LBL-34390
UC-210
Preprint

# Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

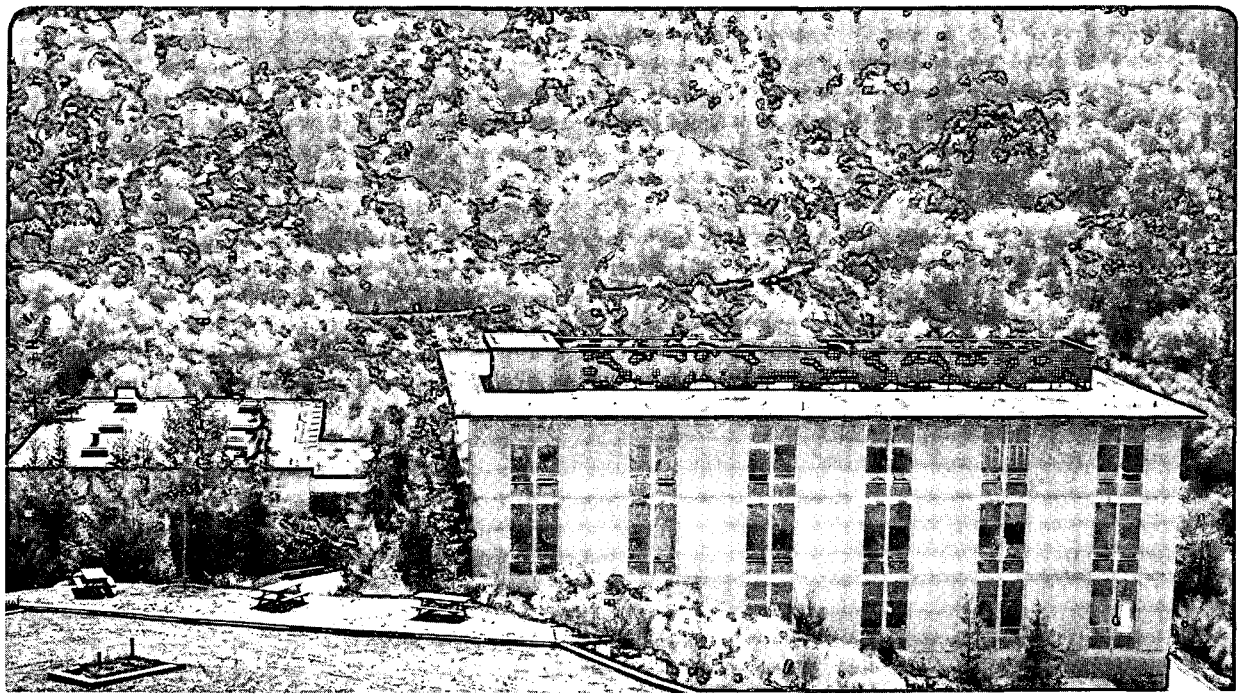
## Materials Sciences Division

Submitted to Modern Aspects of Electrochemistry

# Metal Hydride Electrodes

T.F. Fuller and J. Newman

August 1993



Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098

LOAN COPY
Circulates
for 4 weeks
Bldg. 50 Library.
Copy 2
LBL-34390

## DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-34390
UC-210

# Metal Hydride Electrodes

Thomas F. Fuller and John Newman

Department of Chemical Engineering
University of California
and
Materials Sciences Division
Lawrence Berkeley Laboratory
Berkeley, California 94720

August 1993

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies, Electric and Hybrid Propulsion Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

# Metal Hydride Electrodes

Thomas F. Fuller and John Newman

Department of Chemical Engineering
University of California
and
Materials Sciences Division
Lawrence Berkeley Laboratory
Berkeley, California 94720

## Abstract

The principles of operation of the metal-hydride electrode, including thermodynamics, kinetics, and transport, are reviewed. These fundamentals elucidate the keys to improving the performance of metal-hydride electrodes. The equations presented form the basis for a detailed mathematical model, which would ultimately be used to design and scale-up battery systems. The NiOOH-metal hydride cell is compared critically with competing technologies, and the remaining technical challenges in their development are highlighted.

## Introduction

The energy shock of the seventies and more recently cold-fusion spurred interest in metal hydrides. Because of their ability to store large quantities of hydrogen, they have been considered for a variety of energy-conversion applications.[1,2] Although some applications have not been realized on a large scale and some not at all, several companies are aggressively pursuing the commercialization of the NiOOH-metal hydride battery.[3,4] As the demand for and the production of portable appliances grows, environmental concerns for the disposal of cadmium, a toxic component of the nickel cadmium (Ni/Cd) cell, mount. Many anticipate that the NiOOH-metal hydride battery will replace the traditional Ni/Cd battery.[5] Moreover, the U. S. Advanced Battery Consortium

(USABC)[6] and others[7] are evaluating the NiOOH-metal hydride cell for electric-vehicle applications. Ovshinsky *et al.*[8] recently discussed Ovonics' efforts to develop a metal-hydride battery. Our objectives are to review the fundamentals of operation of the metal-hydride electrode, to compare critically the NiOOH-metal hydride cell with competing technologies, and to highlight the remaining technical challenges in their development.

Hydrides are expected to form when hydrogen is combined with an element less electronegative than itself. For convenience, hydrides are categorized by the nature of the chemical bonding as covalent, ionic, or metallic hydrides. Hydrogen reacts with many transition metals or their alloys to give compounds called metal hydrides, even though there may be no "hydrides" present. The electronic structure of metal hydrides been elucidated only recently.[9] In general, these alloys are complex, with multiple phases and wide divergences from stoichiometry.

Metal hydrides are a class of solid-state systems called interstitial alloys wherein hydrogen is incorporated into empty sites of a simple metal lattice. Figure 1 shows the insertion of hydrogen in a typical alloy; hydrogen is found in tetrahedral or octahedral interstices of a face-centered-cubic metal structure, for example. Often, only partial occupancy is thermodynamically favored. Nonetheless, high hydrogen densities can be obtained in these metals, leading to their application for hydrogen storage and reactor moderator materials.[10] The insertion of hydrogen into interstices only slightly distorts the crystal lattice, and hence the reactions can be highly reversible. The absorption of hydrogen in alloys has many similarities with topochemical reactions of lithium in transition metal oxides and sulfides.[11]

For practical devices, metal hydrides are sought with the following properties: high capacity to store hydrogen, high rates of absorption and desorption, fast kinetics, low cost, light weight, and good stability. This combination is not possible with elemental hydrides. Hydrides formed from pure metals are too stable for use as reversible electrodes.

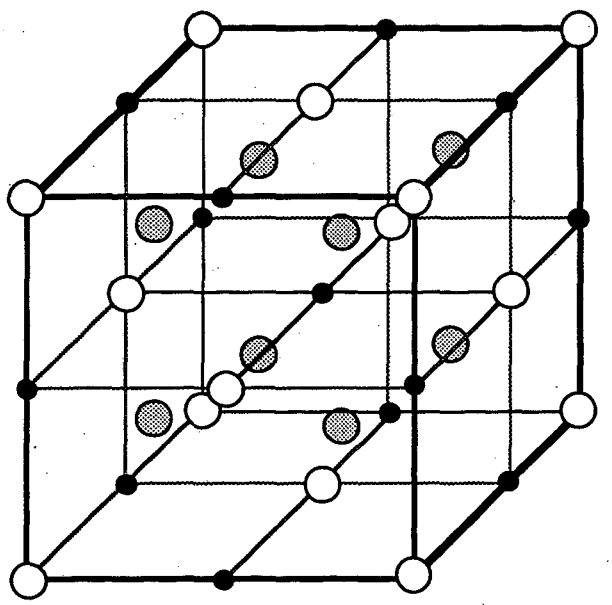


Figure 1. Fcc hydride structure. Open circles are the metal atoms. Small solid circles represent hydrogen atoms in octahedral sites, large shaded circles represent hydrogen in tetrahedral sites.

