Recent advances in NiMH battery technology

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Abstract

Nickel-metal hydride (NiMH) is a commercially important rechargeable battery technology for both consumer and industrial applications due to design flexibility, excellent energy and power, environmental acceptability and cost. [1] From the initial product introduction in 1991 of cylindrical cells having an energy of $54\,Wh\,kg^{-1}$, today's small consumer cells have a specific energy over $100\,Wh\,kg^{-1}$. Numerous licensed manufacturers produce a myriad of NiMH products ranging from 30 mAh button cells to a wide variety of consumer cylindrical products, prismatic cells up to 250 Ah for electric buses and 6 Ah multicell modules for hybrid electric vehicles. Power has increased from under 200 to $1200\,W\,kg^{-1}$ commercially and up to $2000\,W\,kg^{-1}$ at a development level [2].

Early NiMH batteries had limited operating temperatures while today's batteries can provide excellent power at cold temperatures of $-30\,°C$ and provide over 90% capacity at $70\,°C$. Many of these product performance advances are a result of innovations to the metal hydride and nickel hydroxide materials. We will report on some of these key material advances which provide today's NiMH performance and new materials to allow higher energy, power and significant cost reduction.
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1. Introduction

Nickel-metal hydride (NiMH) batteries are in high volume commercial production for small portable battery applications, achieving an annual worldwide production of over 1 billion cells. The driving force for the rapid growth of NiMH is both technical and environmental. Energy performance advantages of NiMH over nickel-cadmium is fueling the explosive growth of portable electronic devices and the replacement of primary alkaline batteries for products such as digital cameras [3].

NiMH batteries have become the dominant advanced battery technology for electric vehicle (EV) and hybrid electric vehicle (HEV) applications by having the best overall performance in the wide-ranging requirements set by automotive companies. In addition to the essential performance targets of energy, power, cycle life and operating temperature, the following features of NiMH have established the technology preeminence [4]:

- Flexible cell sizes from 30 mAh–250 Ah;
- Safe operation at high voltage (320+ V);
- Excellent volumetric energy and power;
- Flexible vehicle packaging;
- Easy application to series and series/parallel strings;
- Choice of cylindrical or prismatic cells;
- Safety in charge and discharge, including tolerance to abusive overcharge and overdischarge;
- Maintenance free;
- Excellent thermal properties;
- Capability to utilize regenerative braking energy;
- Simple and inexpensive charging and electronic control circuits; and
- Environmentally acceptable and recyclable materials.

Development activity in NiMH batteries has focused on further improvements in specific power for both transportation and portable applications under both normal and cold temperature conditions. Our results in raising power and high rate discharge capability, with particular emphasis to the metal hydride electrode surface catalytic activity at the metal/electrolyte oxide interface, will be shown.

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The nickel hydroxide positive electrode has also undergone rapid evolution. It is common for commercial NiMH batteries to contain approximately 10% high capacity gamma phase nickel hydroxide in combination with conventional beta phase nickel hydroxide [5]. The active materials may also contain multiple modifier elements to improve charge acceptance, especially at high temperature [6]. Conductive additives such as filamentary nickel have been added internally to the nickel hydroxide active material during precipitation or as external additives in the pasting process [7]. Significant improvements to voltage stability under storage and cost reduction were accomplished by adopting cobalt encapsulation techniques to the nickel hydroxide active material prior to assembling the battery [8]. This paper will emphasize the nickel hydroxide influence on high temperature charge efficiency.

2. Experimental

Analysis of the metal hydride surface was conducted by disassembly of discharged C cells in an argon glove box, with the metal hydride electrode rinsed and dried of KOH. Samples were prepared for examination by progressive polishing followed by dimple grinding to a specimen thickness of about 50 μm. The samples were then ion-milled at cryogenic temperature using 3–6 keV argon ions to a specimen thickness of about 500 Å. Investigation of the MH surface oxide was performed on a JEOL-2010 scanning transmission electron microscope (STEM) using brightfield and darkfield imaging. Crystal structures were studied using selected area electron diffraction (SAED). Quantitative energy dispersive spectroscopy (EDS) analyses were obtained using a Cliff-Lorimer thin film correction procedure in conjunction with experimental X-ray correction factors (k-factors) obtained from thin film standards [9].

