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High Capacity Technology of Nickel-Metal Hydride Batteries

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The nickel-metal hydride battery has been recognized as an important power source for various cordless appliances since its commercialization in 1990. Therefore, demands for capabilities of the batteries have been increasing. A key technology to meet these demands is improvement of the electrode materials. This work is focused on improving composition and microstructure of the bulk and surface states of hydrogen-absorbing alloys used as the negative electrode material and the composition of the nickel hydroxide and additives used for the positive electrode.

1. Introduction

Recently, portable electronic appliances like cellular phones, personal computers and so on have become very popular. Since their commercialization in 1990, nickel-metal hydride batteries have been used as the power sources of such portable electronic appliances. However, improvement of the batteries' performances has been demanded since lithium ion batteries with higher energy density were developed.

For achieving high performance in nickel-metal hydride batteries, it is important to improve the characteristics of the positive and negative electrode materials. In addition, improvements in other materials such as electrolytes and battery construction are also important.

As a result, we have developed high performance nickel-metal hydride batteries by using the new technologies described in this work.

2. Construction and characteristics of nickel-metal hydride battery

The construction of nickel-metal hydride batteries is very similar to that of nickel-cadmium batteries. The positive electrode material (nickel hydroxide) and electrolyte are essentially the

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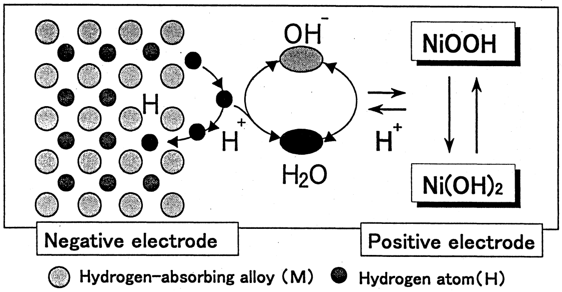
same. However, a hydrogen-absorbing alloy is used as the negative electrode material of nickel-metal hydride batteries.

The charge–discharge reaction of the nickel-metal hydride battery is illustrated in Fig.1. The hydrogen-absorbing alloy used as the negative electrode material absorbs hydrogen during charge and desorbs it during discharge. Nearly no charge-discharge reaction of the nickel-metal hydride batteries accompanies a concentration change in the electrolyte.



$$\mathrm{MH + NiOOH} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} \mathrm{M + Ni(OH)_2}$$

Fig.1 Charge-discharge reaction of the nickel-metal hydride battery

3. High-performance technology of negative electrode materials

To use a hydrogen-absorbing alloy as the negative electrode material, (1) it must allow a large amount of hydrogen to be absorbed and desorbed in an alkaline solution, (2) its reaction rate must be high, and (3) it must have long-term durability under repeated charge-discharge cycling. Many types of hydrogen absorbing alloys, e.g. rare earth-nickel based alloys, Ti-Zr based alloys, and alkaline earth-nickel based alloys have been developed; however, most Japanese battery manufactures are still using rare earth-nickel based alloys. $\mathrm{LaNi_5}$ is a typical rare earth-nickel type alloy, but it shows significant capacity deterioration during repeated charge-discharge cycling. The first step in the development was to obtain sufficient corrosion resistance of the $\mathrm{LaNi_5}$ alloy for its use as an electrode material. It was found that the partial replacement of nickel with cobalt and the substitution of lanthanum with misch metal (Mm)(a mixture of rare earth elements such as lanthanum, cerium, praseodymium and neodymium) were very useful in improving the charge-discharge cycle life. However, the discharge capacity of the alloy was not sufficient for a practical battery. From studying effect of partial substitution of aluminum and manganese, it was concluded that the best alloy composition was Mm(Ni-Co-Al-Mn)x.

