EFFECT OF ELECTROLESS PLATING COBALT UPON CHARACTERISTICS OF NICKEL HYDROXIDE ELECTRODE FOR RECHARGEABLE ALKALINE BATTERIES[①]

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ABSTRACT The electroless plating cobalt of nickel hydroxide particles used as a positive active material for rechargeable alkaline batteries and the effects of the cobalt coating content on the nickel electrode performance were investigated. The characteristics of the electrode deposited cobalt, such as discharging capacity, utilization of active material and reversibility of $Ni(OH)_2/NiOOH$ redox reaction were studied by comparing charging/discharging curves and cyclic voltammetric results. The results indicated that the nickel hydroxide electrode deposited cobalt exhibited better charging/discharging cyclic characteristics and excellent electrode performance. The electrochemical impedance data of the nickel hydroxide electrode before and after electroless plating cobalt were obtained. These data indicated that the cobalt coating could decrease the contact resistance between the nickel hydroxide and the substrate, and increase the proton conductivity and electronic conductivity of nickel hydroxide. The mechanism of improving electrode performance by cobalt coating were discussed.

Key words nickel hydroxide electrode electroless plating cobalt electrode performance electrochemical impedance conductivity

1 INTRODUCTION

Nickel hydroxide electrodes have been widely used as positive electrode in Ni-Cd, Ni-H₂ and Ni-MH secondary batteries. Improvement in the electrode performance has always been one of the important research objectives all along. At the beginning of this century Edison first reported the addition of cobalt to nickel hydroxide which is the positive electrode active material of Ni-Cd batteries[1]. It is well known that cobalt additive in nickel hydroxide electrodes can increase the utilization of the active material, enhance the charging/discharging performance of the positive electrode and raise the overpotential of oxygen evolution reaction[2, 3]. Moreover, other additives introduced into nickel hydroxide lattice can also improve the electrode performance. Corrigan[4] studied binary 9: 1 composite hydroxides of nickel with 13 other metals which were prepared

by cathodic electrocoprecipitation and their electrochemical characteristics, and found that Co and Mn shifted the nickel hydroxide redox potentials to more cathodic values, and Cd, Pb and Zn poisoned the oxygen evolution reaction. Oshitani *et al*[5] developed a nickel electrode consisting of a solid-solution of $Ni(OH)_2$ and an adequate amount of $Co(OH)_2$ and $Cd(OH)_2$ where the content of the latter is relatively high at the electrode surface. The results showed that cobalt lowered the oxidation potential of nickel hydroxide probably by improving the proton conductivity of the electrodes, and cadmium prevented the formation of γ-NiOOH and raised the oxygen evolution potential. Zimmerman[6] found that the addition of 10% $Co(OH)_2$ could decrease the diffusion resistance of the active material and increase the depth of discharging. Armstrong[7] considered that the action of cobalt upon the characteristics of the nickel hydroxide is to raise

the oxygen overpotential and promote greater utilization of the active material. Armstrong[8] also studied the effect of cobalt addition upon the behavior of the nickel hydroxide electrode, showing that the nickel component reached a maximum oxidation level of (IV) when the amount of cobalt exceeded 50%. However, the relatively large amount of cobalt resulted in the increase in cost and a substantial decrease in discharging potential plateau. In addition, Visintin[9] have demonstrated that the distribution of additives in the active material were nonuniform and played a diminished role during activation of the active material.

Recently, in order to increase further energy density of Ni-Cd and Ni-MH batteries, a low-cost and higher performance pasted nickel electrode made from a porous nickel foam or nickel fibre substrate has been developed. Low conductivity of nickel hydroxide, however, which was an electronic insulator or a low conductivity p-type semiconductor[10], resulted in a low charging efficiency and revealed a poor electrode performance. Although addition of cobalt can improve the electronic conductivity of nickel hydroxide, it cannot effectively decrease the contact resistance between nickel hydroxide and nickel foam or nickel fibre substrate and increase the electrode performance due to the uneven distribution of additive.