Spherical high-tap-density nickel hydroxide precipitates were prepared in a continuously fed reactor under strong stirring, at constant pH and temperature [10]. Nickel sulfate, sodium hydroxide, and ammonium hydroxide solutions were continuously fed into the reactor. Through an overflow on the side of the reactor, the nickel hydroxide product and effluent were collected continuously. Using this method, the precipitates do not require pulverization or grinding, are composed of spherical particles, have the high tap density required to achieve packing density and capacity, and have the crystal structure, particle size, and surface morphology required for commercially acceptable battery performance.

Chemical composition was measured using an inductively coupled argon plasma spectrophotometer (Varian Liberty 100). Surface area was measured by the BET adsorption method (Quantachrome instruments, Autosorb-3B). Particle-size distributions were measured with a laser-diffraction instrument (Microtrac system, model SRA 150). X-ray diffraction measurements were obtained using a diffractometer (Philips Analytical). The surface morphology of the nickel-hydroxide particles was also examined using a scanning electron microscope (JEOL 6320F field-emission scanning electron microscope with Thermo-Noran Kevex Sigma 32 digital imaging package).

3. Results and discussion

3.1. Metal hydride alloys

Early NiMH batteries targeted niche markets due to fundamental power limitations. Metal hydride surface oxidation limited conductivity, transport of reactants, and catalytic activity. Power restrictions were overcome by engineering the surface oxide to include extremely small (50–70 Å) metallic nickel particles distributed throughout the oxide, thereby imparting significantly improved catalytic activity [11]. It was found the small catalysts could be engineered smaller still (10–40 Å), could include additional elements, and have finer dispersal. These improvements in catalytic activity enabled dramatic increases in NiMH power [12].

Early AB_5 type metal hydride alloys had a moderate capacity of about 310 mAh g^{-1} [13]. AB_2 materials were known to have a higher capacity of about 390 mAh g^{-1}, but were not widely used for reasons such as cost, activation, power and charge retention [14]. Improved AB_2 alloys warrant further evaluation. Disordered A_2B_7 alloys offer some of the advantages of both AB_5 and AB_2 material systems including capacities of 390 mAh g^{-1} simultaneously with high catalytic activity. NiMH AA cells using such alloys are projected to have a capacity of 3000 mAh.

3.2. Alloy design concept

NiMH batteries are an unusual battery technology in that the metal hydride active material is an engineered alloy made up of many different elements and the MH alloy formulas vary significantly. The active material in the negative electrode is either of the disordered AB_5 (LaCePrNdNiCoMnAl), A_2B_7 (LaCePrNdNiCoMnAl plus Mg), or disordered AB_2 (VTiZrNiCrCoMnAlSn) type, where the "AB_x" designation refers to the ratio of the A type elements (LaCePrNd or TiZr) to that of the B type elements (VNiCrCoMnAlSn). In all cases, the materials have complex microstructures that allow the hydrogen storage alloys to operate in the aggressive environment (30% KOH electrolyte, oxygen gas in overcharge recombining at the MH surface) within the battery where most of the metals are thermodynamically more stable as oxides.

Electrochemical utilization of metal hydride materials as anodes in NiMH batteries requires meeting a demanding list of performance attributes including hydrogen storage capacity, suitable metal-to-hydrogen bond strength, acceptable catalytic activity and discharge kinetics, and sufficient oxidation/corrosion resistance to allow for long cycle life. Multielement, multiphase, disordered alloys of the LaNi$_5$ and VTiZrNiCr type are attractive development candidates for atomic engineering due to a broad range of elemental addition and substitution, availability of alternate crystallographic phases which form the matrix for chemical modification, and a tolerance for non-stoichiometric formulas. Through the introduction of modifier elements, ease of activation and formation has been achieved.

