An Overview of Nickel Metal Hydride Battery Technology for Aerospace Applications

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[Signature]
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An Overview of Nickel Metal Hydride Battery Technology for Aerospace Applications

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Hydrides, Batteries, Lanthanum-Nickel Alloys, Intermetallics

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Summary

For thirty years, intermetallic metal hydrides have attracted interest worldwide as hydrogen reservoirs and electrodes for different battery systems. The nickel metal hydride battery is analogous to the nickel-hydrogen battery with the metal hydride acting as both a catalytic hydrogen electrode and a hydrogen reservoir. It is presently in production as a replacement for nickel-cadmium batteries in small, portable electronics. This review surveys the status of research and commercial development of nickel metal hydride cells and evaluates the potential advantages and applications of nickel metal hydride batteries for aerospace use.

The primary advantage over the nickel-hydrogen battery is that the nickel metal hydride battery permits more flexible battery geometries. Nickel metal hydride batteries do not require high-pressure containers for hydrogen storage, and prismatic cell designs are possible. It is anticipated that self-discharge processes resulting from high hydrogen pressures in the nickel-hydrogen battery will be less active in the nickel metal hydride battery. The functional temperature range of hydride electrodes can be precisely manipulated through macroalloying. However, the heat of formation for the hydride phase is significant, and large battery designs may require thermal monitoring and active control to dissipate heat during charging and supply heat during discharging, particularly under high-rate conditions.

The nickel metal hydride battery suffers from unique degradation modes not seen in nickel-hydrogen batteries, which limit its cycle life. The charge capacity of the metal hydride electrode varies from 250 mAh/g to 400 mAh/g, depending on the intermetallic material used. However, due to intrinsic volume changes during hydride formation, the intermetallic electrode is susceptible to widespread cracking and irreversible oxidation, which decrease its discharge capacity and rate capability. Although metallurgical processes such as electroless plating, macroalloying, and rapid solidification are successful in reducing the rate of degradation, none of these methods completely arrests oxidation, and the maximum cycle life is on the order of 2000. Only cell designs that maintain the intermetallic hydride in a water- and oxygen-free environment may succeed in appreciably extending the cycle life.

Growing consumer markets, safety concerns with nickel-cadmium battery production, and adaptability to existing nickel-cadmium production lines have fueled a nickel metal hydride battery industry in Japan. Numerous recent investigations to optimize metal hydride electrode materials have addressed the effects of alloy composition, microstructure, particle size, crystallinity, and surface modifications on electrode performance. Despite these efforts, the inherent degradation modes of the nickel metal hydride batteries now in production make them unreliable choices for satellite battery systems demanding more than 500–2000 cycles. Significant improvement in cycle life for these nickel metal hydride battery designs in the near future appears unlikely. Additionally, the long-term effects of exposure to potassium hydroxide for low-cycle, long-life missions is not known.
1. Introduction

When hydrogen enters a material, it can either stay in a random solution within the lattice, recombine to form hydrogen gas in defects or grain boundaries, or it can form a new phase within the material. The term *metal hydride* refers to this hydrogen-rich phase, which has chemical and mechanical properties that are different from the host material. In practice, the term *metal hydride* has come to denote materials that reversibly absorb and release hydrogen under relatively mild conditions of pressure and temperature. This review focuses on the class of hydride-forming materials known as *intermetallics*, which are compounds containing stoichiometric ratios of metallic elements in well-defined crystalline structures.

During research on permanent magnets in the 1950s, certain intermetallic compounds, such as SmCo$_5$, became notorious for their ability to absorb large amounts of hydrogen, which diminished their magnetic force. It was in attempting to remedy this adverse effect that, in the late 1960s, the ability of LaNi$_5$ to reversibly absorb large amounts of hydrogen was discovered. The hydride LaNi$_5$H$_6$ was found to store 30% more hydrogen by volume than liquid hydrogen in a form that was stable and required neither high pressures nor refrigeration to maintain. The hydride also decomposed easily, permitting the removal of hydrogen at high rates if necessary.

