Short communication

Surface modification and electrochemical studies of spherical nickel hydroxide

Xianyou Wang [a,*], Jie Yan [a], Huatang Yuan [a], Zhen Zhou [a], Deying Song [a], Yunshi Zhang [a], Ligu Zhu [b]

[a] *Institute of New Energy Material Chemistry, Nankai University, Tianjin 300071, China*
[b] *Department of Chemical Engineering, Xiangtan University, Xiantan 411105, Hunan Province, China*

Abstract

Electroless cobalt on the surface of spherical nickel hydroxide has been used as a surface modifying method of active material for positive electrodes of rechargeable alkaline batteries. Cyclic voltammetric studies show that the electrodes exhibit higher oxygen overpotential and much more reversibility than ones of pure nickel hydroxide or nickel hydroxide with 5 wt.% cobalt added as a conductor. The discharge behaviour of the electrodes is also similar. © 1998 Elsevier Science S.A.

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1. Introduction

Cobalt additives have been widely used in nickel hydroxide battery electrodes since the time of Edison [1]. These increase the number of charge–discharge cycles that are available from nickel hydroxide electrodes in alkaline solutions [2]. It is generally believed that the presence of cobalt bestows many beneficial effects such as increased utilization of the active material, greater dimensional stability [3]. Increased oxygen evolution overpotential [3], reduced electric resistance [4] and improved electrochemical reversibility [5]. Thus, cobalt affects the ionic and electronic conductivity of nickel hydroxide. It was found, for example, that a cobalt additive decreases the diffusion resistance during '1100 discharge' by about an order of magnitude [4], which indicates a substantial increase in ionic conductivity. The electronic conductivity of the nickel hydroxide is also increased by the higher defect concentration provided by the cobalt.

In spite of many apparent advantages attained by the addition of cobalt to nickel hydroxide, some studies [6,7] have reported that the addition will result in a substantial decrease of the discharge potential. Moreover, there is still some controversy over whether the electronic conductivity is increased through the addition of cobalt to the inner crystal of nickel hydroxide. For example, Corrigan and Bendert [8] has reported that there was no evidence that any of the coprecipitated metal ions provided dopant states which increased the electronic conductivity. Thus, the utilization of active material of the nickel hydroxide electrode cannot be satisfactorily improved. On the other hand, most of papers published to date have focused on the electrochemical properties of conventional nickel hydroxide or thin films obtained by chemical impregnation and electrochemical impregnation of cobalt. Only a few studies have discussed the electrochemical properties of spherical nickel hydroxide as active material, especially after electroless depositing of cobalt or nickel on the surface.

It is the purpose of this paper to discuss the electrochemical properties after modifying the electronic conductivity by electroless cobalt deposited on the surface of spherical nickel hydroxide.

2. Experimental details

2.1. Electroless deposition of cobalt

The spherical nickel hydroxide used in this work was β-nickel hydroxide obtained by chemical precipitation. It
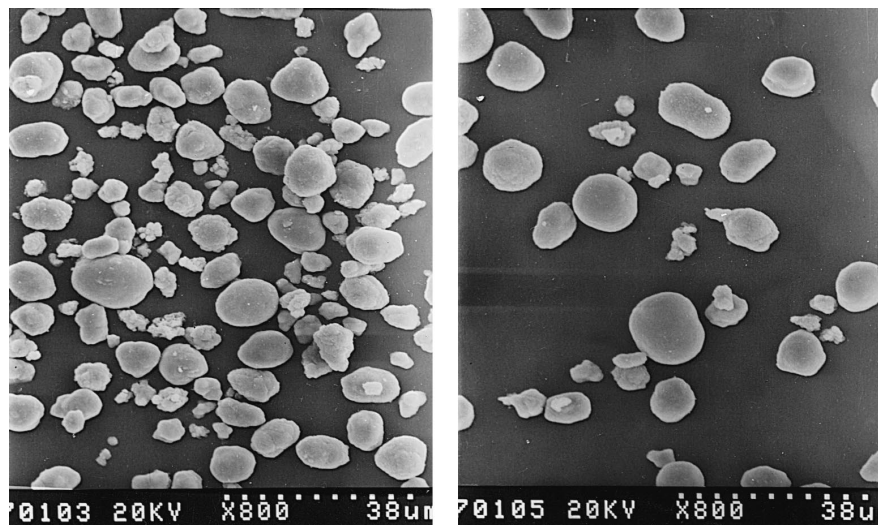
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* Corresponding author.