The metal hydride active material has special design options. The active materials may be adjusted to influence one or more of capacity, power, and/or cycle life. Disorder permits the extra
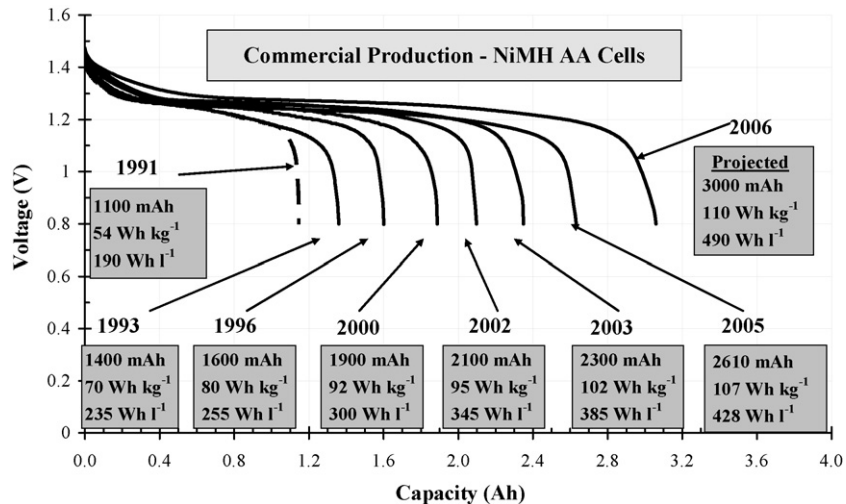
Fig. 1. Evolution of NiMH specific energy.

degrees of freedom which allow for a high level of chemical substitution [15]. For the AB_5 system, a typical formula is $La_{5.7}Ce_{8.0}Pr_{0.8}Nd_{2.3}Ni_{59.2}Co_{12.2}$ $Mn_{6.8}$ $Al_{5.0}$ (atomic percent a/o). While the capacity of various AB_5 alloys is usually around 290–320 mAh g^{-1}, other overall performance attributes can be greatly influenced [16]. It is common for the ratio of La/Ce to be reversed to emphasize cycle life and power. The total amount of Co, Mn and Al significantly affect ease of activation and formation but increased cobalt has cost implications. After production of the AB_5 alloy ingot, it is common to further refine the microstructure of the material by a post anneal treatment of perhaps 1000 °C for 10 h. The annealing treatment can have a significant effect on capacity, discharge rate and cycle life by adjusting crystallite size and grain boundaries, as well as eliminating unwanted phases precipitated during ingot melting and casting [17]. Commercial AB_5 alloys have a predominantly $CaCu_5$ crystallographic structure. However, within that structure, there is a range of lattice constants brought about by compositional disorder within the material that are important to catalysis, storage capacity and stability to the alkaline environment and embrittlement. These materials also precipitate a nickel-cobalt phase which is important to high rate discharge [18].

AB_2 alloys also have formula and processing choices. Popular AB_2 alloy formulas (a/o) include $V_{18}Ti_{15}Zr_{18}Ni_{29}$ $Cr_5Co_7Mn_8$ and $V_5Ti_9Zr_{26.2}Ni_{38}Cr_{3.5}Co_{1.5}Mn_{15.6}Al_{0.4}Sn_{0.8}$.

Alloy capacity may range from 385 to 450 mAh g^{-1}. High vanadium content alloys may suffer from higher rates of self discharge due to the solubility of vanadium oxide and its consequent ability to form a special type of redox shuttle [19]. The concentration of Co, Mn, Al and Sn are important for easy activation, formation, and long cycle life. The ratio of hexagonal C14 to cubic C15 phase is important to emphasize capacity or power.

3.3. Alloy and battery performance

The specific energy of NiMH batteries can vary from 40 to 110 Wh kg^{-1} depending on the particular application require-

ments. Where device run time is paramount, NiMH batteries need not have high power capability or even ultra-long cycle life. On the other hand, for extremely high power charge and discharge, extra current collection, high N/P ratios (proportion of excess negative electrode capacity to positive electrode capacity), and other cell design and construction decisions can additively affect specific energy. Fig. 1 presents specific energy improvements over the last 10 years in consumer (portable), cylindrical NiMH cells. For the most common small consumer NiMH batteries, specific energy is usually about 90–110 Wh kg^{-1}, for EV batteries usually about 65–80 Wh kg^{-1}, and for HEV batteries and other high power applications about 45–60 Wh kg^{-1} [20]. While gravimetric energy usually receives the attention for advanced battery technologies, in many cases volumetric energy density in watt-hours per liter is actually more important. NiMH has exceptional energy density, achieving up to 420 Wh l^{-1}. Cost reduction is at the forefront of NiMH development. High volume consumer battery production has seen NiMH cost at or below the cost per Kilowatt-hour of NiCd, previously thought to be unobtainable. NiMH cost reduction begins with the recognition that the technology cost is primarily materials intensive. Efforts to raise specific energy involves development of metal hydride alloys with higher hydrogen storage capacity (from 320–385 mAh g^{-1} active material to 450 mAh g^{-1}) and higher utilization nickel hydroxide (from 240 mAh g^{-1} active material to 280–300 mAh g^{-1}). Each of these higher utilization active materials involves innovative materials research involving highly modified alloy formulas and advanced processing techniques.

