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Improvement of high- and low-temperature characteristics of nickel-metal hydride secondary batteries using rare-earth compounds

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Abstract

Improvement of high- and low-temperature characteristics of nickel–metal hydride secondary batteries using rare-earth compounds is discussed. High-temperature charge characteristics are improved by coating a sintered positive electrode with yttrium hydroxide due to the increased oxygen evolution overpotential. Low-temperature discharge characteristics are also improved by adding rare-earth oxides into a negative electrode due to the increased ratio of metallic nickel at the surface of the hydrogen-absorbing alloy.

Keywords: Nickel–metal hydride secondary battery; Rare-earth compounds; Sintered nickel positive electrode; Hydrogen-absorbing alloy; Temperature characteristics

1. Introduction

Nickel–metal hydride (Ni–MH) secondary batteries have been widely used for a variety of applications such as digital still cameras (DSCs), notebook computers and power tools. Recently, Ni–MH batteries for retail market have been getting important with the growth of the DSC market since users of DSCs require larger battery capacity for larger filming number than alkaline dry batteries. Meeting this customers' demand, the capacity of the Ni–MH batteries for retail market has been increasing almost linearly year by year and have reached approximately double the capacity at the first introduction in 1996 as shown in Fig. 1 [1]. For the other applications, hybrid electric vehicles (HEVs) have been receiving much attention from both environmental and economical points of view. Ni–MH batteries for HEVs have eventually been getting important since almost all the commercialized HEVs employ Ni–MH batteries because of their better combination of output power, capacity, life, reliability and cost [2–8].

Ni–MH batteries thus need to match with a variety of applications, and in particular, they are required to work in a wide temperature range by improving both high- and low-temperature characteristics. The discharge capacity of a Ni–MH battery charged at high temperature is usually lower than that charged at room temperature [9–13]. This is considered to be due to the oxygen evolution reaction or a side reaction (Eq. (2)) of the charging reaction (Eq. (1)) of the positive electrode at high temperature, either using a sintered nickel electrode or using a non-sintered nickel electrode:

Charge reaction

$$\mathrm{Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e^-} \quad (1)$$

Side reaction of oxygen evolution

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

In the past, the electrolyte composition [10] and co-precipitating elements into nickel hydroxide such as cobalt and calcium [11–15] were investigated in order to improve the high-temperature charge efficiency. Powder additives such as calcium compounds, barium compounds and rare-earth compounds are used for this purpose for a non-sintered nickel electrode [16–20]. However, it is difficult from the

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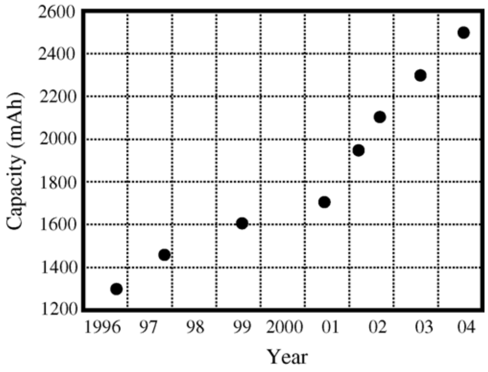

Fig. 1. Increase in the capacity of an AA-size Ni–MH battery for retail market (Sanyo HR-3U).

manufacturing point of view to apply such powder additives to a sintered nickel electrode, which possesses better power characteristics than a non-sintered nickel electrode and is suitable for use in HEVs. As for low-temperature characteristics, it has been reported that the reactivity of the negative electrode using a hydrogen-absorbing alloy dominates the low-temperature characteristics of a whole cell [21].

In this report, we focus on the improvement of the high- and low-temperature characteristics of Ni–MH batteries by using rare-earth compounds. We discuss the improvement of high-temperature charge characteristics by coating a sintered nickel positive electrode with a hydroxide of rare-earth elements. Improvement of low-temperature characteristics by adding rare-earth compounds to the negative electrode is also presented.

2. Experimental

2.1. Modification of sintered positive electrode by rare-earth compounds [22]

First, yttrium from the rare-earth elements was selected as a coating material. Calcium from the alkaline earth metals and cobalt, which is commonly used as an element to be co-precipitated in nickel hydroxide were also selected. After filling nickel hydroxide into a porous sintering body by using a chemical impregnation method, the sintering body with nickel hydroxide was immersed in an yttrium nitrate solution, calcium nitrate solution or cobalt nitrate solution of a specific gravity of 1.2. By immersion in a sodium hydroxide solution, the sintered nickel positive electrodes surface coated with yttrium hydroxide, calcium hydroxide and cobalt hydroxide were obtained, respectively. The amount of coating hydroxide was calculated from the weight difference of the electrode before and after coating. The nickel positive electrode coated with yttrium hydroxide was characterized with scanning electron microscopy (SEM) and electron probe microanalysis (EPMA).

