

Development and commercialization of nickel–metal hydride secondary batteries

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(Received April 7, 1994)

Abstract

Hydrogen-absorbing alloys used for the negative electrode of nickel–metal hydride (Ni–MH) secondary batteries must combine the two roles of a hydrogen storage media and an electrochemical catalyst. Alloys for secondary batteries must also offer endurance during charge/discharge cycles. Hydrogen-absorbing alloys for batteries have been developed from these viewpoints. The hydrogen-absorbing alloys used for Ni–MH can be divided into two main types: the LaNi_5 -type and the TiNi_x -type. In the LaNi_5 -type, we have substituted La for Misch-metal (Mm), which is a mixture of rare earth elements such as La, Ce, Pr and Nd, and we have partially substituted Ni for Co and Al to lengthen the charge/discharge cycle life. To adjust the hydrogen-absorbing equilibrium pressure, we have partially substituted Ni for Mn and Al. Another type of positive electrode, different from that of Ni–Cd secondary batteries, was developed for the use with Ni–MH to study the environment. A Zn–Co additive prevented electrode swelling by suppressing the production of γ -NiOOH at charging. As a result, cadmium-free, low-pollution, nickel electrodes were developed. As for cell construction materials, new separators were also developed that suggest improved cell reliability. Ni–MH can now be practically charged at 1C using the $-\Delta V$ charging method, and discharge at 4C. Its 1C charge/discharge cycle life is more than 500 cycles. This enables the commercial application of Ni–MH to a wide variety of cordless equipment.

Operating principle

Nickel–metal hydride batteries use the same nickel electrode that is used in conventional alkaline batteries for the positive electrode and a hydrogen-absorbing alloy electrode for the negative electrode. This makes the development of a hydrogen-absorbing alloy electrode an important subject.

Hydrogen-absorbing alloys can reversibly absorb and desorb hydrogen. In the gas phase, hydrogen gas is rapidly absorbed, then desorbed on the alloy (gas–solid reaction). In the electrode reaction, the alloy electrochemically absorbs and desorbs hydrogen in an alkaline solution (electrochemical reaction). From the viewpoint of equilibrium behavior, the electrochemical reaction is the same as the gas–solid reaction. Therefore, we will first describe the gas–solid reaction, then the electrochemical reaction.

On the surface of the hydrogen-absorbing alloy, hydrogen gas dissociates to atomic adsorbed hydrogen (H_{ad}). In absorption, H_{ad} diffuses into the alloy and produces a metal hydride. In desorption, the reverse reaction occurs. This equilibrium reaction of absorbing and desorbing is indicated in eqn. (1). In hydrogen absorption, the reaction is exothermic:



A pressure–composition isotherm (P – C isotherm) is useful for indicating the hydrogen-absorbing and desorbing characteristics of the alloy. It indicates the relationship between the hydrogen composition and the equilibrium hydrogen pressure under a constant temperature (Fig. 1).

In a region of low hydrogen composition, the hydrogen exists in the solid–solution phase (α phase) in the alloy. When the hydrogen composition increases, the hydride phase (β phase) appears. At the region of coexistence between these two phases, the P – C isotherm exhibits a plateau in which the hydrogen equilibrium pressure does not increase in spite of an increase in the hydrogen composition. When the hydrogen composition increases further, the α phase disappears and only the β phase remains. Then, the hydrogen equilibrium pressure increases with increases in hydrogen composition [1].

The higher the temperature, the more the hydrogen equilibrium pressure rises. The hydrogen-absorbing reaction obeys the van't Hoff equation (eqn. (2)). The logarithm of the equilibrium pressure is proportional to the inverse of the temperature:

$$\ln P = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \quad (2)$$

where P is the hydrogen equilibrium pressure, ΔH the entropy, ΔS the enthalpy, R the gas constant, and T the temperature.

Van't Hoff plots of several hydrogen-absorbing alloys are shown in Fig. 2. Most of the ΔS is the enthalpy change when hydrogen gas condenses to metal hydride, and any hydrogen-absorbing alloys reveal almost a constant value ($\Delta S = -31 \text{ cal K}^{-1} \text{ mol}^{-1}$) [2].

For battery use, the hydrogen-absorbing alloy must have an equilibrium pressure of about 0.1 MPa under room temperature. Therefore, in Fig. 2, the alloys within the dotted line are suitable.