3.4. MH surface oxide and catalysis

A critical design factor within the metal hydride surface oxide is to achieve a balance between surface oxide passivation and corrosion. Porosity within the oxide is important to allow ionic access to the metallic catalysts and therefore promote high rate discharge. While passivation of the oxide is problematic for high rate discharge and cycle life, unrestrained corrosion is equally
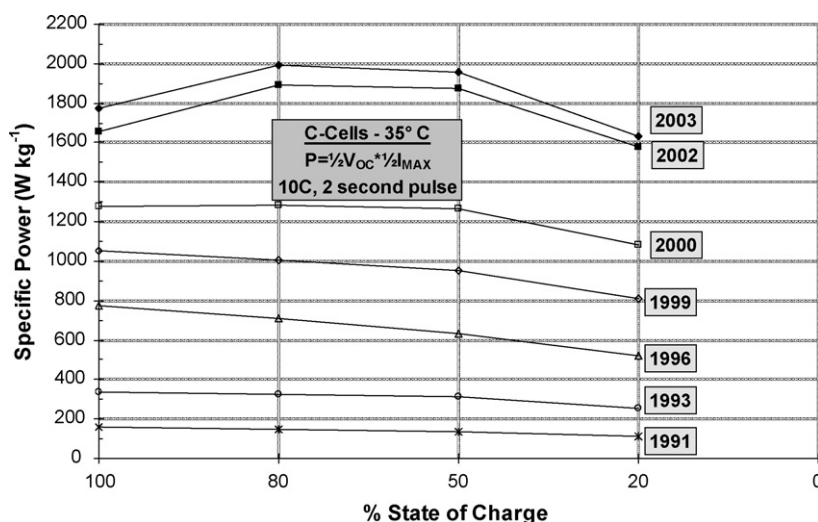
Fig. 2. Evolution of NiMH specific power.

destructive. Oxidation and corrosion of the anode metals consumes electrolyte, changes the state of charge balance by release of hydrogen in the sealed cell, and creates corrosion products which are capable of poisoning the positive electrode by causing premature oxygen evolution. Establishing a balance between passivation and corrosion for stability is a primary function of compositional and structural disorder.

For AB_5, A_2B_7 and AB_2 metal hydride alloys, the metal/electrolyte surface oxide interface is a crucial factor in discharge rate capability and cycle life stability. Fig. 2 shows how specific power for NiMH batteries has undergone significant change since 1991. Original $LaNi_5$ and TiNi alloys extensively studied in the 1970s and 1980s for NiMH battery applications were never commercialized due to poor discharge rate and cycle life capability. The lack of catalytic activity at the surface oxide limits high rate discharge and the lack of sufficient oxidation/corrosion resistance is a critical obstacle to long cycle life. The complicated chemical formulas and microstructures of present disordered AB_5 and AB_2 alloys extends to the surface oxide. At the oxide, important factors include thickness, microporosity and catalytic activity. In particular, the oxide interface between the metal hydride and the electrolyte has been identified as essential for low voltage loss under pulse discharge. Of critical importance to increased discharge rate was the use of ultrafine metallic nickel alloy particles having a size less than 70 Å dispersed within the oxide. These particles are excellent catalysts for the reaction of hydrogen and hydroxyl ions, and are especially important for reducing activation polarization [21].

The ultrafine metallic catalysts are created by preferential corrosion within the multielement hydrogen storage alloy. In particular, the dissolution and precipitation of the less noble vanadium, titanium and zirconium (or La, Ce) allows nickel in the presence of cobalt, manganese and aluminum to form the metallic clusters and requires careful design of the surface composition and structure based on the lack of proximity of nickel atoms in the unit cell. The keys to success of the catalysts are size, number, density, and topology of the metallic particles. Nickel in the metallic state is electrically conductive and cat-

alytically active. By further alloying the catalysts with cobalt ($\sim$20% a/o), the relative size of the catalysts can be reduced from about on average 50–70 Å to about 10–50 Å. Surface segregation via enrichment and selective oxidation of La in $LaNi_5$ to lower surface energy and the formation of surface nickel precipitates has been previously reported. However, there was no disclosure of size, composition, proximity or stability of such precipitates and the resultant surface formation of $La(OH)_3$ and $Ni(OH)_2$ upon electrochemical cycling was discussed [22].