By 1979, scientists had demonstrated that many of the hydride-forming characteristics of LaNi$_5$ could be predictably altered by alloying the compound with small amounts of other elements. For example, LaNi$_5$ has a room-temperature hydride formation pressure above 1 atm; yet, by adding a small amount of tin to produce LaNi$_{4.5}$Sn$_{0.5}$, the hydride formation pressure drops to less than 0.1 atm. Soon after this discovery, LaNi$_5$-based alloys were tailored to operate at specific pressures and temperatures for a host of devices, including gettering compounds, hydrogen storage beds, gas purifiers, hydrogen sensors, compressors, actuators, refrigerators, and heat pumps. Despite this range of applications, actual utilization of these materials fell below expectation in subsequent years, primarily because the newer devices were not cost effective enough to supplant older technology. Although the metal hydrides performed well, particularly in clean applications where no water, oxygen, or poisons such as carbon monoxide were present, the base cost of the LaNi$_5$ material was prohibitive.

LaNi$_5$ is a member of a class of intermetallics known as AB$_5$ compounds. Other classes of intermetallic compounds, such as AB, A$_2$B, and AB$_2$, also reversibly form hydrides, though often not as easily or quickly as LaNi$_5$. TiFe is a low-cost hydride-former that passivates easily by oxides. Mg$_2$Ni requires temperatures near 300°C to reversibly form hydrides. Similarly, Ti$_2$Ni and many of the AB$_2$ intermetallics ($A = Ti, Zr, B = V, Cr, Mn, Fe, Co, Ni, Cu$) suffer slow hydriding kinetics. Like LaNi$_5$, the hydriding pressures of these other intermetallic alloys are easily manipulated by macroalloying. Research on AB, A$_2$B, and AB$_2$ alloys initially preceded the LaNi$_5$ work and continues to parallel it today. While LaNi$_5$ compounds enjoyed early success in meeting desired material performance, these other alloys now rival the performance of LaNi$_5$-based alloys at lower material costs and lighter weights due to advanced material processing techniques.
In the last four years, demand for lighter-weight, lower-emission automobiles has evoked designs to replace gasoline with hydrogen as a fuel for combustion engines and to replace combustion engines with hydrogen-based fuel cells. Lightweight intermetallics such as TiZrNi₂, Mg, and Mg₃Ni are presently under development as low-cost, lighter, and safer alternatives for containing the hydrogen gas over traditional compressed gas or liquefied gas tanks.⁹,¹⁰
2. Metal Hydride Battery Research and Development

Scientists have explored using intermetallic hydrides to replace the hydrogen electrode in the nickel-hydrogen cell since the mid-1970s. By 1981, a 10-Ah cell had been tested by the Atomic Energy Research Establishment.\textsuperscript{11} This cell contained a nickel grid packed with LaNi\textsubscript{5} powder, which was coated with platinum black on the surface in contact with the electrolyte. The cell also employed a potassium titanate separator near the metal hydride electrode and a carbon electrode close to the Ni(OH)\textsubscript{2} electrode to recombine oxygen formed at the end of charge. At temperatures between \(-20^\circ\text{C}\) and \(50^\circ\text{C}\), the cell performance was nearly identical to a high-pressure, nickel-hydrogen cell tested for comparison. At \(-40^\circ\text{C}\), however, the discharge capacity of the metal hydride electrode was much lower than the capacity of the high-pressure cell due to the stability of the hydride. Analysis of the high- and low-pressure batteries showed that the weight saved by eliminating the pressure vessel in the low-pressure cell was almost entirely regained by the additional weight of the LaNi\textsubscript{5}.

