

Effects of metallic cobalt addition on the performance of pasted nickel electrodes

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Received 8 October 1998; accepted 5 November 1998

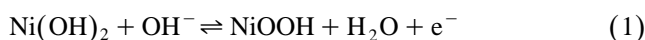
Abstract

A study is made on the performance of Ni-foam pasted nickel electrodes prepared from co-precipitated $\text{Ni}_{1-x}\text{Zn}_x(\text{OH})_2$ with and without cobalt powder. The addition of cobalt provides higher performance in terms of both discharge capacity and cycle life. Cobalt increases remarkably the active-material utilization through enhancement of the discharge depth due to the formation of conducting CoOOH during the first activation charging. The superior capacity stability during cycling is attributed to the synergistic action of zinc and cobalt, especially to the co-precipitation of zinc hydroxide which is considered to inhibit the formation of $\gamma\text{-NiOOH}$. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Nickel electrode; Metallic cobalt; Co-precipitated zinc hydroxide; Capacity; Cycle life

1. Introduction

The performance of nickel-based (Ni–Cd or Ni–MH) alkaline batteries is strongly influenced by the positive Ni electrode which determines the cell capacity. The redox reaction of Ni(II)/Ni(III) in alkaline media is generally expressed as



which is believed to be a solid-state proton intercalation–de-intercalation reaction [1,2]. In the charge–discharge process, both electrons and protons are exchanged and the processes are considered to be controlled by the bulk solid diffusion of protons [1,3–5]. Zimmerman [6] found that during discharge, when at higher potentials (average valence states above about 2.2), the diffusion resistance dominates the electrode resistance characteristics. By contrast, the charge transfer resistance begins to dominate when the electrode is discharged below about 0.3 V. This is due to the formation of a poorly conductive layer.

Cobalt [4,7–11] has been found to exert beneficial effects on the performance of the nickel electrode. The metal is introduced through either co-precipitation or elec-

trochemical co-deposition. In one study [10], however, CoO powder was mixed with the $\text{Ni}(\text{OH})_2$ powder.

Unates et al. [12] investigated co-precipitated zinc hydroxide through a study of the voltammetric behavior of a $\text{Ni}(\text{OH})_2 + \text{Zn}(\text{OH})_2/0.1 \text{ M KOH}$ electrode and found that the metal hydroxide mixture has a beneficial effect for the Ni(II)/Ni(III) redox couple at a Zn(II)/Ni(II) concentration ratio of about 0.2. They further studied [13] the influence of Co, Cd and Zn ions on the voltammetric behavior of the nickel hydroxide electrode in binary and ternary metal hydroxide layers in 0.1 M KOH and 0.08 M KOH + 0.02 M LiOH. The simultaneous presence of Co and Zn ions in the metal hydroxide layer improves the long-term stability and efficiency of the active material. The incorporation of Cd hydroxide increases the polarization of the oxygen evolution reaction. The presence of Li^+ ion in the solution increases the efficiency and hinders the decay of the active material, particularly for $\text{Ni}(\text{OH})_2 + \text{Zn}(\text{OH})_2$ composed electrodes.

Calcium compounds have been found [14,15] to increase the charge efficiency of the nickel electrode due to raising of the oxygen evolution potential. Oshitani et al. [16,17] found that the addition of $\text{Co}(\text{OH})_2$ and $\text{Cd}(\text{OH})_2$ can increase the charge-acceptance of Ni electrodes and prevent the formation of another oxide $\nu\text{-NiOOH}$ which can cause the swelling of Ni electrodes.

This paper is devoted to the study of the influence of doped Co powder on the electrochemical behavior of

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pasted nickel electrodes prepared from nickel hydroxide with co-precipitated Zn.

2. Experimental details

The preparation of Ni electrodes, with and without of Co, was as follows: 0.4 g nickel hydroxide (from Canada, containing 5 wt.% co-precipitated zinc) powder, 5 wt.% metallic cobalt powder or no powder (for comparison) and 5 wt.% graphite were mixed with 5% PTFE dispersion (containing a small amount of 1% MC) as binder. The paste was packed into a foam nickel substrate ($2 \times 2 \text{ cm}^2$). The resulting electrode was dried at 65°C and then pressed to a thickness of 0.5 mm. In order to investigate the conversion reaction of Co, a cobalt electrode was prepared, namely: 0.05 g of metallic cobalt powder was mixed with a 5% PTFE dispersion and the paste was packed into a Ni-foam substrate ($1 \times 1 \text{ cm}^2$). The electrode was then dried and pressed to a thickness of 0.5 mm.

