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The development of hydrogen storage electrode alloys for nickel hydride batteries

Kuochih Hong

Hong Enterprises Co., 1790 Rollingwoods Drive, Troy, MI 48098, USA

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Abstract

The development of hydrogen storage electrode alloys in the 1980s resulted in the birth and growth of the rechargeable nickel hydride (Ni/MH) battery. In this paper we describe briefly a semi-empirical electrochemical/thermodynamic approach to develop/screen a hydrogen storage alloy for electrochemical application. More specifically we will discuss the AB_x Ti/Zr-based alloys. Finally, the current state of the Ni/MH batteries including commercial manufacture processes, cell performance and applications is given.

Keywords: Metal hydrides; Nickel/metal hydride batteries

1. Introduction

In the 1970s, studies of the hydrogen storage alloys and metal hydride technology were initiated and developed [1,2]. One of the fruits of these studies was their electrochemical applications, more specifically the development of commercial hydrogen storage electrodes and the rechargeable nickel hydride batteries in 1980s [3–13]. The rapid growth of wireless 3C-industries (communication, computer and consumer electronics) helped the mass production of commercial nickel hydride (Ni/MH) batteries. In 1999, the sales of Ni/MH cells were estimated to be about 900 million cells.

In this paper, we will review and discuss the development of high capacity and long-life hydrogen storage electrode materials as used for the commercialization of Ni/MH batteries.

2. Metal hydrides for applications in Ni/MH batteries

A hydrogen storage material, M, can form hydride, MH_x, by the interaction with hydrogen gas and/or electrochemical method as shown in Eqs. (1) and (2):

$$M(s) + \tfrac{1}{2}xH_2(g) \rightleftarrows MH_x(s) \quad (1)$$

$$M + xH_2O + xe^- \rightleftarrows MH_x + xOH^- \quad (2)$$

However, not every hydrogen storage alloy can be charged and discharged electrochemically as given in Eq. (2). As the active material of a hydrogen storage electrode, a hydrogen storage alloy has two major roles: an electrochemical catalyst for the charge/discharge of hydrogen and a hydrogen storage reservoir/source. Therefore, a good hydrogen storage (hydride) electrode material must meet the following criteria:

1. high reversible hydrogen storage capacity, i.e. >1 wt.%;
2. good electrochemical catalyst for hydrogen charge (reduction/absorption) and discharge (desorption/oxidation);
3. easy activation;
4. excellent corrosion resistance in alkaline electrolyte;
5. suitable hydrogen equilibrium pressure, not higher than 5 bar at 25°C;
6. good charge/absorption and discharge/desorption kinetics and efficiency;
7. long cycle life;
8. small hysteresis in charge/discharge isotherms;
9. low cost.

3. The development of commercial hydrogen storage electrode alloys

3.1. Three main stages of hydride electrode alloy development

1. The concept of hydrogen storage alloy for electrochemical application began in the 1970s [5–13]. Some

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AB- and AB_5-type hydrogen storage materials were known, such as TiNi, TiFe, $LaNi_5$ and these were tested. However, these alloys are either difficult to activate, have a short cycle life, and/or low capacity. Therefore, they are not suitable for the commercial application.

2. Later, in the early 1980s, Hong and co-workers [3,4] first studied the Ti/Zr-based AB_2-type Ti/Zr–V–Ni–M systems. These alloys include the following three families: (a) $TiV_{2-x}Ni_x$, (b) $Ti_{1-y}Zr_yV_{2-x}Ni_x$ and (c) $Ti_{1-y}Cr_yV_{2-x}Ni_x$ [3,4], which became the basis of Ovonic's Ti/Zr-based AB_2-type alloys. The capacity of these alloys is up to 450 mAh g^{-1} at 25 mA g^{-1} current density. Among these three families, the Ti–V–Ni alloys studied have high capacity, but short cycle life. However, the Ti–Zr–V–Ni and Ti–Cr–V–Ni alloys have a long cycle life. The microstructures of these alloys generally are multiphase and crystalline, consisting of a hydrogen storage phase and one or more electrochemical catalytic phases [14]. On the other hand, about the same time as Hong, Willems et al. [15] reported the rare earth-based AB_5-type Ln–Ni–Co–Mn–Al alloys. These cobalt-containing alloys have less capacity than $LaNi_5$, but have a good cycle life. These early 1980s studies in Ti/Zr-based AB_2-type Ti/Zr–V–Ni–M systems and rare earth-based AB_5-type Ln–Ni–Co–Mn–Al alloys opened the window for the commercialization of rechargeable nickel hydride batteries.
3. Finally, in late 1980s and early 1990s, Hong [16] and Gamo et al. [17] independently studied AB_x-type multi-component alloys away from the stoichiometric restriction of AB_2 and AB_5 types. As a result, more new alloys having improved performance including more capacity and/or long cycle life were developed.

