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The Memory Effect Observed in Partial Charge-Discharge Cycling Process of Alkaline Secondary Batteries Using Nickel Electrode

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Introduction: Rechargeable alkaline batteries using a Ni electrode show working voltage lowering in discharge curves after repeated shallow charge-discharge cycling or overcharging. Such a phenomenon is called the memory effect. We have studied the cause of the memory effect and concluded that the cause of the memory effect is mainly due to γ-NiOOH formed at the collector side [1-4]. Recently, Ni-MH batteries have been used as the power sources for hybrid electric vehicle (HEV), where the batteries in HEV are used in a partially charged state not in full charged state. In the present paper, we discussed whether the memory effect will occur or not by repeating partial charge-discharge cycling under the non-full charged state of Ni electrode between 50-70% state of charge.

Experimental: The positive capacity-limited cell with about 69 mAh was fabricated a using sintered-type nickel electrode (5.95 cm^2) and cadmium electrode (29.82 cm^2). The cell was soaked and tested in 8 M KOH solutions. Partial charge-discharge cycling was conducted to keep constantly charging electricity at 10 mA (1.68 mA/cm^2) of charging current for 75 min (70% SOC) and 10 mA of discharging current for 70 min (50% SOC) and at 30℃. After repeating the partial charge-discharge cycling, the cell was discharged at 10 mA to a 0.8 V to examine the effect of partial charge-discharge cycling.

Results and Discussion: Figure 1 shows the discharge curves of the cell operated under different cycle numbers. Generally, the working voltage of cell after repeated partial charge-discharge cycling (B-E) is lower than that of the normal state (A), suggesting that cell suffers from the "memory effect". Moreover, the larger the cycle number is, the lower the working voltage is. Figure 2 shows Cole-Cole plots of charged state Ni electrode (B-E) after 100-500 cycles of partial charge-discharge cycling. The diameter of the semicircle at the higher frequency part, which is corresponding to the charge transfer resistance, increases as partial charge-discharge cycling number increases. Figure 3 shows the XRD patterns of Ni electrodes cycled for different numbers under partial charge-discharge condition. Compared to the normal state, new diffraction peaks related to γ-NiOOH appear at about 13° and 26° and the peak intensity increases as the cycle number increases. These results suggest that the "memory effect" exists in cell operated under repeating partial charge-discharge cycling and the origin of this effect is mainly due to the formation of γ-NiOOH.

References

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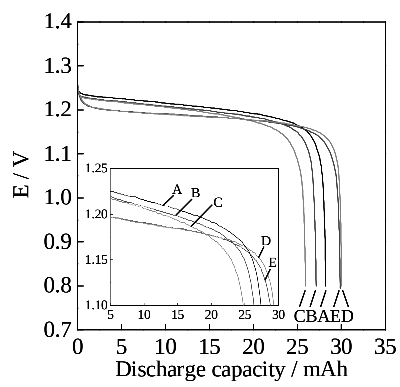

Fig. 1 Discharge curves of Ni capacity limited Ni-Cd cell obtained at 1.68 mA/cm^2 and at 30℃. A: Normal discharge curves at 50% SOC, Discharge curve at 50% SOC after B: 100 cycles, C: 300 cycles, D: 400 cycles, E: 500 cycles of partial charge-discharge (50 - 70% SOC) cycling.

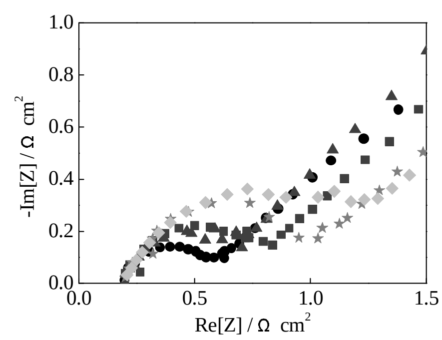

Fig. 2 Cole-Cole plots of charged-state Ni electrodes of ●: normal state and after ▲: 100 cycles, ■: 300 cycles, ★: 400 cycles, ◆: 500 cycles of partial charge-discharge cycling (50 - 70 % SOC) at 1.68 mA/cm^2 and at 30℃.

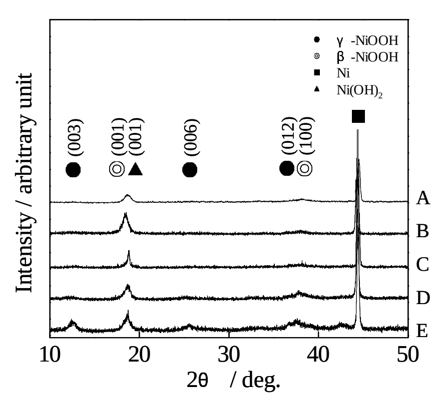

Fig. 3 XRD patterns for charged-state Ni electrodes of A: normal state and after B: 100 cycles, C: 200 cycles, D: 300 cycles, E: 500 cycles of partial charge-discharge cycling (50 - 70 % SOC) at 1.68 mA/cm^2 and at 30℃.