Test cells using the coated positive electrode as the working electrode and a sintered cadmium electrode as the counter electrode were assembled in order to examine the high-temperature characteristics. A three-ingredient solution of potassium hydroxide, sodium hydroxide and lithium hydroxide was used as the electrolyte. The condition testing the high-temperature charge characteristics was as follows: (1) charge the positive electrode up to 160% of the theoretical capacity for a one-electron reaction at $1/5C$ within an environmental temperature range from 25 to 60 °C. (2) Set the environmental temperature at 25 °C. (3) Discharge the positive electrode up to a cell voltage of 0.8 V at $1/3C$.

Cylindrical sealed-type AA-size cells using the coated nickel positive electrode, a hydrogen-absorbing alloy negative electrode and a three-ingredient electrolyte consisting of potassium hydroxide, sodium hydroxide and lithium hydroxide was also prepared. The composition of the hydrogen-absorbing alloy was $MmNi_{3.6}Co_{0.6}Al_{0.3}Mn_{0.5}$ (Mm: misch metal). The conditions testing the high-temperature charge characteristics was as follows: (1) charge the cell up to 120% of the cell capacity at $1/2C$ at an environmental temperature range from 25 to 60 °C. (2) Set the environmental temperature at 25 °C. (3) Discharge the cell up to a cell voltage of 1.0 V at $1/2C$.

2.2. Addition of rare-earth compounds to negative electrode

Cylindrical sealed-type AA-size cells were prepared as follows. A paste-type electrode comprising $MmNi_{3.6}Co_{0.6}Al_{0.3}Mn_{0.5}$ hydrogen-absorbing alloy was used as a negative electrode. The rare-earth oxide additives to the negative electrode were selected from gadolinium oxide (Gd_2O_3), terbium oxide (Tb_4O_7), holmium oxide (Ho_2O_3), thulium oxide (Tm_2O_3) and lutetium oxide (Lu_2O_3). The amount of each additive was 0.5 wt% of the hydrogen-absorbing alloy. A sintered nickel electrode comprising nickel hydroxide co-precipitated with cobalt and zinc and coated with yttrium hydroxide was used as a positive electrode. The negative and positive electrodes were wound with a hydrophilic treated polyolefin separator. The electrolyte was composed of potassium hydroxide, sodium hydroxide and lithium hydroxide.

The DC resistance of the cell was measured as follows. After being charged to SOC 50%, the cell was discharged for 10 s at various currents at 25 and 0 °C and the cell resistance was calculated as a slope from the relationship between the cell voltage and the current. The condition testing the cycle characteristics was as follows: (1) charge up to a cell voltage lowered 10 mV from the maximum at room temperature at $1C$. (2) Discharge up to a cell voltage of 1 V at room temperature at $1C$. The negative electrode alloys added with the rare-earth oxides were also characterized with X-ray photoelectron spectroscopy (XPS) in order to examine change in the surface structure.

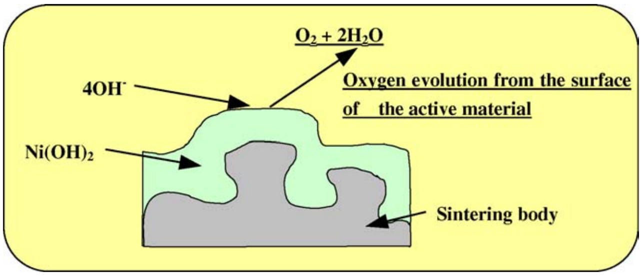

Fig. 2. Oxygen evolution reaction at the surface of the sintered positive nickel electrode.

3. Results and discussion

3.1. Improvement of high-temperature charge characteristics of positive electrode [22]

Our strategy for improving high-temperature charge efficiency is illustrated in Fig. 2. The sintered nickel electrode has a three-dimensional porous structure consisting of a sintered nickel body filled with nickel hydroxide as the active material. When the cell temperature is high, the side reaction in Eq. (2) occurs, generating oxygen and water. Cobalt co-precipitation in nickel hydroxide is often used in order to improve the charge acceptance characteristics. Instead, we focused on the modification of the active material surface by coating the nickel positive electrode with hydroxides of other elements as this side reaction is considered to occur on the active material surface.