Fig. 1. Electron micrographs of spherical nickel hydroxide: (a) before electroless cobalt deposition; (b) after electroless cobalt deposition.

contained about 1.5 wt.% cobalt, added in the form of cobalt hydroxide. Electroless deposition of cobalt on the surface of spherical nickel hydroxide was carried out in a solution containing cobalt sulfate, sodium citrate, ammonium sulfate, sodium hypophosphite and additive. The morphology of the spherical nickel hydroxide before and after electroless cobalt deposition was examined using a scanning electron microscope (SEM) (Hitachi X-650).

2.2. Preparation of electrode

Nickel foam $(1 \times 1 \text{ cm}^2)$ was used as the nickel substrate. Three types of electrode were prepared as follows.

Electrode A. A small amount (1 wt.%) of polytetrafluoroethylene (PTFE) aqueous suspension as a binder was added to spherical nickel hydroxide and mixed. The mix-

ture was put into a nickel–foam electrode, dried in air at 60°C for 1 h and then pressed at 20 MPa for 1 min. Finally, a nickel ribbon was spot welded as a current-collector.

Electrode B was prepared by mixing spherical nickel hydroxide with cobalt powder (5 wt.%). The processing was the same as for electrode A.

Electrode C comprises an electroless deposit of cobalt (~ 5 wt.%) on the surface of spherical nickel hydroxide. The processing was similar to that used for electrode A.

2.3. Electrochemical measurements

Electrochemical measurements were performed in a three-compartment electrolysis cell at 25°C using an EG& G PARC Mode 273 Potentiostat/galvanostat with an IBM
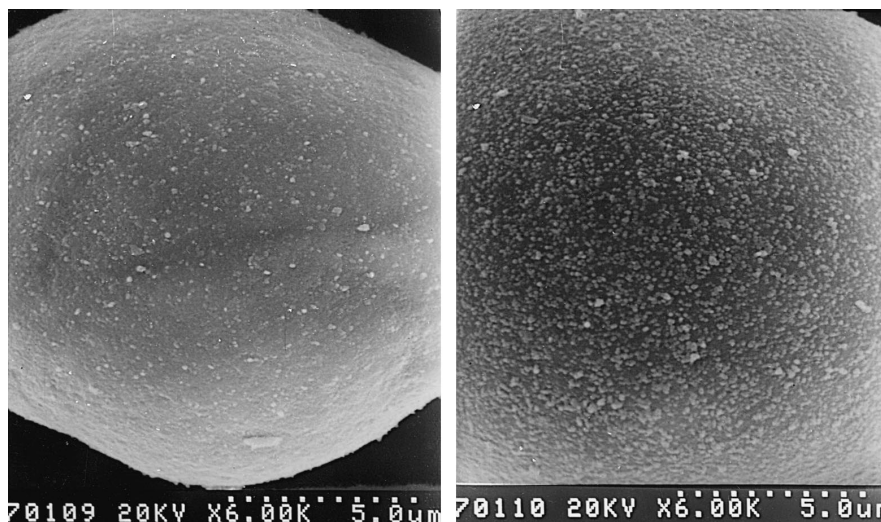

Fig. 2. High-resolution electron micrographs of spherical nickel hydroxide particles (from Fig. 1): (a) before electroless cobalt deposition; (b) after electroless cobalt deposition.
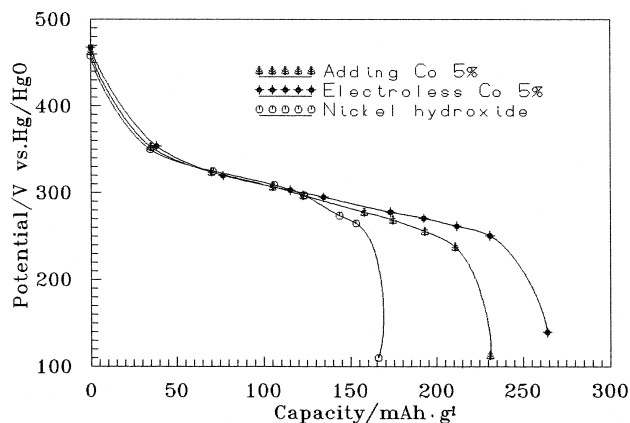
Fig. 3. Constant-current discharge curves at C-5 rate for different electrodes.

computer to control the experimental conditions and to analyze the data. A nickel mesh was used as a counter electrode. The electrolyte consisted of 6 mol/l KOH and 0.6 mol/l LiOH. All potentials were referred to a Hg/HgO/OH reference electrode in the same alkali solution as that used for the working electrode.

