nominal Capacity
Cycle 66% DOD, 1 h Discharge/2 h Charge**

Figure 7. Vented 5-Cell Pack, Life Test

Figure 8. Capacity Stand Test

Figure 9. Weight Breakdown

A stable sealed Ni-MH battery design requires the incorporation of a mechanism to provide for some oxygen recombination during charge and overcharge. This oxygen is evolved on the positive electrode due to its close operating potential to oxygen evolution. The classic approach for stable oxygen recombination is allowing the oxygen to permeate through a porous type separator material where it reacts with the anode; this is the baseline design for this battery concept. However, it is also recognized that designing for direct recombination through a porous, non-woven type separator has some disadvantages. The quantity of electrolyte used in the cell has to be very precise to allow for direct gas recombination. The sensitivity to electrolyte quantity places cell operation on a critical point and small amounts of electrolyte loss by absorption in electrodes or redistribution can result in performance decay. There is some evidence that hydride alloy materials are sensitive to attack by oxygen and that excessive oxygen recombination and overcharge accelerates electrode decay. For these reasons, it is possible to consider alternative design strategies for oxygen recombination and this was evaluated in the program.

The alternative scheme evaluated for oxygen recombination was to place a spacer on the back side of the hydride electrode and allow for oxygen access to the back side of the hydride electrode as shown in Figure 10. The back side of the hydride electrode recombination rate can be enhanced by additional catalysts and/or wet proofing. The spacer on the back side of the hydride electrode can be catalyzed for enhanced recombination. If the design provides for back side recombination, the separator material does not need to be porous for oxygen cross gas transport and a denser separator with higher electrolyte inventories can be employed. A number of single cells using a wet-proof, porous graphite paper on the back side of the hydride electrode were tested in the program. The separator materials employed contained smaller pore size than traditional non-woven materials. These designs have proven to work quite well and exhibited recombination rates within acceptable limits. The trade off of using this approach is the added complexity, weight and volume of an electrode spacer: which must be conductive in a bipolar configuration. Figure 11 shows typical life results on single sealed cells at 50% DOD.

CONCLUSIONS

Conclusions made from the results are described below.

1. A test cell configuration for rapid screenings of cell variables was developed and optimized, which was a basis for all of the testing in the program.
2. The single cell wafer concept utilizing a heat-sealed conductive plastic envelope offers the advantage of:
 - A. Low resistance current path for the electrodes between cells.
 - B. Uniform current density on the working electrodes.

DIRECT OXYGEN RECOMBINATION

BACKSIDE OXYGEN RECOMBINATION

Figure 10. Recombination Approaches

1A Discharge .5hr, 350mA Charge 1.5hr

Figure 11. Sealed Cell Life Test 50% DOD

- C. A construction that has a high active-to-inert weight that doesn't require current collectors within the electrodes and special terminals.
 - D. The ability to seal individually and test cells prior to multi-cell battery assembly.
 - E. Compact packaging for good volumetric energy density.
 - F. A construction approach appearing especially adaptable to automated high volume manufacturing.
3. Unique electrode formulations and fabrication procedures were evaluated that were demonstrated to be compatible with the wafer cell concept.
 4. In the component tests difficulty was encountered in obtaining good utilization and stable capacity in cells with the sintered nickel electrodes. The reason for this was not completely established. It appears that the interface contact with the sintered electrode deteriorated during cycling.
 5. The plastic bonded nickel electrodes performed well and are adaptable to various electrode thicknesses for different designs and power densities.
 6. The pasted foam nickel electrode process yielded electrodes with stable performance. However, these electrodes are more expensive than the plastic bonded type.
 7. A number of the hydride alloy formulations (tested similar to the IBA alloys) exhibited stable performance, extended life, and offered reasonable capacity density.
 8. Of the separator materials tested the pellen or the potassium titanate composite appeared acceptable. The potassium titanate offered some advantages of better electrolyte retention, and wettability due to its finer pore structure. It also limited the migration or shedding of active material from the respective electrodes. One would expect the KT material to be much more chemically stable than the non-woven nylon, which is known to deteriorate over extended periods of time in strong alkaline electrolytes. The tight pore structure of this material, however, probably would adversely affect direct oxygen recombination for sealed operation.
 9. The carbon plastic conductive cell envelope utilized in the program was very stable under the operating conditions tested. No noticeable decay of this material was observed throughout the program.
 10. Acceptable stable contact resistances between the conductive carbon plastic and some of the electrodes were achieved to enable operation at up to the half hour rate.

11. Several electrode formulations exhibited stable life up to 1500 cycles under the test conditions utilized.
12. Energy densities of 28 Wh/lb (61.8 Wh/kg) and 2.1 Wh/in³ (128 Wh/l) were obtained at the single cell level. It is anticipated that improvements readily achievable would increase these levels by 20%. If new hydride materials were developed that have higher capacity density there is a potential for the Ni-MH system to achieve a 50% improvement over the levels demonstrated.
13. Based on the results the viability of the Ni-MH wafer design at the single cell and five cell pack was successfully demonstrated.
14. The cell materials utilized and electrode process developed are much more environmentally acceptable than those encountered with Ni-Cd and Pb-acid batteries. This represents a significant advantage of this type of battery and the fabrication approaches investigated.

FURTHER WORK

Some issues have yet to be resolved before commercialization of bipolar Ni-MH batteries for consumer applications.

1. **Multi-cell Packaging:** Development of multi-cell packaging arrangements to ensure good cell-to-cell electrical contact, and uniform electrode stack compression without a significant sacrifice in weight and volume for the battery system. It is estimated that this is also achievable and would involve a weight and volume penalty equal to 10-20% of the individual cells. This is in line with packaging for multi-cell batteries of other battery types.
2. **Thermal/Charge Control:** Multi-cell batteries will need to be designed for thermally stable operation with appropriate charge control. The Ni-MH system operates endothermically during discharge. Therefore, thermal problems during discharge would be somewhat less than with other types of batteries. This is a potential advantage for very high rate applications.
3. **Charge Retention, Operating Temperature:** Self discharge and various operating temperature modes were not addressed to any significant extent in the program. These are key issues for some battery applications. There are published references that indicate that Ni-MH batteries are poorer than Ni-Cd batteries in these categories. Other references indicated that the self-discharge is caused by impurities in the battery system and shuttle mechanisms. It appears that the metal hydride electrode enhances shuttle mechanism self discharge. This places a greater emphasis on the use of stable materials in hydride cells.

4. **Advanced Hydride Materials:** The most significant energy density improvement and cost reduction for this system could be achieved with an improved hydride hydrogen storage alloy. The cells constructed utilized alloys that operated at approximately 1% hydrogen storage. An increase to 2% hydrogen storage, with all other things being equal, would be a very significant advance.

PUBLICATIONS INCORPORATING RESULTS OF THE PROJECT

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