

Cause of the memory effect observed in alkaline secondary batteries using nickel electrode

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Abstract

The cause of the memory effect observed in alkaline-type rechargeable batteries such as nickel–cadmium and nickel–hydrogen batteries was studied using a positive capacity-limited nickel–cadmium cell and AAA-type commercially available nickel–cadmium and nickel–hydrogen batteries. From the X-ray diffraction (XRD) analysis, γ -NiOOH was observed on the nickel electrode in a charged state after repeating shallow discharge cycling of the cells or overcharging. This γ -NiOOH is initially formed at the collector side of the electrode and it then grows to the solution side during shallow discharge cycling. When the amount of γ -NiOOH formed is small, only β -NiOOH can be detected by conventional XRD, even when the memory effect is observed. In this case, γ -NiOOH can be detected by shaving the surface of the electrode, using an emery paper to remove the β -NiOOH covering. This γ -NiOOH disappeared within a few cycles of the normal charge–discharge cycling and the memory effect disappeared. It is concluded that the cause of the memory effect is mainly due to the formation of γ -NiOOH. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Memory effect; Alkaline secondary battery; Nickel–cadmium battery; Nickel–hydrogen battery; γ -Oxy-nickel hydroxide

1. Introduction

The memory effect observed in nickel–cadmium secondary batteries can be described as an apparent reduction in cell capacity to a predetermined cutoff voltage resulting from highly repetitive patterns of use. If a nickel–cadmium battery has been cycled to a certain shallow depth of discharge for a large number of cycles, for example, the battery will not produce a capacity as large as that corresponding to subsequent normal discharge–charge cycles. There are some papers on the cause of this effect. These are divided into those that are about a Cd electrode origin [1,2] and those that are about an NiOOH electrode origin [3]. However, the memory effect is observed in nickel–hydrogen batteries using a metal hydride (MH) [3,4] and hydrogen gas in space [5]. Therefore, it may be concluded that the cause of the memory effect is mainly ascribed to the nickel electrode.

Recently, the Ni–MH battery has gained much attention as the most promising candidate for the power sources of hybrid vehicles (HEV) and EV [4]. Therefore, it is urgent to clarify the cause of the memory effect. In the previous paper [6], we reported that the memory effect occurred

because β -NiOOH changed to γ -NiOOH by overcharging. However, there was an argument that the memory effect occurred even when γ -NiOOH could not be observed [7]. Therefore, we carried out further study to clarify the cause of the memory effect and concluded that it occurs due to the formation of γ -NiOOH. Although the formation of γ -NiOOH has been studied frequently [8,9] and some additives such as cobalt, cadmium, $\text{Ca}(\text{OH})_2$ and $\text{Zn}(\text{OH})_2$ meant for preventing the formation of γ -NiOOH have been reported [10–14], few of the concerned researchers seem to have given attention to the fact that the formation of γ -NiOOH is the cause of memory effect, except the present authors [6]. This paper reaffirms the fact that the memory effect occurs due to the formation of γ -NiOOH.

2. Experimental

The positive capacity-limited cell with a capacity of about 75 mA h was fabricated using a 1.8 cm \times 1.8 cm nickel sheet electrode cut from a sintered-type nickel electrode of a commercially available AAA battery (Panasonic P-4NPS, nominal capacity 250 mA h), which was then wrapped with a polypropylene nonwoven fabric separator. It was placed between two sheets of a 3.27 cm \times 3.5 cm cadmium electrode with a larger capacity — about 3.6 times larger than

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that of the nickel electrode. These electrodes were then sandwiched between two thin resin plates with many small holes, and the assembly was tightly bolted at the four corners. This cell was soaked and tested in an 8 M KOH solution.