The above requirements (1) and (2) are mainly decided by the bulk characteristics of

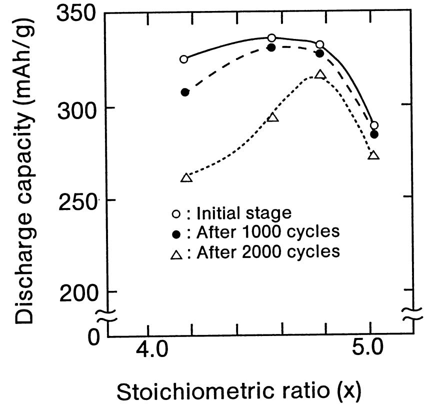


Fig.2 Relationship between stoichiometric ratio (x) and discharge capacity of Mm(Ni-Co-Al-Mn)x alloy in a Ni-MH cell

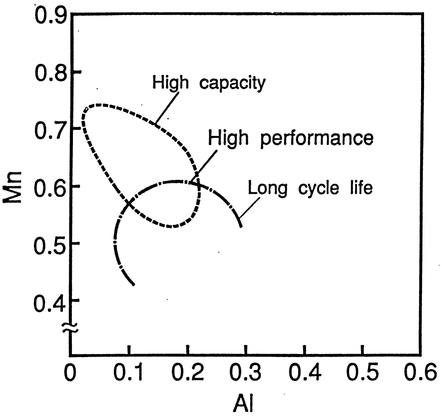


Fig.3 Electrochemical characteristics of MmNiaCobAlcMnd alloys; a+b+c+d=4.76, a/b=3.2

the alloy, while requirement (3) is largely influenced by the surface characteristics of the alloy. Therefore, a technical approach to total improvement requires consideration of both bulk and surface. From the viewpoint of bulk, a study was performed on compositions, stoichiometric number x, and preparation methods of alloys. From the viewpoint of surface, a study was performed on surface treatment. Improvement of Mm(Ni-Co-Al-Mn)x has been achieved in several ways.

The stoichiometric number x of Mm(Ni-Co-Al-Mn)x has largely affected discharge capacity and cycle life. Figure 2 shows the discharge capacity of a Mm(Ni-Co-Al-Mn)x alloy at initial stage, after 1000 cycles, and after 2000 cycles. The alloys with a non-stoichiometric composition [Mm(Ni-Co-Al-Mn)x: 4.7<x<4.8] had a large capacity and a long cycle life1).

Figure 3 shows the influence of a partial substitution of Mn and Al on capacity and cycle life. The optimized area of the partial substitution of Mn and Al is indicated2).

Not only the composition of Mm(Ni-Co-Al-Mn)x but also the preparation method has significantly affected discharge capacity and cycle life. Figure 4 shows P-C isotherms of the alloys prepared by several methods3). The alloys were (a) induction-melted alloy; which was obtained by melting the mixture of raw materials with an induction furnace, followed by casting into a mold; (b) induction-melted and subsequently annealed alloy; (c) rapidly quenched alloy, which was obtained by an induction-melting process followed by a rapid quenching process of strip-casting on a rotating copper roll; and (d) rapidly quenched and subsequently annealed alloy. Plateau regions appeared in the P-C isotherms except for alloy (a); also, the content of hydrogen increased.

Figure 5 shows charge-discharge cycle characteristics of test cells made from the above four alloys. The cell made from alloy (d) exhibited the longest cycle life. The alloy (d), i.e. the rapidly quenched and subsequently annealed alloy, had the lowest segregation of the component element as well as the most homogenous microstructure. Homogenity in microstructure is believed to improve cycle performance.

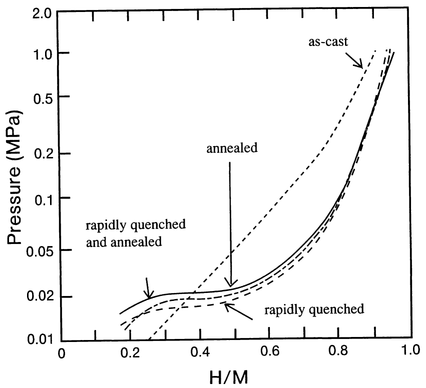


Fig.4 P-C isotherms of Mm(Ni-Co-Al-Mn)$_{4.76}$ alloys prepared by various methods

Alloy (d) exhibited the largest discharge capacity and the best cycle performance.