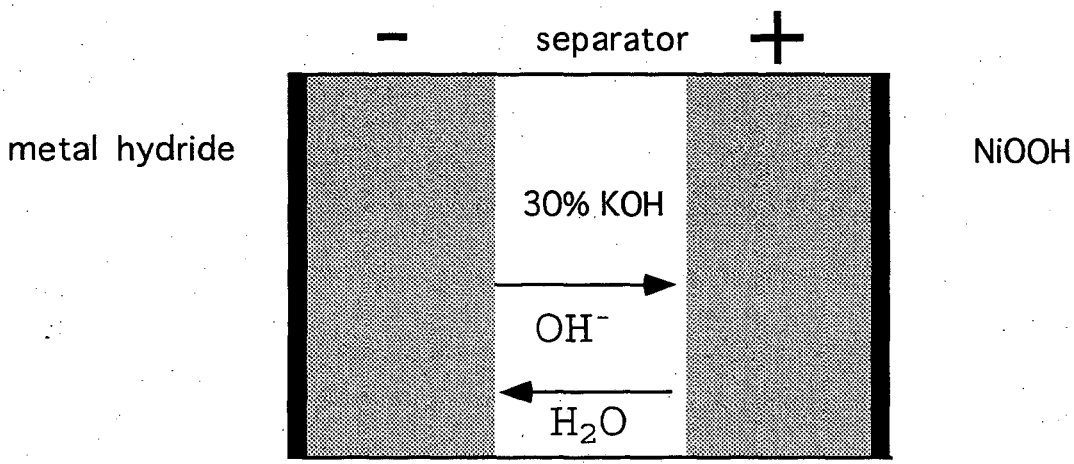
About 200 intermetallic alloys that form hydrides are known and are sometimes grouped according to their structure. The major groups are listed in table 1; the minor classes of intermetallic hydrides are given by Buschow *et al.*[12] and Ivey and Norwood.[13] More detailed information can also be found in references 14 and 15.

**Table 1.**

| Group | Example | Structure |
|---|---|---|
| $AB_5$ | $LaNi_5$, $MmNi_5$ | hexagonal or orthorhombic |
| $AB_2$ | $ZrMn_2$ | Laves phases |
| AB | TiFe | CsCl |
| $A_2B$ | $Ti_2Ni$ | complex |

A is an alkaline earth, transition metal, rare-earth, or actinide; B is a transition metal of the iron group. Mm, or Mischmetal, is a combination of lanthanum and other rare-earth elements. $LaNi_5$ is often referred to as the conventional material. It should be noted that the classifications are only generalizations; typical alloys contain multiple phases and complex structures.

The study of hydrides, in particular hydrogen in metals, is a broad interdisciplinary research topic. Metal hydrides have been the subject of several international symposia.[14,15,16] We concentrate on the electrochemical applications of metal hydrides, where our expertise lies. Originally these alloys were used to reduce the pressure of stored hydrogen in the $Ni/H_2$ cell, a well-established energy-storage system for satellites.[17] More recently, the metal-hydride electrode has been considered as a replacement for the cadmium negative electrode in the nickel-cadmium cell. Figure 2




$$MH + OH^- \rightarrow M + H_2O + e^-$$

$$NiOOH + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$$

Figure 2. NiOOH-metal hydride cell. The cell potential is about 1.2 V. There is no net production or consumption of water. During discharge hydroxyl ions are transported from the negative to the positive electrode, and water is transported from positive to negative, resulting in a shuttle of hydrogen between electrodes.

depicts a typical cell; the potential of the cell is about 1.2 V, similar to the Ni/Cd cell. The first reversible metal-hydride electrode was reported by Justi *et al.*[18] These cells had poor performance; dramatic improvement in the cycle life and durability were obtained by Willems.[20] The NiOOH-metal hydride cell will be discussed in detail later in this paper. The status of research and development of the metal hydride electrode has been addressed in earlier reviews.[19,20] We will focus on the recent research and development activities on intermetallic hydrides and the NiOOH-metal hydride battery.

Before analyzing the NiOOH-metal hydride cell, we should like to discuss the principles of operation of metal-hydride electrodes. The fundamentals of thermodynamics, kinetics, and transport will provide us with the tools to identify the keys to improving the performance of metal hydride electrodes. In addition, the equations presented would be the basis for a detailed mathematical model, which could ultimately be used to design and scale-up battery systems.

## Fundamentals

*Thermodynamics.*— First, let us consider the open-circuit potential of the cell shown below. Here, we measure the potential of the metal-hydride electrode with a mercury-mercuric oxide electrode.

| $\alpha$ | $\beta$ | $\delta$ | $\varepsilon$ | $\beta'$ | $\alpha'$ |
|---|---|---|---|---|---|
| Pt(s) | M(s) | KOH | HgO(s) | Hg(l) | Pt(s) |
| | $H_2$ | $H_2O$ | | | |

The cell potential is

$$FU = -F\left(\Phi^{\alpha} - \Phi^{\alpha'}\right) = \mu_{e^-}^{\alpha} - \mu_{e^-}^{\alpha'}. \qquad (1.)$$

At equilibrium, we can equate the electrochemical potential of species in adjacent phases. For the mercury-mercuric oxide electrode,

$$Hg + 2OH^- \Leftrightarrow HgO + H_2O + 2e^-. \tag{2.}$$

Thus,

$$\mu^{\beta}_{Hg} + 2\mu^{\delta}_{OH^-} = \mu^{\varepsilon}_{HgO} + \mu^{\delta}_{H_2O} + 2\mu^{\alpha}_{e^-}. \tag{3.}$$

For the metal hydride, two reactions are possible

$$M + H_2O + e^- \Leftrightarrow M{\cdot}H_{ad} + OH^-, \tag{4.}$$

and

$$2M{\cdot}H_{ad} \Leftrightarrow H_2 + 2M. \tag{5.}$$

If the above reactions are equilibrated,

$$\mu^{\alpha}_{e^-} = \frac{1}{2}\mu^{\beta}_{H_2} + \mu^{\delta}_{OH^-} - \mu^{\delta}_{H_2O}. \tag{6.}$$

In effect, the metal-hydride electrode functions as a hydrogen electrode in an alkaline medium. We can express the cell potential as,

$$U = U^{\theta} + \frac{RT}{2F}\ln\frac{p^{\beta}_{H_2}}{a^{\delta}_{H_2O}}, \tag{7.}$$

where

$$U^{\theta} = \frac{1}{2F}\left(\mu^{*}_{H_2} + \mu^{o}_{HgO} - \mu^{o}_{H_2O} - \mu^{o}_{Hg}\right) \approx 0.926. \tag{8.}$$

The potential of the cell is related to the fugacity of hydrogen through equation 7. These two quantities are plotted against the stoichiometry of a hypothetical hydride in figure 3, the shape being typical of the absorption isotherm for a single-phase system. In the simplest analysis, we would relate the fugacity of hydrogen in the gas phase to a concentration in the metal using a Langmuir or similar isotherm based on equation 5. Often phase changes accompany the absorption of hydrogen, and the isotherms are complex. For a typical two-phase system, a small amount of hydrogen dissolves into the metal, occupying interstitial sites in the metal lattice. This is referred to as the α-phase. Further absorption of hydrogen causes a phase transformation. The new hydrogen-rich phase is called the β-phase. Such a phase transformation results in a plateau in the absorption isotherm. After the phase transformation is complete, the hydrogen pressure increases with increasing hydrogen concentration. The monograph by Lewis,[21] detailing the palladium hydrogen system, contains a wealth of information, applicable to most metal-hydride systems, and provides a historical perspective of the field.

The adsorption of hydrogen is an exothermic reaction. The effect of temperature on the equilibrium, quantified by the Gibbs-Helmholtz relationship, has been exploited in heat engines using metal hydrides. The effect of temperature on the absorption of hydrogen has been measured in detail for the palladium system.[22] With increasing temperature, the maximum solubility of hydrogen in the α-phase increases, and at the critical point the two phases are miscible. At constant composition, the equilibrium pressure of hydrogen increases with increasing temperature.