Electroless plating methods have been widely used to prepare electronic devices and other industrial parts because they provide uniform surface. They are especially suitable for functional plating which utilizes the properties of the film itself. Electroless plating cobalt has been studied extensively due to its potential use in magnetic recording media[11]. In our previous study[12], electroless plating cobalt on the surface of spherical nickel hydroxide particles has been developed. In the present study, we will examine the changes of the electrochemical impedance and voltammograms of nickel hydroxide before and after electroless cobalt plating, and investigate the effect of various amount of deposited cobalt on nickel hydroxide electrode performance. Simultaneously, we will also discuss the mecha-

nism of improving electrode performance by cobalt deposit.

2 EXPERIMENTAL

2. 1 Electroless plating cobalt

The spherical nickel hydroxide was β-Ni(OH)$_2$ obtained by chemical precipitation. It incorporated about 1. 5% cobalt, which existed in the form of cobalt hydroxide.

Electroless plating cobalt was conducted according to our previous study[12]. The solution constituted cobalt sulfate, rochelle salt, ammonium sulfate and sodium hypophosphite. All the reagents used were analytical reagent (A. R.) grade. The pH of the solution was adjusted with a diluted NH$_3$•H$_2$O. The operating temperature was controlled using a CS-501 constant temperature water bath.

2. 2 Electrodes preparation

Electrode substrate was prepared from 1 cm × 1 cm square thin sheets of nickel foam, to which a nickel ribbon was spot welded as a current collector.

Electrode A was prepared by mixing spherical nickel hydroxide with cobalt powder (5% of the total active material), adding an appropriate amount of 1% polytetrafluorethylene (PTFE) aqueous suspension (60%) as a binder and then kneading to obtain a paste. The paste was filled into the nickel foam substrate using a spatula, dried at 60 ℃ for 1 h and then pressed at 20 M Pa for 1 min in order to assure a good electronic contact between the nickel foam substrate and the active material. Finally, the electrode was immersed in the electrolyte solution for 24 h.

Electrode B was directly made from spherical nickel hydroxide modified by electroless cobalt coating, which the amount of deposited cobalt coating was 5% of the total active material, mixing with 1% PTFE aqueous suspension (60%) to paste. The other details were the same as Electrode A.

2. 3 Electrochemical measurements

The electrolyte consisted of 6 mol/L KOH and 0. 6 mol/L LiOH. A three-compartment

electrolysis cell was used for the experimental measurements. Two nickel sheet counterelectrodes were placed to both sides and the working electrode was positioned in the center. Hg/HgO reference electrode was used with a Luggin capillary in close approach to the working electrode and contained the same alkali solution as that used in the working electrode cell.

Cyclic voltammetry experiments were performed using E G & G PARC Mode 273 Potentiostat/galvanostat, meanwhile M270 electrochemical analyzing system with IBM computer was used to controll experiment and for analyzing data. The electrodes were activated by charge/discharge cycling prior to experiment.

The a. c. impedance spectrum was obtained using a potentiostat (Model 273) and a lock-in amplifier (Model 5210). Electrochemical impedance system software (Model 388) was used to the interfaces between computer, lock-in amplifier and potentiostat.

Charge/discharge experiments were carried out using one nickel electrode with two metal hydride(MH) electrodes (provided by our institute). The electrodes were protected by a separator film. Charge was initially carried out at a rate of 0. 2 C for 150% theoretical capacity, holding for 30 min, then discharge was performed at a rate of 0. 2C to 0. 1V(vs Hg/HgO).

3 RESULTS

Fig. 1 shows the typical constant current discharging curves for Electrode A and Electrode B. As seen from Fig. 1, the discharging capacity of Electrode B was markedly higher than that of Electrode A. The discharging potentials for the two types of electrodes had an initial fall from 400~ 500mV to less than 350mV, followed by a more stable region on each curve. Below 250 mV the discharging potentials decrease rapidly. But, in Fig. 1 Electrode B exhibited a slightly increased discharging potential plateau region.

