Effect of cupric oxide addition on the performance of nickel electrode

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Abstract

Nickel hydroxide is widely used as the active material in positive electrodes of rechargeable alkaline batteries. In this paper, the effects of cupric oxide additive on the characteristics of the nickel electrode have been investigated. The results indicate that the addition of cupric oxide in the nickel electrode can prevent swelling of the nickel electrode during charging and thus prolong the cycle-life of rechargeable batteries. Cupric oxide additive can also promote the transformation from cobalt powder to β-CoOOH and make cobalt additive be well-spread on nickel hydroxide particles, thus facilitate the charging process in the initial stage. © 1999 Elsevier Science S.A. All rights reserved.

1. Introduction

With the increasing demand for portable electronic devices and electric vehicle applications, much interest is focusing on the development of alkaline batteries with high specific energies [1]. In particular, the development and commercialization of nickel/metal hydride (Ni–MH) technology provides the possibility for producing such batteries with high specific energy because the metal hydride negative electrode has a higher capacity per unit volume and longer cycle-life than the cadmium negative electrode in nickel/cadmium batteries [2–5]. Rechargeable alkaline batteries are usually positive limited, however, so that the capacity and cycle-life are determined mainly by the performance of the nickel electrodes. Although the active material in the nickel electrode has a theoretical specific energy of 289 mA h g^{-1}, the practical specific capacity of this electrode in the battery is far below this value [6]. Therefore, in order to increase effectively the specific energy and cycle-life of alkaline batteries, it is necessary to improve further the performance of the nickel electrode and increase the active-material utilization of the nickel electrodes [7–10].

Many studies have revealed that incorporating other transition metal atom additives, such as cobalt compounds, into the nickel electrode is one of the most effective approaches to improve active-material utilization and cycle-life [11–16]. The cobalt compound reduces both the oxidizing and reducing potentials of the nickel electrode and increases the overpotential of oxygen evolution; thus, the utilization of the active material is improved [17]. Thus, addition of cobalt compound into the nickel electrode has been widely adopted by battery manufactures. In addition, adding cadmium, zinc, manganese, barium, magnesium and calcium compounds into the nickel electrode are reported to have beneficial effects (such as inhibiting the swelling of the nickel electrode during cycling) [18,19]. In this study, the influence of cupric oxide additive on the electrochemical performance and structure of the nickel electrode is investigated.

2. Experimental

The test nickel electrodes were prepared by paste-type technology. All the materials used to prepare the electrodes were commercial available. Nickel foam served as the substrate, to which a nickel wire was welded to provide electrical contact. Nickel hydroxide powder (β-nickel hydroxide), cobalt metal powder, nickel metal powder and cupric oxide powder were mixed thoroughly in a weight ratio of 100:5:8:0 ~ 0.5. A suitable amount of aqueous suspension containing carboxymethyl cellulose (CMC) and polytetrafluoroethylene (PTFE) dispersion solution as binders were added to the mixed powder and mixed again

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Table 1
Effect of different cupric oxide powder content on utilization of active material

Cupric oxide content (weight ratio)	Real capacity (mA h)	Theoretical capacity (mA h)	Utilization (%)
0.0	211	234	90.3
0.1	228	246	92.5
0.3	242	256	94.5
0.4	224	238	94.1
0.5	229	241	94.9

to obtain a slurry. The slurry was pasted on to the nickel foam, and then dried in air in an oven at 80°C, pressed and cut into a dimension of $20 \times 30 \times 0.7$ mm. The weight of the active materials in the resultant electrodes was about 1 g.

