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Effect of rare earth oxide additives on the performance of NiMH batteries

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Abstract

To date, we have performed research on nickel–metal hydride (NiMH) batteries used in many applications and have found that addition of rare earth oxides to the nickel electrode and the hydrogen-storage alloy (MH) electrode improves battery performance significantly. Because heavy rare earth oxides of such as Er, Tm, Yb and Lu have remarkable properties that shift the oxygen evolution overpotentials of nickel electrodes to more noble potentials, it is possible to improve high-temperature charge efficiency of nickel–metal hydride secondary batteries by adding them to nickel electrodes. Furthermore, addition of heavy rare earth oxides to MH electrodes depresses an acceleration of the alloy corrosion and improves service life of the battery at high temperatures. Accordingly, addition of heavy rare earth oxides is effective for NiMH batteries used in high-temperature applications such as electric vehicles (EVs), hybrid vehicles (HEVs) and rapid charge devices. In this study, we discussed how the addition of heavy rare earth oxides affects NiMH battery characteristics.

Keywords: Nickel–metal hydride battery; Rare earth oxides; Charge efficiency; Rapid charge

1. Introduction

In recent years, nickel–metal hydride (NiMH) batteries have grown both in capacity and power; manufacturers are developing AA-sized cylindrical cells exceeding 2000 mAh and batteries exceeding 1000 W/kg for hybrid vehicles (HEVs). They are also beginning to develop batteries that can be rapidly charged within 15 min. However, higher capacity and higher power lead battery to generate much heat and cause the low charge efficiency of nickel electrode and the corrosion of hydrogen-storage alloy (MH) electrode. As a consequence, the electrolyte amount decreases and service life of the battery is shortened.

In nickel electrodes, the charging reaction in Eq. (1) is followed by the oxygen evolution reaction in Eq. (2).

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

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

Because the oxygen overpotential of nickel electrode drops rapidly in the high-temperature range of over 35 °C, the charging reaction and the oxygen evolution reaction occur in conflict with one another, thereby it causes the charge efficiency to decrease. While various ways to improve charge efficiency have been reported by others [1–4], we have reported that addition of heavy rare earth oxides can achieve substantial improvement [5–7]. The use of this technique has attained excellent charge efficiency in EVs and HEVs applications [8,9].

The main corrosion reaction in MH electrodes is the reaction, shown in Eq. (3) below, that forms hydroxides of misch metal, primarily La.

$$\mathrm{Mm + 3H_2O \rightarrow Mm(OH)_3 + 3H} \qquad \text{(Mm : misch metal)} \qquad (3)$$

The $\mathrm{Mm(OH)_3}$ has poor conductivity and deteriorates the charge and discharge characteristics of MH electrode. And, because the hydrogen evolved in Eq. (3) is absorbed into the hydrogen-storage alloy, the state of charge (SOC) of MH electrode increases. It results a change of capacity balance

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between nickel and MH electrodes, accelerates a pulverization of the alloy into fine powder and finally causes a deterioration of service life. Focusing on the fact that the magnitude of hydrogen overpotential has a major effect on alloy corrosion resistance, we confirmed the effect of addition of rare earth oxides to MH electrode to inhibit the corrosion reaction in Eq. (3) [10].

In this paper, we report the high-temperature operating characteristics and durability of NiMH batteries to which rare earth oxides are added, and further explore the application of power and rapid charge characteristics.

2. Experimental

2.1. Preparation of NiMH battery

We prepared high-density nickel hydroxide powder added with 3.5 wt% zinc and 1.5 wt% cobalt in solid solution, which surface was coated with 5.5 wt% cobalt oxy-hydroxide. We then made a paste by mixing 2 wt% rare earth oxides from La to Pr and Er to Yb into this nickel hydroxide powder and adding an aqueous solution of 1 wt% carboxymethylcellulose, loaded this paste into a foam nickel substrate, dried and pressed them and produced nickel electrodes as positive electrodes with a capacity of 2000 mAh. To investigate rapid charge characteristics, we produced nickel electrodes into which Yb_2O_3 was mixed in the range of 1–3 wt%.