Next, we will describe the electrochemical reaction of the hydrogen-absorbing alloy. The absorption and desorption reaction is indicated in eqn. (3):

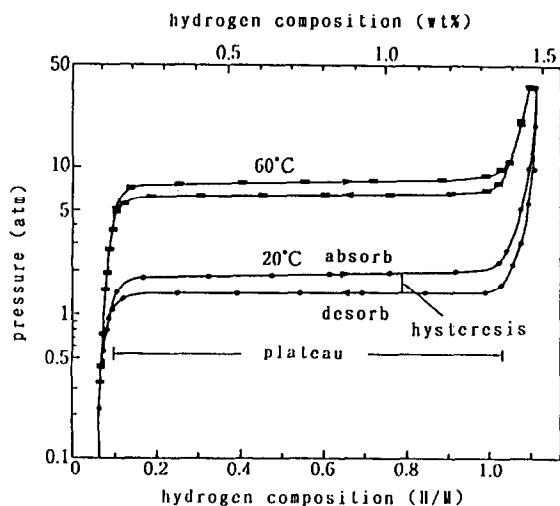


Fig. 1. Pressure–composition isotherm for $\text{LaNi}_5\text{-H}_2$ system.

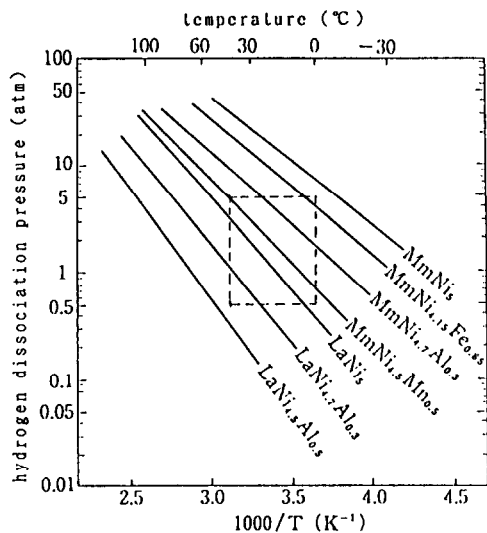


Fig. 2. Van't Hoff plots of several hydrogen-absorbing alloys. Mm: La (28%), Ce (40%), Nd (14%).

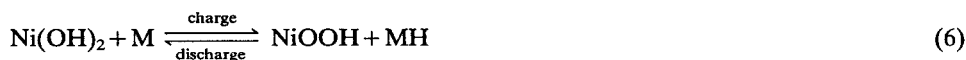
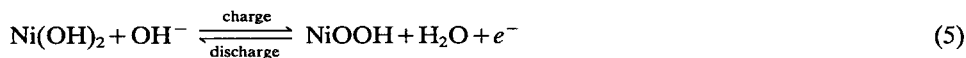


Electrochemically produced metal hydride (MH) is simultaneously in equilibrium with hydrogen gas, as shown in eqn. (1).

Equation (3) obeys the Nernst equation, so the potential is induced from the hydrogen equilibrium pressure (eqn. (4)) [3].

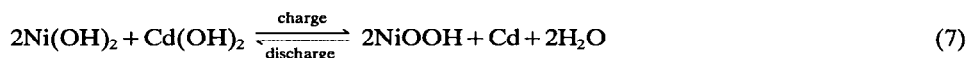
$$E_0 = - \frac{RT}{2F} \ln P_{\text{H}_2} \text{ (versus NHE)} \quad (4)$$

And the charge/discharge reaction of the nickel electrode and the nickel–metal hydride battery are indicated in eqns. (5) and (6), respectively:



$$E_{\text{emf}} = 1.32 \text{ V}$$

On the other hand, the charge/discharge reaction of the nickel–cadmium battery is given by eqn. (7):



$$E_{\text{emf}} = 1.32 \text{ V}$$

The two batteries are also interchangeable because the nickel–metal hydride battery has almost the same electromotive force (E_{emf}) as the nickel–cadmium battery, and the same operating voltage (about 1.2 V).

Because $\text{Cd}(\text{OH})_2$ is deposited on the surface of the cadmium electrode in discharging, the electron transfer and ionic conduction are disturbed. Therefore, the availability of the reactant degrades and the capacity become lower. However, in the hydrogen-absorbing alloy electrode, the electron transfer is good, both in charging and discharging, because only hydrogen permeates into the alloy. Moreover, ionic migration does not occur in the solid phase, only in the liquid phase, so the ionic conduction is also good. In addition, electric conduction in the electrode is good because of the high electric conductivity of hydrogen-absorbing alloy. As a result, the utilization of the reactant is almost 100%, and the alloys have a large capacity.

In the charge/discharge cycle, the cadmium electrode becomes also passive and the utilization of reactant gradually degrades. However, this does not occur in the hydrogen-absorbing alloy, but in the charge/discharge cycle, cracks are formed in the alloy and the active surface appears. For these reasons, it is possible to design a higher capacity battery by using hydrogen-absorbing alloy for the negative electrode than would be possible with a nickel–cadmium battery.

Current status

Recent advances in electronics technology have accelerated the trend towards smaller and lighter electrical and electronic devices. For the secondary batteries that serve as power supplies for these devices, there is also an increasing demand for the development of more compact, lighter batteries with high energy density and high performance.