Electrochemical measurements of the nickel electrodes were performed using a glass beaker, in which 7 M KOH was used as the electrolyte. Two-nickel meshes as the counter electrodes were placed either side of the working electrode. Hg/HgO was used as the reference electrode, all potentials are reported with respect to this electrode. Constant-current charge–discharge cycles were performed at $30°C \pm 1°C$ on a charge–discharge instrument controlled by a computer. The test cell was charged at the 0.2 rate, kept for 0.5 h at open-circuit, and then discharged at the same rate down to 0.1 V. The stable capacity of the test cell after several cycles was taken as the real capacity of the nickel electrode. In all cycling tests, an overcharge corresponding to 50% of the theoretical capacity was always applied. The surface morphology of the nickel electrodes was observed by means of a scanning electron microscopy (SEM), and the crystal structure of the active material was determined by using X-ray diffractometry (Cu $K\alpha$ radiation and graphite filter at 40 kV and 100
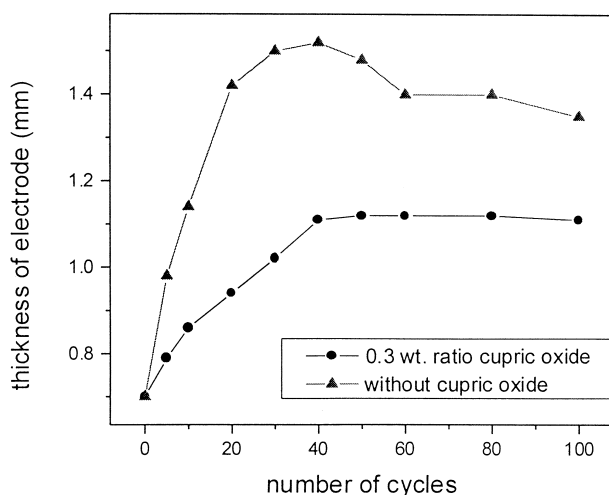
mA). The variation in thickness of the nickel electrode during cycling was measured with a micrometer.

A–A-size Ni–MH batteries were each assembled with a $70 \times 40 \times 0.7$ mm nickel positive electrode and a $80 \times 40 \times 0.4$ mm metal hydride negative electrode. The capacity of the negative electrode was 1.2 times larger than that of the nickel electrode. The rechargeable batteries were charged initially at the 0.1 C rate for 10 h, and then discharged at the 0.2 C rate down to 1.0 V. After the discharge capacity had become stable, each battery was cycled under the following regime: charge at 0.5 C for 2.5 h, discharge at the same rate down to 1.0 V. The change in internal resistance of the battery with cycling was measured with a DK-3000 precision internal resistance instrument.
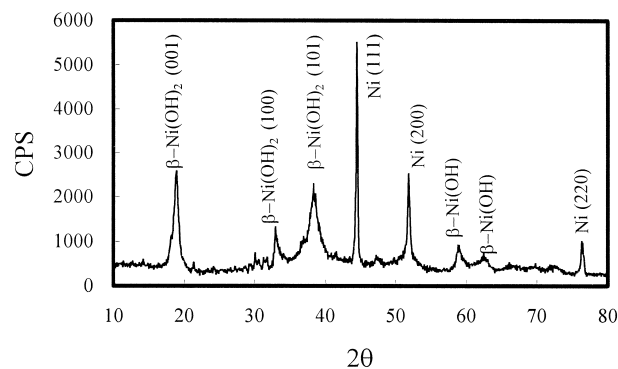
3. Results and discussion

3.1. Effect of cupric oxide on capacity of nickel electrode

Test electrodes with different weight ratios of cupric oxide were charged and discharged at a constant rate of
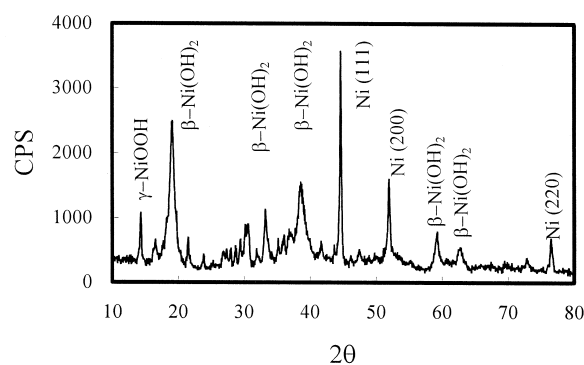
(a)

(b)

Fig. 2. X-ray patterns of nickel electrodes after 100 cycles: (a) without cupric oxide; (b) with 0.3 weight ratio cupric oxide.

Fig. 1. Variation in thickness of doped and undoped nickel electrodes with cycling.

0.2 C. The measured real capacities of the electrodes, corresponding theoretical capacities and their active material utilization are listed in Table 1. The theoretical capacity of the electrode was calculated from the total amount of nickel hydroxide loaded in the electrode and assuming the electrode reaction to be:

$$Ni(OH)_2 + OH^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} NiOOH + H_2O + e^-. \qquad (1)$$

The data shows that the addition of small amount of cupric oxide powder to the nickel electrode can slightly increase the utilization of the active material.