The catalyst size is important in that at less than 70 Å, there are an approximately equivalent number of surface atoms and bulk atoms. The close proximity of the metallic catalysts, typically about 100 Å apart, may also be referred to as "density of sites". It is the interaction of the local chemical electronic bonds with the reacting H^+ and OH^- that makes these catalysts so effective, and it is their metallic nature, size and number which provide excellent poisoning resistance.

The investigation of the MH surface oxide was conducted using a scanning transmission electron microscope having the capability for EDS, SAED and EELS. Fig. 3 presents a high magnification darkfield TEM image of the surface oxide exhibiting high catalytic activity. The bright inclusions are useful for determining the size of the catalyst and are indicative of very strong electron diffraction from nanocrystals having high crystallinity. Wide area EDS shows an enriched nickel surface to be expected from the preferential corrosion of the other base alloy constiuents. Fine beam EDS of the inclusions shows almost no oxygen relative to a high nickel or nickel-cobalt peak intensity while the area surrounding the nickel inclusion is rich in oxygen. To provide further corroboration, SAED indexing is consistant with metallic nickel rather than nickel oxide. Comparable tests on earlier low catalytic activity MH materials showed the absence of inclusions within the oxide under darkfield imaging, a high oxygen signal throughout the oxide under EDS, SAED patterns characteristic of nickel oxide and EELS spectra indicative of nickel in the +2 oxidation state.

AC impedance measurements of the highly catalytic MH materials revealed a charge transfer resistance two to three
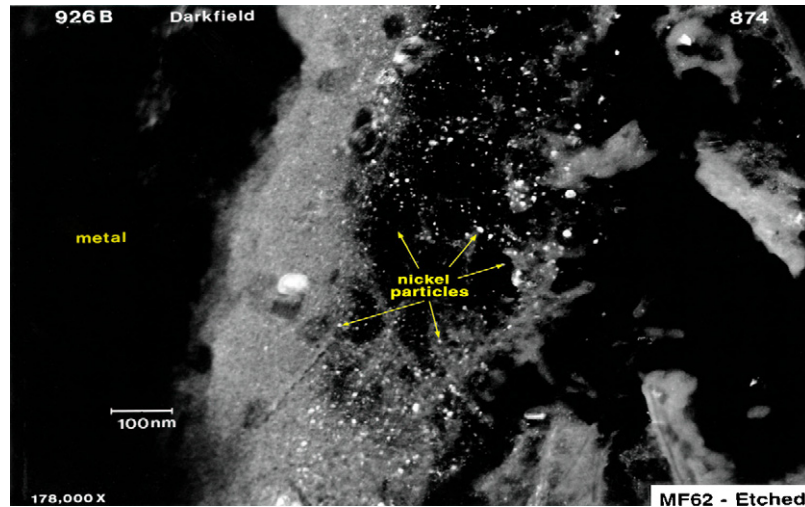
Fig. 3. TEM Darkfield micrograph of VTiZrNiCrCoMnAlSn alloy surface oxide having high catalytic activity.

times lower in the alloys having the surface oxide catalytic sites [23,24]. The resulting higher exchange current density of the surface modified materials reflects the higher catalytic activity of the metal oxide surface interface with the electrolyte.

Continued efforts to engineer the surface oxide resulted in vastly improved cold temperature performance. The oxide formed a support matrix surrounding the ultrafine metallic catalysts, but contained insufficient pore structure to allow rapid transfer of reactants at cold temperature. By engineering increased porosity and specifically sized pore channels, cold temperature power increased from practically zero at $-30\,^{\circ}\mathrm{C}$ to over $300\,\mathrm{W\,kg^{-1}}$.