One major consideration for the utility of a metal-hydride electrode is the hydrogen storage capacity of the alloy. Hydrogen can be stored in gaseous, liquid, or solid forms. Table 2 compares the capacity of some metal-hydride electrodes with pure hydrogen. The parameter $c_t$ is the maximum concentration of hydrogen in the compound. Although these alloys are capable of storing hydrogen in high concentrations, the capacity

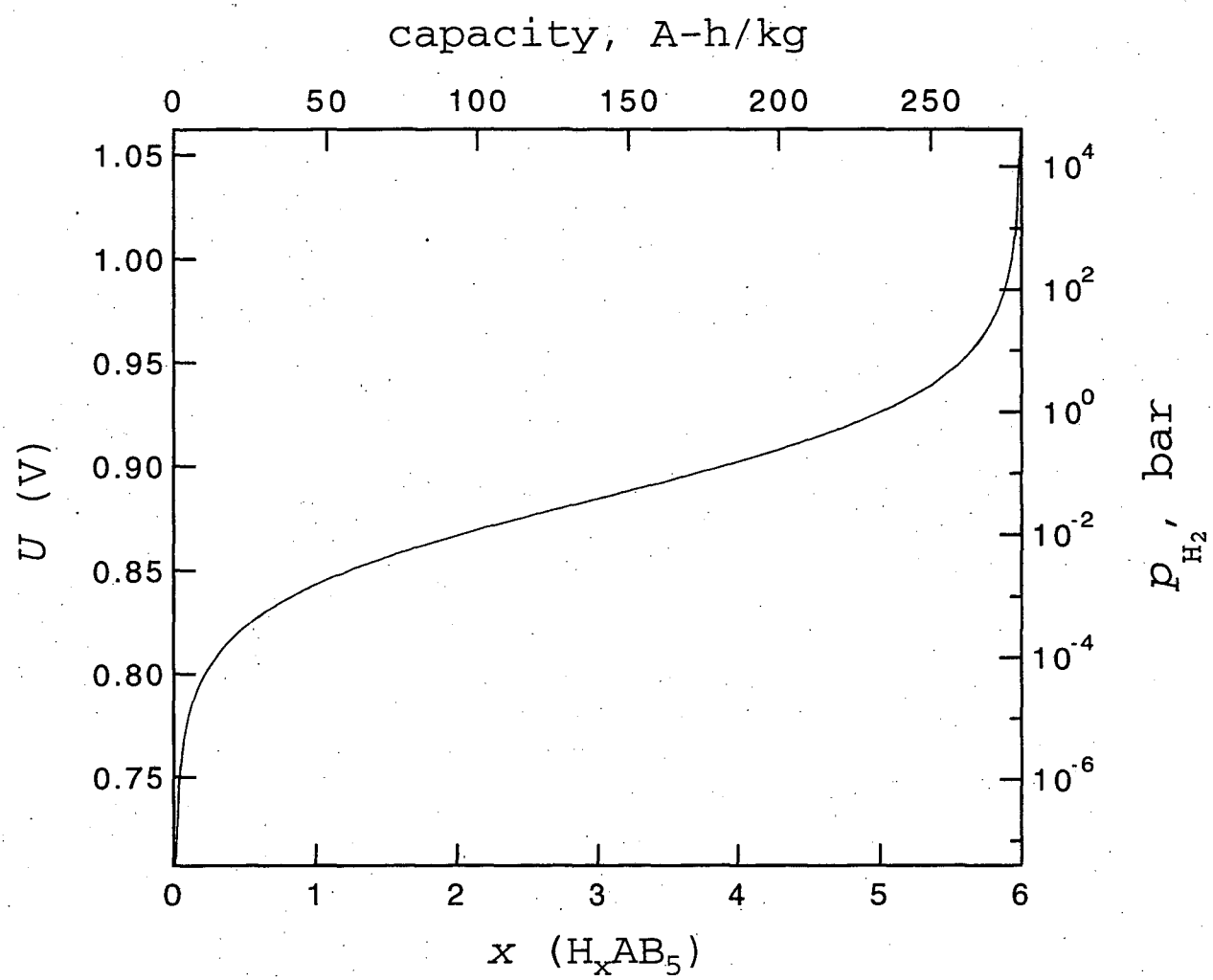



Figure 3. Open-circuit potential of a typical metal hydride electrode. The potential is that of the Hg/HgO reference electrode relative to the metal hydride electrode. $x$ is related to the capacity assuming a molecular weight of 590 g/mol for $AB_5$.

per mass is low compared to pure forms of hydrogen. The capacities listed do not include the mass of the containers used to store the hydrogen.

**Table 2.**

| **Compound** | $c_t$, mol/dm$^3$ | **Theoretical capacity**, A·h/g |
|---|---|---|
| $H_2$ gas, 150 bar | 11.6 | 26.8 |
| liquid $H_2$, 20 K | 66.41 | 26.8 |
| liquid $CH_4$ | 99.6 | 6.7 |
| $LaNi_5H_6$ | 91.3 | 0.372 |
| $TiFeH_{1.93}$ | 100.2 | 0.501 |
| $ZrMn_2H_{3.6}$ | | 0..480 |

*Electrode Kinetics.*— Because the rates of reaction can limit the rate of charge or discharge of the metal-hydride electrode, the surface or kinetic properties of the alloys are important. The main reactions for metal hydride electrodes are:

Volmer $$M + H_2O + e^- \Leftrightarrow M{\cdot}H_{ad} + OH^-, \quad (9.)$$

Heyrovský $$M{\cdot}H_{ad} + H_2O + e^- \Leftrightarrow M + H_2 + OH^-, \quad (10.)$$

Tafel $$2M{\cdot}H_{ad} \Leftrightarrow H_2 + 2M, \quad (11.)$$

and $$M{\cdot}H_{ad} \Leftrightarrow M{\cdot}H_{ab}. \quad (12.)$$

The last reaction represents the diffusion of hydrogen from the surface of the particle into the metal lattice. These reactions are fundamental to the hydrogen electrode and have been studied extensively.[23,24] Along with the above reactions, for the metal-hydride electrode, there are self-discharge, recombination, over-discharge, and corrosion reactions; these are important to the operation of the cell and will be considered in more detail in the analysis of the NiOOH-metal hydride battery. The overall reaction at the electrode is

$$M + H_2O + e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} MH + OH^- . \qquad (13.)$$

The rates of electron-transfer reactions are commonly described with the Butler-Volmer equation;

$$i = i_o \left\{ \exp\left[ \frac{(1-\beta)nF}{RT} \eta_s \right] - \exp\left[ \frac{-\beta nF}{RT} \eta_s \right] \right\}. \qquad (14.)$$

The kinetics of the reaction may be limiting if it is slow compared to the ohmic resistance or when compared to diffusion of hydrogen in the particles.

The catalytic properties of the alloy are critical to the battery designer. Some reactions that are thermodynamically favorable may proceed at such a slow rate as to be negligible, with desirable or undesirable effects. For example, if the kinetics for recombination of atomic hydrogen (eq. 11) is poor, then substantial amounts of hydrogen may be electrochemically inserted into the lattice without significantly raising the cell pressure (a favorable situation), assuming the cell is discharged shortly thereafter. This also suggests that if hydrogen is generated on the negative electrode during overcharge, it will be slow to be absorbed into the negative electrode. The area of the electrode is important for heterogeneous reactions. Often these alloys are activated, *i.e.*, the alloy is

cycled several times to break the metal into smaller fragments. The finely divided alloys have a high specific area, reducing the kinetic resistance. Thus, they are termed "activated" because of their ability to absorb and desorb hydrogen rapidly.

Schlapbach[25] has reviewed surface properties of metals with respect to the formation of metal hydrides. Flanagan[26] points out the difficulties of kinetic measurements and interpretation of results for two-phase alloys. Notten and Einerhand measured the exchange current densities for several $AB_5$ materials.[27] Because the alloys are in a strongly oxidizing environment, the surface may be passivated. A metal oxide film could form, inhibiting the adsorption of hydrogen and catalyzing other reactions. The rate of mass transfer can also limit the performance of the electrode and is discussed below.