After these tests and other similar work on metal hydride cells, it was soon evident that the charge capacity of LaNi\textsubscript{5} electrodes in contact with potassium hydroxide or water vapor\textsuperscript{12,13} rapidly decayed with cycling. New surfaces, generated by brittle fracture of the material during hydriding, were quickly oxidized. However, optimism was renewed in 1984 when it was shown that cobalt additions with aluminum or silicon reduced fracturing and increased cycle life to about 1000.\textsuperscript{1} This led to the construction of a 300-mAh sealed cell by Philips Research Laboratories in Eindhoven using a La\textsubscript{0.8}Nd\textsubscript{0.2}Ni\textsubscript{5}Co\textsubscript{4.5}Si\textsubscript{0.1} alloy. Philips reported only a 16% capacity loss after 5000 cycles, though the degree of charging and depth of discharge were not specified.\textsuperscript{1}

Fueled by the success of macroalloying with cobalt and aluminum to depress capacity decay, myriad LaNi\textsubscript{5}-based compounds containing nearly every element were fabricated and tested in laboratories around the world in an effort to radically increase capacity and cycle life. But better alloys were not forthcoming, and many complex alloys were discarded with little insight as to how all the alloying elements acted together to produce the behavior seen. It still cannot be well predicted how a particular alloying element, whether acting alone or together with other alloying elements, will affect electrode performance. Though some additional alloying elements, such as cerium, have demonstrated excellent corrosion resistance, no single alloy has emerged with distinctly superior capacity, rate capability, or cycle life. The closest optimized alloy to date is MmNi\textsubscript{5.8}Mn\textsubscript{0.4}Al\textsubscript{1.2}Co\textsubscript{0.75} (Mm = Mischmetal, a combination of the rare earth elements containing mostly La and Ce).\textsuperscript{14,15}

The majority of today's research on metal hydride electrodes still focuses on LaNi\textsubscript{5} compounds, although successes with AB\textsubscript{2} compounds such as (Ti, Zr),Ni\textsubscript{2} are attracting more interest in developing alloys from other intermetallic classes. Present materials strategies concentrate on combining different phases and microstructures to overcome shortcomings in the bulk metal hydride behavior. They include manipulating crystallinity,\textsuperscript{16} different phases, porosity,\textsuperscript{17} microstructures,\textsuperscript{18} surfaces,\textsuperscript{19} and particle sizes. Large surface area materials are fabricated by powder sintering, mechanical alloying,\textsuperscript{20} and etching\textsuperscript{21} to increase rate capabilities. Although successful in increasing discharge rates, these compounds invariably suffer lower cycle lives due to increased oxidation of the surface. As a result,
surface treatments such as electroless plating of copper and nickel\textsuperscript{20-23} or doping with palladium and cerium are applied to resist the oxidation. To retard the mechanical breakdown of the electrode, techniques such as gas-phase hydrogen cycling, gas atomization, and grinding are used to produce smaller initial particle sizes.\textsuperscript{24} Other efforts are directed towards maintaining electrical contact during the 14–24\% volume change that the metal lattice endures during hydride formation. These strategies include the use of carbon/polymer binders, compaction in porous nickel foams, surface plating, doping, and compaction with other conductive powders.\textsuperscript{24}

Although still an active area for scientific investigation, research in metal hydride batteries is waning in favor of lithium-ion research. In the United States, agencies like the DOE have reduced funding levels for metal hydrides to support lithium-ion research for advanced batteries. Most of the metal hydride research continues in Japan, where the majority of the nickel metal hydride batteries are currently in production.
3. Battery Production

The market for advanced battery systems such as nickel metal hydride is lucrative. New products such as video cameras, power tools, laptop computers, and cellular phones have increased demand for high-cycle, low-Ah batteries. In the United States, OSHA regulations have sharply reduced the maximum allowable cadmium exposure limits for workers, thereby increasing production costs of nickel-cadmium batteries. Other countries such as Sweden have passed legislation curtailing the sale of nickel-cadmium batteries in an effort to reduce cadmium levels in landfills. Finally, nickel metal hydride batteries outperform nickel-cadmium batteries in discharge capacity and have no cadmium memory effect.