The discharging curves of the electrodes with various cobalt coating content are shown clearly in Fig. 2. It can be seen that there is a complex relationship between cobalt coating content and the discharging capacity, but that the

general trend is to increase capacity with the increase of cobalt coating content when cobalt coating content is less than 5 % and to decrease capacity when cobalt coating content is more than 7. 5 %. Thus, the optimum range of cobalt coating is about 5%.
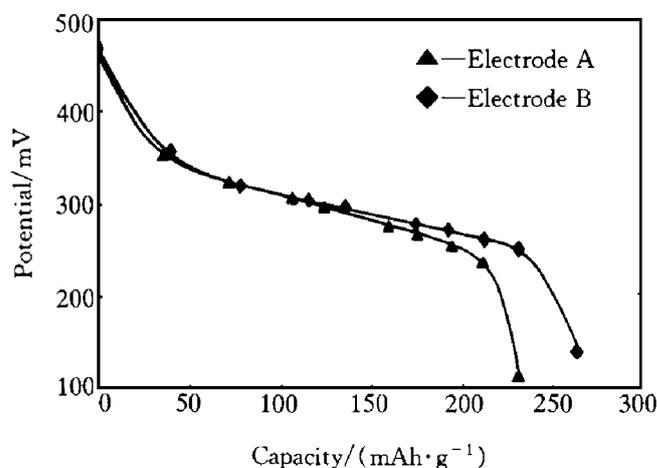

Fig. 1 Constant current discharging curves of different electrodes at a rate of 0. 2 C
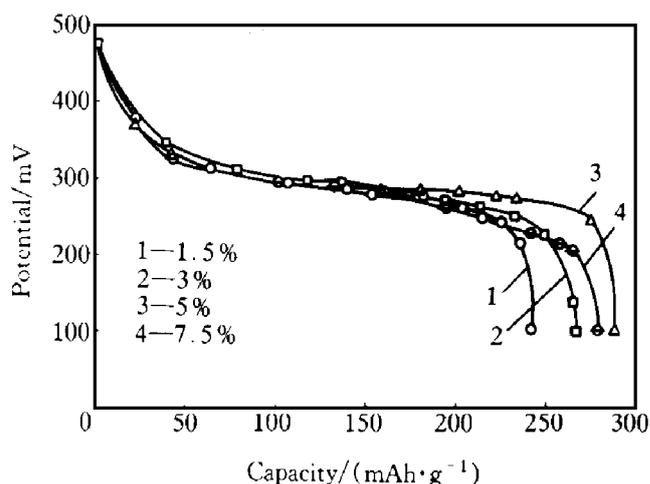

Fig. 2 Constant current discharging curves of electrodes in different cobalt coating content at a rate of 0. 2C

Fig. 3 shows the cyclic voltammograms of Electrode A and Electrode B. Apparently, for Electrode B deposited cobalt, only one anodic oxidation peak appearing at about 500 mV was recorded prior to oxygen evolution. Simultaneously, only one nickel oxyhydroxide reduction peak at about 240 mV was observed on the reverse sweep. Similar voltammograms has been

seen for Electrode A mixed 5 % cobalt powder as a conductor. But for Electrode A the anodic peak corresponding to nickel hydroxide oxidation reaction shifts to a more positive potential, and the cathodic peak potential corresponding to nickel oxyhydroxide reduction reaction shifts to less positive compared to that of Electrode B; this is in agreement with other observations[3, 4, 8] which incorporated cobalt in the lattice of nickel hydroxide in the form of Co(OH)$_2$.
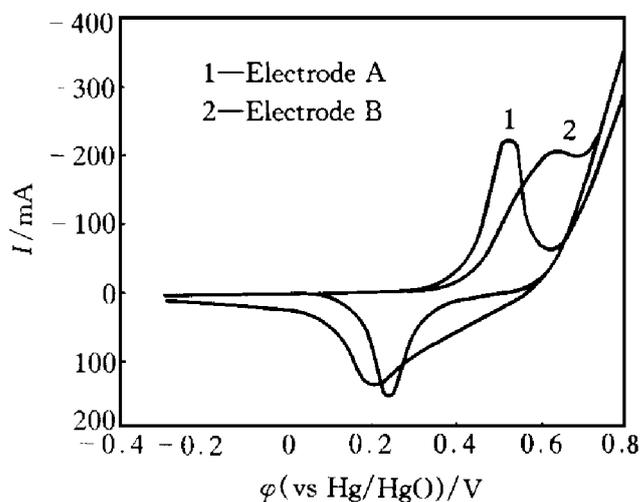