The nickel electrodes were tested using a cell-performance testing instrument (DC-5) controlled by a micro-computer. A three-compartment glass cell containing 6 M KOH solution was used. A hydrogen-storage alloy electrode with a capacity well in excess of the nickel electrode was used as a counter electrode and Hg/HgO (6 M KOH) electrode was employed as the reference electrode. The discharge cut-off potential was 0.1 V vs. Hg/HgO reference electrode.

Voltammetric and a.c. impedance measurements were performed under potentiostatic control using a Solartron SI 1287 electrochemical interface in conjunction with a 1250 frequency response analyzer.

The crystal structure of the active material, viz., $\text{Ni}(\text{OH})_2$ (co-precipitated zinc), was determined by X-ray powder diffraction analysis using a Philips PC-APD diffractometer with $\text{Cu K}\alpha$ radiation. Scanning electron microscopic observations were carried out with a Hitachi S-570 microscope.

3. Results and discussion

3.1. Active-material utilization of nickel electrode

The specific capacities of nickel hydroxide (co-precipitated zinc), with and without the addition of metallic

Table 1

Specific capacities of nickel hydroxide, with and without addition of metallic cobalt, at various charge–discharge rates ($\text{mA h g}^{-1} \text{Ni}(\text{OH})_2$)

Active material	C/10	C/5	C/2	1 C
Pure $\text{Ni}(\text{OH})_2$ [15]	215	175	152	122
$\text{Ni}(\text{OH})_2 + \text{Zn}(\text{OH})_2$	213	191	183	171
$\text{Ni}(\text{OH})_2 + \text{Zn}(\text{OH})_2 + \text{Co powder}$	246	234	225	216

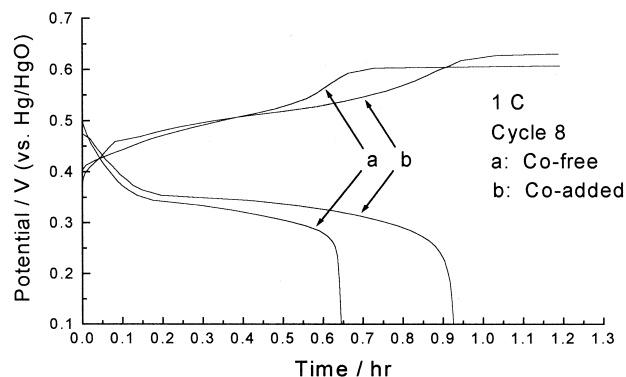


Fig. 1. Charge–discharge curves of nickel electrodes with and without Co.

cobalt, at various charge–discharge rates are listed in Table 1. The data show that the specific capacities of the electrode with addition of co-precipitated zinc hydroxide and mixed cobalt powder are much higher than the pure nickel hydroxide electrode, particularly at higher charge–discharge rates. This is mainly attributed to the metallic cobalt added. This will be discussed later.

The charge–discharge characteristics of Ni electrodes, with and without Co, at the 1 C rate are shown in Fig. 1. The oxygen evolution potential of the Co-added electrode is higher than that of the Co-free electrode which demonstrates that cobalt can improve the oxygen evolution overpotential. In addition, the depth-of-discharge (DOD) for the Co-added electrode is larger than that without Co (see Fig. 1) which can be also proved by the recovery potential after discharge at the 1 C rate, which is 0.337 and 0.311 V (vs. Hg/HgO) for Co-free and Co-added, respectively. It

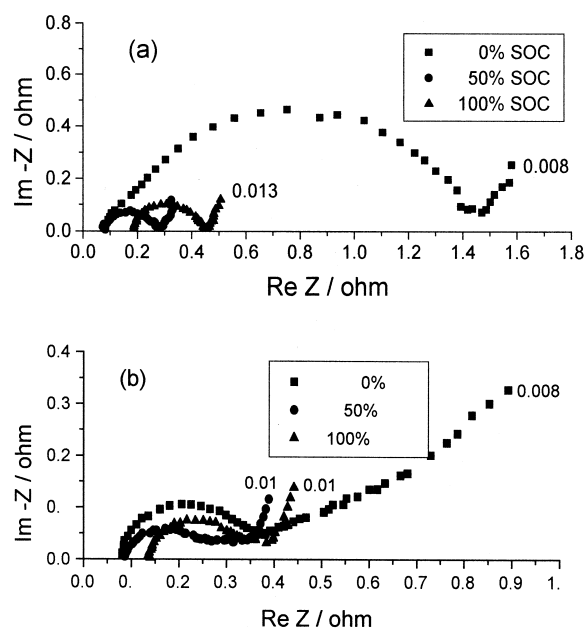


Fig. 2. Nyquist plots of nickel electrodes with and without Co.