Charge–discharge cycling was carried out at $30 \pm 1^\circ\text{C}$ using a charge–discharge unit (Hokuto Denko Co., 6ch, 10 V, 1 A) and a Y-T recorder (Yokogawa Electric Corp., micro R180, Model 4176) or a charge–discharge unit (Toyo System Co., TYS-30TU00) with a personal computer (PC) and charge–discharge controlling software. Charge–discharge cycling modes and conditions were as follows. At first, five normal charge–discharge cycles were conducted for the positive capacity-limited cell, where charging was conducted at a constant current of 20 mA (3.2 mA/cm^2) for 5 h and discharge was at 20 mA (3.2 mA/cm^2) to a 0.8 V cutoff voltage. Then, cycling at 20 mA (3.2 mA/cm^2) of charging current for 5 h and at 20 mA (3.2 mA/cm^2) of discharging current to a 1.2 V cutoff voltage was conducted for appropriate cycles to produce a memory effect (shallow discharge cycling). After repeating the given charge–discharge cycles under these conditions, the cell was discharged at the normal discharge rate of 20 mA (3.2 mA/cm^2) to a 0.8 V cutoff voltage to examine the effect of the preceding shallow discharge cycles and then charged for 5 h at 3.2 mA/cm^2 to obtain the second discharge curve. A paste-type AAA (height: 43 mm, diameter: 9.1 mm) commercially available nickel–hydrogen secondary battery with a nominal capacity of 550 mA h (Toshiba TH-4A) was used for cycling tests demonstrating the memory effect. For the AAA nickel–hydrogen battery, five normal charge–discharge cycles were conducted, where charging was conducted at a constant current of 50 mA for 16 h and a discharging current of 250 mA to a 0.8 V cutoff voltage. Then, 300 charge–discharge cycles were conducted at a charging current of 50 mA for 16 h and a discharging current of 50 mA to a 1.20 V cutoff voltage. After repeating this shallow discharging and overcharging, normal discharge was conducted at a constant current of 250 mA to 0.8 V. For a nickel–cadmium and a nickel–hydrogen battery, overcharging was conducted at 50 mA h for 1000 h for the former and 5000 h for the latter and then discharged at 250 mA h.

X-ray diffraction (XRD) analysis of the surface of nickel electrode was conducted using a Geigerflex RAD- γ A (Rigaku Co., Cu $K\alpha$, 40 kV, 100 mA).

3. Results and discussion

Fig. 1 shows the discharge curves of the positive capacity-limited nickel–cadmium cell. Curve A is the normal discharge curve. Curve B is the first discharge curve for the cell after five shallow discharge cycles. The normal charge–discharge and shallow charge–discharge cycling conditions for obtaining the memory effect have been given in Section 2. As seen in the enlarged figure, clearly, the work-

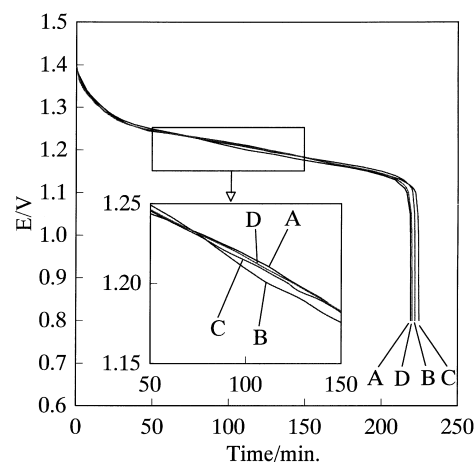


Fig. 1. Discharge curves of positive capacity-limited cell at 3.2 mA/cm^2 and at 30°C : (A) discharge curve of normal-state cell, i.e. a cell subjected to five normal charge–discharge cycles (see text), and discharge curves for the electrode after five shallow discharge cycles; (B) first discharge process; (C) second discharge process; (D) third discharge process. Charging was carried out at 3.2 mA/cm^2 for 5 h in curves A–D.

ing voltage of curve B is lowered, i.e. a memory effect appeared, and this voltage depression recovered to a normal discharge curve after the next normal charge–discharge cycling as seen in curves C and D. XRD analysis was conducted for a charged-state nickel electrode obtained from normal charge–discharge cycling and for that obtained from five shallow discharge cycles. These XRD patterns are shown in Fig. 2. The diffraction pattern of the charged state of normal electrode A and electrode B, which is the charged-state electrode after five shallow discharge cycles, did not exhibit diffraction peaks assigned to γ -NiOOH. However, after shaving 0.11 or 0.17 mm of the surface of this five-cycled electrode B using an emery paper, diffraction peaks

