



Electrochemical characteristics of Ni–Pd-coated MmNi₅-based alloy powder for nickel–metal hydride batteries

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Abstract

Negative electrodes were made from a multicomponent alloy (Mm_{0.9}Ti_{0.1}Ni_{3.9}Mn_{0.4}Co_{0.4}Al_{0.3}) powder coated with 10 wt.% palladium and nickel. The capacity decay of the Ni–Pd-coated alloy electrode was only 3% after 200 cycles compared with its saturated value at 27 °C. Experimental Ni–MH batteries (AA size, 1 A h) using the Ni–Pd-coated and uncoated alloy powders were assembled to clarify the discharge characteristics. The average discharge voltage of the battery using the Ni–Pd-coated alloy powder was 1.27 V at 0.4 C rate and the discharge capacity at 3 C rate was 76% of the value at 0.4 C rate.

Keywords: MmNi₅; Nickel-metal hydride batteries; Discharge capacity; Cycle lifetime

1. Introduction

Nickel–metal hydride (Ni–MH) batteries using hydrogen storage alloys as the negative electrode material have several advantages over conventional Ni–Cd batteries, e.g. high energy density and low level of pollutants [1]. The capacity decay of LaNi₅-based alloys with charge–discharge cycling has been ascribed to oxidized decomposition of the alloys to La(OH)₃ [2]. Microencapsulation of the alloy powder with various kinds of electroless coating such as Cu, Ni–P and Ni–B has been confirmed to be effective for improving the cycle lifetime and the high rate dischargeability [3–7]. The discharge capacity and high rate dischargeability of the negative electrode for MmNi₅-based alloys have also been improved by mixing with Co, Co₃O₄ and RuO₂ powder [8–10]. In our previous work the electrochemical characterization of Mm_{0.9}Ti_{0.1}Ni_{3.9}Mn_{0.4}Co_{0.4}Al_{0.3} alloy powder coated with 10 wt.% palladium and nickel was studied [11]. It was found that the Ni–Pd-coated alloy powder had a higher rate dischargeability than the uncoated alloy powder.

In this work the cycle lifetime of the Ni–Pd-coated Mm_{0.9}Ti_{0.1}Ni_{3.9}Mn_{0.4}Co_{0.4}Al_{0.3} alloy powder was studied in detail. Small cylindrical sealed Ni–MH batteries (AA size, 1 A h) using the Ni–Pd-coated and uncoated alloy powders were constructed and researched.

2. Experimental details

The hydrogen storage alloy Mm_{0.9}Ti_{0.1}Ni_{3.9}Mn_{0.4}Co_{0.4}Al_{0.3} (where Mm denotes misch metal, which comprised 43.1 wt.% La, 3.5 wt.% Ce, 13.3 wt.% Pr and 38.9 wt.% Nd) was prepared by induction melting and rapid cooling. The cast alloy was pulverized mechanically to 40–60 μm particle size. The alloy powder was activated by immersing in 60 ml l⁻¹ hydrochloric acid and 40 g l⁻¹ stannous chloride aqueous solution and then in 5 ml l⁻¹ hydrochloric acid and 0.3 g l⁻¹ palladium chloride aqueous solution. The activated powder was coated with 1 wt.% palladium in an aqueous solution containing 2 g l⁻¹ palladium chloride, 4 ml l⁻¹ hydrochloric acid, 10 g l⁻¹ sodium hypophosphite and 27 g l⁻¹ ammonium chloride (40–80 °C, pH=9–10) for 20 min and then the Pd-coated alloy powder was immersed in a chemical plating solution containing 36 g l⁻¹ nickel sulphate, 38 g l⁻¹ sodium hypophosphite, 18 g l⁻¹ sodium citrate and 38 g l⁻¹ ammonium chloride (30–60 °C, pH 9–10) aqueous solution to achieve microencapsulation of 10 wt.% palladium and nickel. The Ni–Pd-coated and uncoated alloy powders (100 mg) were mixed with nickel powder in a weight ratio of 1:3 together with a small amount of polyvinyl alcohol (PVA) solution as a binder and then pressed at a pressure of 150 kgf cm⁻² after vacuum drying at 150 °C. To prevent the electrode plate breaking into pieces with the charge–