3.2. Effect of cupric oxide on structure of nickel electrode

The variation in thickness of the nickel electrodes, without and with a 0.3 weight ratio of cupric oxide powder, with cycling, is shown in Fig. 1. Obviously, the thickness of both electrodes tends to increase with cycling, but the rate of increase of the nickel electrode without cupric oxide is larger than that of the electrode with cupric oxide. The increase in thickness of the electrode is considered to be due to the formation of γ-NiOOH during charging, especially during overcharging [20]. The crystal form of nickel hydroxide changes from β-Ni(OH)$_2$ to β-NiOOH and then from β-NiOOH to γ-NiOOH during charging. Since the density of γ-NiOOH is much smaller than that of β-NiOOH, the electrode swells with increase in the content of γ-NiOOH and thus increases in thickness. This swelling reduces the integration of the active material and decreases the cycle-life of the electrode. The sudden reduction in thickness of the nickel electrode shown in Fig. 1 resulted from spalling of the active material. The reduced increase in thickness of the nickel electrode with cupric oxide indicates that the addition of cupric oxide can effectively inhibit the formation of γ-NiOOH during charging. This was confirmed by X-ray diffraction analysis of 50% overcharged electrodes. In the overcharged stage, the active material consisted of β-NiOOH and γ-NiOOH, but the content of γ-NiOOH in the electrode with 0.3 weight ratio cupric oxide was far lower than that in the electrode without cupric oxide.

After 100 cycles, the nickel electrode with 0.3 weight ratio cupric oxide still appeared to be compact and flat, while the electrode without cupric oxide additive became loose and much of the active material became dislodged. The X-ray diffraction patterns of the active materials in

× 1000   × 5000
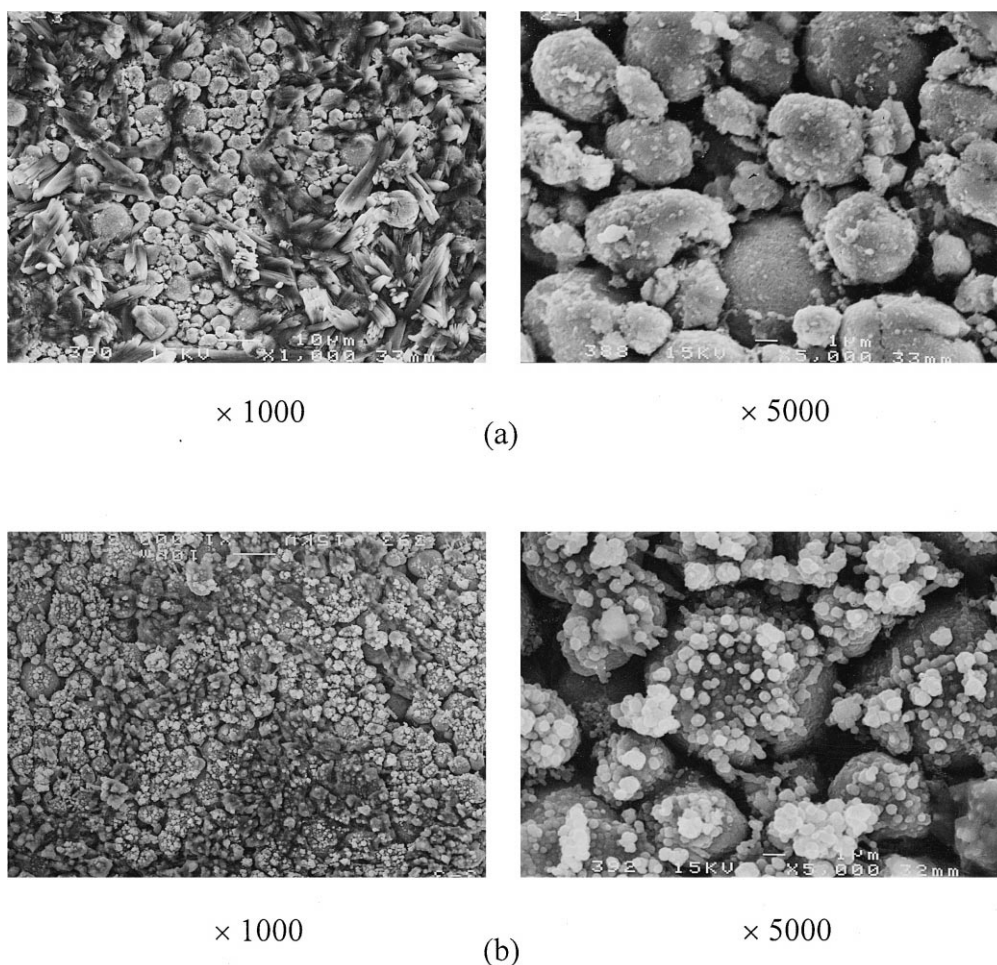
(a)