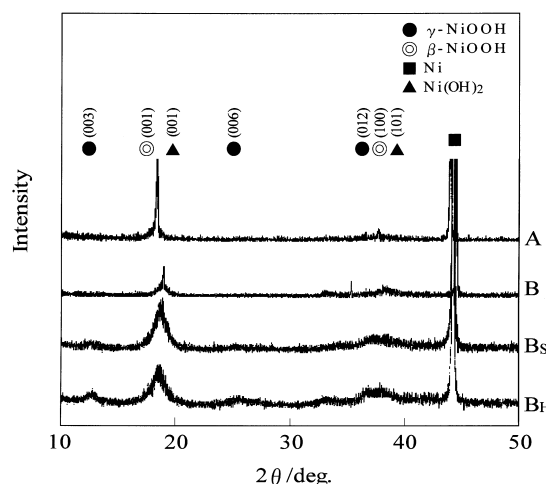


Fig. 2. XRD patterns for charged-state nickel electrode: (A) normal electrode; (B) electrode after five shallow discharge cycles; (Bs) 0.11 mm shaved electrode (electrode thickness: 0.12 mm) after five shallow discharge cycles; (BII) 0.17 mm shaved electrode (electrode thickness: 0.06 mm) after five shallow discharge cycles.

assigned to γ -NiOOH clearly appeared at 2θ equal to about 13° and 26° as seen in B_S (slightly shaved) and B_H (heavily shaved). This observation suggests that γ -NiOOH is present on the inner side of the electrode. For the discharged-state electrode after measuring curve B in Fig. 1, and charged-state electrodes after measuring curve B (i.e., the electrode before measuring curves C in Fig. 1) and curve C (the electrode before measuring curve D in Fig. 1), diffraction peaks due to γ -NiOOH could not be observed even after shaving had been carried out. It is clear that γ -NiOOH observed on electrode B in Fig. 2 disappeared after normal discharge to 0.8 V. On the shaved electrode in a charged state after repeating normal charge–discharge cycling, γ -NiOOH was not observed.

Upon increasing the number of cycles for shallow discharge cycling, the depression in working voltage became more pronounced as seen in curve B in Fig. 3, compared to curve B in Fig. 1. After 100 shallow discharge cycles, the low voltage observed at the discharge curve did not easily recover as is shown in curves C and D. The voltage difference observed in the initial parts of discharge curves A, B, C and D seems to be influenced by the quantity of γ -NiOOH left in the interface between the substrate and active materials. In the charged state after 100 shallow discharge cycles, a very small diffraction peak due to γ -NiOOH appeared at about 13° as shown in the diffraction pattern B in Fig. 4. After shaving this electrode, diffraction peaks due to γ -NiOOH became clearer as seen in the diffraction patterns of B_S and B_H . For the charged-state electrode obtained after measuring the discharge curve D in Fig. 3, XRD analysis was conducted (curve D in Fig. 4). In this case, diffraction peaks due to γ -NiOOH were observed for the shaved electrodes (D_S and D_H), but their intensities were smaller

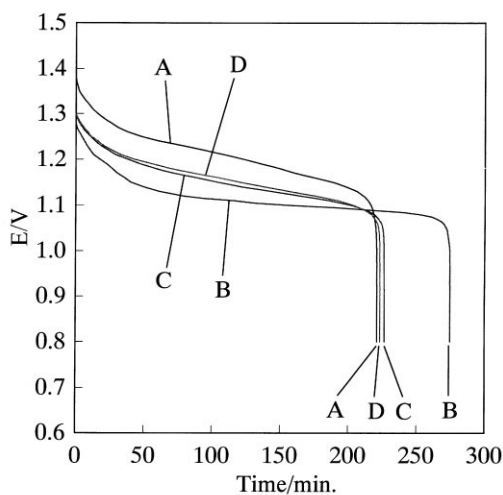


Fig. 3. Discharge curves of positive capacity-limited cell at 3.2 mA/cm^2 and at 30°C : (A) discharge curve of normal-state cell, and discharge curves for the electrode after 100 shallow discharge cycles; (B) first discharge process; (C) second discharge process; (D) third discharge process. Charging was carried out at 3.2 mA/cm^2 for 5 h in curves A–D.