The test sequence was charged at the 0.1 C rate, held for 30 min, discharged at the 0.2 C rate. The cut-off potential for discharging was 0.1 V vs. Hg/HgO. The theoretical capacity of nickel hydroxide is 289 mAh (g-active material) given that the electrode reaction is:

$$Ni(OH)_2 + OH \rightleftarrows NiOOH + H_2O + e \qquad (1)$$
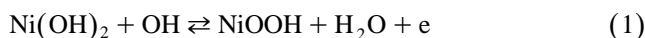
Prior to cyclic voltammetric experiments, the three electrodes were activated by charge–discharge cycling until the capacity stabilized.

3. Results

3.1. Surface morphology of spherical nickel hydroxide particle

Electron micrographs of spherical nickel hydroxide before and after electroless cobalt deposition are shown in Fig. 1a and b, respectively. The corresponding particles are shown at higher magnification in Fig. 2. Clearly, the size of the nickel hydroxide particles after electroless cobalt deposition is larger than that before such treatment. More-

over, the particles change colour from green into gray–black. The surfaces of the particles before electroless cobalt deposition are smooth but became coarse in the presence of cobalt (Fig. 2a and b). The coarse appearance increases the real surface area of the particle and, thus, improves the activity of nickel hydroxide and modifies its electrode performance.

3.2. Discharging behavior of the electrodes

Typical discharging curves for the three electrodes at the 0.2°C rate are given in Fig. 3. There is an initial decline on potential between 450 and 500 mV to less than 350 mV. This is followed by a more stable region. Limiting current regions are observed below 250 mV. The discharge capacity of electrode A is the lowest among the three types of electrodes. When 5 wt.% cobalt powder was added as a conductor, the discharge capacity was improved to a certain degree (electrode B). After depositing cobalt on the surface of the nickel hydroxide particles, however, the discharge capacity increased markedly (electrode C).

The discharge capacity, utilization and mean discharge potential are listed in Table 1. The data show that the discharge capacity and utilization of active material are a little improved after cobalt powder is added as a conductor. By contrast, after electroless deposition of cobalt on the surface of nickel hydroxide particles, these parameters greatly increase.

Previous investigations [5,8] have shown that cobalt decreases substantially the discharge potential of the nickel hydroxide redox reaction. Though these results relate to nickel hydroxide particles or film obtained by electrochemical impregnation of cobalt or chemical coprecipitation of cobalt, analogous discussion can also be obtained for electrodes using cobalt powder as a conductor. Similarly, after electroless deposition of cobalt on the surface of the particles, the mean discharge potential also will slightly decrease, but the magnitude of the decrease will be very small.

3.3. Cyclic voltammetric studies of the electrodes

Cyclic voltammetric technology is a useful method for studying cell characteristics. It enables independent estimation of oxidation as well as reduction reaction potentials and throws light in their mechanism. Further, within certain limitations, it enables estimations to be made [6,8] of

Table 1
Capacity and utilization of the active material for different electrodes

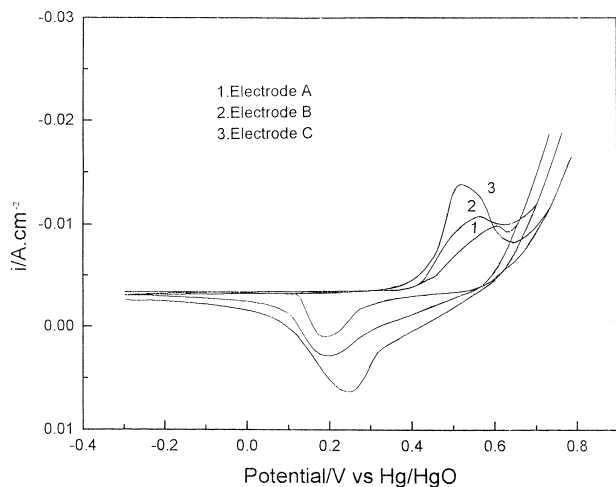| Electrode	Utilization (%)	Specific capacity (mA h/g)	Specific volume capacity (mA h/cm^3)
A	57.2	165	421
B	81.9	237	542.7
C	94.1	272	597.3