In the 1980s, research and development led to the sealed nickel–metal hydride battery as a higher energy density battery for the next generation. However, this battery still presented numerous problems in achieving higher energy density, a long cycle life, superior charge/discharge characteristics and high reliability.

A number of battery manufacturers tackled these problems, and in 1990, Sanyo Electric and Matsushita Battery succeeded in the large-scale commercialization of the world's first sealed nickel–metal hydride batteries. Since then, other battery makers have commercialized or announced plans for commercializing similar products.

Technical challenges

Development of the negative electrode – hydrogen-absorbing alloy for use in batteries

Hydrogen-absorbing alloys were discovered in the 1960s [4], and various studies on metal hydride electrode materials were done in the 1970s and 1980s [5–8]. To use a hydrogen-absorbing alloy as the negative electrode material for a high-performance cell, it must allow a large amount of hydrogen to be absorbed and desorbed in an alkaline solution, its reaction rate must be high, and it must have a long charge/discharge cycle life.

Much of this study was conducted on LaNi_5 based alloys [9–17] and TiNi_x -based alloys [5, 18, 19]. Sanyo Electric, Matsushita Battery and most other battery manufacturers have been using LaNi_5 -based rare earth–nickel-type alloys [19, 20]. Some manufacturers are using a TiNi_x -based alloy [21].

It was thought that rare earth–nickel-type alloys had a large exchange current density and that they absorbed a large amount of hydrogen, thereby enabling the construction of high energy density batteries. The first step in this development was

to obtain a sufficient cycle life for use as an electrode material. Figure 3 shows the charge/discharge cycle characteristics of alloys in which part of the nickel component was replaced with cobalt. Misch-metal (Mm), which is a mixture of rare earth elements such as lanthanum, cesium, praseodymium and neodymium, was used in place of lanthanum. It was found that the partial replacement of nickel with cobalt and the substitution of the lanthanum content with Mm was very useful in improving the charge/discharge cycle life. But such alloys have insufficient capacity, as shown in Fig. 4 [22]. After studying the effect that their compositions had on the charge/discharge capacity, it was concluded that the best alloy elements were $\text{Mm}(\text{Ni-Co-Al-Mn})_x$. This alloy led to the commercialization of sealed nickel-metal hydride batteries. All of the battery manufacturers who use a rare earth-nickel-type alloy for the negative electrode material use similar alloys with slightly different compositions. Figure 5 [15] shows P - C isotherms of the hydrogen-absorbing alloy. To obtain a sufficient amount of hydrogen for the charge/discharge reaction, it is necessary to lower the hydrogen-absorbing equilibrium pressure. It was found that the partial replacement of nickel

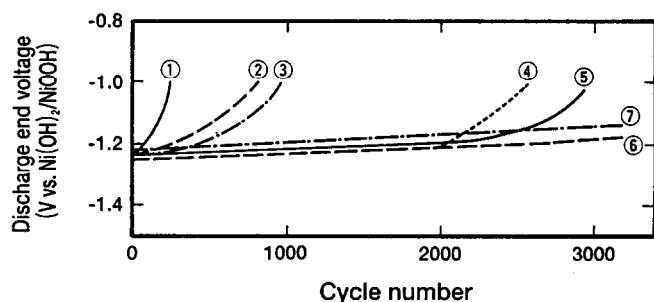


Fig. 3. Cycle characteristics of rare earth-nickel-type hydrogen-absorbing alloy electrodes. Charge: $(190 \text{ mAh g}^{-1}) \times 0.8 \text{ h}^{-1}$; discharge: $(190 \text{ mAh g}^{-1}) \times 0.6 \text{ h}^{-1}$, and pressure: 5.0 atm. Hydrogen-absorbing alloy: 1, LaNi_5 ; 2, LaNi_4Co ; 3, LaNi_3Co_2 ; 4, LaNi_2Co_3 ; 5, $\text{La}_{0.8}\text{Ce}_{0.2}\text{Ni}_2\text{Co}_3$; 6, $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_2\text{Co}_3$; 7, MmNi_2Co_3 (Mm: 25 wt.% La, 50 wt.% Ce, 7 wt.% Pr, 18 wt.% Nd).

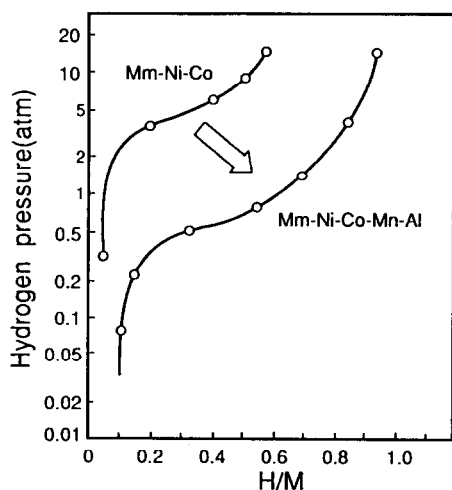


Fig. 4. Pressure-composition isotherms of rare earth-nickel-type hydrogen-absorbing alloys.