3.2. A semi-empirical method for developing a hydrogen storage electrode alloy

Hong [16,18–21], based on the thermodynamic and electrochemical studies, presented a semi-empirical method to develop good AB_x-type multi-component hydrogen storage electrode alloys. In this approach, a potential candidate alloy, $A_aB_bC_c\ldots$ for a rechargeable hydrogen storage electrode has to satisfy three basic conditions:

1. $A_aB_bC_c\ldots$ contains at least 5–85 at.% of Ni, preferably 15–65 at.%;
2. contains at least 10–80 at.% of hydride formers selected from Ti, Zr, and rare earth metals, preferably 15–65 at.%;
3. contains 0.1–15% of two or more modifiers preferably selected from but not limited to the group of V, Nb, Mg, Ca, Hf, Mn, Cr, Co, Mo, Cu, Al, Sn, Bi, Si, Sb, Fe, Zn and Ag;
4. the calculated heat of hydride formation H_h is between -2.5 and -10.50 kcal $mole^{-1}$ H. When the elements A, B, C, ... are chosen, a set of atomic ratio, a, b, c, ... can be obtained by the following equation:

$$H_h = -\frac{aH_h(A) + bH_h(B) + cH_h(C) + \cdots}{2(a+b+c+\cdots)} + K \quad (3)$$

where $H_h(A)$, $H_h(B)$, $H_h(C)$, ... are the heat of formation of hydrides of metals A, B, C, ..., respectively, in the unit of kcal $mole^{-1}$ H_2; K is a constant depending on the heat of formation (H^f) of the alloy, $A_aB_bC_c\ldots$ and the heat of mixing (H_h^m) of the hydride AH, BH, CH, ..., as shown in Eq. (4):

$$H_h = -\frac{aH_h(A) + bH_h(B) + cH_h(C) + \cdots}{2(a+b+c+\cdots)} + H_h^m \quad (4)$$

The values of K were given as 0.5, -0.2 and -1.5 kcal $mole^{-1}$ H for $a+b+c+\cdots$ equal to 2, 3 and 6, respectively [15,20]. For $a+b+c+\cdots$ not equal to 2, 3 and 6, it can be normalized to 3 for Ti/Zr-based alloy and 6 for rare earth-based alloy before calculation. The heats of hydride formation of metals, in kcal $mole^{-1}$ H_2, are given as $H_h(Mg) = -17.9$, $H_h(Ti) = -15.0$, $H_h(V) = -7.0$, $H_h(Cr) = -1.81$, $H_h(Mn) = -2.0$, $H_h(Fe) = 4.0$, $H_h(Co) = 3.5$; $H_h(Ni) = 1.8$, $H_h(Al) = -1.38$, $H_h(Y) = -27$, $H_h(Zr) = -19.5$, $H_h(Nb) = -9.0$, $H_h(Zr) = -19.5$, $H_h(Hf) = -19.5$; $H_h(Pd) = -4.0$, $H_h(Mo) = -1.0$, $H_h(Ca) = -21.0$, $H_h(Si) = -1.0$, $H_h(C) = -1.0$, $H_h(Cu) = 2.0$, $H_h(Ta) = -10.0$; H_h(rare earth metals) $= -27.0$, $H_h(Li) = -21.0$, $H_h(Na) = -13.4$, $H_h(K) = -13.7$, $H_h(Rb) = -12.5$, $H_h(B) = 2.83$; $H_h(Sn) = 2.05$, $H_h(Sb) = 5.5$, $H_h = -20.2$, $H_h(Sc) = -28.9$, $H_h(Zn) = -1.2$, $H_h(Ag) = 1.0$, $H_h(S) = -1.0$, $H_h(N) = -0.5$; $H_h(W) = -0.50$, $H_h(P) = -0.30$.

This semi-empirical approach is totally free of any crystal structure restriction and has been found very useful in developing new Ti/Zr transition metal-based and rare earth-based electrode alloys [16,18–26]. Table 1 lists some useful hydrogen storage electrode alloys including both Ti/Zr-based and Mm-based alloys (Mm is the mischmetal, a mixture of rare earth metals).