Fig. 4. Voltammograms of different electrodes: (1) Electrode A; (2) Electrode B; (3) Electrode C. Scan rate: 0.1 mV s^{-1}.

various parameters such as charge capacity, coulombic efficiency, reversible potential and reversibility.

Voltammograms for the three electrodes are shown in Fig. 4. Each electrode displays one anodic and one cathodic peak, corresponding to the nickel hydroxide redox reaction. The average peak potential, E_{rev}, is taken as an estimate of the reversible potential and the difference in the anodic and cathodic peak positions. $\Delta E_{a,c}$, is taken as an estimate of the reversibility of the reaction [6,8]. The difference between the oxygen evolution potential and the oxidation peak potential (DOP) is used as an indicator for raising the oxygen evolution overpotential [9]. These estimates are given in Table 2. As seen from Fig. 4, the oxidation peak of electrode B is slightly shifted to a cathodic potential compared with electrode A, while electrode C is significantly shifted to cathodic potential. The changes in reduction peak potentials of the electrodes are a complex relationship. Shifts in the reduction peak potential showed cathodic shift with electrode B and anodic shift with electrode C. Comparing the results in Table 2, the reversibility, charge capacity and oxygen evolution overpotential of the electrodes increase in the order:

Electrode C > Electrode B > Electrode A

This indicates that electrode C has a greater discharge

capacity and better reversible characteristics. Thus, electroless cobalt on the surface of nickel hydroxide particles is beneficial when using this material as positive electrodes in rechargeable alkaline batteries.

4. Discussion

Cobalt additives are generally considered to improve significantly the performance of nickel hydroxide through affecting both the ionic and the electronic conductivity of the active material [4]. The distribution of cobalt in the lattice of nickel hydroxide is heterogenous and thus the conductivity of nickel hydroxide is not maximized and the positive active-material cannot be fully used in the charge–discharge process. Because the conductivity of nickel hydroxide is very low, nickel(II) species accumulate at the hydroxide/electrolyte interface. These species are insulating and, consequently, prevent discharge of the crystallite core [1]. On the other hand, the presence of Co(III) which is oxidized during charge, may maintain the current path and hence allow a more complete discharge of the active material. But, whether chemically coprecipitating cobalt hydroxide into the nickel hydroxide lattice or forming a cobalt hydroxide film by electrochemical impregnation, the heterogeneous distribution of cobalt in the lattice of nickel hydroxide will cause the nickel oxyhydroxide which is formed during charge to be incompletely reduced back to nickel hydroxide. This results in a low utilization of active material, especially for a pasted electrode with a highly porous substrate. Thus, in order to improve the discharge behaviour of the electrode, most battery producers add cobalt powder as a conductor (see electrode B), cobalt. Nevertheless, mere mixing of cobalt powder with nickel hydroxide does not provide a good electrical path due to distribution of isolated cobalt powder that does not sufficiently connect nickel hydroxide with the adjacent substrate. A Japan patent [10] has presented a method for the electroless deposition of nickel on the surface of nickel hydroxide particles. Such a nickel coating will be oxidized to nickel oxyhydroxide during charge and therefore, cannot efficiently improve the conductivity of nickel hydroxide particles.
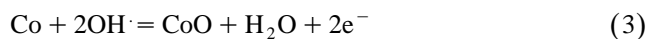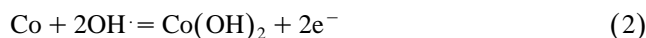
The electroless deposition of cobalt on the surface of nickel hydroxide particles can effectively improve the performance of electrodes (see electrode C in Table 1). This is considered to be due to the formation of cobalt oxyhydroxide (β-CoOOH) on the surface of nickel hydroxide particles during charge. The compound is expected to provide a good electrical path. Benson [11] found that β-CoOOH had a high conductivity of about 50×10^{-1} mho/cm when compressed as a powder at 1000 kg cm^{-2}. By contrast, β-NiOOH powder has a conductivity of only about 10^{-1} mho/cm. The formation of cobalt oxyhydrox-