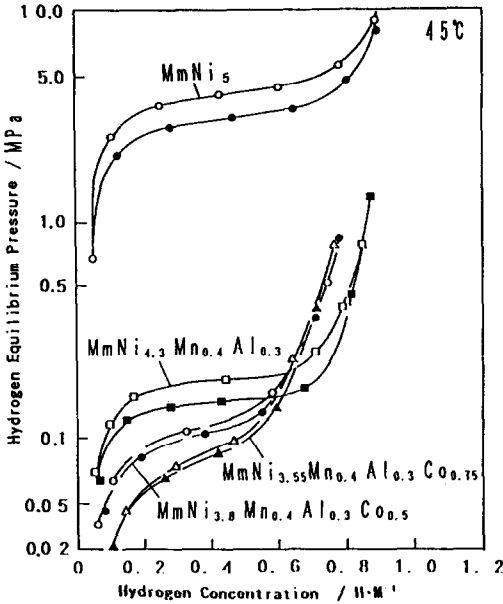


Fig. 5. Influence of manganese, aluminum, and cobalt substitution for MmNi_5 alloy system.

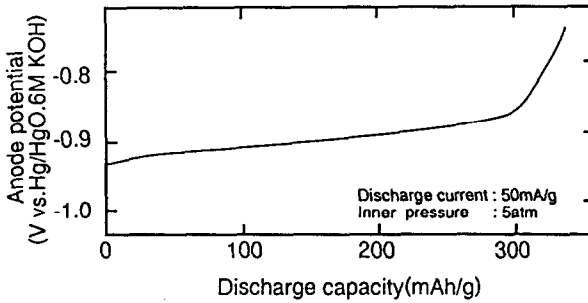


Fig. 6. Discharge characteristics of an electrode using the alloy $\text{MmNi}_{3.05}\text{Co}_{0.95}\text{Al}_{0.19}\text{Mn}_{0.57}$.

and cobalt by aluminum and manganese is useful for lowering the hydrogen-absorbing pressure [15, 17, 20, 23]. Aluminum was also found to be effective in improving the cycle life [22].

Improvement of $\text{Mm}(\text{Ni-Co-Al-Mn})_x$ -type alloys were achieved in various ways. Figure 6 [17] shows the discharge characteristics of an electrode using an alloy ($\text{MmNi}_{3.05}\text{Co}_{0.95}\text{Al}_{0.19}\text{Mn}_{0.57}$) with a long cycle life as well as a high capacity of 330 mAh g^{-1} which has a non-stoichiometric composition [24].

It was found that $\text{Mm}(\text{Ni-Co-Al-Mn})_x$ -type alloys with boron, molybdenum, tungsten, tantalum or zirconium added showed superior high-rate discharge characteristics [25, 26]. Figure 7 [25] shows the relationship between discharge rate and discharge capacity for the initial charge/discharge cycle of alloys in which various elements were added to $\text{Mm}(\text{Ni-Co-Al-Mn})_x$. Without the additive, the discharge capacity dropped significantly. However, it was found that alloys with these elements added showed less of a decrease in discharge capacity at a high discharge current. It

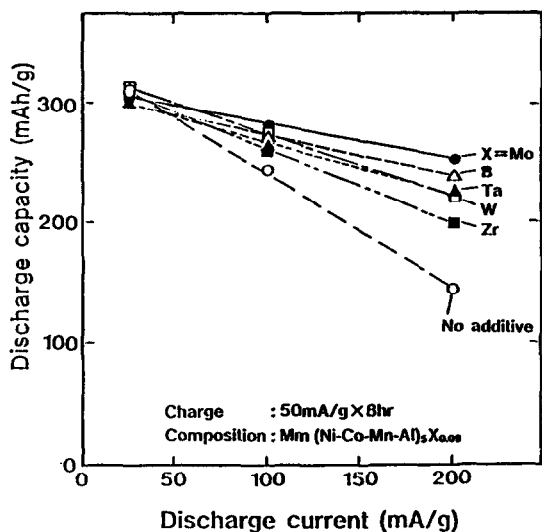


Fig. 7. Discharge rate vs. discharge capacity for the initial charge/discharge cycle of alloys. Charge: $(50 \text{ mA g}^{-1}) \times 8 \text{ h}$; discharge: $MmNi_{3.2}Co_{1.0}Mn_{0.6}X_{0.09}$, X: Mo, B, Ta, W or Zr. Mm: La (25%), Ce (50%), Pr (7%), Nd (14%).