Fig. 3   Cyclic voltammograms of Electrode A and Electrode B

In order to compare conveniently the features of the electrodes, cyclic voltammetric results in Fig. 3 are tabulated in Table 1. The difference in the anodic and cathodic peak position, $\Delta E_{a, c}$, is taken as an estimate of reversibility of the redox reaction[4]. Oxygen evolution is a parasitic reaction during charging of nickel battery electrodes. To illustrate effects of two kinds of electrodes on the oxygen evolution reaction, the overpotential at 150 mA was estimated from voltammograms. For this reason, it was assumed that the return sweep provided the best approximation of the steady-state condition since there would be less interference from the nickel hydroxide redox relation[4]. Thus, the overpotential was taken as the potential on the return sweep required to produce 150 mA of anodic current minus the reversible oxygen potential (taken as 303 mV(vs Hg/Hg O)[4]).

It can be noticed from Fig. 3 and Table 1 that the presence of cobalt coating on the surface of nickel hydroxide particles allows the electrode to be charged at a significantly less positive potential (510 mV instead of 620 mV). The charging/discharging process appears to be more reversible in the presence of cobalt coating (Electrode B) than in its absence (Electrode A) ($\Delta E_{a, c}$ is 270 mV instead of 418 mV). Besides, oxygen evolution overpotential shifts to more positive value in the presence of cobalt coating than in its absence (397 mV instead of 357 mV).

Table 1   Results of cyclic voltammetry experiment for different electrodes

Electrode	E_a / mV	E_c / mV	$\Delta E_{a, c}$ / mV	Oxygen evolution overpotential / mV
Electrode A	510	240	270	397
Electrode B	620	202	418	357

Fig. 4 shows the electrochemical impedance plot of Electrode A, at high frequency the plot starts a well defined semi-circle, and as the frequency decreases it changes to a straight line with an angle of 45° respect to the real axis; when the frequency further decreases, this angle increases to 55°, indicating a capacitive behavior. Fig. 5 shows the complex plane plot of the impedance for Electrode B, at high frequency, a small section of capacitive arc indicating charge transfer resistance can be seen, but the overall plot mainly shows a shape which subtends an angle of 45° with the real axis at lower frequency, indicating a pure diffusion behavior. The above results are in good agreement with Murugesamorthi's study for nickel hydroxide electrode in Ni-H$_2$ batteries[13]. Barral et al[14] studied the Nyquist diagram of electrochemical formed Ni(OH)$_2$ layer and found similar phenomena, the diagram consisting of a high frequency semi-circle, then a linear part with 45° slope.

