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INVESTIGATION OF "STEPPED" DISCHARGE CURVES IN SINTERED TYPE NICKEL-CADMIUM CELL

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Abstract

Formation of the nickel-cadmium alloy in the negative electrode of nickel-cadmium cell subjected to continuous charging at elevated temperatures (40~45℃) is shown to be one of the causes of the "stepped" discharge curves. The alloy has been characterized by electrode potential measurement and X-ray diffraction method. The potential lowering during discharge is related to discharge of the alloy. X-ray diffraction suggests that the nickel-cadmium alloy can be formed during charge in negative electrode by interaction of the two metals. Addition of Ni $(OH)_2$ into Cd $(OH)_2$ active material is found to form the alloy more readily than sintered negative electrode alone.

Key words : *Alkaline Storage Battery, Nickel-Cadmium Cell, Stepped Discharge Curve, Cadmium Electrode, Nickel-Cadmium Alloy*

1. Introduction

Sintered type nickel-cadmium cell has excellent high rate discharge properties over a wide temperature range. Low temperatures and high rates less affect the capacity of this cell than that of any other rechargeable system. It has a very good cycle life and is very reliable in most applications. However, after extended charge condition particularly at elevated temperatures nickel-cadmium cell may show on subsequent discharge two plateau regions separated by 100~150mV. Although various explanations have been given for this "stepped" discharge behavior the cause is still uncertain. Barnard *et al*[1]. reported that overcharged sintered cadmium electrode containing some Ni $(OH)_2$ additive showed a small potential arrest about 100mV lower than the normal Cd discharge potential. X-ray diffraction studies revealed lines that could not be attributed to Cd metal, Ni metal or any expected impurity. Several workers[2),3)] concluded that the second lower plateau of discharge curve might be attributed to a nickel-cadmium alloy. They suggested that this phase was Ni_5Cd_{21}. The objective of this study is to establish whether nickel-cadmium alloys are practically formed in the sintered cadmium electrode containing Ni $(OH)_2$ of nickel-cadmium cells, which are long time trickle charge at 45℃ and high rate charge-discharge cycles at 40℃.

2. Experimental

Positive and negative electrodes were obtained by conventional chemical impregnation of nickel sinters with requisite levels of Ni $(OH)_2$ and Cd $(OH)_2$. The positive electrodes were of the dimensions 8.0×5.0×0.1cm and contained 4.85g Ni $(OH)_2$ (nominal capacity 1.40Ah). Negative electrodes of the same size contained 3.00g Cd $(OH)_2$ (nominal capacity 1.10Ah) and additional level of Ni $(OH)_2$ about 10% based on the total weight of active material. The flooded electrolyte (s.g. 1.30 KOH solution at 25℃) nickel-cadmium test cells were subjected to two conditions charge-discharge cycles as shown in table 1.

3. Result and discussion

Fig. 1 demonstrates the effect of repeated shallow 1.25C discharge at 40℃ on shape of 0.2C discharge curves given by cadmium electrode.

Table 1. Conditions of charge and discharge to give rise to "stepped" discharge for sintered cadmium electrode

1. Repeated high rate charge and discharge cycles : Charge ; 1.25C*A, 70min. (Amount of 140% of discharge capacity), Discharge rate ; 1.25C, Cut-off voltage of discharge ; 1.050V, Temperature ; 40℃ 2. Repeated trickle charge and 1C rate discharge cycles : Charge ; 1/30CA, 50hours, Discharge rate ; 1C, Cut-off voltage of discharge ; -700mV (negative potential vs. Hg/HgO/6M KOH), Temperature ; 45℃
C : Rated capacity (5-Hour rate

Fig. 1a shows the preferred type of discharge curve in the initial stable condition. On the other hand, Fig. 1b shows secondary plateau at -800mV to -740mV in addition to the normal discharge plateau for cadmium metal (-910mV to -890mV). Fig. 2 demonstrates 0.2C discharge curves obtained by trickle charging cadmium electrode at 45℃. Fig. 2b also shows "stepped"