Table 2
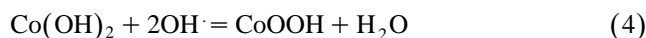Results of cyclic voltammetry measurements for different electrodes

Electrode	E_{anodic} / mV	$E_{cathodic}$ / mV	$\Delta E_{a,c}$ / mV	$E_{res.}$ / mV	DOP[a] / mV
A	637	191	446	414	17
B	591	203	389	397	89
C	508	242	−266	375	168

[a]Oxygen evolution potential taken as the value where the anodic current density = 0.0125 mA/cm^{-2}.

ide is attributed to the conversion of Co to Co (II) [12], i.e.,

$$Co + 2OH^. = Co(OH)_2 + 2e^- \qquad (2)$$

$$Co + 2OH^. = CoO + H_2O + 2e^- \qquad (3)$$

and

$$Co(OH)_2 + 2OH^. = CoOOH + H_2O \qquad (4)$$

$$CoO + OH^. = CoOOH \qquad (5)$$

Thus, $Co(OH)_2$ and CoO will be changed to a lightly conductive β-CoOOH. Because of the irreversibility of Co(II)/Co(III) and the good electrical conduction between the nickel hydroxide particles and the substrate [13], the higher active-material utilization is clearly correlated with the uniform distribution of cobalt on the electrode. Consequently, it is clear that uniform distribution of cobalt through electroless deposition of cobalt is responsible for the high active-material utilization of electrode C (see Table 1).

Battery producers are well aware that the addition of cobalt to the nickel electrode leads to a decrease in the half discharge potential. Armstrong et al. [1] has reported that the addition of 12 wt.% cobalt to the nickel hydroxide electrode produces a general depression of the plateau potential. A similar phenomenon is displayed in Fig. 3. This result differs, however, from those obtained either for an anodically grown nickel hydroxide layer on a nickel electrode under voltammetric conditions [14] or a chemically coprecipitated nickel hydroxide layer with a cobalt additive [1,2] namely, the decrease in the half discharge potential after electroless deposition of cobalt on the surface of nickel hydroxide particles is much smaller than that observed with other methods and is only 6 mV.

From a comparison of the curves in Fig. 4 and the results in Table 2, it is evident that the cathodic and anodic peak potentials of nickel hydroxide are shift significantly for the three electrodes, but for each type of electrode, only one anodic peak (at about 590 mV) is recorded prior to oxygen evolution. Similarly, only one oxyhydroxide reduction peak (at about 300 mV) is observed on the reverse sweep. Similar voltammograms have been reported for nickel hydroxide electrodes in alkaline solution [2,5,6]. The results in Table 2 demonstrate that electrode C has a higher oxygen evolution overpotential greater reversibility for $Ni(OH)_2/NiOOH$ electrode and a higher DOP value. These characteristics suggest that electrode C exhibits an apparent increase in the depth-of-discharge and excellent performance.

Armstrong et al. [1] considered that the action of cobalt is likely to be a surface effect where the additive alters the enthalpy of chemisorption. The change in thermodynamics thus alters the kinetics of the process. In this study, the cobalt distribution is more uniform and thus good electrical connection will be provided. Also, the electrode will display higher active-material utilization and better performance.

5. Conclusions

This study has examined the effects of surface modification of nickel hydroxide particles on positive electrode behaviour in rechargeable alkaline batteries. The main improvements are as follows.

(1) The shift of the nickel hydroxide redox reaction to less anodic potentials and the decrease in the oxidation potential of the active material improve both the reversibility of the Ni(II) Ni(III) redox reaction and the utilization of active material.

(2) Electroless deposition of cobalt increases the oxygen overpotential and thus allows full oxidation of the nickel hydroxide.

(3) A highly conductive cobalt oxyhydroxide layer on the surface of nickel hydroxide particles can be formed during charge after electroless deposition of cobalt and this allows a greater depth-of-discharge.

(4) Electroless deposition of cobalt for nickel hydroxide particles requires smaller amounts of cobalt than direct addition of cobalt to the electrode and also exhibits better electrode performance. Thus, this method is economically attractive to battery manufacturers.

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