The actual production of nickel metal hydride batteries for commercial sale has been rapid because the component materials and fabrication methods used are almost identical to those used in the production of nickel-cadmium cells. Most battery companies worldwide have built at least experimental cells based on metal hydride electrodes. Companies now in the advanced stages of commercial development include Matsushita, Panasonic, Sanyo, Sharp, and Toshiba (Japan), and the Ovonic Battery Company (USA). Batteries ranging from mAh button cells to 200-Ah prismatic cells have been produced for sale. Other companies working on developing metal hydride batteries include Varta (Germany), Gates (USA), SAFT (France), and Yuasa Battery, Shin-Kobe Electric Machinery, Hitachi, and Japanese Storage Battery (Japan).

Matsushita Battery Industrial Companies marketed one of the first commercially available nickel metal hydride batteries in 1990, a AA cylindrical sealed cell with a 1.07-Ah capacity at a weight of 24 g. The stated cycle life was 500 cycles at a temperature range of 0 to 45°C. However, the battery developed high internal pressures during rapid battery charging and fast self discharge rates. Soon thereafter, Toshiba Battery sold a AA-size battery with low overcharge pressures and a discharge capacity that stayed within 95% of its rated value when discharged at a 6C rate. By 1992, 1-Ah, 500-cycle, cylindrical and prismatic cells were available from Sanyo and Panasonic.

In the United States, large companies such as Duracell purchase pre-fabricated metal-hydride alloys from Japan for their electrodes. The Ovonic Battery Company (Michigan) is engaged in the development and production of metal hydrides for electric vehicles and military applications. The Ovonic Battery Company has claimed legal proprietorship over many of the AB2 and AB3 systems, thereby keeping competition from other small U.S. companies low. Although little technical information on their materials is available, Ovonic has built 40-Ah nickel metal hydride cells using AB2 alloys such as V2Ti1-xZrxNiyCr7. Alloys similar to these have been studied by other research groups worldwide; however, the material performance claimed by the Ovonic Battery Company has not been reproduced.

Leclanché (Switzerland) has built a range of metal-hydride batteries ranging in capacity from a few mAh to 25-Ah prismatic cells. Cells use LaNi5-based hydrides that have been mixed with a polymeric binder such as PTFE and pressed into nickel foam or felt, polypropylene or polyamide separa-
tors, and larger cells are vented. Heat management problems have been encountered during charging. However, better than 2000 cycles at C/2 discharge to 80% DOD have been realized for a 9-Ah prismatic cell.
4. Battery Design Concerns

As of yet, many of the material challenges in using intermetallic hydrides as battery electrodes have not been solved. A recent review article provides a comprehensive technical summary of the known chemistry and physics controlling the nickel metal hydride system. The following briefly discusses various performance concerns of the nickel metal hydride battery.

4.1 Discharge Capacity

The highest density hydride of the AB$_3$ intermetallics is LaNi$_5$H$_6$, which has a maximum theoretical discharge capacity of 370 mAh/g. Although much research has focused on increasing the base storage capacity of LaNi$_5$, either through alloying or manipulating the degree of crystallinity and microstructure of the material, there has been little success. The reason for this appears to be electronic, and can be explained through conduction band theory. Alloying elements added to LaNi$_5$ compete electronically with hydrogen for holes in the nickel 3d band, thereby lowering the total amount of hydrogen the intermetallic can absorb.

In the case of the AB$_2$ systems, porosity, multiphase regions, and crystalline disorder are manipulated to increase hydrogen storage capacity. Researchers at the Ovonic Battery Company assert that by controlling the porosity of the surface oxide layer through etching, hydrogen mobilities through the oxide can be increased. It is also claimed that the metal-hydrogen bond energies can be controlled by changing the degree of crystalline disorder in the alloy, thereby increasing the reversible capacity. A similar link between capacity and disorder has been demonstrated in an amorphous Mg$_{50}$Ni$_{50}$ compound that showed an initial 500-mAh/g capacity; however, the capacity quickly decayed with cycling. It is worth noting that disorder in LaNi$_5$ alloys always results in lower hydrogen capacities and higher, poorly defined, hydride formation pressures characteristic of material that has been heavily cycled in the gas phase. Performance in both cases can be restored by vacuum annealing. In LaNi$_5$ alloys prepared by melt spinning and gas atomization, annealing after processing causes substantial increases in capacity and cycle life.