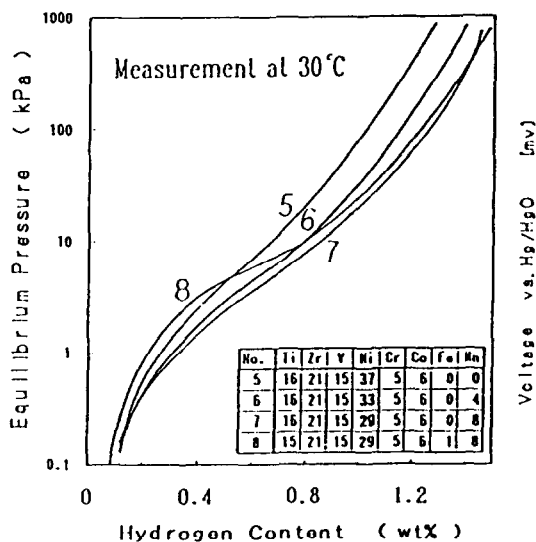


Fig. 8. Pressure-composition isotherms of Ti-Zr-Ni system alloys.

was assumed that reactivity is improved by the increased reaction surface area of the hydrogen-absorbing alloy and its catalytic activity.

Ti-Ni-type alloys for electrode materials have also been developed. Figure 8 [21] shows the $P-C$ isotherms of a Ti-Ni-type alloys. Multi-component alloys (Ti-Zr-V-Ni-Cr-Co-Fe-Mn) have been studied and it has been reported that the alloy raises the discharge capacity of the cell.

Development of the positive electrode

Nickel electrodes have been used for nickel–cadmium batteries, and they are usually given a cadmium additive to suppress the deterioration of the electrode characteristics [27]. It is also known that a cadmium additive raises the oxygen overvoltage and improves the charge efficiency at high temperatures [28]. Most of the Japanese battery manufacturers have been studying cadmium-free nickel electrodes which are suited to the nickel–metal hydride battery and are better for the environment.

The technology for a cadmium-free nickel electrode was thus developed. Figure 9 shows the swelling rate of sintered nickel electrodes with various additives. The result shows that eliminating cadmium from the usual additives (cadmium and cobalt) negates the effects of swelling prevention. However, substituting zinc for cadmium has almost the same effect as the cadmium–cobalt additive. It is believed that the swelling prevention was due to suppressing the production of γ -NiOOH at charging [29]. It was found that utilization of the active material when charging at a high temperature was significantly influenced by the electrolyte. Figure 10 [20] shows an example of the results. The Figure indicates that a three-component electrolyte, KOH–NaOH–LiOH, provided the highest discharge capacity when charged at a high temperature [30]. This three-component electrolyte is considered to be the best match for the nickel hydroxide-active material with a zinc–cobalt additive.

To increase the energy density of the nickel electrode, it is important to put as many nickel hydroxide particles as possible into a given substrate, and improve its utilization. Figure 11 [31] shows that the use of a highly porous nickel fiber felt and cobalt monoxide powder makes it possible to obtain a high energy density.

Development of cell materials and cell construction

To improve the performance of positive and negative electrodes and obtain a high reliability, it is also important to develop materials for constructing the cell and optimizing the cell construction.

Outside of the electrode materials, one of the most important materials is the separator. It influences virtually all cell characteristics, including cycle life and storage

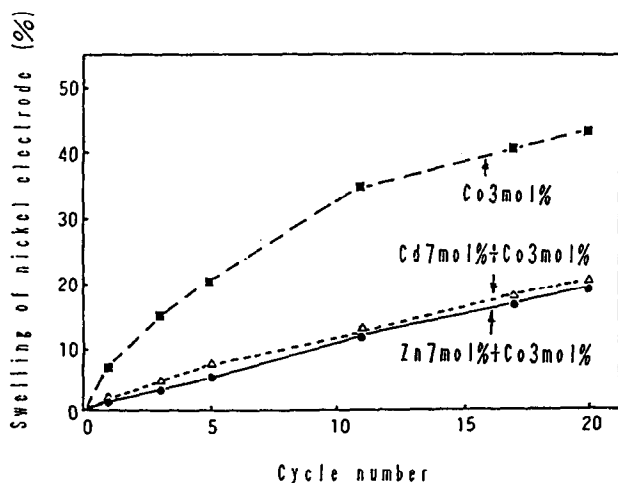


Fig. 9. Swelling rate of sintered nickel electrodes with various additives. Nickel electrode: sintered type; charge: $(289 \text{ mA g}^{-1}) \times 1.5 \text{ h}$, discharge: 289 mA g^{-1} to 1.0 V vs. Hg/HgO.