However, it should be noted that

1. for the Ti/Zr-based alloy the heat of hydride formation is preferably in the range between -4.5 and -8.0 kcal $mole^{-1}$ H;
2. for the rare earth-based alloys, the boundary of the heat of hydride formation is between -2.35 and -4.80 kcal $mole^{-1}$ H;
3. for high rate applications, the nickel content is no less than 35 at.%, preferably greater than 43 at.% for the Ti/Zr-based alloy and no less than 50 at.% for the rare earth-based alloy. Table 2 shows the comparison of the electrochemical performance between the AB_x Ti/Zr-based and AB_x rare earth-based alloys.

Furthermore, based on this approach, we found that a Ti/Zr-based alloy having a calculated heat of hydride formation

Table 1
The capacity (mAh g^{-1} at 100 mA g^{-1}) of some AB_x hydrogen storage electrode alloys

Alloy no.	Composition	C (mAh g^{-1})	H_h (kcal $mole^{-1}$ H)
601	$Ti_{10}Zr_{20}Ni_{35}Cr_{3.5}Mn_{4.5}V_{25}Al_{2.0}$	375	−7.10
602	$Ti_8Zr_{29}Ni_{44}Cr_{3.0}Mn_{10.0}V_{3.0}Mm_{2.0}$	360	−7.01
603	$Ti_{24}Zr_{17}Ni_{41}Cr_{2.0}Mn_{7.0}V_{9.0}Al_{0.0}$	358	−6.90
604	$Ti_{12}Zr_{27}Ni_{48}Cr_{1.5}Mn_{8.0}V_{1.5}Mm_{2.0}$	354	−6.90
605	$Ti_9Zr_{29}Ni_{47}Cr_{2.0}Mn_{10}Nb_{2.0}Mm_{2.0}$	322	−6.86
606	$Ti_{10}Zr_{30}Ni_{48}Cr_{1.7}Mn_{7.0}Nb_{3.0}Hf_{0.3}$	334	−6.80
607	$Ti_{10}Zr_{29}Ni_{47}Cr_{2.0}Mn_{8.0}V_{4.0}Al_{1.0}$	342	−6.70
608	$Ti_{22}Zr_{18}Ni_{40}Cr_{4.0}Mn_{8.0}V_{7.0}Al_{1.0}$	335	−6.65
609	$Ti_{30}Zr_{10}Ni_{47}Cr_{2.0}Mn_{7.0}Nb_{3.0}$	308	−5.94
610	$Mm_{17}Ni_{61.6}Co_{12.5}Mn_{6.7}Al_{2.2}$	285	−4.71
611	$Mm_{16.8}Ni_{59.5}Co_{12.4}Mn_{6.7}Al_{4.5}$	280	−4.72
612	$Mm_{16}Ni_{64.9}Co_{10.4}Mn_{4.8}Al_{4.0}$	295	−4.44
613	$Mm_{16.4}Ni_{60}Co_{14}Mn_{4.9}Al_{4.7}$	275	−4.52
614	$Mm_{16}Ni_{74}Sn_{5.0}Mn_{4.0}Mo_{1.0}$	285	−4.53
615	$Mm_{16}Ni_{58}Co_{10}Mn_{9.4}Al_{5.0}Ti_{1.0}$	295	−4.81

Table 2
Comparison of the electrochemical performance of AB_x Ti/Zr-based and AB_x rare earth-based alloys

Performance	Ti/Zr-based alloy	Rare earth-based alloy
Capacity (mAh g^{-1})	230–430	230–310
Electrode preparation	Dry pressing	Dry or pasting
Pre-assembly activation	Generally required	Not needed
Rate capability	Good/excellent	Excellent
Cycle life	Good/excellent	Good/excellent

more negative than −6.5 kcal $mole^{-1}$ H can have an electrochemical capacity of 340–430 mAh g^{-1} and that a Ti/Zr-based alloy having a calculated heat of hydride formation between −6.0 and −4.5 kcal $mole^{-1}$ H will only have an electrochemical capacity of 230–310 mAh g^{-1}, the same range as that of rare earth-based alloys. In later case, the rate capability and working potential of a Ti/Zr alloy is similar to that of a rare earth-based alloy.

4. The Ni/MH_x battery

The combination of a hydride electrode with a nickel positive electrode forms a Ni/MH cell. The electrochemical reaction of a Ni/MH cell can be represented by the following half-cell reactions.