A comparison of the two impedance diagrams (Fig. 4, 5) shows that the semi-circle of high frequency is apparently different. The semi-circle of the electrode deposited cobalt has a slightly small diameter and only a small section of arc of semi-circle can be seen (Fig. 4), while the semi-circle of Electrode A is clearly seen. Generally, at a higher frequency the semi-circle
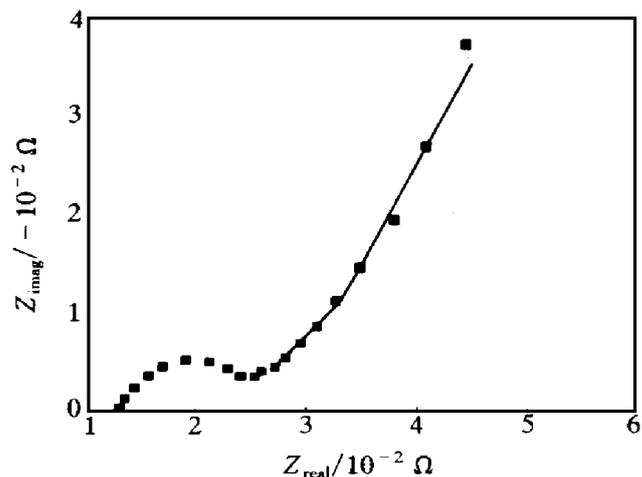
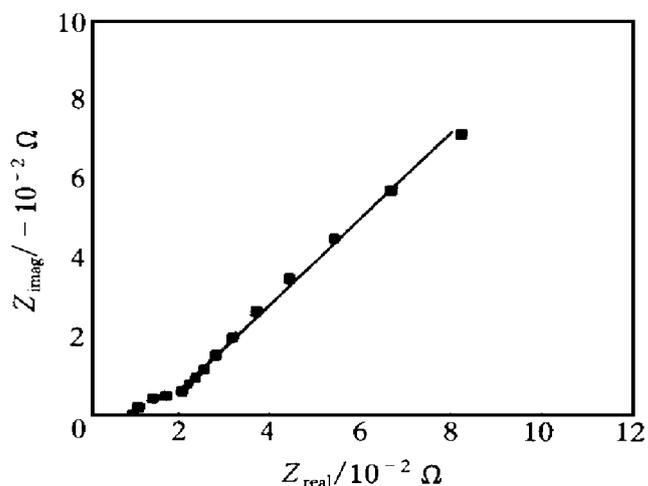**Fig. 4** Complex plane impedance diagram for Electrode A

Fig. 5 Complex plane impedance diagram for Electrode B

is the characteristics of the charge-transfer resistance acting in parallel with the double-layer capacitance[15]. This means that Electrode B deposited cobalt has a relatively lower charge-transfer resistance than Electrode A has. At low frequencies, the linear Warburg portion due to slow diffusion processes can be seen for Electrode A and Electrode B, the Warburg slope of Electrode A is about 45° at first, and afterwards 55°, while the Warburg slope of Electrode B is approximately 45° . In general, a higher slope signifies a slower rate of diffusion, and a lower slope a more rapid rate of diffusion.

For a planar electrode, the Warburg slope is proportional to $1/CD^{1/2}$ and is about 45°, where

C is the concentration of diffusing species and D is the diffusion coefficient. The behavior of porous electrode is more complicated. Karumathilaka and Hampso[16] concluded that the Warburg slope of porous electrode is between 22. 5° and 45° based on characteristics of an electrode with semi-infinite pores. It can be seen that the behavior of the electrode deposited cobalt is similar to that of planar electrode (Fig. 5). This is possibly attributed to compress more compact when the electrode is prepared due to existence of cobalt coating on the surface of nickel hydroxide and looks as a planar electrode. The higher Warburg slope for Electrode A at lower frequency may be attributed to hindered diffusion in the electrode pores.

In the impedance diagrams, the real component of the impedance at the highest frequency corresponds to the sum of the ohmic resistance. The main component is the resistance of electrolyte in the pores of the electrode and the separator but the electrode matrix also makes a contribution[17]. Comparing ohmic resistances of Electrode A and Electrode B, we can find that the value of Electrode B is lower than that of Electrode A (Table 2) . Table 2 is the results using a non-linear least squares procedure to fit the data of Nyquist diagrams (EQUIVCRT. PAS program) , where R_1 is the sum of the ohmic resistance; R_2 is the charge-transfer resistance; C is the double layer capacitance and Z_w is the Warburg impedance. It can be known from Table 2 that the electrode process of Electrode B is mainly controlled by diffusion and that of Electode A is controlled by charge-transfer process and diffusion.