× 1000   × 5000

(b)

Fig. 3. Electron micrographs of nickel electrodes after 10 cycles: (a) without cupric oxide; (b) with 0.3 weight ratio cupric oxide.

these electrodes, are presented in Fig. 2. The active material with cupric oxide additive consisted only of β-Ni(OH)$_2$ (Fig. 2(b)); by contrast, the active material in the electrode without cupric oxide contained a small amount γ-NiOOH, even after discharging to a cut-off voltage of 0.1 V (Fig. 2(a)). Electron micrographs of the surfaces of the two electrodes after 10 cycles are shown in Fig. 3. The nickel hydroxide active materials are mainly spherical. The cobalt compound and other additives in the electrode without cupric oxide are aggregated in the form of rhomboids and some of the spherical nickel hydroxide active material has broken up. In the electrode containing 0.3 weight ratio cupric oxide, microcrystals of the cobalt compound and other additives are observed and are uniformly distributed on the nickel hydroxide active materials. This indicates that the addition of the cupric oxide in the active material is able to cause the cobalt additive to be well spread on the surface of the nickel hydroxide particles, and thus enhance the utilization and cycle-life of the nickel electrode.

3.3. Effect of cupric oxide on electrochemical behaviour of nickel electrode

The first and second charging curves for electrodes containing 0 and 0.3 weight ratio cupric oxide, respec-
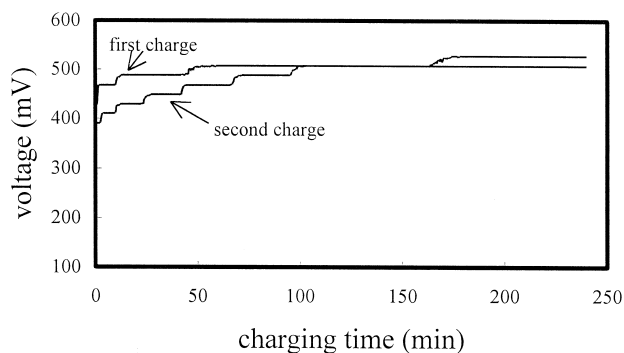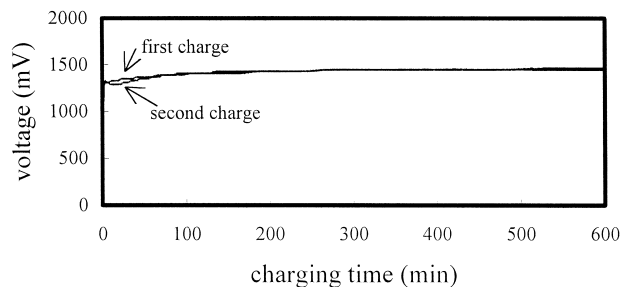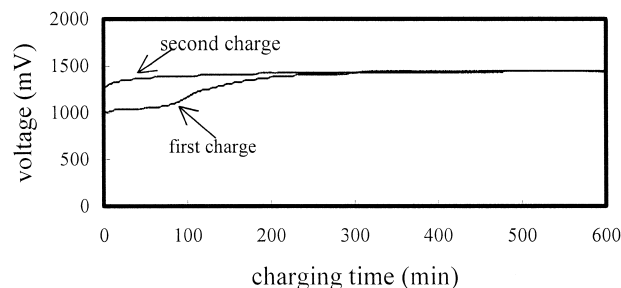