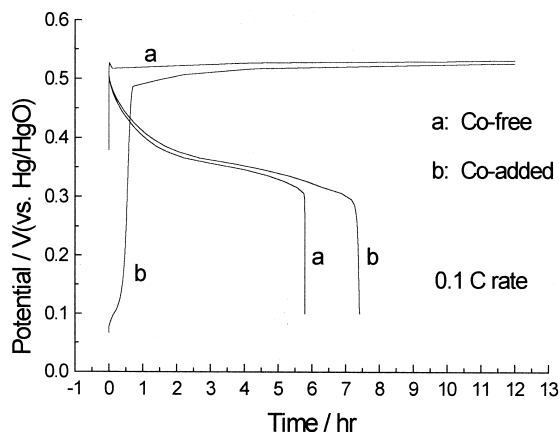
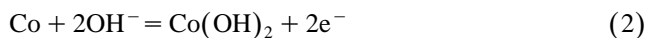


Fig. 3. First activation charge–discharge curves for Co-free and Co-added nickel electrodes.

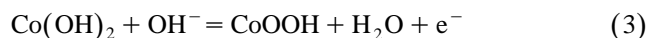
is well known that nickel hydroxide has poor conductivity due to its semi-conductive nature [4,18]. This is particularly true for pasted Ni electrodes, in which the particles are not tightly contacted unlike in thin-film or sintered nickel electrodes.

The impedance spectra of a Co-free and a Co-added Ni electrode are shown in Fig. 2. It can be seen that, in the case of Co-free electrode, the impedance in the discharged state is much greater than that in the charged state. While, for the Co-added electrode, the impedance on discharge is only slightly larger than that on charge. In the former case, with discharge proceeding, the NiOOH particles directly contacted with the foamed-Ni substrate are reduced to Ni(OH)₂, which is a poor conductor of electrons. Thus, the NiOOH particles located in the middle of the foamed-Ni pores are not efficiently reduced and the experimental apparent electrochemical reaction impedance is high. The addition of Co decreases the impedance of the nickel electrode in the discharged state.

The first-charge characteristics of Co-free and Co-added Ni electrodes are presented in Fig. 3. The lower potential plateau is characteristic of the Co transformation reaction. During the first activation charge process, the added Co is oxidized to a higher valency state, CoOOH, which cannot be reduced during the subsequent discharge process. Thus, converted CoOOH provides a good electrical path between the nickel hydroxide particles and the foamed-Ni substrate and increases the active-material utilization of the electrode. In order to elucidate the conversion reactions of Co in alkaline solution, a metallic cobalt powder electrode was prepared and cycled in 6 M KOH solution. Its cyclic voltammetric behaviour is illustrated in Fig. 4. The first anodic peak current occurs at about -0.65 V, which corresponds to the reaction:



This reaction is irreversible because its cathodic peak is negligible compared with the anodic. The second anodic peak at about 0.4 V is likely to correspond to the reaction:



When the electrode potential is beyond the potential region (about -1.2 to 0.6 V), the solution becomes unstable and hydrogen or oxygen evolution takes place.

3.2. Cycle life of nickel electrode

Figs. 5 and 6 show, respectively, the XRD pattern and electron micrographs for co-precipitated nickel/zinc hydroxide powder. As shown in Fig. 6a, the particles are spherical with a size distribution from about 2 to 20 μm . This provides a high filling-density during the preparation of Ni electrodes. Furthermore, the characteristic peaks in Fig. 5 show that the hydroxide has a crystal structure of β -Ni(OH)₂ and some disorder in the crystal lattice which is characterized by the full width at half maximum (FWHM) values of the (001)($d_{4.666}$), (101)($d_{2.338}$) and (102)($d_{1.760}$) diffraction lines. Fig. 6b shows the fine crystal texture (sub-structure of a particle in Fig. 6a); this is beneficial for the active-material utilization, high rate charge–discharge and cycle life of Ni electrodes [19].