4 DISCUSSION

The charging-discharging processes of the nickel hydroxide in alkaline solution can be described as a proton deintercalation-intercalation mechanism:

$$NiOOH + H_2O + e \underset{charge}{\overset{discharge}{\rightleftharpoons}} Ni(OH)_2 + OH^-$$ (1)
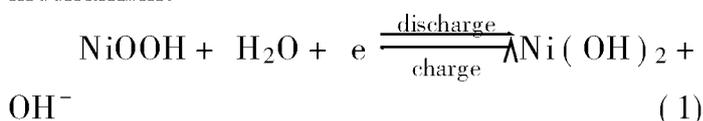
Reduction reaction of nickel hydroxide electrode has been found to follow diffusion kinet-

ics[18]. MacArthur[19] identified the solid-state proton diffusion from the oxidation state to the electrode-electrolyte interfaces is a rate-limiting process. The reduction process may be represented as[18]:
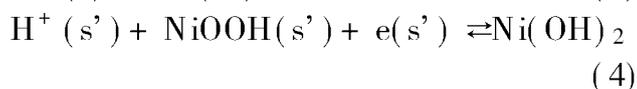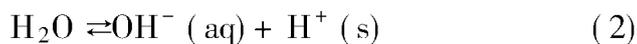
$$H_2O \rightleftharpoons OH^- (aq) + H^+ (s) \qquad (2)$$

$$H^+ (s) \rightleftharpoons H^+ (s') \qquad (3)$$

$$H^+ (s') + NiOOH(s') + e(s') \rightleftharpoons Ni(OH)_2 \qquad (4)$$

Table 2 Data from Nyquist diagrams for two electrodes

Parameters	Electrode A	Electrode B
Warburg slope/ ($^\circ$)	45~ 55	45
R_1/ Ω	1.28×10^{-2}	9.79×10^{-3}
R_2/ Ω	1.48×10^{-2}	5.35×10^{-3}
C/ F	2.80	2.27
Z_w/ Ω	1.62	28.8

Reaction (2) represents the formation of a proton at catalytic site (s) on the electrode/ electrolyte interface, reaction (3) involves diffusion of the proton from site (s) into the electrode to the charge transfer site (s'), and reaction (4) is the charge-transfer process involving the reduction of one of the higher valence species of active material in the lattice, represented here as simply NiOOH. However, it has been reported that the high-charged phase is an n-type semiconductor and the low-charged one is an electronic insulator or a low conductive p-type semiconductor[10]. To certain extent the addition of cobalt powder as a conductor can decrease the contact resistance between nickel hydroxide and the substrate. But it can be seen from Table 2 that R_1 value of Electrode A is apparently higher than one of Electrode B.

Cobalt coatings on the surface of nickel hydroxide particle can be oxidized into cobalt oxyhydroxide during charging, which henceforth remains as cobalt oxyhydroxide because of irreversibility of Co (II)/Co (III) couple to the capacity of the electrode[7]. Moreover, cobalt oxyhydroxide is highly conductive, its conductivity measured as compressed (1 000 kg/ cm^2) powder is found to be 12.8 S/ cm, which is far higher than that (0.15 S/ cm) of nickel oxyhydroxide in a fully charged state[10]. Thus, it is expected to provide continuity of a good electrical path between the active material and the substrate (see R_1 value in Table 2) and to increase the proton conductivity of nickel hydroxide, thereby improve the performance of electrode (Table 2). Zimmerman[18] reported that 10% cobalt additive decreased the diffusion resistance during the C/ 100 discharging by about one order of magnitude, indicating substantially increased ionic conductivity. However, after the surface of nickel hydroxide particle was deposited cobalt, the cobalt is uniform distribution on the surface of nickel hydroxide and the conductivity of nickel hydroxide can be effectively increased. Consequently, this can make nickel hydroxide be fully oxidized during charging and nickel oxyhydroxide be thoroughly reduced during discharging. It is obvious that the presence of cobalt coating on the surface of nickel hydroxide is essential for the better performance of electrode, such as higher utilization of active material, greater discharging capacity and better reversibility of Ni (II)/Ni (III) redox reaction. Moreover, due to the decrease of contact resistance between nickel hydroxide and nickel substrate, kinetic mechanism of electrode process has changed into diffusion control from mixing control of charge-transfer and diffusion.