(a)
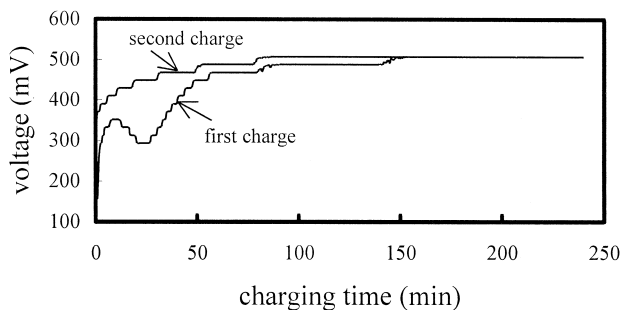
(b)

Fig. 4. First and second charging curves of nickel electrodes: (a) without cupric oxide; (b) with 0.3 weight ratio cupric oxide.

(a)

(b)

Fig. 5. First and second charging curves of A–A size Ni–MH batteries: (a) nickel electrode without cupric oxide; (b) nickel electrode with 0.3 weight ratio cupric oxide.

tively, are shown in Fig. 4. At the beginning of charging stage, the charging potential of the electrode without cupric oxide in the first cycle is slightly higher than that in the second cycle. By contrast, in the first charging curve for the electrode containing cupric oxide additive, the charging potential is lower than that in the second cycle and far below that of the electrode without cupric oxide at the same charging time. This is probably because the Cu^{2+} species in cupric oxide has an oxidizing property to some extent. On the first cycle, the presence of cupric oxide is beneficial to the oxidation of cobalt powder to β-CoOOH, which is spread on the surface of the nickel hydroxide particles and constructs a conductive network which connects the nickel hydroxide particles to the current collector [21]. Thus, cupric oxide additive results in an easier charging process in the initial stage. On the second cycle, the difference between the charging curves of the electrodes with and without cupric oxide additive is not pronounced due to the presence of less cobalt.

3.4. Effect of cupric oxide on properties of A–A size Ni–MH battery

A–A size Ni–MH batteries with a nominal capacity of 1200 mA h were assembled with nickel electrodes contain-

Table 2
Effect of cupric oxide additive in nickel electrode on capacity and internal resistance of battery with cycling

Number of cycles	Battery with no cupric oxide		Battery containing 0.3 weight ratio cupric oxide	
	Capacity (mA h)	Internal resistance (Ω)	Capacity (mA h)	Internal resistance (Ω)
0	1090	20.8	1180	19.6
10	1100	21.2	1178	19.8
50	1098	22.9	1180	20.7
100	1098	30.0	1180	20.9
150	1096	41.2	1178	24.3
200	1048	53.8	1172	29.6
250	1022	86.1	1170	36.2
300	1007	126.7	1166	43.0

ing 0 or 0.3 weight ratio cupric oxide additive and with metal hydride electrodes. The first and second charging curves of these batteries at the 0.1 C rate are shown in Fig. 5. Obviously, the results are in general agreement with the observations of the nickel electrode during initial charge–discharge cycles. This suggests that the nickel electrode is the performance-determining component in the Ni–MH battery and the battery containing cupric oxide additive in the nickel electrode has better initial charge behaviour. The variations in the capacity and internal resistance of the batteries with cycling is given in Table 2. In comparison with the battery with no cupric oxide, the battery with cupric oxide additive exhibits a slower, decrease in capacity and a slower increase in internal resistance. The increase in internal resistance of Ni–MH batteries is due to the consumption of electrolyte that results from the evolution of oxygen and to the poor current conduction that is caused by swelling of the electrodes. Since the addition of cupric oxide can effectively prevent the nickel electrode from swelling and improve the conductive network of the cobalt additive, the properties of the battery are improved.

4. Conclusions

The present study has indicated that the addition of a small amount of cupric oxide to the nickel electrode can effectively prevent the formation of γ-NiOOH during charging and thus prevent the swelling and prolong the cycle-life of the electrode.

Furthermore, cupric oxide can promote the formation of a β-CoOOH conductive network from cobalt powder and enhance the utilization of cobalt additive, which leads to an easier initial charging of the nickel electrode. Compared with a rechargeable battery without cupric oxide additive, a battery containing cupric oxide has a better cycle-life and exhibits a slower increase in internal resistance with cycling.

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