Improved cold temperature performance is vital for propulsion applications requiring instant start capability in low temperature climates. Rather than only requiring capacity, these applications demand specific power be sufficient to operate the vehicle. Even for commercial HEV NiMH batteries with power over $1000\,\mathrm{W\,kg^{-1}}$ at $20\,^{\circ}\mathrm{C}$, essentially no power capability was available at $-30\,^{\circ}\mathrm{C}$. Fig. 4 shows the dramatic increase in cold temperature power when using a modified metal hydride

alloy having a surface engineered to provide improved reactant transfer. Fig. 5 illustrates the modified surface oxide. The oxide surrounding the ultrafine metallic catalysts exhibited pore channels of approximately 10–20 Å extending in three directions throughout the surface layer. The channels or voids provide pathways to and from the ultrafine catalytic particles which promote access of reactant species to the catalysts and removal of reaction products from the catalytic particles. A conventional metal hydride alloy surface having excellent room temperature rate capability but poor cold temperature performance may only contain approximately 4% void volume while the engineered surface may contain approximately 20% void as shown in Fig. 6 [25].

NiMH batteries have traditionally suffered very poor low temperature discharge performance due to the use of aqueous KOH electrolyte and the resultant generation of H_2O at the surface of the metal hydride electrode during discharge. Power and high rate discharge capability at $-30\,^{\circ}\mathrm{C}$ are diminished in conventional NiMH batteries as the water reaction product freezes and inhibits the diffusion of the KOH ionic species within the
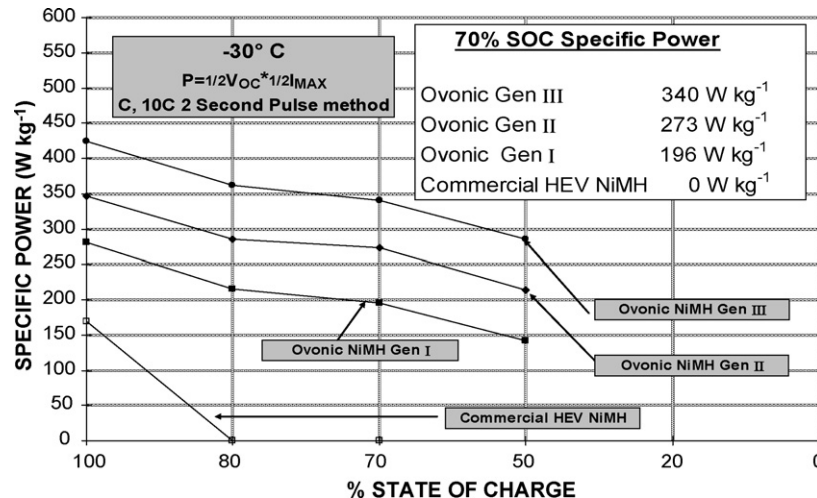

Fig. 4. Improved NiMH specific power at $-30\,^{\circ}\mathrm{C}$ resulting from incorporation of void channels within support oxide.
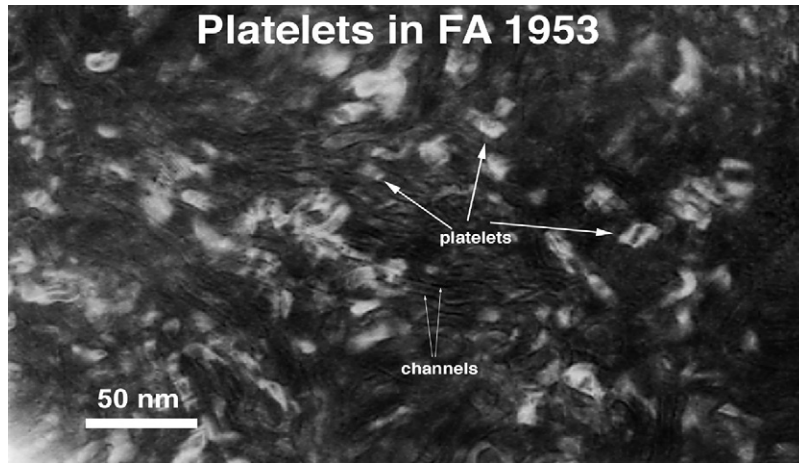
Fig. 5. TEM darkfield micrograph of MH surface oxide containing pore channels within support oxide.

surface oxide. It is believed the larger and increased amount of pore channels within the engineered oxide facilitate the rapid diffusion of water and ionic species, and mitigate the inherent limitations of using an aqueous electrolyte. The mechanism is the same, but the effect of reaction water freezing during cold discharge causing power degradation has been moved from $0\,^{\circ}$C in conventional NiMH to now providing good power even to $-30\,^{\circ}$C.