A hydrogen-storage alloy was prepared with an average particle size of 20 μm and an alloy composition of $MmNi_{4.00}Co_{0.65}Mn_{0.30}Al_{0.28}$. We then made a paste by mixing 1.2 wt% rare earth oxides from La to Pr and Er to Yb into this hydrogen-storage alloy, coated it onto punching metal substrates, then dried and pressed them to produce MH electrodes as negative electrodes with a capacity of 2500 mAh.

These nickel and MH electrodes were wound in a spiral shape together by spacing with polyolefin split fiber separators. We put them into a cell container with an aqueous solution of 6.8 M KOH + 0.8 M LiOH as the electrolyte and sealed to produce AA-sized cylindrical cells that were activated according to the prescribed charging and discharging conditions.

2.2. NiMH battery testing

2.2.1. Charge efficiency and charge-capacity retention tests at high temperatures

AA-sized cylindrical cells were charged at a constant current of 0.5 C rate for 2 h at 40 °C, rested for 0.5 h and then discharged at a 0.5 C rate to 0.9 V. This cycle was repeated 10 times and the maximum discharge capacity was determined.

Next the cells were charged at a 0.1 C rate for 16 h at 20 °C, rested for 1 h and determined the discharge capacity at a 0.2 C rate to 1.0 V. After this measurement, the batteries were charged at a 0.1 C rate for 16 h at 20 °C, then placed in a thermostatic chamber at 60 °C for 7 days. After 7 days, the discharge capacity was determined as a residual capacity at a 0.2 C rate to 1.0 V at 20 °C.

2.2.2. Power characteristics after high-temperature tests

After high-temperature tests, the cells were charged at a 0.5 C rate for 1 h at 20 °C (50% SOC) and measured with an alternating current at the frequency of 1 kHz for the internal a.c. resistance. Then, discharge current of 2, 4 and 6 A was fed to the battery. We plotted each discharge current (I) and the voltage (V) at the 10th second, calculated its slope (V/I) and used that for the internal d.c. resistance value.

2.2.3. Rapid charge characteristics

The cells having nickel electrodes to which Yb_2O_3 had been added were charged at a constant voltage of 1.6 V for 15 min at 20 °C, and then, the discharge capacity at a 1.0 C rate to 1.0 V was determined.

3. Results and discussion

3.1. Effect on high-temperature charge efficiency

Fig. 1 plots the charge efficiency at 40 °C of NiMH batteries to which rare earth oxides were added. When adding heavy rare earth oxides (Er, Tm and Yb) provided a charge efficiency of 90%. This happens because the oxygen evolution overpotential of nickel electrodes shifted to the noble potentials [5–7] and indicates that heavy rare earth oxides effectively raise high-temperature charge efficiency. On the other hand, when light rare earth oxides (La, Ce and Pr) were added to nickel electrodes, charge efficiency was the same as when there were no additives. In case of adding La_2O_3 to the nickel electrode, the remarkable decrease was observed.

Further, adding heavy rare earth oxides to MH electrodes likewise raises the charge efficiency of NiMH batteries.

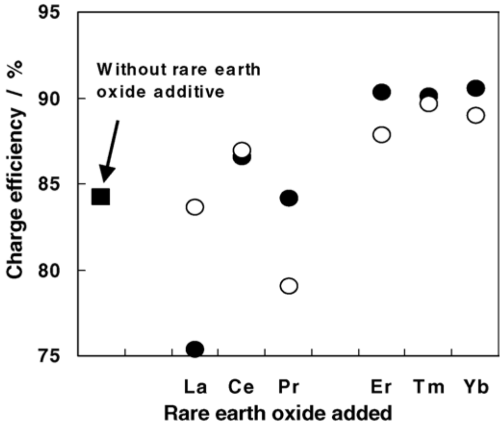

Fig. 1. Charge efficiency of NiMH batteries at 40 °C. Rare earth oxides not added (■); added to nickel electrode (●); added to MH electrode (○).