The charge–discharge cyclic behaviour of co-precipitated Ni(OH)₂ + Zn(OH)₂ electrodes, with and without Co powder, are shown in Fig. 7. Clearly, the Co-added electrode not only has higher discharge capacity but also exhibits superior stability of capacity during charge–discharge cycling. This can be attributed to the synergistic effect of co-precipitated zinc and added cobalt. During charging of a pure Ni(OH)₂ electrode, especially during overcharge, the product, β -NiOOH, can be easily transformed into γ -NiOOH which has a density that is lower than β -Ni(OH)₂ or β -NiOOH [20]. Hence, the formation of γ -NiOOH during cycling can cause swelling and blistering of the electrode, so as to induce the degradation of the

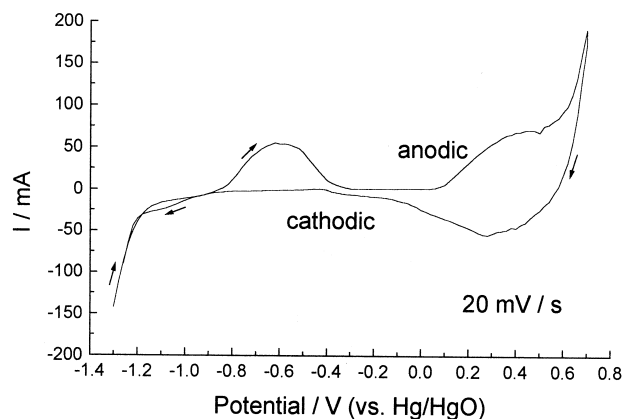


Fig. 4. Voltammogram for Co powder electrode.

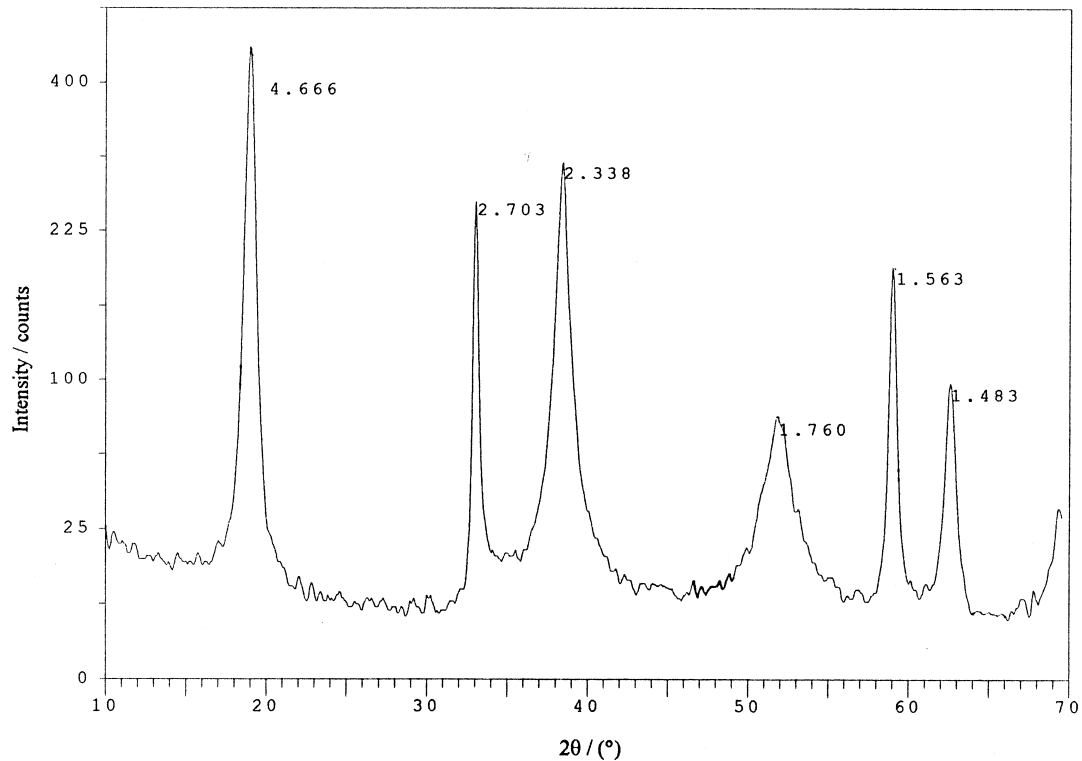


Fig. 5. X-ray powder diffraction pattern for co-precipitated Ni(II)/Zn(II) hydroxide.