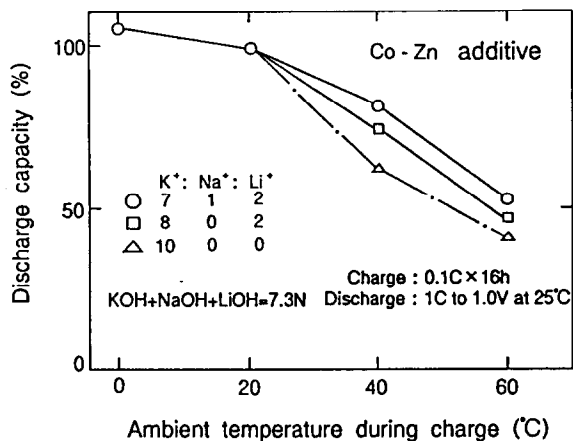
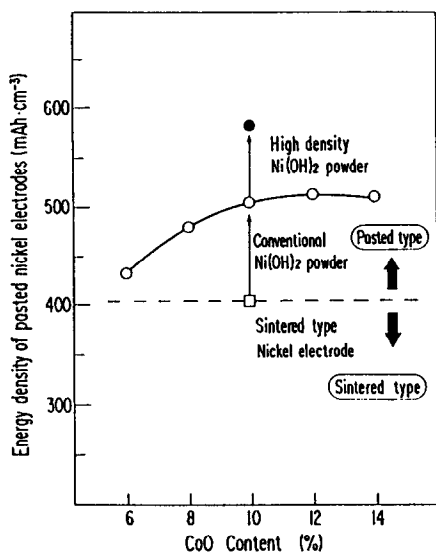


Fig. 10. Discharge capacity of test cells using nickel electrode with a zinc-cobalt additive vs. ambient temperature during charge. Charge: $0.1C \times 16$ h; discharge: 1C; end voltage: 1.0 V, and temperature at discharge: 25 °C.



Energy density of posted nickel electrodes

Fig. 11. Energy density of posted nickel electrodes.

characteristics. Figure 12 [23] shows that the use of a sulfonated polypropylene separator improves the storage characteristics.

One important factor in the cell construction technology is reliability. When considering the reaction mechanism of nickel-metal hydride batteries, the charging product of the hydrogen-absorbing pressure of the electrode must be controlled. It was found that the upper limit for a suitable value is 20 atm at 70 °C [32]. To obtain this value, we had to select a hydrogen-absorbing alloy with an adequate equilibrium

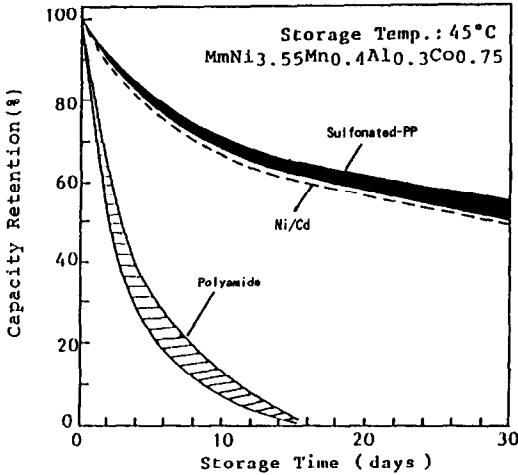


Fig. 12. Storage characteristics of batteries using various separators. PP: polypropylene.

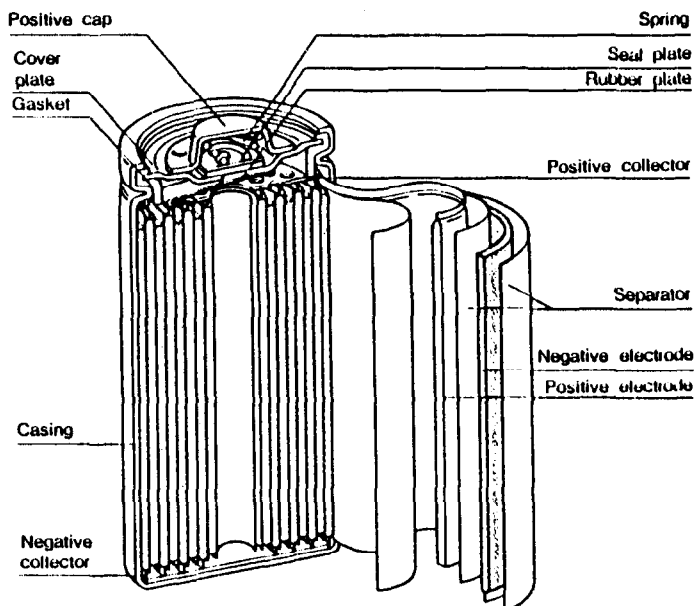
absorbing pressure and an adequate capacity balance between positive and negative electrodes. Cases outside of this value do not provide sufficient reliability. This discharge product of the hydrogen-absorbing alloy electrode is water, which diffuses to the electrolyte solution. This is different from the instance of nickel-cadmium batteries, and the electrolyte concentration must be properly controlled for nickel-metal hydride batteries. We found the upper limit for a suitable electrolyte concentration to be 35 wt.% [32]. This is independent of battery scale or shape. A higher concentration will result in a considerable degradation of the positive electrode. In addition, the operating pressure of the safety vent and the constructed pressure of the electrodes in the cell are also important.