discharge cycling, it was clamped and pressed by porous nickel. As counter- and reference electrodes a sintered nickel hydroxide ($\text{Ni}(\text{OH})_2/\text{NiOOH}$) plate and Hg/HgO 6 M KOH electrodes were employed respectively. The charge current was 150 mA g^{-1} and the discharge currents were 100 and 400 mA g^{-1} . The end of discharge was set to -0.5 V vs. Hg/HgO .

Both Ni–Pd-coated and uncoated alloy powders were mixed with 3 wt.% polytetrafluoroethylene (PTFE) dispersion, 0.3 wt.% carboxymethylcellulose (CMC), 0.5 wt.% PVA aqueous solution and a small amount of carbon powder. The mixture was filled into a porous nickel substrate and roller pressed in order to get a sheet, which was used to construct a small cylinder sealed cell. The sealed cell (AA size, 1 A h) was also constructed by rolling the MH electrode ($40 \times 85 \text{ mm}^2$, greater than 1.6 A h), the separator and the sintered nickel electrode ($40 \times 75 \text{ mm}^2$, greater than 0.9 A h). The cell was charged at 0.5 C rate (at 0.5 A charge current) for 2.5 h and discharged to 1.0 V at various rates. The charge–discharge characteristics of the battery using the Ni–Pd-coated alloy powder in comparison with those of the battery using the uncoated alloy powder were examined.

The crystal structure of the alloy powder after 200 charge–discharge cycles was identified by X-ray diffraction experiments with $\text{Co K}\alpha$ radiation.

3. Results and discussion

The discharge capacity of the alloy powder coated with 10 wt.% palladium and nickel is shown in Fig. 1 as a function of the cycle number. The saturated

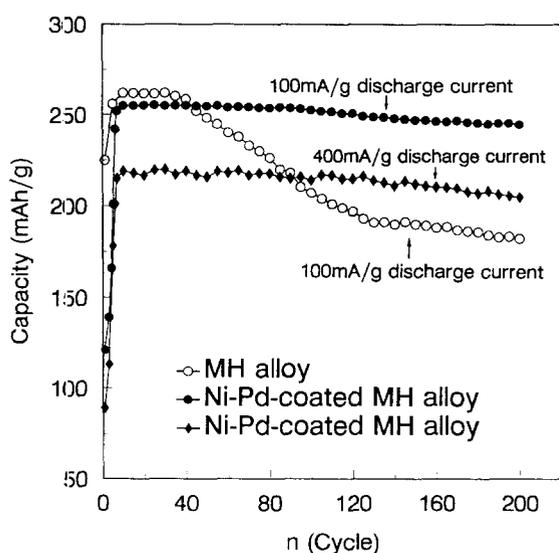


Fig. 1. Discharge capacities of Ni–Pd-coated $\text{Mm}_{0.5}\text{Ti}_{0.1}\text{Ni}_{3.9}\text{Mn}_{0.4}\text{Co}_{0.4}\text{Al}_{0.3}$ alloy powder and uncoated alloy powder as a function of cycle number at 27°C (at discharge currents of 100 and 400 mA g^{-1}).