4.1. Normal charge reactions (forward reaction is charging, the reverse reaction is discharging)

Nickel (positive) electrode:

$$x\mathrm{Ni(OH)_2} + x\mathrm{OH^-} \rightleftarrows x\mathrm{NiOOH} + x\mathrm{H_2O} + x\mathrm{e^-} \quad (5)$$

Hydride (negative) electrode:

$$\mathrm{M} + x\mathrm{H_2O} + x\mathrm{e^-} \rightleftarrows \mathrm{MH}_x + \mathrm{OH^-} \quad (6)$$

Overall reaction:

$$x\mathrm{Ni(OH)_2} + \mathrm{M} \rightleftarrows x\mathrm{NiOOH} + \mathrm{MH}_x \quad (7)$$

4.2. Over-charge

In the construction of an actual cell especially a sealed cell, the capacity of the hydride negative electrode is higher than that of nickel positive electrode. In this positive-limited cell, oxygen evolution will occur in the positive electrode during over-charge. The oxygen generated will diffuse to the hydride negative electrode to combine the hydrogen to form water as indicated in Eqs. (10) and (11). This is the so-called oxygen recombination in a cell. Therefore, the internal pressure build-up will be eliminated or reduced substantially.

Nickel electrode:

$$2y\mathrm{OH^-} \rightleftarrows y\mathrm{H_2O} + \tfrac{1}{2}y\mathrm{O_2} + 2y\mathrm{e^-} \quad (8)$$

Hydride electrode:

$$\mathrm{MH}_x + 2y\mathrm{H_2O} + 2y\mathrm{e^-} \rightleftarrows \mathrm{MH}_{x+2y} + 2y\mathrm{OH^-} \quad (9)$$

$$\tfrac{1}{2}y\mathrm{O_2} + \mathrm{MH}_{x+2y} \rightleftarrows \mathrm{MH}_x + y\mathrm{H_2O} \quad (10)$$

$$\mathrm{O_2} + 2\mathrm{H_2O} + 4\mathrm{e^-} \rightleftarrows 4\mathrm{OH^-} \quad (11)$$

$$\tfrac{1}{2}p\mathrm{O_2} \rightleftarrows \mathrm{MH}_{x-2r}\mathrm{O}_p + r\mathrm{H_2} \quad (12)$$

$$q\mathrm{H_2O} + q\mathrm{e^-} \rightleftarrows q\mathrm{OH^-} + \tfrac{1}{2}q\mathrm{H_2} \quad (13)$$

4.3. Over-discharge

For a positive-limited and negative-pre-charged Ni/MH cell, hydrogen evolution will occur at the nickel electrode during over-discharge. The hydrogen generated at the nickel electrode will diffuse to the hydride electrode and be absorbed by the alloy in the electrode. Thus, the hydride electrode will not be oxidized and no internal pressure is

build-up. These reactions are given in the following equations:

At the nickel electrode:

$$pH_2O + pe^- \rightleftarrows pOH^- + \tfrac{1}{2}pH_2 \quad (14)$$

At the hydride electrode:

$$H_p + pOH^- \rightleftarrows M + pH_2O + e^- \quad (15)$$

$$M + \tfrac{1}{2}pH_2 \rightleftarrows MH_p \quad (16)$$

During a prolonged and/or in a high current over-discharge, the hydrogen recombination rate at the hydride electrode is generally not fast enough to keep recharging the hydride electrode. Therefore, the electrode will eventually discharge completely and oxygen evolution will occur at the hydride electrode. Consequently the internal pressure of the cell will build-up and the hydride electrode may be partially oxidized and damaged.

5. Current status of commercial nickel hydride batteries

5.1. The manufacture process [26–29]

The making of nickel hydride batteries mainly includes (1) a negative hydride electrode line, (2) a nickel positive electrode line, (3) a cell assembly line, and (4) a cell formation line. The active material in negative electrodes is hydrogen storage alloy(s). The negative electrode can be made by a wet slurry pasting method or a dry pressing process with or without sintering. The current collector substrate is nickel or nickel plated steel or copper in the form of mesh, perforated foil or expanded sheet. The dry press method with sintering method generally gives a better rate performance. The nickel positive electrode generally is made by a pasting method in which the slurry of the active material ($Ni(OH)_2$ plus additives) is impregnated into the nickel foam/fiber substrate.

5.2. Performance

The performance of a nickel hydride cell depends on many factors, including the electrode preparation, active material and its amount, and additives in each electrode, negative/positive capacity ratio, volume and concentration of KOH electrolyte, separator and activation. In general, a well-made Ni/MH cell can show a very good electrochemical properties.

1. High capacity: the capacity of a Ni/MH cell keeps increasing. For example, the capacity of a AAA-sized cell increased from 500 in 1996 to 550, then 600 and now (in 2000) to 750 mAh.
2. High working potential: the discharge capacity above 1.20 V is up to more than 80% of the total at 1*C*-rate for a AAA size Ni/MH cell, as shown in Fig. 1.
3. Excellent rate capability: a high rate Ni/MH Sc-sized cell can discharge up to 20*C*-rate, the power is higher than 500 W kg^{-1} when fully charged and 400 W kg^{-1} nearly fully discharged, equal to or better than a Ni/Cd Sc cell. Fig. 2 shows the discharge curves of a high rate Ni/MH Sc cell.
4. Low self discharge rate: the charge retention after 1 month at ambient temperature is above 80%.
5. Long cycle life: higher than 1000 cycles on a 1*C*-rate charge–discharge cycle, 100% depth of discharge.