Presently, nominal discharge capacities of around 250 mAh/g are common for LaNi$_5$-based systems. These values are based on the weight of the active metal hydride only, and do not include the weight of the metal-hydride binding material, the nickel grid it adheres to, or any other battery components. Additionally, the values are valid for room-temperature operation only, and discharge capacities decrease with increasing temperature. Discharge capacities of AB and AB$_2$ compounds found in the literature are usually higher, about 350–400 mAh/g, owing to the lower molecular weight of the material. For nickel-hydrogen cells, it is anticipated that the effective energy density of the system may be increased by permitting more flexible geometries, such as a prismatic cell. However, these weight reductions might be offset by the weight of the intermetallic itself because the density of LaNi$_5$ rivals that of steel.
4.2 Cycle Life

Much of the present research effort is aimed at increasing the cycle life of the metal-hydride electrode. Commercial cells reliably achieve 300–500 cycles, and claims for 2000 cycle lives are becoming routine. However, little significant progress on extending cycle life has been made since the first battery using LaNi₅ was tested in 1981. Aside from poisons such as SO₂, H₂S, CO, and CO₂ there are three basic modes in which LaNi₅ alloys degrade: oxidation, mechanical breakdown, and disproportionation.

4.2.1 Oxidation

LaNi₅ alloys readily oxidize to LaₓOₚ, La(OH)ₓ, and nickel when in contact with oxygen, water, or potassium hydroxide. Although free nickel in the intermetallic surface catalyzes the absorption of hydrogen, surface oxide layers reduce the percent of active bulk material, which can be significant for small particle sizes. The oxide layer for LaNi₅ is not compact or strongly adherent, and oxidation continues by diffusion to consume bulk material throughout exposure to water or air. If the oxide layer is thick enough, the hydriding reaction becomes passivated. Vacuum annealing or exposure to high hydrogen pressures at room temperature is required to breakdown the oxide layers prior to hydride formation.

Different approaches have been taken to minimize oxidation with varying degrees of success. Nickel and copper coatings on the surface of intermetallic particles have decreased the rate of oxidation and extended cycle lives; however, oxidation was not completely arrested in these surface-modified materials. Invariably, mechanical breakdown caused by hydride expansion generated new surfaces that were not resistant to oxygen attack. Alternatively, denser and more stable oxides surfaces have been generated by replacing some of the lanthanum with cerium. While electrodes containing cerium show reduced oxidation rates with cycling, discharge capacities are lower.

In order to maximize the use of existing nickel-cadmium production technology, present commercial designs do not incorporate provisions to prevent oxygen recombination on the metal-hydride electrode. However, designs of early nickel metal hydride cells took care to protect the metal hydride from oxygen evolution and recombination during overdischarging and overcharging by either physically separating the metal hydrides from the potassium hydroxide or by using separators and ancillary electrodes for the oxygen recombination reaction to occur. Both of these studies reported cycle lives in the thousands on alloy compositions that have since been found to fail by a different mechanism (disproportionation) in gas-phase cycling. Smarter alloying and additional oxygen/water barriers such as palladium foil might produce higher cycle lives for these types of designs.