*Transport Phenomena.*— Transport phenomena in the metal-hydride particles as well as in the electrolyte can affect the performance of the metal-hydride electrode. The metal hydride electrode is similar to the lithium ion insertion systems. The interested reader is referred to the work of Doyle *et al.*[28,29] or of Newman.[30]

Transport of hydrogen in the alloy is typically analyzed with the diffusion equation;

$$\frac{\partial c_s}{\partial t} = -\nabla \cdot N. \tag{15.}$$

The relevant physical property for the solid particle is the diffusion coefficient of hydrogen in the metal lattice. Conway and Wojtowicz[31] investigated the maximum rate of charge or discharge in systems limited by solid-state diffusion in a single-phase system. Züchner *et al.*[32] used the current-pulse method to measure the diffusion coefficient in the α-phase of H in $LaNi_5$. They found that the diffusion coefficient depended on the crystal orientation. There are often phase changes associated with insertion, and the alloys have complex structures, suggesting that simple diffusion may be a severe approximation. Li *et al.*[33]

presented a relationship between discharge capacity and current density for two-phase $AB_5$ materials, assuming diffusion of hydrogen is rate limiting. Sakamoto *et al.*[34] modeled diffusion in the metal particles, treating diffusion in the two phases of the palladium system, and compared the calculated potentials of the electrode with experimental values. Pollard and Newman[35] developed a shrinking core model for a two-phase alloy. Reilly *et al.*[36] used a shrinking core model to describe the isothermal decomposition of $LaNi_5$, assuming that the phase change was rate limiting.

For the $LaNi_5$ electrode, Willems[20] compared the time of discharge to the time of diffusion in the particles and found no transport limitations for his system. In battery applications, the metal hydride electrode would have a porous structure, and this ratio of time constants can be generalized;

$$S_s = \frac{R_s^2 I}{D_s nF(1-\varepsilon)c_t \delta}. \tag{16.}$$

This expression assumes spherical particles and galvanostatic charge or discharge. $R_s$ is the particle radius, $I$ the separator current density, and ε is the porosity of the electrode. For small particles (S<<1), the time for diffusion is small compared to the time of discharge, and diffusion would not be limiting.

The typical electrolyte is concentrated potassium hydroxide. For such a binary electrolyte, the important transport properties are the electrical conductivity (κ), the transference number of hydroxyl ions ($t_-^0$), and the diffusion coefficient of the salt ($D$). Potassium hydroxide is widely used in other cells and is reasonably well characterized. The fluxes can be represented by

$$N_+ = c_+ v^{\square} - \varepsilon D \nabla c_+ + \frac{(1-t_-^0)}{z_+ F} i_2, \tag{17.}$$

and

$$N_0 = c_0 v^{\square} - \varepsilon D \nabla c_0. \tag{18.}$$

These equations are for a concentrated binary electrolyte, using a volume average velocity.[37,38] At steady state, the flux of cations is zero, and a concentration gradient develops even though there is no net consumption of electrolyte. Although steady-states, other than $I$=0, are not obtainable in battery systems, concentration gradients will develop during charge and discharge.

There are two important issues regarding electrolyte transport. First, we can compare the time of discharge with the diffusion time for the electrolyte as we did above for the particles. For a cell of thickness $L$,

$$S_e = \frac{L^2 I}{DnF(1-\varepsilon)c_t \delta}. \tag{19.}$$

This expression is based on the time to discharge the cell completely and tells us whether there is sufficient time for concentration gradients to be established. We can also examine a short pulse of high current. Although a cell may not be able to sustain a large current density over the full discharge, it may be able to deliver a short pulse of power without significant concentration polarization. Second, we can estimate the magnitude of the concentration difference. This will be determined by the transference number of $OH^-$, the diffusion coefficient of potassium hydroxide in the solvent, and the current density.

$$\Delta c \approx \frac{(1-t_-^0)LI}{z_+ FD}. \tag{20.}$$

This equation suggests that the larger the anion transference number the smaller the concentration gradients.

The potential $\Phi_2$ in the electrolyte, measured with a Hg-HgO electrode in solution, is related to the superficial current density in the pore system by

$$i_2 = -\kappa\nabla\Phi_2 - \frac{\kappa}{F}\left(t_+^0 + \frac{c}{2c_o}\right)\nabla\mu_e \ . \tag{21.}$$

This is a modified form of Ohm's law, accounting for concentration polarization. Similarly for the electronically conducting solid phase,

$$i_1 = -\sigma\nabla\Phi_1 \ . \tag{22.}$$

One advantage of these metal electrodes is that the electrodes have high electronic conductivity. This is in contrast to the NiOOH electrode, which forms a poorly conducting hydroxide.

Vitanen[39] developed a mathematical model of the metal hydride electrode but did not examine the performance of the electrode in detail. White *et al.*[40,41] have modeled the nickel hydrogen cell. Heat transfer in metal-hydride beds has been studied extensively. Thermal effects are frequently neglected for electrochemical applications, but undoubtedly they play an important role and should be studied in detail. Bernardi *et al.*[42] presented a general energy balance for battery systems.

## Analysis

*The* NiOOH-Metal-hydride *Cell.*—Clearly one of the most promising applications of metal hydrides is the NiOOH-MH cell. The potential of the cell is about the same as that of the Ni/Cd cell, but the metal hydride electrode has a greater energy density. The major advantage, however, is that the battery does not contain toxic materials. Other advantages of this cell include: no dendrites are formed, the main reactions do not involve precipitation or dissolution, and there is no net consumption or production of water. The NiOOH electrode has been studied extensively;[43,44] we will

review its operation only in connection with the NiOOH-metal hydride cell. The negative metal hydride electrode is typically made by compressing the metal hydride powder onto a nickel grid. The negative and positive electrodes and separator are then impregnated with aqueous potassium hydroxide. As was mentioned in the preceding section, this cell has many similarities to the dual lithium ion insertion cells. Here hydrogen is inserted and deinserted from the metal electrodes. In contrast to the lithium systems, hydrogen ions are not available for transport in the alkaline medium. On discharge, for example, hydrogen from the metal combines with hydroxyl ions to produce water (eq. 13). The net effect is that the hydroxyl ions move from the positive to the negative electrode and water is transported from negative to positive, resulting in a shuttle of hydrogen between the two electrodes.

The success of the metal hydride electrode depends on a few critical issues:

- capacity to absorb hydrogen reversibly
- cycle life and mechanical stability of the electrode
- nominal operating pressure
- cost

The amount of hydrogen absorbed by the hydride determines the specific energy of the electrode. The absorption must be rapid and reversible. Although there are numerous factors (discussed in more detail below) that affect the characteristics listed above, there are two avenues to enhance the performance: modifying the intermetallic alloys or alternatively improving the cell design and control of the operating conditions.

*Optimization of alloys.*—The composition of the alloy is the most important factor in the performance of the cell, and optimization of the alloy compositions is an active area of research.[45,46,47] There have been two approaches to improving the characteristics of metal hydride materials: modification of existing alloys and development new alloys. Most current work centers on the conventional $AB_5$ materials and $AB_2$ compounds. The goals of alloy modification are:

- increasing the capacity to absorb hydrogen reversibly
- reducing the rate of corrosion
- controlling the catalytic/surface properties
- reducing the cost of raw materials and processing
- lowering the equilibrium hydrogen pressure

For the conventional lanthanum based materials, numerous combinations of metal have been tried, making trade-offs between the desired properties: high capacity for hydrogen absorption, minimal expansion of the metal lattice, resistance to corrosion, and highly catalytic surfaces. $LaNi_5$ is a conventional metal hydride electrode and has good hydrogen absorption capacity but poor stability. Attempts to improve the stability generally result in lower capacity and poor kinetics. Small amounts of Al and Si were found to improve the stability dramatically;[48] replacing half the nickel with cobalt improved the cycle life.[20] The cobalt reduces the expansion of the lattice, and the Al and Si help to form a more protective layer on the surface of the alloy. Mischmetals are commonly used in place of pure elements. These are a mixture of naturally occurring rare-earth elements (Ce, La, Nd, Pr), often added as they are found in nature because of the difficulty and expense of separation. Tadokoro *et al.*[49] varied the value of $x$ between 3.85 and 5.56 in $Mm(Ni\text{-}Co\text{-}Mn\text{-}Al)_x$ to optimize the hydrogen absorption capacity. They found that, with lower values of $x$, the equilibrium pressure was lower, but the capacity diminished. At the same time they observed minimal loss of capacity on cycling. Alloys with Mo, B, Ta, W, and Zr improved the discharge characteristics because of increased surface area and better catalytic properties. Notten and Einerhand[27] reported improved catalytic activity with the addition of palladium to $AB_5$ materials and with double-phase alloys.