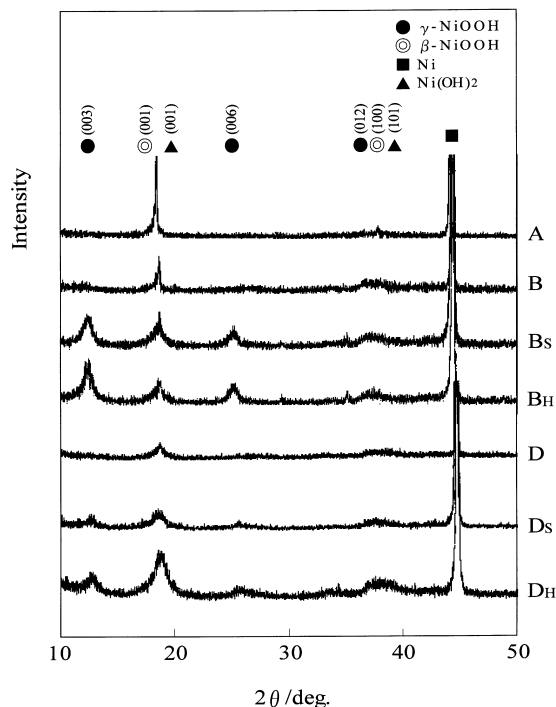


Fig. 4. XRD patterns for (A) charged-state normal nickel electrode, (B) charged-state electrode after 100 shallow discharge cycles, (B_S) 0.10 mm shaved electrode (electrode thickness: 0.13 mm) of electrode B, (B_H) 0.20 mm shaved electrode (electrode thickness: 0.04 mm) of electrode B and (D) charged-state electrode after measuring curve D in Fig. 3, (D_S) 0.10 mm shaved electrode (electrode thickness: 0.13 mm) of electrode D and (D_H) 0.17 mm shaved electrode (electrode thickness: 0.06 mm) of electrode D.

than those for B_S and B_H . This means that the amount of γ -NiOOH decreased by two or three normal discharge cycles. However, the voltage depression phenomena remained remarkably as seen in curve D in Fig. 3. It is well known that the discharge potential of γ -NiOOH is lower than that of β -NiOOH and the discharge capacity is, as a rule, larger for γ -NiOOH than for β -NiOOH, which is caused by a higher oxidation state of γ -NiOOH [15–18]. Our experimental results are not inconsistent with these descriptions for γ -NiOOH.

The shallow discharge cycle seems to cause overcharging. Therefore, using commercially available AAA-size nickel–cadmium battery, 1000 h of overcharging at 50 mA of charging current was carried out. As seen in curve B in Fig. 5, clearly, voltage depression and prolonged discharge time were observed as seen in curve B in Fig. 3. The shaved electrode in this overcharged state also showed the presence of γ -NiOOH as seen for shaved electrodes B_S and B_H in Fig. 6.

Next, commercially available AAA-size nickel–hydrogen battery was also tested, i.e. 5000 h of overcharging and 300 cycles of shallow discharge cycling were carried out. These are shown in Figs. 7 and 8. Curve B in Fig. 7 is the first discharge curve for 5000 h of overcharging, and Curve B in Fig. 8 is the first discharge curve after 300 cycles. Both of