Fig. 6 illustrates an assumed mechanism that the cobalt coating brings about a good electrical connection between each nickel hydroxide particle and the nickel foam substrate. At first, cobalt coating deposites homogeneously on the surface of nickel hydroxide and thoroughly connects the nickel hydroxide particle with the substrate (Fig. 6(a)). After charging (Fig. 6(b)), cobalt can be oxidized into Co (OH)$_2$ or CoO, then Co (OH)$_2$ or CoO is further oxidized into highly conductive cobalt oxyhydroxide. The overall reactions can be represented approximately as:

$$Co + 2OH^- \rightleftharpoons Co(OH)_2 + 2e \qquad (5)$$

$$Co + 2OH^- \rightleftharpoons CoO + H_2O + 2e \qquad (6)$$

$$Co(OH)_2 + OH^- \rightleftharpoons CoOOH + H_2O + e \qquad (7)$$

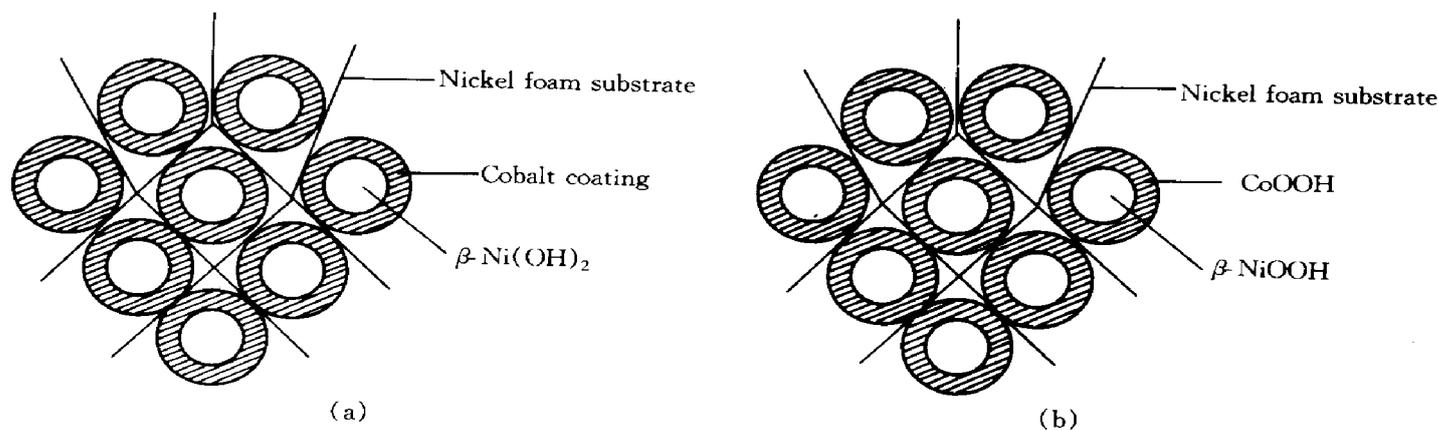$$CoO + OH^- \rightleftharpoons CoOOH + e \qquad (8)$$
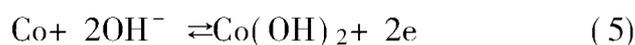
Fig. 6　Schematic diagrams of effect of cobalt coating
(a) —Before charging;　(b) —After charging

5　CONCLUSIONS

(1) The cobalt coating on the surface of nickel hydroxide particles can be oxidized into highly conductive cobalt oxyhydroxide during charging process and provide a good electrical conductivity network between the nickel hydroxide and the nickel foam substrate.

(2) The optimum content of cobalt coating is about 5%. When cobalt content is more than 7.5%, it is not economic and results in the slight decrease of discharging potential plateau.

(3) The presence of cobalt coating can increase electronic conductivity and protonic conductivity of nickel hydroxide, thus improve the performance of nickel hydroxide electrode, resulting in higher utilization of active material, greater discharging capacity and better reversibility of Ni(II)/Ni(III) redox reaction.

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