discharge capacity for the Ni–Pd-coated alloy powder was found to be 255 mA h g^{-1} at 27°C . After 200 charge–discharge cycles the capacity decay of the Ni–Pd coated alloy powder was 3% at 100 mA g^{-1} discharge current, which was less than that of the uncoated alloy powder. The discharge capacity of the uncoated alloy powder decreased by about 30% compared with its saturated value after 200 cycles (at 100 mA g^{-1} discharge current). At 400 mA g^{-1} discharge current the discharge capacity of the Ni–Pd-coated alloy powder decreased from 219 to 208 mA h g^{-1} after 200 cycles. The discharge capacity of the uncoated alloy powder after 10 cycles was about 141 mA h g^{-1} at 400 mA g^{-1} discharge current [11], but after 100 cycles it had decreased to 123 mA h g^{-1} at the same discharge current. Thus the capacity decay is almost prevented by coating the surface of the alloy powder with nickel–palladium and the Ni–Pd-coated alloy powder is also suitable for high rate discharge. In previous work [11] it was indicated that hydrogen atoms could easily penetrate the Ni–Pd layer of the powder surface but that oxygen atoms found it harder to penetrate this surface layer. Thus the metallic elements in the surface covered with the Ni–Pd layer would not be easily oxidized with increasing charge–discharge cycles.

After 200 charge–discharge cycles the crystal structures of the alloy electrodes were examined by X-ray diffraction. The X-ray diffraction spectra of the alloy electrodes are shown in Fig. 2. Because of the addition of nickel powder to the alloy electrodes, the diffraction peaks of nickel are present in Figs. 2b and 2c. A small

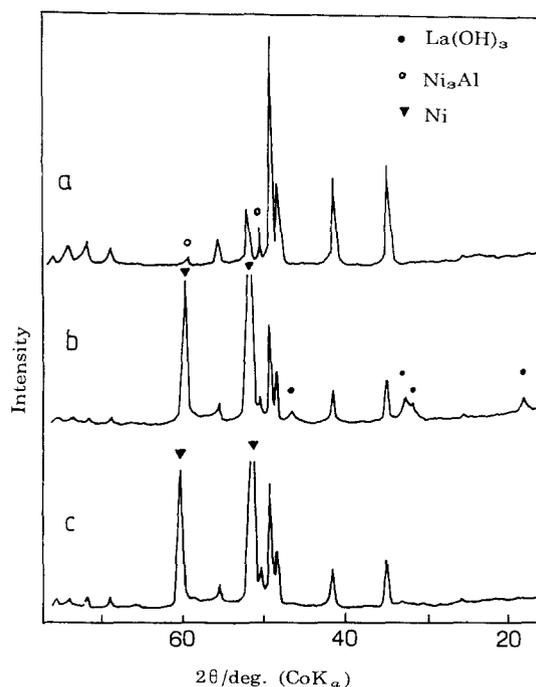


Fig. 2. X-Ray diffraction spectra of (a) uncoated alloy powder, (b) uncoated alloy powder after 200 cycles and (c) Ni–Pd-coated alloy powder after 200 cycles.

amount of Ni₃Al phase also exists in the alloy [10]. Because La was easily segregated into the surface and grain boundaries of the alloy powder with increasing charge-discharge cycles, the diffraction peaks of La(OH)₃ were observed in the uncoated alloy electrode after 200 cycles (Fig. 2c). The spectrum of Fig. 2c was obtained from the Ni-Pd-coated alloy powder after 200 cycles. It is seen in Fig. 2c that La(OH)₃ is no longer present. Thus the segregation of La is prevented in the Ni-Pd-coated alloy powder and the Ni-Pd-coated alloy powder has a long cycle lifetime.

From the discharge curves of the cylindrical sealed Ni-MH batteries with the Ni-Pd-coated and uncoated alloy powders after 10 cycles (Fig. 3), the battery using the Ni-Pd-coated alloy powder exhibited a higher discharge voltage than that with the uncoated alloy powder. The average discharge voltage of the battery using the Ni-Pd-coated alloy powder was 1.27 V at 0.4 C rate (at 0.4 A discharge current), while the average discharge voltage of the battery using the uncoated alloy powder was 1.21 V. With increasing charge-discharge cycles the average discharge voltage of the battery using the uncoated alloy powder decreased, e.g. to an average discharge voltage of 1.17 V at 0.4 C rate after 50 cycles (broken curve in Fig. 3a). Because oxygen atoms easily penetrate the surface layer of the uncoated alloy powder, the diffusion of hydrogen atoms in the surface layer will meet with obstruction, which influences the discharge voltage and high rate dischargeability of the battery. The average discharge voltage of the battery using the Ni-Pd-coated alloy powder remained at the same value of 1.27 V at 0.4 C rate after 50 cycles.