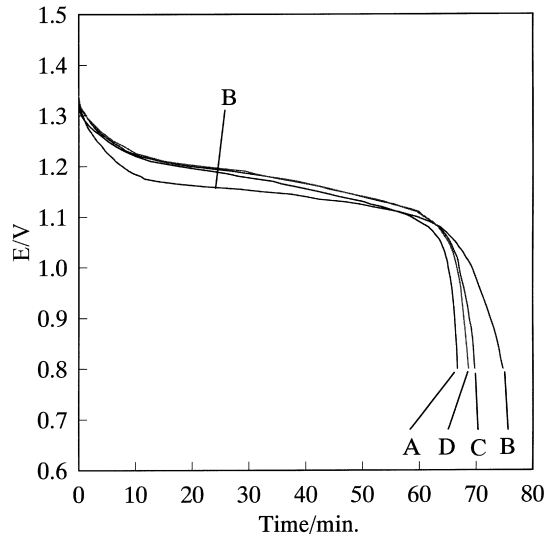


Fig. 5. Discharge curves of AAA-size nickel-cadmium battery at 250 mA and at 30°C: (A) discharge curve of normal-state battery, and discharge curves for the battery after 1000 h of overcharging at 50 mA; (B) first discharge process; (C) second discharge process; (D) third discharge process. Charging was carried out at 50 mA for 7 h in curves A–D.

these two curves clearly show the memory effect caused by overcharging and shallow discharge cycling, where the working voltage is lowered and discharge time is prolonged, i.e. a memory effect was also observed in the nickel-hydrogen battery. Second (curve C) and third (curve D) discharge curves for both cases recovered almost to the normal discharge curve A. XRD analysis for the charged-state nickel electrode after 300 cycles of charge-discharge cycling were conducted. NiOOH powder obtained from this 300-cycled electrode showed a small diffraction peak due to γ -NiOOH at about 13° (Fig. 9, B_p). As this electrode was a

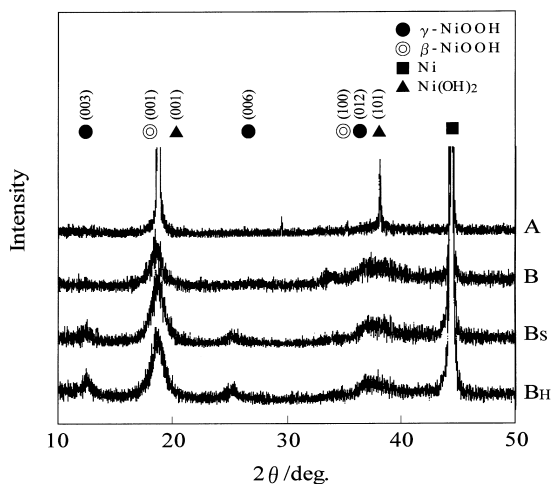


Fig. 6. XRD patterns for charged-state nickel electrode obtained from AAA-size nickel-cadmium battery: (A) normal electrode; (B) electrode after 1000 h of overcharging at 50 mA; (B_s) 0.10 mm shaved electrode (electrode thickness: 0.13 mm) of electrode B; (B_H) 0.19 mm shaved electrode (electrode thickness: 0.03 mm) of electrode B.

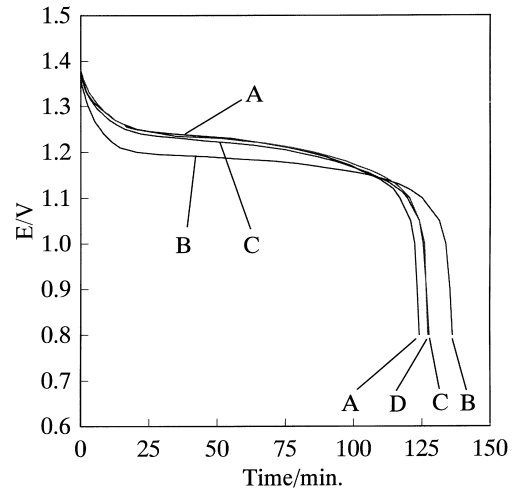


Fig. 7. Discharge curves of AAA-size nickel-hydrogen battery at 250 mA and at 30°C: (A) discharge curve of normal-state cell, and discharge curves for the battery after 5000 h of overcharging at 50 mA; (B) first discharge process; (C) second discharge process; (D) third discharge process. Charging was carried out at 50 mA for 7 h in curves A–D.

paste-type one, prepared by impregnating a nickel fiber substrate with nickel hydroxide, shaved electrodes could not be obtained, unlike a sintered-type nickel electrode of the nickel-cadmium battery. For the NiOOH powder of the 5000 h-overcharged battery, the XRD pattern was almost the same as B_p in Fig. 9. The reason why the shapes of diffraction patterns of NiOOH for nickel-cadmium and nickel-hydrogen cells are different seems mainly to be ascribable to the products of different battery makers, i.e. different materials may be added.