4.2.2 Mechanical Breakdown

The volume of LaNi₅ expands nearly 25% upon hydriding. During cycling of LaNi₅-based electrodes, this large volume change causes the inherently brittle intermetallic to break down into fine particles on the order of a micron in diameter. If in contact with potassium hydroxide, the resulting surface areas oxidize, and significant bulk capacity is lost. Furthermore, commonly used binding materials such as PTFE often fail to maintain physical contact during the fracturing process, leading to electrical dead areas and particle fallout. Figure 1 shows a SEM micrograph of a LaNi₅Sn₀.25
Figure 1. LaNi₅Sn₀.₃ in a carbon/PTFE binder after 100 cycles in 31 wt.% potassium hydroxide at 39% depth of charge. Note the extensive cracking and loss of contact in the metal hydride particles and the cracking in the binding material as well.

electrode after 100 cycles at only 39% depth of charging. Note the fragmentation of the intermetallic and the loss of adhesion between the intermetallic and PTFE/carbon binder. The change of volume of this alloy on hydriding to LaNi₅Sn₀.₃H₅₄ is about 17%.

The amount of discharge capacity lost with cycling has been shown to scale linearly with the percent volume expansion during hydriding.¹ Through macroalloying, the unhydried LaNi₅ unit cell can be expanded, and volume changes during hydriding can be reduced to as low as 12%. Similarly, high solidification rate casting techniques can be used to create microstructures that better accommodate volume changes. Melt spinning has been used to create a flake-like alloy with a 2–3 μm columnar grains with a higher cycle life than the cast alloy.¹⁶ Although both of these methods produce materials that suffer smaller lattice strains and less mechanical breakdown with hydrogen cycling, decay rates are not entirely arrested because the volume changes, though smaller, are still destructive.

Alloying elements that increase the ductility of the inherently brittle LaNi₅, as indicated by a lower Vickers hardness number, have been linked with reduced mechanical breakdown.²⁴ Although inter-
metallics are notoriously brittle, more ductile AB and AB₂ systems may prove tougher in withstanding the strain of hydride formation. However, hydride phases of any material are usually brittle, and cracking may still occur while the material is in the hydried state.

Although most of the particle breakdown in a metal hydride electrode occurs within the first 10 hydriding cycles, the damage due to the volume change on each cycle continues to degrade performance throughout the life of the electrode. Figure 2 demonstrates the effect of different charging times on the discharge capacity of LaNi₅Sn₀.₂₅ as a function of cycle number. In the gas phase, this alloy has an equivalent discharge capacity of 340 mAh/g. As shown in Figure 2, decay rates decrease with depth of charge, and an electrode charged to only 39% of its capacity showed no decay in 100 cycles. Previous studies have shown that degradation follows an exponential relationship, implying that material is lost in proportion to the remaining active material on each step.¹ Thermodynamic modeling has shown that even materials charged to low hydrogen concentrations contain domains of fully stoichiometric hydrides surrounded by unhydried material.³⁷ These regions still suffer the degradation modes intrinsic to the volume change during hydride formation. This argues that although there is less cyclic degradation in electrodes charged to lower states of charge, there is no charge limit at

![Graph showing discharge capacity as a function of cycle number for LaNi₅Sn₀.₂₅](image)

**Figure 2.** Discharge capacity as a function of cycle for a 75-mg sample of LaNi₅Sn₀.₂₅ in 31 wt.% potassium hydroxide for different charging times at 10 mA. Electrodes charged to lower capacities suffer less overall capacity loss on each cycle.
which degradation will not occur. The bottom curve on Figure 2 shows no decay only because the
test was stopped before the decay would have been evident for the state of charge used.

4.2.3 Disproportionation

Energetically, the LaNi₅H₆ is less stable than lanthanum hydride and nickel. If lanthanum has signifi-
cant mobility, LaNi₅H₆ spontaneously disproportionates into lanthanum hydride and nickel. Although
lanthanum mobilities in LaNi₅ are small at room temperature, while the lattice is expanded during
hydriding, the activation energy for lanthanum diffusion is much lower, and LaH₃ formation is facili-
tated. This disproportionation mechanism has been observed in heavily cycled LaNi₅. The forma-
tion of lanthanum hydride is irreversible, and any hydrogen stored as lanthanum hydride cannot be
recovered, except by decomposition annealing at 400°C.