Figure 13 shows a typical structural design for nickel-metal hydride batteries of the cylindrical and rectangular type. Basically, their structure is similar to that of the nickel-cadmium battery. The difference is in the volume ratio of the nickel electrode, which is higher than that in nickel-cadmium batteries.

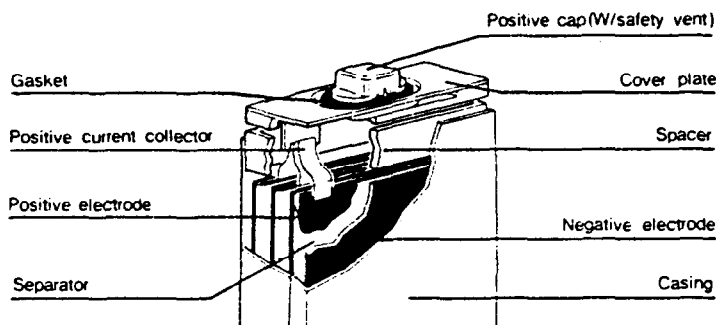
Types of nickel-metal hydride batteries and their characteristics

Japanese battery manufacturers have developed various types of batteries. Figure 14 shows the charge/discharge characteristics of the AA-size nickel-metal hydride battery in comparison with the nickel-cadmium battery produced by Sanyo Electric. Its capacity density is 1.5 to 1.8 times higher than that of nickel-cadmium batteries. The other characteristics are very similar to those of the nickel-cadmium battery. Using the $-\Delta V$ charging method, a charge at 1C is possible. The battery can be discharged at a 4C rate, as shown in Fig. 15 [33]. Figure 16 [33] shows the charge/discharge cycle characteristics of the AA-size battery under the condition of a 1C charge using the $-\Delta V$ method and a 1C discharge to 100% depth-of-discharge. At the 600th cycle, the batteries maintain their initial discharge capacity, which shows their long cycle life.

Figure 17 [34] shows the discharge characteristics of a rectangular-type battery. The rectangular-type battery also has a higher capacity than the same size nickel-cadmium battery. Rectangular-type batteries are effective from the viewpoint of energy density



(a)



(b)

Fig. 13. Designs for cylindrical-type and rectangular-type nickel-metal hydride batteries.

in a packed battery. However, they have disadvantages in production. Battery manufacturers have developed a structure for the rectangular-type battery.

Commercial impact

- The outstanding characteristics of the nickel-metal hydride battery are as follows:
- (i) the discharge capacity is 80% higher than the standard nickel-cadmium battery;
 - (ii) a low internal resistance which enables a high-rate discharge;
 - (iii) a long charge/discharge cycle life which can last over 500 cycles, and
 - (iv) cell materials which are adaptable to the environment.

As a result, the nickel-metal hydride battery has been a good seller right from the start of commercialization.

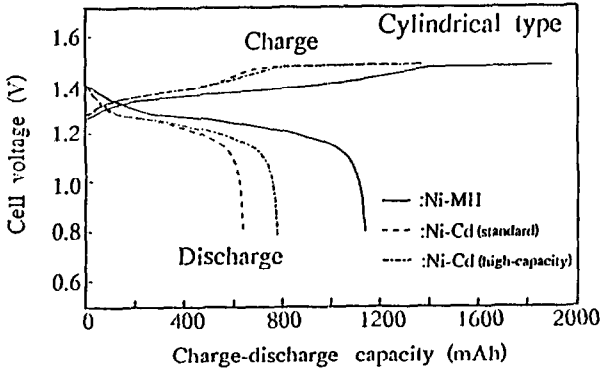


Fig. 14. Comparison of charge/discharge characteristics of a nickel-metal hydride battery and nickel-cadmium batteries; cell AA size.

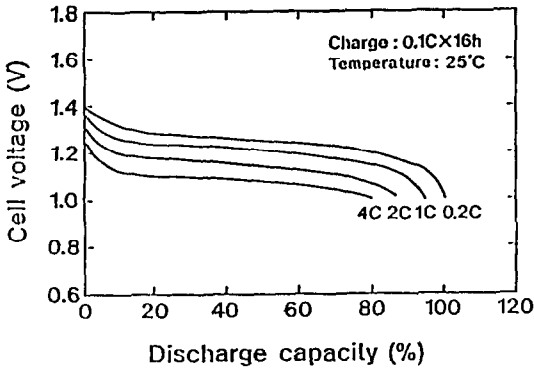


Fig. 15. Discharge rate characteristics; cell AA size.