An alternative approach is to use the laves phase ($AB_2$) alloys; there are several strategies to improve the characteristics of these intermetallic alloys. Moriwaki *et al.*[50] attempted to optimize the composition of $ZrMn_{0.6}Cr_{0.2}Ni_{1.2}$ by adjusting the A:B ratio and the Mn:Cr ratio. Fetcenko *et al.*[51] compared and contrasted the $AB_5$ and $AB_2$ materials and outlined their approach of compositional and structural disorder to identify

improved electrode materials. By adding different elements, the capacity to store hydrogen, bond strength, catalytic properties, and corrosion resistance of the alloys can be modified.

Sakai *et al.*[52] found that heat treatment was effective in prolonging cycle life, suggesting that the microstructure of the alloy is important. Thin films of alloys were found to behave differently depending on how the films were prepared; however, Sakai *et al.*[53] concluded that the thin films were unsuitable for common applications. Other methods to improve the electrodes include preactivation of the alloy, surface pretreatment, and the use of composite electrodes. Petrov *et al.*[54] added binder and carbon to the electrode, attempting to improve the performance.

For the NiOOH-metal hydride cell, increasing the capacity of the alloy (the negative electrode) results in progressively smaller increases in the specific energy of the cell when the mass of other battery components is considered. Table 3 gives theoretical energy densities for several systems. Ovonics reported a theoretical capacity of 400 A-h/kg for current alloys and projected much larger capacities in the near future. The capacity of the NiOOH electrode is about 300 A-h/kg. This, of course, limits the maximum energy density obtainable for the NiOOH-metal hydride battery. Furthermore, the equilibrium hydrogen pressure must be considered. The more hydrogen that is inserted the greater the equilibrium pressure; consequently not all the capacity may be accessible without raising the cell pressure excessively.

*Stability.*—The importance of the corrosion resistance of the alloys cannot be overstated. The stability of the alloys directly affects the cycle life of the electrode. The goal of the USABC is to obtain 500 to 1000 cycles. It is well known that many of the hydride phases are not thermodynamically stable. Nevertheless, the kinetics are slow at ambient temperatures, and thus this is not a problem for electrochemical applications. Repeated cycling stresses the alloy and tends to break the particles into small fragments (pulverization). The smaller particles have a greater surface area available for adsorption,

there could be loss of contact between particles, and the rate of corrosion may increase as well.

**Table 3.**

| Battery | Theoretical capacity W•h/kg |
|---|---|
| $Pb\text{-}PbO_2$ | 161 |
| Cd-NiOOH | 209 |
| $LaNi_5H_6$-NiOOH | 216 |
| $H_2$-NiOOH | 378 |
| $LaNi_5H_6$-air | 458 |
| $Li\text{-}Li_yMn_2O_4$ | 478 ($0.2<y<1$) |
| $LiC_6\text{-}Li_yCoO_2$ | 644 ($0<y>1$) |
| Na/S | 758 |

Notten and Hokkeling[55] give the corrosion stability of several $AB_5$ systems in strong alkaline solutions and discuss the kinetics of the electrochemical reactions. Willems[20] showed that the capacity of $LaNi_5$ (without additives) decreased rapidly with cycling and that $La(OH)_3$ is formed. Other concerns with corrosion of the alloys are: loss of electrolyte through irreversible reactions and changing of the balance of the electrodes (positive-to-negative capacity ratio). Oxygen generated at the nickel electrode, a mechanism of self-discharge, may oxidize the negative electrode. Markin *et al.* have suggested that the alloy can be protected by coating the surface with Pt black, catalyzing the recombination reaction given in equation 25. Sakai *et al.*[56] microencapsulated the alloy in porous copper or nickel, protecting the alloy from attack by oxygen. The copper

increases the effective electronic conductivity of the solid matrix, acting as a microcurrent collector, and the microencapsulation also increases the thermal conductivity of the electrodes.

*Cell Design.*—The battery designer has substantial control over the performance of the cell. Although a better design does not increase the theoretical capacity to absorb hydrogen or reduce the equilibrium pressure of hydrogen, the operating conditions and design of the battery can be modified to increase the utilization of active material and to reduce the maximum pressure of the cell during charge, for example. Some of the variables that should be considered are:

- particle size
- using partially electrolyte-starved electrodes
- thickness of electrodes and separator
- positive-to-negative-electrode capacity ratio
- temperature of operation and thermal control
- rates of charge/discharge and charge termination
- porosity of the electrode

*Cell pressure.*—Commercial success depends on the amount of hydrogen that can be reversibly cycled without loss of capacity or excessive build up in pressure of hydrogen. A completely sealed system is required for most applications, and a gauge pressure above about 1 bar will require a metal casing, adding significant weight to the system. If excess pressure is vented, water is lost from the cell, and the relative states of charge of the electrodes changes.

When the metal hydride is coupled with a NiOOH positive electrode, the following reactions must also be considered. If the cell is overcharged, oxygen can be generated at the positive electrode

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^-, \qquad (0.401\ V) \qquad (23.)$$

and hydrogen at the negative electrode

$$H_2O + e^- \rightarrow \tfrac{1}{2} H_2 + OH^-, \qquad (-0.828\ V) \qquad (24.)$$

There are also recombination reactions, in an oxygen atmosphere, at the negative electrode

$$\tfrac{1}{2} O_2 + 2M{\cdot}H_{ad} \rightarrow H_2O + 2M, \qquad (25.)$$

and for a hydrogen atmosphere, at the positive electrode

$$\tfrac{1}{2} H_2 + NiOOH \rightarrow Ni(OH)_2 . \qquad (26.)$$

For recombination to occur, the gases must have access to the electrode surface, and the kinetics should be facile. The critical issues are: the rate of mass transfer of $H_2$ or $O_2$, the solubility of the gases in the electrolyte for immersed electrodes, and the catalytic properties of the surface. Hydrogen pressure can build up when the rate of transport in the particles or the kinetics is slow or when the cell is overcharged. If the rate of charge transfer (eq. 9) is greater than the rate of diffusion into the alloy, *i.e.*, $S > 1$, the concentration of hydrogen at the surface of the particle will increase. When the maximum surface concentration is reached, hydrogen gas will be evolved (eq. 24). An analogous situation occurs at the positive electrode, generating oxygen. If the rate of oxygen or hydrogen generation is greater than the rate of recombination, the cell pressure will rise.

Overcharge mechanisms are important to the operation of the cell, particularly for cells in series. It is generally recognized that the recombination of hydrogen at the nickel electrode has poor kinetics and hydrogen generation is not a practical approach for overcharge protection. Consequently, one must rely on oxygen recombination (generated at the positive electrode) for an overcharge mechanism. Making the capacity of the negative electrode larger than that of the positive will promote oxygen generation on

overcharge. This also suggests that electrolyte-starved electrodes may be desirable, allowing the oxygen access to the negative electrode if significant overcharge is anticipated. Because of the poor kinetics of hydrogen recombination, any hydrogen produced on overcharge must be reabsorbed into the alloy. This may require limiting the range over which the electrode is cycled. Making the negative electrode larger than the positive electrode should reduce the hydrogen pressure in the cell. Microencapsulation, mentioned above, was also reported to reduce the operating pressure of the cell, presumably because of more effective oxygen reduction and possibly the prevention of hydrogen evolution.