The amount of the coating materials is approximately 2 wt% as shown in Table 1. SEM and EPMA images of the surface of the nickel positive electrode coated with yttrium hydroxide are shown in Fig. 3. The white dots in the EPMA image indicate the presence of yttrium, showing that the surface of the nickel hydroxide, which is the active oxygen evolution site is coated with yttrium hydroxide.

Table 1
Amount of coating hydroxides with respect to the nickel positive electrode material

Coating	Amount of coating hydroxides (wt%)
Cobalt hydroxide	1.8
Yttrium hydroxide	2.4
Calcium hydroxide	2.1

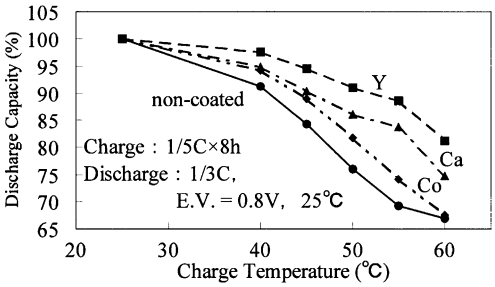

Fig. 4. Effect of hydroxide coating on high-temperature charge efficiency of test cells.

The effect of hydroxide coating on the high-temperature charge efficiency of the test cells is shown in Fig. 4 in terms of the discharge capacity ratio versus the charging temperature. The charge efficiency at high temperature has been improved for all the three hydroxides. In particular, the electrodes using yttrium hydroxide and calcium hydroxide show a large discharge capacity even for charging at 60 °C. The cobalt hydroxide shows the same characteristic as the non-coated electrode for charging at 60 °C, while it shows a superior capacity compared to the non-coated electrode up to 55 °C.

In order to interpret the difference depending on the coating materials, we analyzed the voltage behavior during charging. Fig. 5 shows the charge characteristics of the test cells at 25 °C. The potential difference between oxygen evolution and nickel hydroxide oxidation is large when using the electrodes coated with yttrium hydroxide and calcium hydroxide

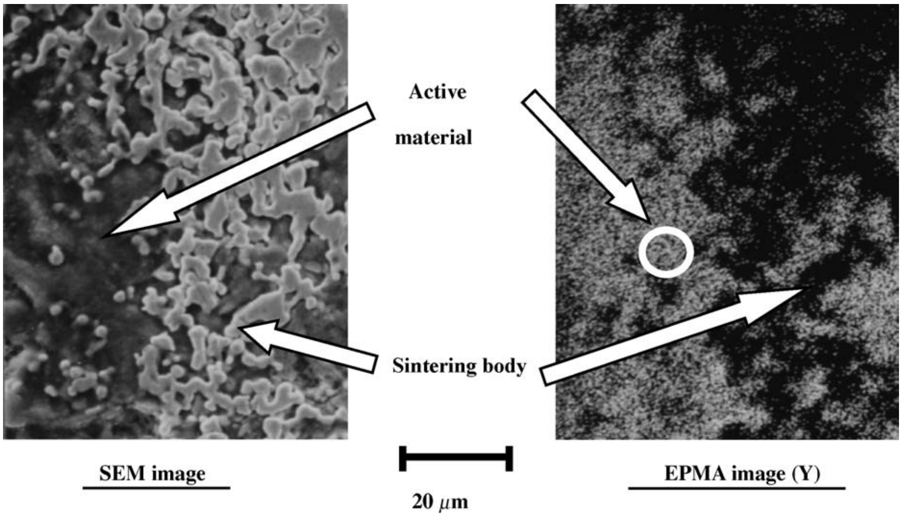

Fig. 3. Surface SEM and EPMA images of a nickel positive electrode coated with yttrium hydroxide.

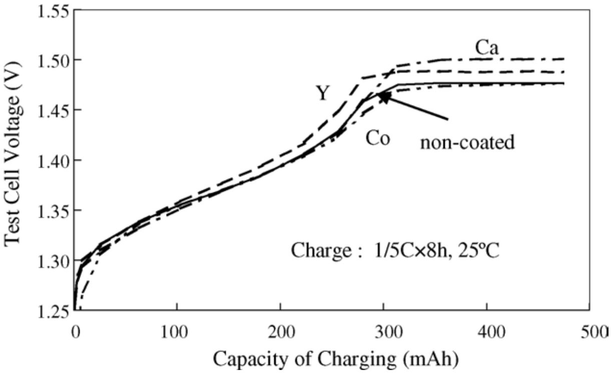

Fig. 5. Charge characteristics of test cells at 25 °C.

compared to the non-coated electrode. Coating with yttrium hydroxide and calcium hydroxide suppresses the oxygen evolution reaction. The timing of the oxygen evolution reaction is delayed for the electrode coated with cobalt hydroxide although the oxygen evolution overvoltage does not change.