Fortunately, the physics of alloy disproportionation is fairly well understood, and its effects have all
but been eradicated through macroalloying. By alloying with large elements such as aluminum and
tin, lanthanum is effectively pinned in the crystal structure, and the disproportionation into nickel and
lanthanum hydride does not occur while the lattice is expanded.

4.3 Charge/Discharge rates

The kinetics of hydrogen in an intermetallic particle are determined by bulk diffusivities and surface
processes. For large metal-hydride particles, the kinetics for charging are limited by the diffusivity of
hydrogen through the material and through its hydride at higher states of charge. The kinetics for
discharging appear to be limited by a surface process. Rates for charge and discharge often improve
initially with cycling once the material has broken down into finer particles due to the increased sur-
face area and the shorter diffusion paths in the intermetallic particles, as well as the generation of low
oxide-containing surfaces. Similarly, high surface area materials obtained by mechanical alloying
have also demonstrated markedly increased rate capabilities. However, such improvements are
often short-lived due to subsequent oxidation of the larger surface areas, which also reduces the dis-
charge capacity.

Most intermetallics are passivated in oxygen or water-containing environments, and hydrogen diffu-
sion through the surface oxides becomes the rate-limiting step. Palladium macroalloying has been
shown to increase the exchange current density of electrodes and other coatings such as nickel and
copper permit higher discharge rates as well.

4.4 Charge Efficiency

The charge efficiency of a metal-hydride electrode depends on the composition of the alloy used and
the states of charge attained during charging. For alloys with low hydride formation pressures and
low states of charge, charge efficiencies are about 90%. The pressures at which an intermetallic
forms or decomposes a hydride phase can be related to the voltage plateau regions in the charge and
discharge curves by the Nerst equation:

\[ E_{eq}(H) \text{ vs } E_{eq}(HgO/Hg) = -0.9324 - 0.0291 \log_{10} P(H_2) \]  

(1)
This equation indicates that large decreases in hydride formation pressures cause only slightly lower working voltages for the cell. However, alloys with high hydride formation pressures suffer poor charging efficiencies as the hydrogen preferentially forms hydrogen gas, whereas alloys with low hydride decomposition pressures show poor discharge performance because the hydride is more stable. Thus, it is generally desired that the hydride formation pressure fall between 0.1 and 5 atm. at 45°C. Although the operating pressure at a given temperature can be easily controlled through macroalloying, the extra alloying elements almost always lower the discharge capacity of the material.

The pressures for hydride formation and decomposition in intermetallics vary strongly with temperature. Table 1 shows the variation in hydride formation pressure with temperature for LaNi₅. Note that the pressures for this alloy fall outside the desirable range for temperatures less than −10°C and greater than 40°C.

<table>
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<tr>
<th>T (°C)</th>
<th>P (atm)</th>
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<tr>
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### Table 1 - Hydride formation pressures for LaNi₅ calculated from Ref. 3.

#### 4.5 Overcharge/Overdischarge/Voltage Reversal

The nickel-hydrogen battery is protected from overcharge and overdischarge by the hydrogen cycle, and, in this regard, the nickel metal hydride system is no different if recombination rates are rapid. Hydrogen formed at the nickel electrode during overdischarging diffuses to the metal hydride and dissociates into atomic hydrogen. There it combines with OH⁻ to form water. During overcharge, oxygen formed at the nickel electrode recombines at the metal hydride electrode to form water. These mechanisms prevent internal pressure rises in the cell, permitting hermetically sealed cell designs. However, if recombination is slow, internal pressures can be generated during rapid charging and high discharge rates.