Fig. 4 shows the discharge current dependences of the discharge capacity and average discharge voltage for the cylindrical sealed cell at 27 °C in which the negative electrode was made from the Ni-Pd-coated alloy powder. The discharge capacity at 3 C rate (at

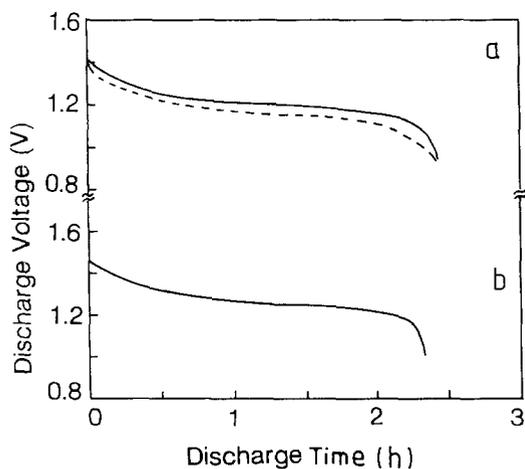


Fig. 3. Discharge characteristics of Ni-MH batteries using (a) uncoated alloy powder and (b) Ni-Pd-coated alloy powder after 10 cycles (the broken curve was obtained after 50 cycles).

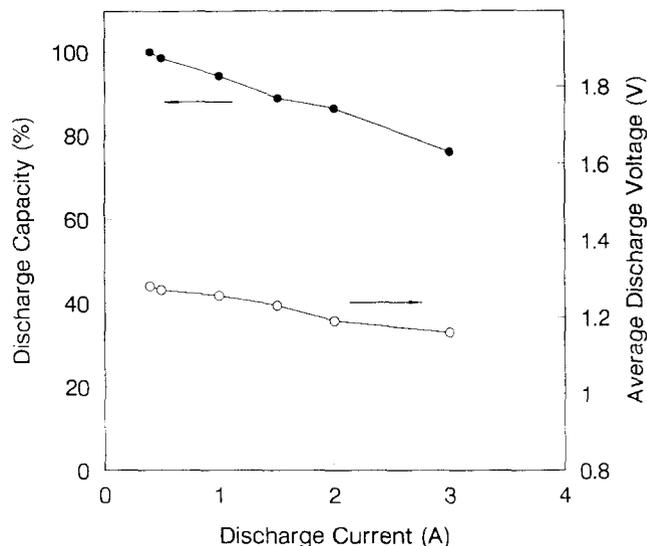


Fig. 4. Discharge rate dependences of capacity (●) and average voltage (○) at 27 °C for battery (AA size, 1 A h) using Ni-Pd-coated alloy powder.

3 A discharge current) was 76% of the value at 0.4 C rate. The average discharge voltage decreased from 1.27 V at 0.4 C rate to 1.16 V at 3 C rate. The reduced average discharge voltage is equal to the internal resistance multiplied by the discharge current. Thus the average discharge voltage of the battery decreases with increasing discharge current. The low average discharge voltage at higher discharge current can also be improved by decreasing the internal resistance of the battery.

4. Conclusions

The saturated discharge capacity of the alloy electrode coated with 10 wt.% palladium and nickel was 255 mA h g⁻¹ at 27 °C. After 200 cycles the capacity decay of the Ni-Pd-coated alloy electrode was only 3% and that of the uncoated alloy electrode was about 30% compared with the corresponding saturated values. This indicates that the Ni-Pd-coated alloy has a long cycle lifetime. The discharge capacity at 3 C rate for the sealed battery using the Ni-Pd-coated alloy powder was 76% of the value at 0.4 C rate and the average discharge voltage for the battery at 0.4 C rate was 1.27 V.

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