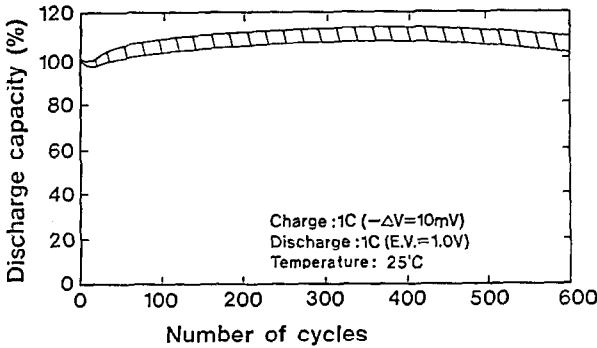


Fig. 16. Charge/discharge cycle characteristics; cell: AA size, charge: 1C ($-\Delta V = 10\text{ mV}$); discharge: 1C (EV=1.0), and temperature: 25 °C.

Today, a rectangular-type battery joins the conventional cylindrical models, extending the range to meet a growing number of applications. Tables 1 and 2 show the ratings of cylindrical- and rectangular-type nickel-metal hydride batteries produced by Sanyo

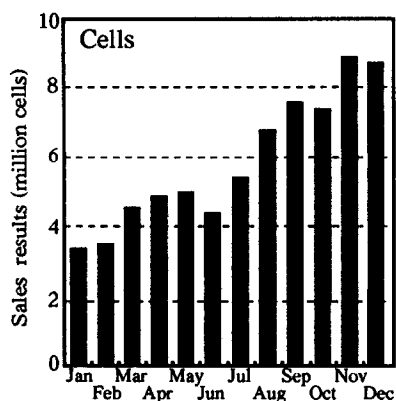
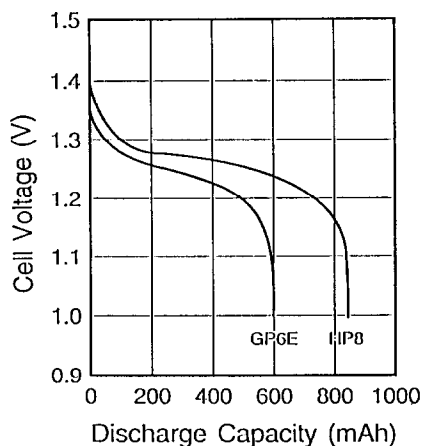


Fig. 17. Discharge characteristics of rectangular-type batteries. Comparison of HP8 (Ni-MH) and GP6E (Ni-Cd) batteries. Charge: 1C mA for 1.3 h, discharge: 160 mA to 1.0 V, and temperature: 25 °C.

Fig. 18. Nickel-metal hydride secondary batteries sales results in Japan, 1993. Source: Japan Storage Battery Association.

TABLE 1

Rating of nickel-metal hydride secondary batteries, cylindrical-type

	Cylindrical-type			
Model number	HR-AA	HR-4/3A	HR-4/5A	HR-A
Voltage (V)	1.2	1.2	1.2	1.2
Capacity (mAh) ^a	1200	2500	1600	1800
Quick charge				
Current (mA)	1200	2500	1600	1800
Time (h)	1.2	1.2	1.2	1.2
Dimensions (incl. tube)				
Diameter (mm)	14.2	17.0	17.0	17.0
Height (mm)	50.0	67.0	43.0	50.0
Weight (g)	26	51	30	35

^aAverage capacity at 0.2C rate.

Electric. Table 3 shows typical applications of the nickel-metal hydride battery. The nickel-metal hydride battery has become one of the keys to down-sizing electrical and electronic devices and raising the level of their functions.

Figure 18 shows the sales results for nickel-metal hydride batteries in Japan, in 1993 (Japan Storage Battery Association).

In addition to the favorable characteristics mentioned above, these sealed nickel-metal hydride batteries offer voltage which are similar to those of nickel-cadmium batteries, and are interchangeable with nickel-cadmium batteries, so they are expected to find widespread application as a new type of battery for compact cordless equipment.

TABLE 2

Rating of nickel-metal hydride secondary batteries, rectangular-type

	Rectangular-type		
	HF-B1	HF-B2	HF-A1
Model number	HF-B1	HF-B2	HF-A1
Voltage (V)	1.2	1.2	1.2
Capacity (mAh) ^a	600	850	850
Quick charge			
Current (mA)	600	850	850
Time (h)	1.2	1.2	1.2
Dimensions (incl. tube)			
Width (mm)	17.0	17.0	17.0
Height (mm)	48.0	48.0	67.0
Thickness (mm)	6.1	8.3	6.1
Weight (g)	17	24	24

^aAverage capacity at 0.2C rate.

TABLE 3

Typical applications of nickel-metal hydride secondary batteries

Application	Types
Personal computer	cylindrical
Cellular phone	cylindrical, rectangular
Transceiver	cylindrical
VCR camera	cylindrical
Shaver	cylindrical

The demands has rapidly increased for nickel-metal hydride batteries to be used as power sources for handy type computers, communications equipment, video cassettes recorders, shavers, etc.

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