Combining with our previous results and discussion, it is concluded that γ -NiOOH can not be detected for the charged-state Ni electrode after some shallow discharge

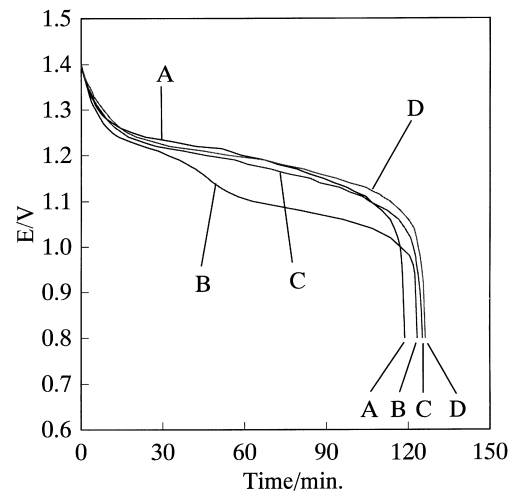


Fig. 8. Discharge curves of AAA-size nickel-hydrogen battery at 250 mA and at 30°C: (A) discharge curve of normal-state cell, and discharge curves for the battery after 300 shallow discharge cycles; (B) first discharge process; (C) second discharge process; (D) third discharge process. Charging was carried out at 0 mA for 16 h in curves A–D.

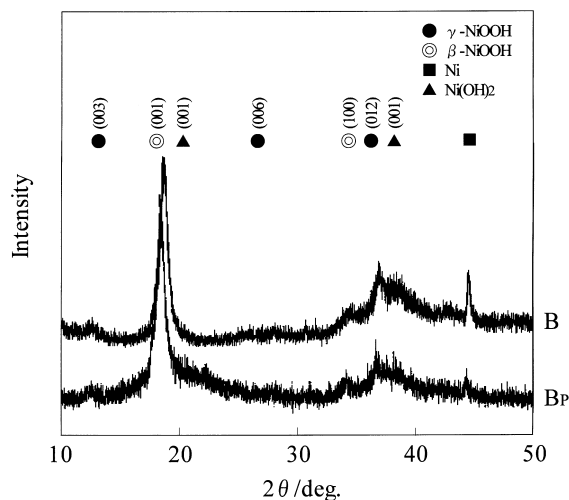


Fig. 9. XRD patterns for charged-state nickel electrode obtained from AAA-size nickel–hydrogen battery: (B) electrode after 300 shallow discharge cycles; (B_p) nickel oxide powder obtained from electrode B.

cycling, if its amount is small and the X-ray can not reach the γ -NiOOH phase. In this case, if the surface of the Ni electrode is shaved to remove the β -NiOOH covering, γ -NiOOH can be detected. Thus, β -NiOOH is formed under normal charging conditions; however, γ -NiOOH is formed at the collector side and it grows to the solution side during the overcharging conditions such as repetitive shallow discharge cycling.

4. Conclusions

From all these results and discussion, we have come to the following conclusions:

1. The cause of the memory effect observed in alkaline-type rechargeable batteries using nickel electrode is mainly due to the formation of γ -NiOOH.
2. This γ -NiOOH disappears within a few cycles of normal charge–discharge cycling.
3. γ -NiOOH initially forms at the collector side and it grows to the solution side as shallow discharge cycling progresses. Therefore, if the amount of formed γ -

NiOOH is small, X-ray can not reach the γ -NiOOH phase and only β -NiOOH can be detected. We think this is the reason why γ -NiOOH can not be detected on a nickel electrode even when a memory effect is observed.

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