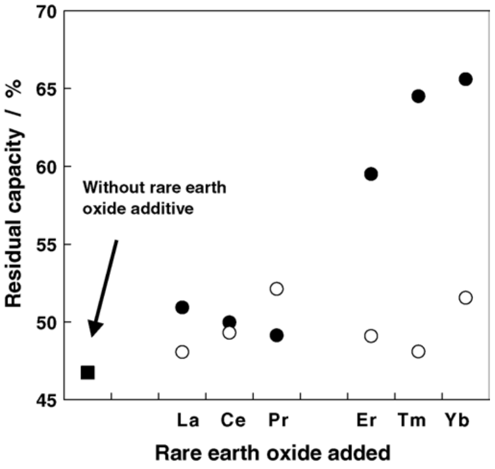

Fig. 2. Residual capacity of NiMH batteries after storage for 7 days at 60 °C. Rare earth oxides not added (■); added to nickel electrode (●); added to MH electrode (○).

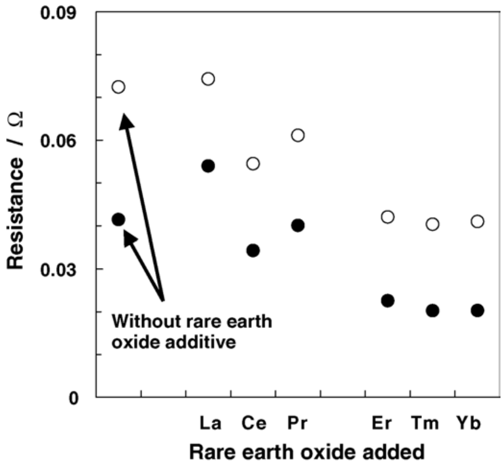

Fig. 3. Internal a.c. resistance (●) and d.c. resistance (○) after high-temperature tests of NiMH batteries to which nickel electrodes rare earth oxides were added.

A conceivable reason for this is the increased hydrogen overpotential. Considering the reports that more f-electrons increases hydrogen overpotential [11], it would seem that heavy rare earth elements with many electrons in 4f orbitals are very effective for increasing the hydrogen overpotential. The increased hydrogen overpotential delays the evolution of hydrogen from MH electrodes and holds down the buildup of internal cell pressure, which appears to improve charge efficiency.

3.2. *Effect on high-temperature charge-capacity retention*

Fig. 2 plots the capacity retention for 7 days at 60 °C of NiMH batteries to which rare earth oxides were added. Addition of heavy rare earth oxides to nickel electrodes has improved capacity-retention characteristics. We had expectations that this would mitigate the autolysis of nickel electrodes [6,7,12,13] and their reduction due to hydrogen evolved from MH electrodes, and this experiment showed that addition of rare earth oxides was effective for mitigating autolysis of the nickel electrode. On the contrary, there was no effect of adding rare earth oxides to MH electrodes on capacity retention.

3.3. *Effect on power characteristics after high-temperature tests*

Fig. 3 shows the internal a.c. resistance and the internal d.c. resistance at 50% SOC of NiMH batteries in which rare earth oxides were added to the nickel electrodes after high-temperature tests. There were differences in these resistances depending on kinds of rare earth oxides. This confirmed that NiMH batteries to which heavy rare earth oxides were added had low internal a.c. and d.c. resistances and continuous excellent power characteristics during high-temperature test. On the other hand, NiMH batteries in which light rare earth oxides were added to the nickel electrodes had high internal a.c. resistance, which suggests that the electrolyte amount in the separators decreased. Judging by the extensive corrosion of MH electrodes as noted below, the primary cause was electrolyte consumption due to alloy corrosion.