5.3. Applications

The applications of Ni/MH cells have been broadened to many areas such as (1) cellular phones, (2) cordless phones, (3) toys, (4) portable computers, (5) CD players, (6) Camcorders, (7) power tools, (8) two-way radios, (9)

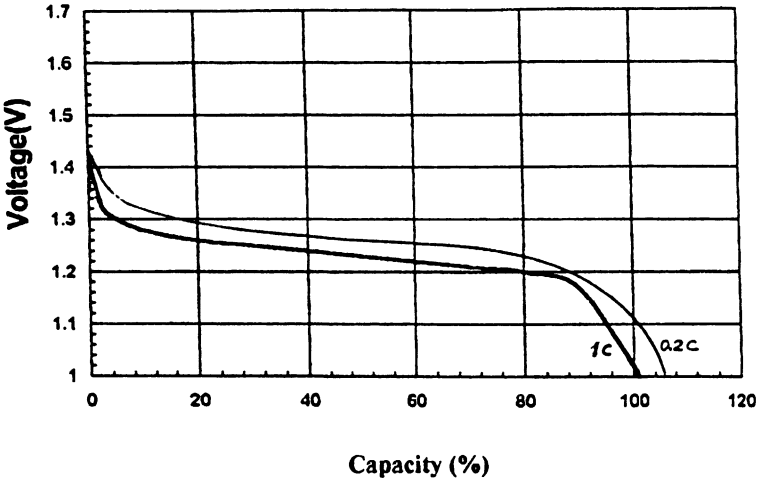

Fig. 1. The typical discharge curves for an AAA-650 mAh cell using a Ti/Zr-based alloy $Ti_{10.2}Zr_{30.0}Ni_{48.2}Cr_{2.0}Nb_{2.8}Mn_{6.8}$.

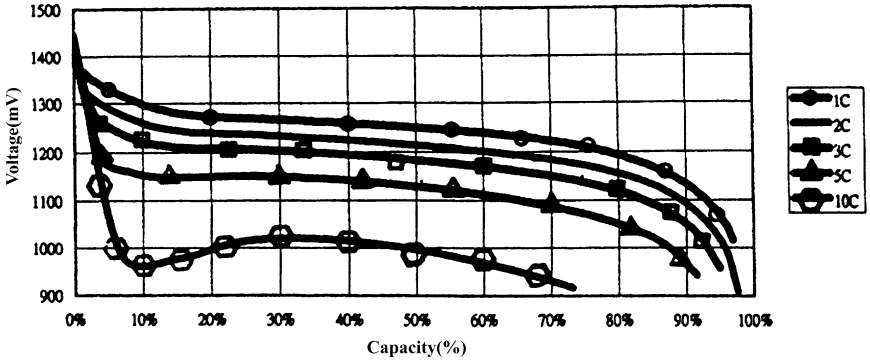

Fig. 2. Typical discharge curves for an EFBC Ni/MH Sc-size cell (1*C*-rate = 3.0 A).

uninterrupted power sources (UPS), and (10) electric vehicles, especially electric bicycles. Ni/MH batteries will increase the applications into the new portable wireless electronic products. However, Ni/MH batteries are facing very strong competition from lithium batteries in small size cells. It is expected that Ni/MH batteries will focus on areas such as high power and/or high capacity types to penetrate and replace the Ni/Cd battery market.

6. Conclusions

Hydrogen storage alloys have been applied successfully to the rechargeable Ni/MH batteries. A semi-empirical electrochemical/thermodynamic method can be used to develop/screen these hydrogen storage electrode alloys. This method is suitable both for the Ti/Zr-based and rare earth metal-based alloys. From the heat of hydride formation calculation, one can obtain a Ti/Zr-based alloy having a useful capacity from 230 up to 450 mAh g^{-1}, and rare earth metal-based alloys having a capacity from 230 to about 320 mAh g^{-1}. In the same capacity range, a Ti/Zr-based alloy has a similar high rate capability and high working potential as that for a rare earth metal-based alloys. The performance of a Ni/MH cell is excellent, superior to that of a Ni/Cd cell. Therefore, there are many applications for Ni/MH batteries. Ni/MH cells are on the way to replace the market of Ni/Cd cells.

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