Surface treatment using an HCl aqueous solution for alloys (b) and (d) was examined in order to improve the initial electrochemical activity.

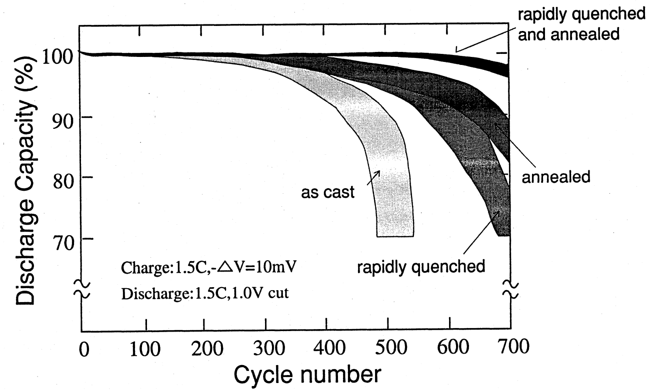


Fig.5 Charge-discharge cycle characteristics of Mm(Ni-Co-Al-Mn)$_{4.76}$ alloys prepared by various methods with an AA size test cells

Figure 6 shows XPS spectra of La 3d$_{5/2}$ and Ni 2p$_{3/2}$ of the surface of an alloy particle before and after surface treatment. In the untreated alloy, La metal and La_2O_3 and/or $La(OH)_3$ peaks were observed, while they were not observed in both surface-treated alloys. The Ni metal peaks of both surface-treated samples were observed to be larger than those of the untreated ones.

Figure 7 shows the initial discharge characteristics of the alloys before and after the surface treatment. The treated alloys exhibited high discharge capacity and showed the same charge-discharge cycle performances as those of the untreated alloys. These results indicate that surface treatment promotes the discharge reaction at the interface between the alloy surface and the electrolyte without disturbing bulk property[4].

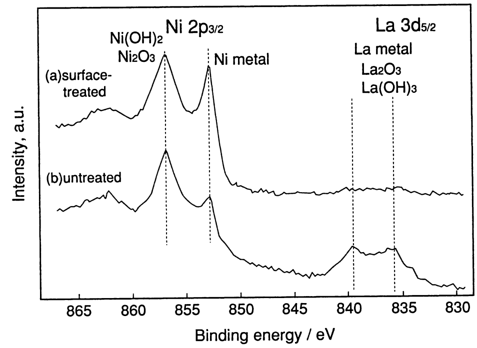


Fig.6 XPS spectra of $La3d_{5/2}$, Ni $2p_{3/2}$ of rapidly quenched and annealed $Mm(Ni_{0.64}Co_{0.20}Al_{0.04}Mn_{0.12})_{4.76}$ alloys

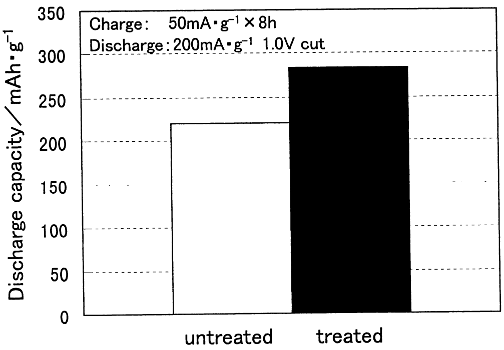


Fig.7 Initial discharge capacity of surface untreated / treated rapidly quenched and annealed alloys

4. High performance technology of positive electrode materials

The capacity of the positive electrode (nickel hydroxide) is less than that of the negative electrode (hydrogen absorbing alloy) to seal nickel-metal hydride batteries. Therefore, an increase in the capacity of the positive electrode is inevitable for achieving high- performance batteries.

Figure 8 shows the relationship between charge-discharge products of the nickel hydroxide electrode and the density of each product.