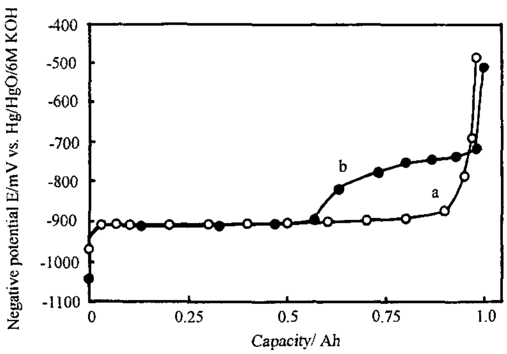

Fig. 1 0.2C discharge curves for the negative electrode.
(a) Normal curve for electrode.
(b) "Stepped" curve for electrode repeated high rate cycles at 40℃. Discharge temperature 28℃.

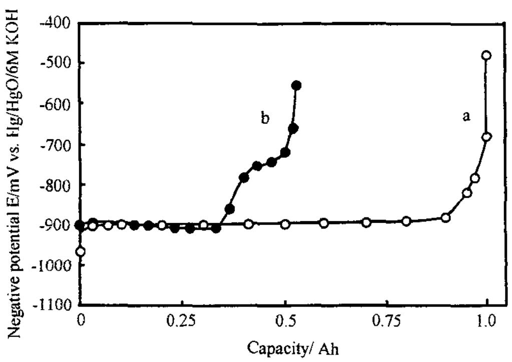

Fig. 2 0.2C discharge curves for the negative electrode.
(a) Normal curve for electrode.
(b) Curve for electrode repeated trickle charge at 1/30C rate and 1C rate discharge cycles. Discharge temperature 28℃.

discharge curve, but discharge capacity was decreased considerably. It was also demonstrated that the magnitude of lower plateau length and discharge capacity is smaller than repeated high rate cycles (Fig. 1b).

The X-ray diffraction patterns are shown in Fig. 3. Fig. 3b is the sample of charging state negative electrode after repeated high rate cycles. The peak of nickel-cadmium alloy Ni_5Cd_{21} at $2\theta=39.2°$ identified by Barnard *et al*[4]. could be detected as well as the peaks of Cd on the surface. After 0.2C discharge, the peak of Ni_5Cd_{21} disappeared on sample (Fig. 3C). It was suggested that the alloy be formed in the active material during the charging process. The alloy is seems to be discharged in the secondary potential plateau region.

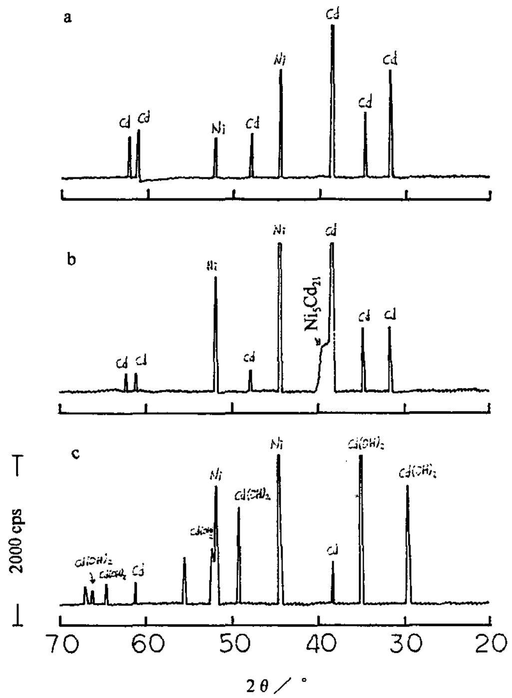

Fig. 3 X-ray diffraction patterns for negative electrodes.
(a) Normal pattern for electrode after charging.
(b) After charging at high rate cycles repeated.
(c) After the second plateau discharge.

4. Conclusion

This work demonstrates that formation of Ni_5Cd_{21} alloy in the negative electrode can give rise to a step of 100~150mV in cell discharge curves. The formation of alloy depends on the $Ni(OH)_2$ present in the electrode and also on temperature and on charge-discharge conditions. It is suggested that the Ni_5Cd_{21} alloy be discharged in the secondary plateau region.

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