Fig. 6 shows the charge characteristics of the test cells at 60 °C. Among the three elements, yttrium hydroxide and calcium hydroxide suppress the oxygen evolution reaction more effectively, and high-charge efficiency is achieved even at high temperatures. Contrary to this, the electrode with cobalt hydroxide exhibits the same characteristic as the non-coated electrode, because the drop in oxygen evolution potential is large. Thus, high-temperature characteristics of a sintered nickel positive electrode are greatly enhanced when coated with yttrium hydroxide and calcium hydroxide.

The effect of the hydroxide coating on the high-temperature charge efficiency of AA cells is shown in Fig. 7. Similarly to the results for the test cells, the AA cells using the coated positive electrodes show a large discharge capacity at the charge temperature above 40 °C. In particular, the electrodes using yttrium hydroxide and calcium hydroxide give a large discharge capacity even when charged at 60 °C compared to the non-coated electrode.

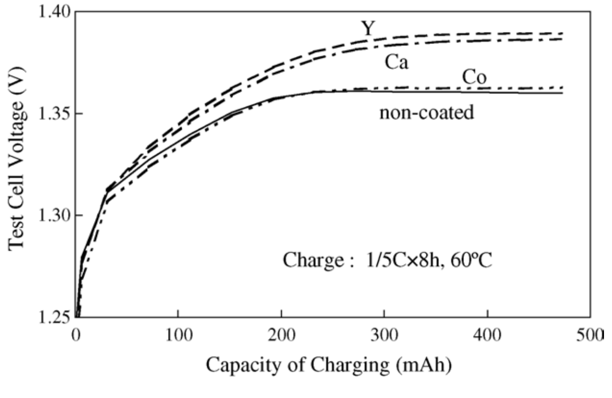

Fig. 6. Charge characteristics of test cells at 60 °C.

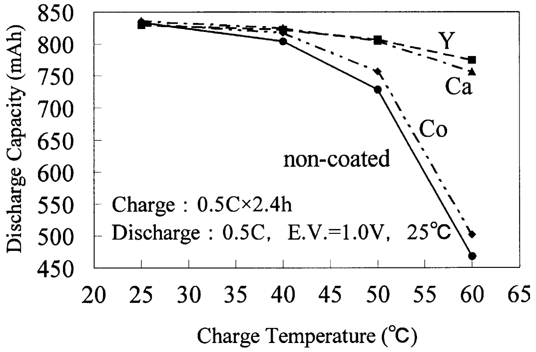

Fig. 7. Effect of hydroxide coating on high-temperature charge efficiency of AA cells.

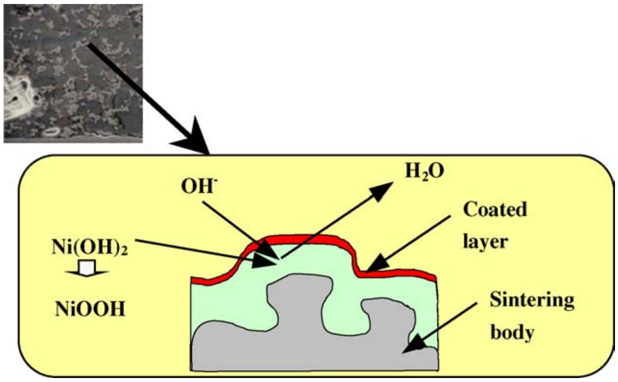

Fig. 8. Function of the surface coating material.

Fig. 8 illustrates a microstructural cross-section of the coated sintered electrode. The sintered body is originally nickel metal sintered powders. On the sintered body surface, the nickel hydroxide active material is maintained to hold the current collectiveness. This time we coated the surface of the nickel hydroxide active material with yttrium hydroxide and calcium hydroxide as shown in Fig. 8 and increased in the oxygen overvoltage.