In general, β-$Ni(OH)_2$, with a higher density than α-$Ni(OH)_2$, is used for the starting positive electrode material of nickel-metal hydride batteries.

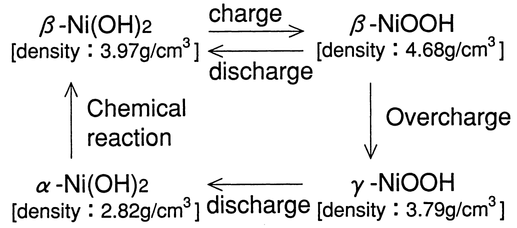


Fig.8 Relationship between charge-discharge products of the nickel hydroxide electrode and the density of each product

Trivalent β-NiOOH is formed during charging of β-$Ni(OH)_2$. The reaction is associated with removal of a proton. β-$Ni(OH)_2$ and β-NiOOH have the same crystal structures with hexagonal unit cells. In addition, nearly no volume change accompanies the reaction because of the relatively low change in lattice coefficients.

On the other hand, γ-NiOOH, with a higher valence than β-NiOOH, is formed when β-NiOOH is overcharged. A volume increase is associated with the formation of γ-NiOOH due to the intercalation of water and cations such as K^+ into the NiO_2 layer. As a result, the formation of γ-NiOOH causes the shortening of the battery life due to the lack of electrolyte.

Figure 9 shows the relationship between the swelling ratio of the electrode and additives in the electrode. Substitution of divalent ions such as Co and Zn for Ni in Ni(OH)2 suppressed the expansion of the electrode5).

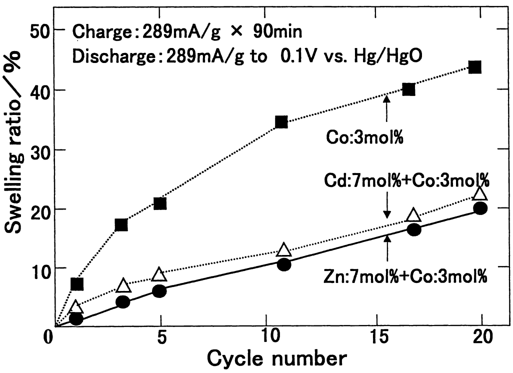


Fig.9 Influence of additives on the swelling ratio of the positive electrodes

The development of new conductive materials for the nickel hydroxide electrode is also an important factor in improving discharge capacity. Cobalt compounds like $Co(OH)_2$ and CoO are used for the conductive material because $Ni(OH)_2$ has low conductivity6). These cobalt compounds change into highly conductive β-CoOOH during the first charging, and the active material utilization of the nickel hydroxide electrode is increased.

It was found that the specific conductivity of a cobalt compound obtained by an oxidation treatment to $Co(OH)_2$ with an NaOH aqueous solution in an air atmosphere showed about four orders of magunitude larger than that of β-CoOOH.

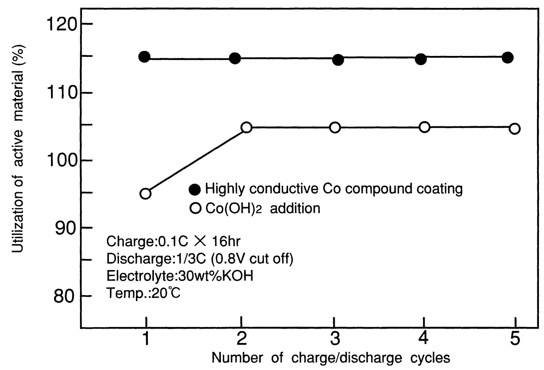


Fig.10 Effect of cobalt compounds on utilization of active material

Figure 10 shows the relation between cobalt compouds and active material utilization. The active material utilization of the nickel hydroxide electrode modified with the highly conductive cobalt compound is 10% larger than that of the electrode with $Co(OH)_2$ addition[7].