Overcharging and overdischarging generates oxygen, which may oxidize the metal hydride instead of recombining with hydrogen to form water. The testing of cells open to the atmosphere allows oxygen to escape instead of forcing it to recombine at the metal-hydride electrode. Thus, some alloys that have shown good robustness against oxidation in open cells have failed within a few cycles when tested in sealed cells. Cell designs that transfer the recombination reaction to an ancillary electrode have demonstrated remarkably improved cycle lives.
4.6 Self Discharge

The first commercial nickel metal hydride batteries produced by Matsushita, Sanyo, Toshiba, and Ovonic all suffered self-discharge rates up to three times greater than rates seen in nickel-cadmium batteries.\textsuperscript{12,42} Subsequent analysis showed that the nylon separators used in the nickel-cadmium cells could not be used in the metal-hydride cells. Ammonium ions produced by the nylon separators were identified with a shuttle reaction involving \(\text{NH}_4^+\) and nitrate ions (\(\text{NO}_3^-\) and \(\text{NO}_3^-\)), which reduced the nickel electrode and oxidized the metal-hydride electrode.\textsuperscript{24} Replacing the nylon separators with sulfonated-polypropylene separators decreased self-discharge rates to equal those of nickel-cadmium batteries.\textsuperscript{26,43} Likewise, electrodes fabricated from nickel-coated metal hydrides show less self discharge than uncoated alloys.\textsuperscript{22} Presently, commercial button cells lose about 20\% of their discharge capacity after six months at 0°C.\textsuperscript{25} Because nickel metal hydride batteries have low overall hydrogen pressures, self-discharge mechanisms in the nickel electrode evident in nickel-hydrogen batteries at high hydrogen pressures should be less active.\textsuperscript{12}

4.7 Heat Generation

Hydride formation in intermetallic alloys is almost always exothermic, and accommodating material heating has hindered the use of metal hydrides in applications such as hydrogen storage beds.\textsuperscript{44} As shown in Table 1, hydride formation pressures follow the Arrhenius equation, and both hydride formation and decomposition reactions can become self limiting if temperature is not controlled. Unless high heat conduction paths are available, the heat generated during charging forces the hydride reaction to higher voltages, and the heat lost during discharge similarly lowers the discharge rate. The change in enthalpy for hydride reactions in LaNi\textsubscript{5}-based systems is 30–60 kJ/mol.\textsuperscript{3}

4.8 Cost

LaNi\textsubscript{5}-based alloys are expensive because of the cost of reducing and purifying lanthanum from Misch metal ore. In 1991, the International Battery Materials Association, Inc. (IBA) sold LaNi\textsubscript{5}-based alloys for electrode fabrication at about $600 per kg.\textsuperscript{45} By 1994, the price had dropped to $200 per kg.\textsuperscript{46} Despite this trend, the cost of novel processing to achieve new microstructures continues to keep cost estimates for intermetallic hydride electrodes high. While AB and AB\textsubscript{2} hydrides have lower material costs, their processing costs are considered prohibitively high for large-scale applications such as load leveling.
5. Unresolved Challenges for the Nickel Metal Hydride Battery

Projected estimates are that by 2002, sales of lightweight portable batteries for small electronics will constitute a $12 billion dollar market.47 Although nickel metal hydride batteries are heavier and less energy dense than lithium-ion batteries, it is estimated that the lower material costs for nickel metal hydride batteries will keep them competitive with the more expensive lithium-ion batteries. For AA-size batteries, nickel metal hydride batteries presently cost 1.35 times more than nickel-cadmium batteries, whereas lithium-ion batteries cost 2 to 3 times as much.25

For aerospace applications, the challenge of fabricating a metal hydride able to withstand the 20,000 charge/discharge cycles necessary for LEO employment remains. Despite the latest research efforts, metal hydrides in potassium hydroxide seem unable to resist intrinsic degradation during cycling, probably due to the large volume expansion of hydried domains in the material. Although reducing the depth of charge in these materials leads to slower degradation rates, losses in capacity cannot be completely arrested by using lower depths of charge and discharge. Designs that promote oxygen recombination away from the metal hydride or physically separate the metal hydride from any contact with oxygen, potassium hydroxide, or water appear to be the most promising.

Additionally, it is not known how well these materials might perform for GEO mission profiles. The present studies on metal hydrides reported in the scientific literature have yet to address the issues of long-term exposure to potassium hydroxide electrolyte for a low number of charge and discharge cycles.
References


TECHNOLOGY OPERATIONS

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