On overdischarge it is possible to form hydrogen at the NiOOH electrode and oxygen at the negative electrode, although these reactions are unlikely in an alkaline environment unless the cell is severely overdischarged, a consideration for multiple cells in series.

*Self-discharge*.—The rate of self-discharge is an important characteristic of the cell. Oxygen and hydrogen can be generated from the following reactions:

$$NiOOH + \tfrac{1}{2} H_2O \Leftrightarrow Ni(OH)_2 + \tfrac{1}{4}O_2 \qquad (27.)$$

$$M{\cdot}H \Leftrightarrow M + \tfrac{1}{2} H_2 \qquad (28.)$$

Iwakura *et al.*[57] and Sakai *et al.*[52] reported the self-discharge rates for metal hydride electrodes. They distinguished between reversible and irreversible capacity loss. The reversible losses are from the reactions given above and are larger than the rate of self-discharge for the Ni/Cd cell. As expected, they found that for an alloy with a lower equilibrium hydrogen pressure, the rate of self-discharge is reduced. For a sealed system, hydrogen stored in the alloy may desorb from the metal according to equation 28, be transported to the positive electrode, and recombine according to equation 26, but the

kinetics is slow. Oxygen generated (eq. 27) can also diffuse to the negative electrode and recombine (eq. 25), resulting in transport of hydrogen from the negative to the positive electrode.

There are several strategies for reducing the rate of self-discharge. First, select a material with a low equilibrium pressure of hydrogen for the desired range over which $x$ ($H_xAB_5$) is cycled. When the partial pressure of hydrogen in the cell header is equal to the equilibrium pressure, desorption of hydrogen will stop at equilibrium. Second, a barrier can be placed between electrodes, preventing the transport of hydrogen to the positive electrode and transport of oxygen to the negative electrode. This will, however, increase the operating pressure of the cell, and is not considered a practical approach.

Fetcenko *et al.*[58] were able to reduce the rate of self-discharge by: modifying the composition of the alloy, using a more inert separator, and using NiOOH electrodes without nitrate impurities. Their results suggest that shuttle mechanisms for self-discharge are present. Nitrate impurities in NiOOH electrodes are known to increase the rate of self-discharge in the Ni/Cd cell, and the nitrates, as well as other impurities, may contribute to the rate of self-discharge. We are not aware of a detailed analysis of shuttle mechanisms in the literature.

*Competing technologies.*—The absence of toxic materials alone will ensure greater acceptance of the NiOOH-metal hydride cell over Ni/Cd cells. Nonetheless, it is useful to compare the advantages and disadvantages of the metal hydride cells with other batteries. The Ni/Cd cell has a slightly lower specific energy but has a lower rate of self-discharge, greater tolerance for overcharging, better temperature range, and a greater cycle life.[5] The NiOOH-metal hydride cells do not exhibit the "memory effect" seen in Ni/Cd cells (attributed to the cadmium electrode). Metal hydride batteries, however, cannot be charged with the "peak-detect fast chargers" currently used with Ni/Cd cells. Attempts are underway to standardize the size and capacity of the NiOOH-metal hydride

cells and to make them compatible with Ni/Cd chargers.[59] Today NiOOH-metal hydride cells cost about twice as much as comparable Ni/Cd cells.

The lead acid cell is a widely used and well-understood secondary battery. The specific energy of the cell is low, and lead is a toxic. The sodium sulfur cell has exceptional specific energy, but is a high-temperature battery. As a consequence there are problems with materials corrosion, sealing, and freeze-thaw cycles. Cycle life is short for cells in series, largely attributed to failure of the β"-alumina separators. The NiOOH-metal hydride cell has a comparable specific energy, but the required supply of pressurized hydrogen presents a safety issue. A sealed system is required to allow for the recombination of hydrogen and oxygen, and the $H_2$-NiOOH cell is not practical for traction applications. Characteristics and prospects for other battery systems can be found in the literature.[60]

The NiOOH-metal hydride cell has a much lower specific energy than lithium cells (see table 3). Although there are some secondary lithium cells on the market, they are not widely used. The lithium cells have two serious drawbacks. First, pure lithium is unstable and reacts irreversibly with the electrolyte. This has been circumvented to some extent by replacing the lithium foil negative electrode with an intercalation material, such as carbon. This concept (dual lithium ion insertion or "rocking-chair" cells) has been used in commercial cells for portable appliances.[61] Second, there is no practical overcharge or overdischarge mechanism in these cells, making control of charging and operation of series of cells more difficult. The lithium rechargeable cell is an active area of research, and improvements can be expected.

*Assessment of Research Needs.*—Numerous technical challenges remain in the development of the NiOOH-metal hydride cell, particularly for electric-vehicle applications, where low cost and high performance are required. Some possible future research areas are:

- detailed mathematical modeling
- design and scale-up of large batteries
- analysis of thermal effects
- optimization of alloy composition
- charging/discharging multiple cells in series
- fundamental studies of kinetic mechanisms including overcharge/overdischarge mechanisms
- development of a positive electrode with a larger specific energy
- fundamental studies of transport in intermetallic alloys
- fundamental studies of the state of hydrogen in candidate metal-hydride electrodes

Detailed mathematical modeling and design and scale-up considerations are important to the development of metal-hydride cells. Electric vehicles, for example, require much larger batteries than commercially available NiOOH-metal hydride cells. Matsumoto *et al.*[62] identified several problems with the scale-up of NiOOH-metal hydride cells. In particular, they saw high temperatures and high pressures and lower utilization of active material in larger batteries. They postulated that the low utilization was due to the distribution of electrolyte in the cell. Little work has been published on modeling and design of metal-hydride electrodes.

Thermal management is critical for the NiOOH-metal hydride cell. Achieving a large number of cycles, low cell pressure, and high specific energy, will depend on a good understanding of temperature distributions in large cells. As we have seen, the equilibrium pressure of hydrogen increases with temperature. Physicochemical properties are strongly dependent on temperature. In addition, the charge acceptance of the NiOOH electrode is poor above 35°C. A thorough analysis of thermal effects on the performance of these cells is needed.

Some researchers have investigated solid-state metal hydride batteries requiring a polymer or other solid electrolyte.[63] Advantages usually cited include: no corrosive solvent present, the cell can easily be configured into a variety of shapes, ease of

manufacture, and combining the functions of separator and electrolyte. Some of the possible problems are: polymer electrolytes have low conductivity at room temperature, loss of contact with the electrolyte, and poor overcharge and overdischarge capabilities.

Optimization of the composition of the alloys can be expected to continue as an active area of research. Klein and Salkind[64] estimated the costs of $AB_5$ alloys. Although not critical for space applications and less critical for small appliances, cost is a key consideration for electric-vehicle applications. They point out that major improvement is needed in this area. Research would focus on development of alloys made from raw materials of lower cost and reducing the manufacturing costs.

Because the specific energy of the NiOOH-metal hydride cell is limited by the positive electrode, it should be viewed as a candidate for meeting only the midterm goals of the USABC. To meet the long-range goals, the positive electrode must be improved or replaced to achieve a significantly larger specific energy in metal hydride cells.

Individual cells connected in series will inevitably be at different states of charge. Although it is possible to monitor the potential of single cells, it may not be practical to monitor individual cells in a large battery or to provide for charging of individual cells. Overcharge and overdischarge mechanisms provide a means to pass current without altering the state of charge of the cell. A theoretical study of the effect of operating multiple cells in series with and without overcharge mechanisms is warranted. This analysis would also apply to batteries other than the NiOOH-metal hydride cell.