3.4. *Effect on hydrogen-storage alloy corrosion*

Fig. 4 shows the X-ray diffraction patterns of MH electrodes removed from batteries after high-temperature tests. We observed the extent of corrosion from the peak intensity due to (1 1 0) and (1 0 1) line of $La(OH)_3$, appearing at a 2θ of about 28°. More $La(OH)_3$ was formed when light rare earth oxides were added to nickel or MH electrodes, whereas

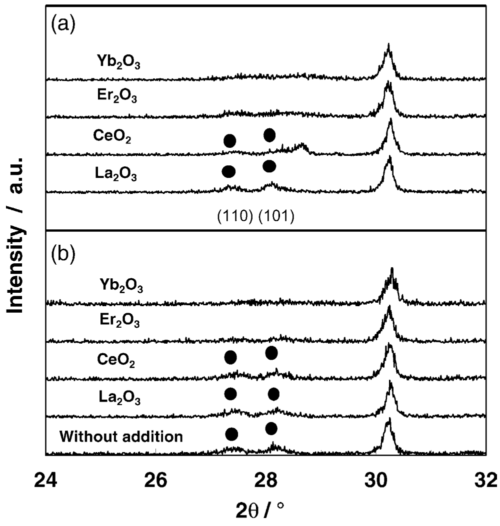

Fig. 4. XRD patterns obtained by Cu Kα radiation, of MH electrodes after high-temperature tests for NiMH batteries in which rare earth oxides were added to: (a) MH electrodes and (b) nickel electrodes. The closed circles show the peaks due to $La(OH)_3$.

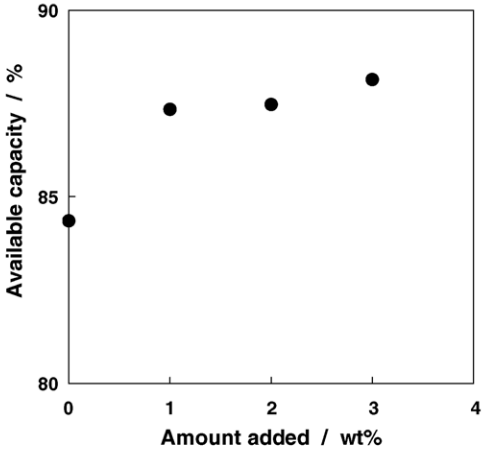

Fig. 5. Rapid charge characteristics of NiMH batteries to which nickel electrodes Yb_2O_3 were added.

its formation was suppressed when heavy rare earth oxides were added to them. Since the addition to nickel electrodes raised battery charge efficiency, this is considered to suppress oxygen evolution in the final charging stage, which in turn restrains corrosion of MH electrodes by oxygen. On the other hand, it appears that rare earth oxides added to MH electrodes directly inhibit the dissolution of lanthanide from the hydrogen-storage alloy. The rare earth oxides added is considered to form thin film on the surface of alloy and prevent corrosion as sacrificial anodes.

3.5. *Effect on rapid charge characteristics*

We evaluated the rapid charge characteristics of NiMH batteries by constant voltage charge. Available capacity of the batteries in which Yb_2O_3 was added to the nickel electrodes was plotted against the amount added in Fig. 5. In this experiment, batteries generated considerable heat, since a current of at least 4 C rate was kept in the initial charging stage. For this reason, NiMH batteries without additives had small capacities stemming from declining charge efficiency in the final charging stage. Available capacity was improved when more Yb_2O_3 was added, and we confirmed that addition of Yb and other heavy rare earth oxides to positive electrodes is also effective in improving rapid charge characteristics.

4. Conclusion

We investigated the effect on NiMH batteries when rare earth oxides were added to both nickel and MH electrodes. In particular, batteries had excellent charge efficiency and capacity-retention characteristics at high temperatures when heavy rare earth oxides were added. Alloy corrosion was also suppressed. Additionally, we confirmed that addition of heavy rare earth oxides to nickel electrodes improves power characteristics during cycling and rapid charge characteristics. Accordingly, NiMH batteries to which rare earth oxides are added are promising for batteries that can be counted on under harsh conditions, which impose demands such as higher capacity, higher power and rapid charging. Especially, since these NiMH batteries give excellent capacity-retention characteristics and rapid charge characteristics, the development of NiMH batteries is hopeful in replacing dry cells.

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