electrode by decreasing the subsequent charging efficiency and discharge depth. A high charging current density favours the formation of γ -NiOOH [10]. The addition of $\text{Cd}(\text{OH})_2$ to $\text{Ni}(\text{OH})_2$ crystals has been found to inhibit the formation of γ -NiOOH and the swelling can be almost completely prevented by the addition of cobalt and cadmium together, even with overcharging at the 1 C rate [16,17]. Zinc also inhibits the development of γ -NiOOH.

Solid solutions of Ni/Zn hydroxide, $\beta\text{-Ni}_{1-x}\text{Zn}_x(\text{OH})_2$ electrodes have been studied [21] and compared with a Zn-free electrode. The results showed that co-precipitated $\text{Zn}(\text{OH})_2$ can inhibit the formation of γ -NiOOH, and suggested that insertion of an inert cation additive reduces the effective negative charge of three-layer stacks during

hydroxide oxidation, hence, inhibits the transformation of β -type solid solutions to the γ -phase. Inhibition of γ -phase formation, as a rule, correlates with higher disordering of the nickel hydroxide structure which, in turn, correlates with higher reversibility of Ni electrode during discharging. The detailed mechanism of zinc in providing cycle stability of nickel electrodes deserves further investigation.

On the other hand, the addition of cobalt has an enhancing effect on the cycle stability of the $\text{Ni}(\text{OH})_2 + \text{Zn}(\text{OH})_2$ electrode. First, the added Co increases the number of reaction sites and, hence, decreases the current density of the active material due to its good conductivity. Second, the addition of Co may relieve the internal electrode stresses and retain the charge–discharge efficiency during cycling and, thereby, reduce the rate of capacity degradation.

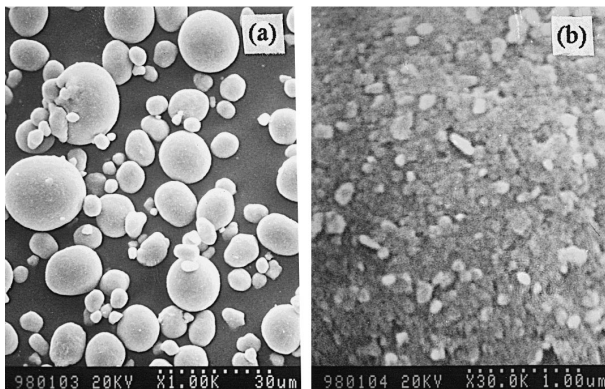


Fig. 6. SEM micrographs for co-precipitated Ni(II)/Zn(II) hydroxide.

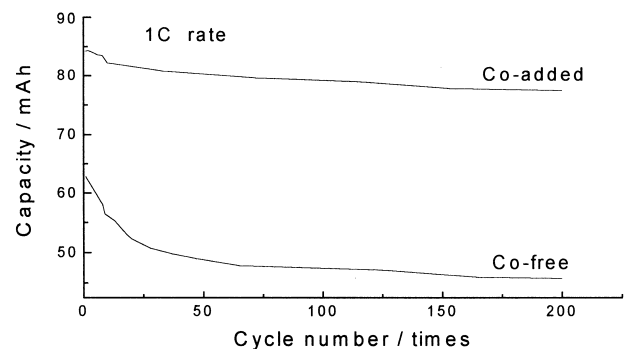


Fig. 7. Cycle life of the Co-free and Co-added Ni electrodes.

4. Conclusions

The present study has centred on the positive effects of cobalt and zinc for pasted nickel electrodes. The experimental results have showed that the electrode prepared by chemically co-precipitated $\text{Ni}(\text{OH})_2 + \text{Zn}(\text{OH})_2$ doped physically with metallic Co powder exhibits a superior performance, both in discharge capacity and in cycle life. Cobalt plays an important role in improving the active-material utilization in nickel electrodes. The good cycle stability is due to the synergistic effect of metallic cobalt and co-precipitated zinc, the latter may restrict the formation of the γ -NiOOH phase and thus slow down the loss of capacity.

Acknowledgements

This work has been supported by the Chinese ‘863’ Project and the Zhejiang Provincial Natural Science Foundation of China.

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