## Acknowledgments

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies, Electric and Hybrid Propulsion Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

## List of Symbols

| | |
|---|---|
| $c_i$ | concentration of species $i$, mol/m$^3$ |
| $D$ | diffusion coefficient, m$^2$/s |
| F | Faraday's constant, 96,487 C/mol |
| $i$ | current density, A/m$^2$ |
| $I$ | superficial current density, A/m$^2$ |
| $L$ | width of cell, m |
| $n$ | number of electrons transferred |
| $N_i$ | flux of species $i$, mol/m$^2$-s |
| $p$ | pressure or fugacity, bar |
| $R_s$ | radius of solid particles, m |
| $S$ | dimensionless ratio defined in equations 16 and 19 |
| $t_i^o$ | transference number of species $i$ |
| $U$ | open-circuit potential, V |
| $v$ | velocity, m/s |
| $z_+$ | charge number |
| $\delta$ | thickness of electrode, m |
| $\Phi$ | electrical potential, V |
| $\kappa$ | electrical conductivity, S/m |
| $\mu_i$ | electrochemical potential of species $i$, J/mol |
| $\varepsilon$ | porosity of electrode |

## Subscripts

| | |
|---|---|
| s | solid phase |
| t | maximum concentration |
| + | cation |
| - | anion |
| o | solvent |

| | |
|---|---|
| e | electrolyte |
| 1 | solid phase |
| 2 | electrolyte phase |

**Superscripts**

| | |
|---|---|
| θ | standard cell potential |
| * | secondary reference state |
| o | pure component |
| ❒ | volume average quantity |

---

## References


1 A. F. Andresen and A. J. Maeland, eds., *Hydrides for Energy Storage*, Proceeding of an International Symposium, International Association for Hydrogen Energy, Pergamon Press, Oxford (1978).

2 F. E. Lynch, "Metal Hydride Practical Applications," *J. Less-Common Met.*, **172-174**, 943-958 (1991).

3 D. Malinik, "Better Batteries for Low-Power Jobs," *Electronics Design*, p. 18, July 23, 1992.

4 "Nickel Hydride Extends Battery Life, but T2000SX Could be Trimmer, Faster," *PC Magazine*, p. 36, May 28, 1991.

5 C. H. Small, "Nickel-Hydride Cells Avert Environmental Headaches," *EDN*, pp. 156-161, December 10, 1992.

[6] E. J. Cairns, "A New Opportunity for Electrochemical Energy Conversion," *Interface*, **1**, 38-39 (1992).

[7] T. Sakai, H. Miyamura, N. Kuriyama, I. Uehara, M. Muta, A. Takagi, U. Kajiyama, K. Kinoshita, and F. Isogai, "Nickel-metal Hydride Battery for Electric Vehicles," *J. Alloys and Compounds*, **192**, 159-160 (1993).

[8] S. R. Ovshinsky, M. A. Fetcenko, and J. Ross, "A Nickel Metal Hydride Battery for Electric Vehicles," *Science*, **260**, 176-181 (1993).

[9] A. C. Switendick, "Electronic Structure of Transition Metal Hydrides," in *Transition Metal Hydrides*, R. Bau, ed., Advances in Chemistry Series, Vol 167, 264-282 (1978).

[10] W. M. Mueller, J. P. Blackledge, and G. G. Libowitz, *Metal Hydrides*, Academic Press, New York (1968).

[11] M. S. Whittingham, "The Role of Ternary Phases in Cathode Reactions," *J. Electrochem. Soc.*, **123**, 315-320 (1976).

[12] Buschow, *Rep. Prog. Phys.*, **45**, 937-1039 (1982).

[13] D. G. Ivey and D. O. Northwood, "Storing Energy in Metal Hydrides, A Review of the Physical Metallurgy," *J. Mater. Sci.*, **18**, 321-347 (1983).

[14] L. Schlapbach, ed., *Hydrogen in Intermetallic Compounds II*, in Topics in Applied Physics, Vol. 67, Springer-Verlag (1992).

[15] D. A.. Corrigan and S. Srinivasan, eds., *Proceedings of the Symposium on Hydrogen Storage Materials, Batteries, and Electrochemistry*, The Electrochemical Society, Pennington, N. J. (1992).

16 Metal-Hydrogen Systems. Fundamentals and Applications, Proceedings of the First International Symposium Combining "Hydrogen in Metals" and "Metal Hydrides," *Zeit. für Phys. Chem. Neue Folge*, **164**, 747 (1989).

[17] Z. P. Zagrodnik and K. R. Jones, "Multiple Cell Common Pressure Vessel Nickel-Hydrogen Battery," *J. Power Sources*, **36**, 375-384 (1991).

[18] E. W. Justi, H. H. Ewe, A. W. Kalberlah, and N. M. Saridakis, "Electrocatalysis in the Nickel-Titanium System," *Energy Conv.*, **10**, 183 (1970).

[19] H. F. Bittner and C. C. Badcock, "Electrochemical Utilization of Metal Hydrides," *J. Electrochem. Soc.*, **130**, 193C-198C (1983).

[20] J. J. G. Willems, "Metal Hydride Electrodes Stability of LaNi5-Related Compounds," *Philips J. Res.*, **39**, Suppl. No.1, 1-94 (1984).

[21] F. A. Lewis, *The Palladium Hydrogen System*, Academic Press, London (1967).

[22] H. Frieske and E. Wicke, "Magnetic Susceptibility and Equilibrium Diagram of PdHn," *Ber. Bunsenges. Phys. Chem.*, 77, 48 (1973).

[23] P. K. Subramanyan, "Electrochemical Aspects of Hydrogen in Metal," in *Comprehensive Treatise of Electrochemistry*, J. O'M Bockris, B. E. Conway, E. Yeager, R. E. White, eds., Vol. 4, Plenum Press, New York (1981).

[24] A. N. Frumkin, "Hydrogen Overvoltage and Adsorption Phenomena," in *Advances in Electrochemistry and Electrochemical Engineering*, C. W. Tobias and P. Delahay, eds., Vol. 3, pp. 287-391, Wiley-Interscience.

[25] L. Schlapbach, "Surface Properties and Activations," in *Hydrogen in Intermetallic Compounds II*, Topics in Applied Physics, Vol. 67, L. Schlapbach, ed., Springer-Verlag, 15-95(1992).

[26] T. B. Flanagan, "Kinetics of Hydrogen Absorption and Desorption," in *Hydrides for Energy Storage*, A. F. Andresen and A. J. Maeland, eds., Proceeding of an International Symposium, International Association for Hydrogen Energy, Pergamon Press, Oxford (1978).

27 P. H. L. Notten and R. E. F. Einerhand, "Electrocatalytic Hydride-Forming Compounds for Rechargeable Batteries," *Adv. Mater.*, **3**, 343-350 (1991).

[28] M. Doyle, T. F. Fuller, and J. Newman, "Modeling of Galvanostatic Charge and Discharge of the Lithium/Polymer/Insertion Cell," *J. Electrochem. Soc.*, **140**, 1526-1533 (1993).

[29] T. F. Fuller, M. Doyle, and J. Newman, "Simulation and Optimization of the Dual Lithium Ion Insertion Cell," May 1993, LBL-33426, *J. Electrochem. Soc.*, submitted.

[30] John Newman, *Electrochemical Systems*, Prentice-Hall, Englewood-Cliffs, N. J. (1991).

[31] B. E. Conway and J. Wojtowicz, "Time-scales of Electrochemical Desorptions and Sorption of H in Relation to Dimensions and Geometries of Host Metal Hydride Electrodes," *J. Electroanal. Chem.*, **326**, 277-297 (1993).

[32] H. Züchner, T. Rauf, and R. Hempelmann, "Electrochemical Measurements of Hydrogen Diffusion in the Intermetallic Compound $LaNi_5$," *J. Less-Common Met.*, **172-174**, 611-617 (1991).

[33] Z. Li, Y. Lei, C. Chen, J. Wu, and Q. Wang, "The Relation between Discharge Capacities and Discharge Current Densities of Hydride Electrodes," *J. Less-Common Met.*, **172-174**, 1260-1264 (1991).