3.5. Nickel hydroxide

Extensive work has been done on the positive (nickel hydroxide) electrode to improve the charge efficiency of the battery over a wide temperature range. Since NiMH batteries are frequently utilized at temperatures that rise well above room temperature, especially in fast charge applications, high-temperature performance is an active area of research and development.

It is well known that as the temperature of the battery increases, the charge acceptance of the positive electrode

decreases, and the battery cannot be fully charged [26]. One of the problems associated with the nickel electrode is the oxygen-evolution reaction observed at higher temperatures (Eq. (1)). This parasitic reaction decreases the battery capacity because a fraction of the charging current is consumed in the oxygen evolution reaction rather than in the charging of the nickel electrode itself (Eq. (2)):

$$4OH^- \rightarrow O_2 + 4e^- + 2H_2O \tag{1}$$

$$Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + 1e^- \tag{2}$$
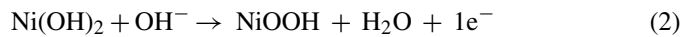
One way of avoiding the oxygen-evolution reaction and improving the high-temperature performance of a battery is to increase the voltage gap between the oxygen evolution potential and the midpoint voltage of the cell measured during charge. An important approach for improving the performance of the nickel hydroxide is to replace a small fraction of the nickel atoms in the crystal lattice by other atoms. This changes the electrochemical properties of the material and can affect the performance of
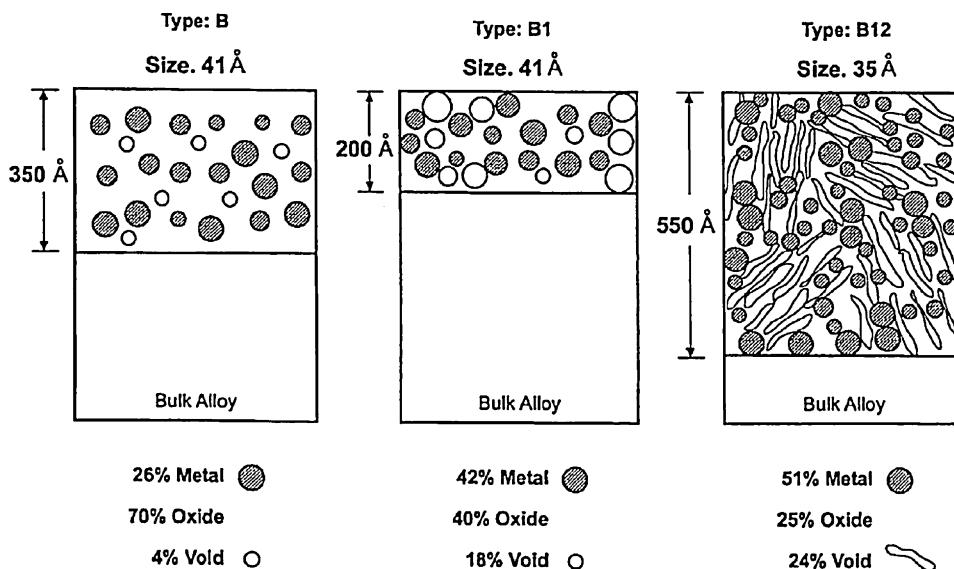

Fig. 6. Schematic of surface oxide containing engineered void volumes to assist reactant transfer.

Table 1
Chemical and physical properties of nickel hydroxide materials studied for high-temperature charge efficiency

