Improvement of High-temperature Characteristics
of Sintered Nickel Positive Electrode
for Nickel-metal Hydride Battery

K. Shinyama, Y. Magari, T. Tanaka,
Y. Harada, T. Nohma and I. Yonezu
New Materials Research Center, Sanyo Electric Co., Ltd.
1-1 Dainichi-higashimachi Moriguchi,
Osaka, 570-8502, Japan

Introduction

Nickel-metal hydride batteries are widely used at present, and they often incorporate a sintered nickel positive electrode particularly for high-power uses. Generally speaking, when a nickel-metal hydride battery is charged at a high temperature, the charging efficiency drops compared with the case of charging at room temperature and the discharge capacity decreases[1]. The cause of this is considered to be due to an oxygen evolution reaction, that is, a side reaction of the charging reaction of the positive electrode, when the temperature is increased. We think it is possible to improve the charging efficiency at a high temperature by suppressing this oxygen evolution reaction.

Accordingly, in our aim to improve the charging efficiency at high temperatures in this research, we report test cells produced with a sintered nickel positive electrode that is coated with one of several compounds, and show evaluations on charge-discharge characteristics at high temperatures.

Experimental

After filling nickel hydroxide (i.e., active material) into a porous sintering body by a chemical impregnation method, we carried out immersion in a cobalt nitrate solution, yttrium nitrate solution or calcium nitrate solution with a specific gravity of 1.2. Then, after drying the sample, we produced the sintered nickel positive electrode surface-coated with cobalt hydroxide, yttrium hydroxide or calcium hydroxide, respectively, by immersion in a sodium hydroxide solution.

We produced test cells by making this positive electrode the working electrode and a sintered cadmium electrode the counter electrode, and by using a three-ingredient solution including potassium hydroxide, sodium hydroxide and lithium hydroxide as the electrolyte. The examination was as follows. After charging the positive electrode up to 160% of the theoretical capacity for a one-electron reaction at a 1/5C current within the environmental temperature range of 25 ℃ to 60℃, the environmental temperature was set to 25 ℃ and discharging was carried out up to a cell voltage of 0.8V at a 1/3C current.

Results and discussion

It was confirmed that each coating existed from the electrode surface to the inside, from SEM and EPMA cross section analysis of the sintered nickel positive electrodes surface-coated with various types of hydrates. The high temperature charging characteristics of the test cells produced with the coated sintered nickel positive electrode are shown as discharge capacity ratios versus the charging temperature in Fig. 1. Throughout the observations, it was clear that the charging efficiency improved at high temperatures with either the cobalt hydroxide, yttrium hydroxide or calcium hydroxide, in comparison with a non-coated sample. Among the results, the differences with the case of non-coating were large with the yttrium hydroxide and calcium hydroxide, even for charging at 60℃. On the other hand, although the cobalt hydroxide showed predominance over the case of non-coating up to 55℃, it showed the same characteristic as the case of non-coating for charging at 60℃.

To make the cause of this clear, we analyzed the voltage behavior in the charging period. Fig. 2 and Fig. 3 show charging curves of 25℃ and 60℃, respectively. From the charging curve of 25℃, it was considered that since the charging final voltage is high for the sample coated with yttrium hydroxide or calcium hydroxide, the oxygen over-voltage becomes high and the sample restrains the oxygen evolution reaction. This tendency appears particularly conspicuously in the charging curve of 60℃. However, for the sample coated with cobalt hydroxide, the charging time up to the oxygen evolution reaction is long at 25℃, while in the case of the charging curve of 60℃, it was believed that it gets the same characteristic as the case of non-coating because the drop of the oxygen evolution potential is large.

From these results, it was proved that the high-temperature characteristics of a sintered nickel positive electrode coated with yttrium hydroxide or calcium hydroxide are greatly enhanced.

References

1) K. Shinyama et al., Extended Abstracts of the 65th Meeting of the Electrochemical Society of Japan, p. 162 (1998)
2) K. Shinyama et al., Extended Abstracts of the 41th Battery Symposium in Japan, p. 186 (2000)

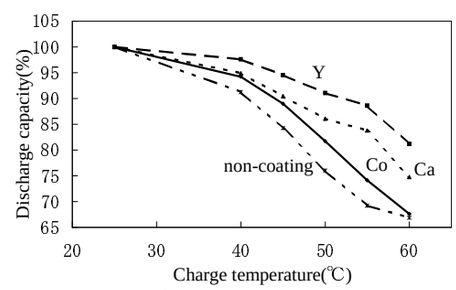

Fig.1 Charge temperature characteristics

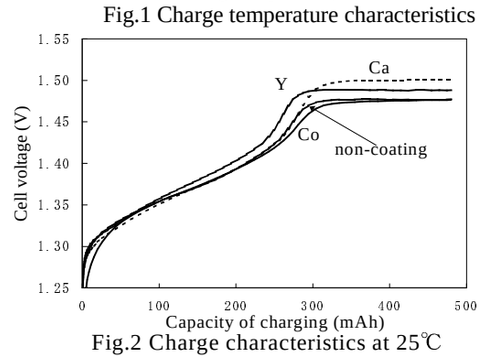

Fig.2 Charge characteristics at 25℃

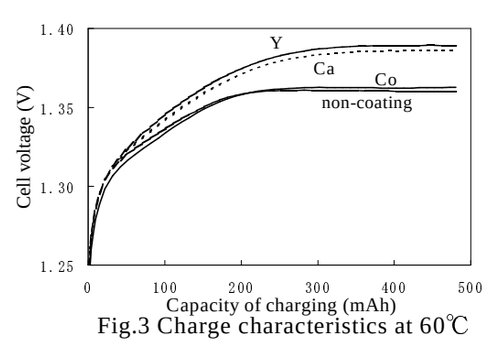

Fig.3 Charge characteristics at 60℃