[34] Y. Sakamoto, K. Kuruma, and Y. Naritoma, "Electrochemical Hydrogen Charge Characteristics of Metal Hydride Electrodes," *Ber. Bunsenges. Phys. Chem.*, **96**, 1813-1818 (1992).

[35] R. Pollard and J. Newman, "Mathematical Modeling of the Lithium-Aluminum, Iron Sulfide Battery, " *J. Electrochem. Soc.*, **128**, 491-502 (1981).

36 J. J. Reilly, Y. Josephy, and J. R. Johnson, "Kinetics of the Isothermal Decomposition of Lanthanam Nickel Hydride, *Zeit. für Phys. Chem. Neue Folge*, **164**, 1241-1247 (1989).

37 J. Newman and T. W. Chapman, "Restricted Diffusion in Binary Solutions," *AIChE J.*, **19**, 343-348 (1973).

38 J. Newman and W. Tiedemann, "Porous-Electrode Theory with Battery Applications," *AIChE J.*, **21**, 25-41 (1975).

39 M. Vitanen, "A Mathematical Model for Metal Hydride Electrodes," *J. Electrochem. Soc.*, **140**, 936-942 (1993).

40 J. B. Kim, T. V. Nguyen, and R. E. White, "Thermal Mathematical Modeling of a Multicell Common Presssure Vessel Nickel-Hydrogen Battery," *J. Electrochem. Soc.*, **139**, 2781-2787 (1992).

41 D. Y. Fan and R. E. White, "A Mathematical Model of a Sealed Nickel-Cadmium Battery - Effects of Intercalation and Oxygen Reactions," *J. Electrochem. Soc.*, **138**, 2952-2960 (1991).

42 D. Bernardi, E. Pawlikowski, and J. Newman, "A General Energy Balance for Battery Systems," *J. Electrochem. Soc.*, **132**, 5-12 (1985).

[43] J. McBreen, "The Nickel Oxide Electrode," in *Modern Aspects of Electrochemistry*, Vol. 21, R. E. White, J. O'M Bockris, and B. E. Conway, eds., Plenum Press, New York, (1991).

[44] D. A. Corrigan and A. H. Zimmerman, eds., *Proceedings of the Symposium on Nickel Hydroxide Electrodes*, The Electrochemical Society, Inc., Pennington, N. J. (1990).

[45] T. Sakai, T. Hazama, H. Miyamura, N. Kuriyama, A. Kato, and H. Ishikawa, "Rare-earth-based Alloy Electrodes for a Nickel-metal Hydride Battery," *J. Less-Common Met.*, **172-174**, 1175-1184 (1991).

[46] M. Tadokoro, M. Nogami, Y. Chihano, M. Kimoto, T. Ise, K. Nishio, and N. Furukawa, "Development of Hydrogen-absorbing Alloys for Nickel-metal Hydride Secondary Batteries," *J. Alloys and Compounds*, **192**, 179-181 (1993).

[47] T. Sakai, H. Miyamura, N. Kuriyama, A. Kato, K. Oguro, and H. Ishikawa, "Metal Hydride Anodes for Nickel-Hydrogen Secondary Battery," *J. Electrochem. Soc.*, **137**, 795-799 (1990).

[48] T. Sakai, H. Miyamura, N. Kuriyama, A. Kato, K. Oguro, H. Ishikawa, and C. Iwakura, "The Influence of Small Amounts of Added Elements on Various Anode Performance Characteristics for $LaNi_{2.5}Co_{2.5}$-Based Alloys," *J. Less-Common Met.*, **159**, 127-139 (1990).

[49] M. Tadokoro, K. Moriwaki, K. Nishio, M. Nogami, N. Inoue, Y. Chihano, M. Kimoto, T. Ise, R. Maeda, F. Mizutaki, Mi Takee, and N. Furukawa, "Development of Hydrogen Absorbing Alloys for Nickel-metal Hydride Secondary Batteries," *Proceedings of the Symposium on Hydrogen Storage Materials, Batteries, and Electrochemistry*, D. A.. Corrigan and S. Srinivasan, eds., The Electrochemical Society, Pennington, N.J. (1992).

[50] Y. Moriwaki, T. Gamo, H. Seri, and T. Iwaki, "Electrode Characteristics of C15-type Laves Phase Alloys," *J. Less-Common Met.*, **172-174**, 1211-1218 (1991).

[51] M. A. Fetcenko, S. Venkatesan, and S. R. Ovshinsky, "Selection of Metal Hydride Alloys for Electrochemical Applications," Proceedings of the Symposium on Hydrogen Storage Materials, Batteries, and Electrochemistry, D. A.. Corrigan and S. Srinivasan, eds., The Electrochemical Society, Pennington, N.J. (1992).

[52] T. Sakai, H. Miyamura, N. Kuriyama, H. Ishikawa, and I. Uehara, "Rare-earth Based Hydrogen Storage Alloys for Rechargeable Nickel-metal Hydride Batteries," *J. Alloys and Compounds*, **192**, 155-157 (1993).

[53] T. Sakai, H. Ishikawa, H. Miyamura, and N. Kuriyama, "Thin Film Preparation of Hydrogen Storage Alloys and Their Characteristics as Metal Hydride Electrodes," *J. Electrochem. Soc.*, **138**, 908-915 (1990).

[54] K. Petrov, A. Visitin, S. Srinivasan, and J. Appleby, "Optimization of Composition and Structure of Metal-Hydride Electrodes," Abstract No. 27, 183rd Meeting of the Electrochemical Society, Honolulu, HI (1993).

[55] P. H. L. Notten and P. Hokkeling, "Double-phase Hydride Forming Compounds: A New Class of Highly Electrocatalytic Materials," *J. Electrochem. Soc.*, **138**, 1877-1885 (1991).

[56] T. Sakai, H. Ishikawa, K. Oguro, C. Iwakura, and H. Yoneyama, "Effects of Microencapsulation of Hydrogen Storage Alloy on the Performance of Sealed Nickel/Metal Hydride Batteries," *J. Electrochem. Soc.*, **134**, 558-562 (1987).

[57] C. Iwakura, Y. Kajiya, H. Yoneyama, T. Sakai, K. Oguro, and H. Ishikawa, "Self-discharge Mechanism of Nickel-Hydrogen Batteries Using Metal Hydride Electrodes," *J. Electrochem. Soc.*, **136**, 1351-1355 (1989).

[58] M. A. Fetcenko, S. Venkatesan, and S. R. Ovshinsky, "Self-discharge Characteristics of V-Ti-Zr-Ni Based Alloys," Abstract No. 51, 183rd Meeting of the Electrochemical Society, Honolulu, HI (1993).

[59] T. Albano, "Sizing Up Laptop Batteries," *PC Magazine*, January 12, 1993, p. 29.

[60] C. W. Tobias, Chairman, *Assessment of Research Needs for Advanced Battery Systems*, National Materials Advisory Board Commision on Engineering and Technical Systems, Publication NMAB-390, Washington (1982).

[61] "Sony's Lithium Manganese Rechargeable Battery (AA Size)," *JEC Press*, Inc., p. 26 (February 1988).

[62] I. Matsumoto, M. Ikoma, A. Ohota, H. Matsuda, and Y. Matsushita, "A Sealed Ni/MH Battery for EV," Abstract No. 26, 183rd Meeting of the Electrochemical Society, Honolulu, HI (1993).

[63] N. Kuriyama, T. Sakai, H. Miyamura, A. Kato, and H. Ishikawa, "Proton Conduction of Tetramethylammonium Hydroxide Pentahydrate $(CH_3)_4NOH \bullet 5H_2O$, and its Applications to Nickel-Metal Hydroxide Battery," *J. Electrochem. Soc.*, **137**, 355-356 (1990).

[64] M. Klein and A. Salkind, "Design and Cost Analysis of a Nickel-Metal Hydride Electric Vehicle Battery," Abstract No. 25, 183rd Meeting of the Electrochemical Society, Honolulu, HI (1993).

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
TECHNICAL INFORMATION DEPARTMENT
BERKELEY, CALIFORNIA 94720

ABH488
LBL Libraries