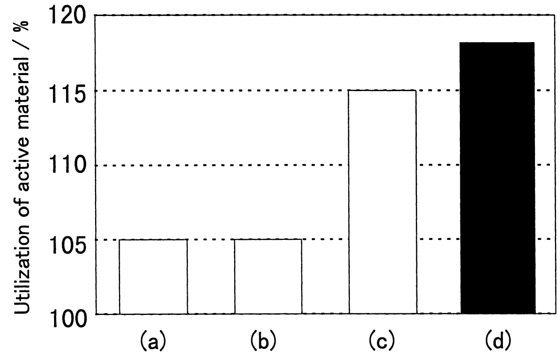


Fig.11 Effect of additives on utilization of active material; (a)CoO addition, (b)CoO and Y_2O_3 addition, (c)Highly conductive Co compound coating, (d)Highly conductive Co compound coating and Y_2O_3 addition

Various kinds of additives were also investigated for improving the discharge capacity of the nickel hydroxide electrode. It was confirmed that a Y_2O_3 addition to the nickel hydroxide electrode modified with a highly conductive cobalt compound has the effect of increasing the active material utilization (Figure 11)[8]. It is believed that a Y_2O_3 addition increases the charge acceptance of the nickel hydroxide electrode due to the increase in oxygen overvoltage[9].

5. Optimization for battery construction.

Development of new positive and negative electrode active materials is important for improving the capabilities of batteries. The technologies of battery construction are also important in using these active materials effectively.

Figure 12 shows the capacity states of each electrode at the initial stage and after charge-discharge cycles.

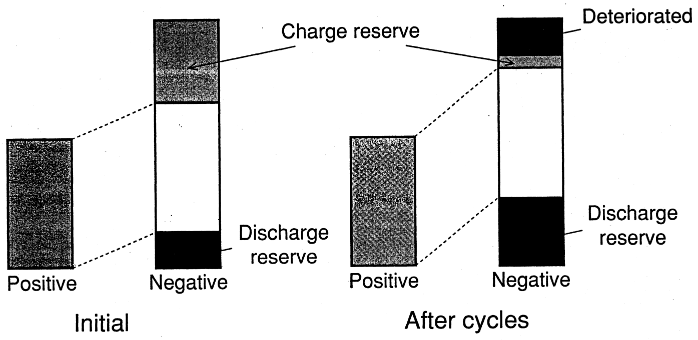


Fig.12 Change of the reserve in a negative electrode

The capacity of the negative electrode is greater than that of the positive electrode to seal the batteries. In general, a non-charging part of the negative electrode at the full-charge state is called a "charge reserve", and a non-discharging part after discharge is called a "discharge reserve".

The charge reserve is indispensable for prohibiting hydrogen gas evolution from the negative electrode during overcharging. In addition, oxygen gas evolved from the positive electrode during overcharging has to be absorbed at the negative electrode to seal the batteries. The discharge reserve is also necessary because the capacity decay of the negative electrode in high rate charge or discharge is larger than that of the positive electrode.

As the charge-discharge cycle passes, the charging reserve decreases with the deterioration of the negative electrode, and the discharging reserve increases, as shown in Fig.12. It is believed that an oxidation of the hydrogen-absorbing alloy has an influence on the change in the capacity in the electrode.

The nickel-metal hydride battery is designed to include a sufficient amount of hydrogen-absorbing alloy, a quantity estimated against expected deterioration. Furthermore, a corrosion-resistant alloy enables the loading of more positive electrode material into the cell and construction of higher-capacity battery.

6. Conclusions

The new technologies of high-performance nickel-metal hydride batteries were discussed. The energy density of these batteries has rapidly increased in the past few years. Customers now demand new nickel-metal hydride batteries that have the same energy density as lithium ion batteries.

Therefore, the development of new materials is expected to improve the discharge capacity of the batteries. In addition, it is believed that additional improvement in such battery capabilities as cycle performance and high power are necessary to broaden the market for nickel-metal hydride batteries.

7. References

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