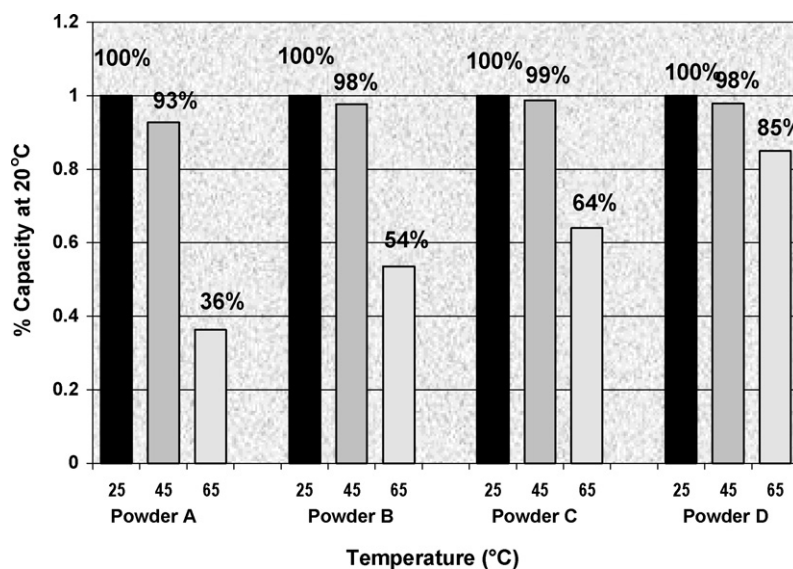| Powder	Cationic hydroxide composition	X-ray FWHM $\langle 1\,0\,1 \rangle$	Particle size (um)	Tap density (g cc^{-1})	BET surface area (m^2 g^{-1})
Powder A	$Ni_{91.3}Co_{2.4}Zn_{5.7}Ca_{0.5}Mg_{0.1}$	1.02	12.0	2.15	16.5
Powder B	$Ni_{91.0}Co_{4.5}Zn_{4.5}$	1.05	10.8	2.20	12.8
Powder C	$Ni_{85.5}Co_{7.0}Zn_{6.0}Ca_{1.0}Mg_{0.5}$	0.88	8.3	2.19	17.8
Powder D	$Ni_{91.0}Co_{7.0}Zn_{0.5}Ca_{1.0}Mg_{0.51}$	0.93	9.8	2.2	10.6

Fig. 7. Improved NiMH high temperature charge efficiency as a result of nickel hydroxide material modification.

the battery at higher temperatures [27]. Compositional modification is accomplished by co-precipitating metal cations with nickel cations to form the metal hydroxide composed primarily of nickel (usually >85% by weight) and now alloyed with the modifier elements. Table 1 shows the chemical formulas and the physical parameters for the studied materials.

X-ray diffraction analysis shows the presence of hexagonal crystal structure with the brucite characteristic of nickel hydroxide in the beta phase. The absence of other species confirms that the co-precipitated elements mainly enter the nickel hydroxide structure, and that they do not form oxides or segregated hydroxides. This may be considered an unusual result, as many processes for precipitation of nickel hydroxide result in segregation and non-uniformities.

These powders were tested in sealed, cylindrical C-cell size nickel metal hydride batteries to study the effect of chemical composition on high-temperature performance. Charging measurements were made at 25, 45, and 65 °C. It was found that co-precipitated cobalt in the presence of magnesium, zinc and calcium increases the voltage gap between the oxygen-evolution potential and the mid-point voltage of the battery. The larger voltage gap dramatically increases the charge acceptance of the battery, improving its charging efficiency (normalized to the room-temperature value) from around 50% for conventional nickel hydroxide to 85% for the improved materials when measured at 65 °C.

Fig. 7 displays the temperature dependence of the battery capacity obtained using each of the powders, normalized with respect to the capacity at room temperature (25 °C). At 45 °C the decrease in performance is small for all four powders, though A is not quite as good as the others. But at 65 °C the differences are very appreciable. The decrease in capacity is only 15% for powder D but is 64% for powder A. High-temperature performance, from best to worst, follows the order D, C, B, A. In particular powder D was the best, yielding 98% and 85% of the room-temperature capacity when measured at 45 and 65 °C, respectively. Powder A, with the smallest VG and with the least amount of cobalt (2.4 atomic%), showed the worst performance, yielding only 36% of the room-temperature at 65 °C.

4. Conclusions

Specific power and high rate discharge of metal hydride alloys for electrochemical application in NiMH batteries was significantly improved by modification of the surface oxide of the metal hydride alloy. By introducing extremely small metallic nickel alloy inclusions throughout the oxide by the method of preferential corrosion, catalytic activity was significantly increased through reduced charge transfer resistance and a specific power of 1900 W kg^{-1} was attained. By further modification of the support matrix surrounding the metallic nickel inclusions to increase

porosity and reactant transfer channels, the specific power was increased to 340 W kg^{-1} at -30 °C.

Excellent high-temperature performance was obtained for a cobalt-rich zinc-poor powder containing co-precipitated calcium and magnesium. NiMH charging efficiency at 65 °C was increased from 36% to 85% by formulating the nickel hydroxide active material to suppress oxygen evolution.

NiMH battery product performance has improved significantly and can be traced to innovative improvements in materials technology. Development efforts are focused on advanced materials to improve performance in energy, power, temperature ultra-fast recharge capability, and cost reduction.

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