3.2. Improvement of low-temperature characteristics of negative electrode

The cell resistance of AA cells using the negative electrodes containing the rare-earth additives at 0 and 25 °C is shown in Table 2. All the additives brought a decrease in the cell resistances at both 0 and 25 °C. In particular, the cell

Table 2
Cell resistance at 25 and 0 °C of AA cells using negative electrode added with rare-earth oxides

Additive	Cell resistance at 25 °C (mΩ)	Cell resistance at 0 °C (mΩ)
Gd_2O_3	24.7	46.2
Tb_4O_7	23.6	44.2
Ho_2O_3	24.6	46.8
Lu_2O_3	23.9	46.1
No additive	24.8	47.4

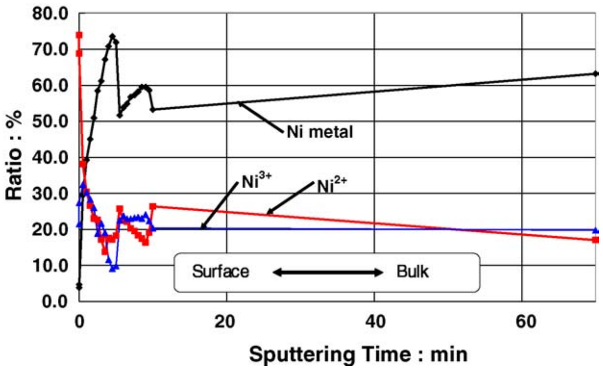

Fig. 9. Profile of nickel valence state near the surface of the hydrogen-absorbing alloy added with terbium oxide.

resistance at 0 °C decreased by 7% for the addition of terbium oxide compared to the cell without additive.

In order to examine the changes caused by the rare-earth additives, the valence state of nickel at the surface was measured using XPS. The nickel valence state of nickel at the surface for the hydrogen-absorbing alloys with terbium oxide and without additive is shown in Figs. 9 and 10, respectively. The ratio of metallic nickel at the surface was increased by adding the terbium oxide. The metallic nickel at the surface is considered to work as an active site for the charge and discharge reactions. The addition of rare-earth oxides thus improves the reactivity of the surface of the hydrogen-absorbing alloy, bringing the decrease in the cell resistance even at a low temperature.

The cycle characteristics of the AA cell containing the terbium oxide were also evaluated at 1*C* charge–discharge current in order to examine the effect of the additives on the cycle life as shown in Fig. 11. The addition of terbium oxide prolonged the cycle life by 6% compared to the cell without additive. It has been considered that the low-temperature characteristics and cycle characteristics are usually in a trade-off relationship. The addition of terbium oxide, however, improved both the low temperature and cycle characteristics.

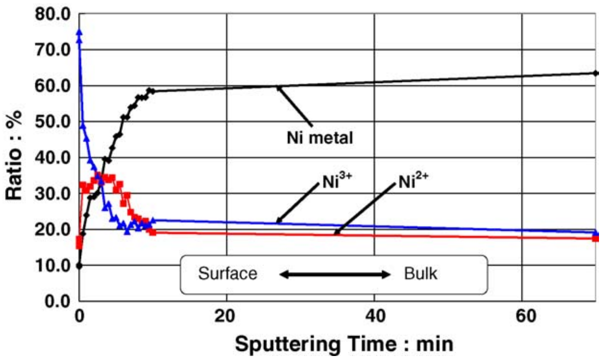

Fig. 10. Profile of nickel valence state near the surface of the hydrogen-absorbing alloy with no additive.

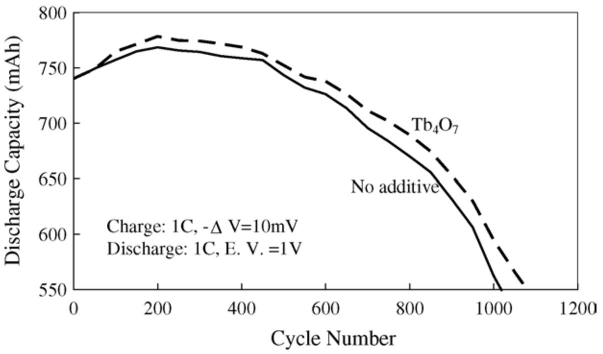

Fig. 11. Cycle characteristics of AA cells using the negative electrodes with terbium oxide and without additive.

4. Conclusions

In order to improve high- and low-temperature characteristics for nickel–metal hydride secondary batteries, coating the positive electrode by hydroxides including yttrium hydroxide and adding rare-earth oxides to the negative electrode have been investigated. The high-temperature charge efficiency of a sintered nickel positive electrode is greatly improved when coated with yttrium hydroxide and calcium hydroxide by increasing the oxygen overvoltage at active oxygen evolution sites.

For the low-temperature characteristics, the addition of rare-earth oxides to the negative electrode decreased the dc resistance of the negative electrode and the cell at low temperature by increasing the ratio of metallic nickel at the surface of the hydrogen-absorbing alloy. The reactivity of the negative electrode is considered to be improved by the surface modification with nickel. The cycle characteristics are also improved by the addition of terbium oxide.

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