

Electrochemical properties of the pasted nickel electrode using surface modified Ni(OH)₂ powder as active material

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Abstract

Nickel hydroxide powder was modified by immersing the mixture of nickel hydroxide powder with cobalt compounds in an alkali solution or by chemical deposition. Electrochemical properties of the pasted nickel electrodes consisting of surface modified Ni(OH)₂ powder in a porous nickel substrate were studied. The results show that the active material utilization of the modified nickel electrodes greatly increases due to the uniform distribution of a Co(OH)₂ layer on the surface of the nickel hydroxide powder resulting in the improvement of the electrochemical activity and conductivity. The EIS results show that the Co(OH)₂ layer decreases the charge-transfer resistance and increases the active surface area of the nickel electrode. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cobalt hydroxide; Nickel electrode; Surface modification; Active material utilization

1. Introduction

Recently pasted nickel electrodes have been greatly developed to meet the requirement of high capacity in secondary batteries such as Ni–Cd, Ni–MH, Ni–Fe and Ni–Zn, due to their simple fabrication and high filling of active materials. However, the pasted nickel electrodes show low active material utilization due to the poor conductivity of Ni(OH)₂ powder and a relatively long distance between nickel hydroxide particles and the nearest portion of the substrate. To overcome this drawback, the addition of additives such as C, Ni, Co and CoO was usually added into the electrode [1–10]. The use of highly conductive CoOOH, which is formed in situ through dissolution/precipitation and charging of cobalt compounds, added to the electrode to provide a good electrical conductive network between the nickel hydroxide and the substrate, was found to be quite effective to improve the active material utilization of the nickel electrode [10]. The addition of cobalt compounds has been extensively studied previously [8,10–13]. The addition of calcium compounds, such as Ca(OH)₂, CaS, CaF₂ and CaCO₃, has been found to hinder oxygen evolution during charging of the electrode and therefore increase the charge efficiency, and to improve the active material utilization of the nickel electrode [14,15]. Combined

addition of several additives was found to be more effective in improving the active material utilization of the nickel electrodes [16–18]. Two ways are usually used to add the additives into the nickel electrode. One is surface modification by mechanical mixing of nickel hydroxide powder with additives. However, the additives are not utilized efficiently due to the fact that the additives on the surface of nickel hydroxide are not well-distributed. Another way is by chemical or electrochemical co-precipitation of zinc or cobalt during the preparation process of nickel hydroxide powder. In this way, though the additives can uniformly exist between crystal lattices of nickel hydroxide, the surface modification of the nickel hydroxide powder is limited.

In this paper, we report a way to form a uniform modification layer on the surface of nickel hydroxide powder by immersing a mixture of nickel hydroxide powder with additives in alkali solution or by chemical deposition. The electrochemical properties of the electrodes formed using treated nickel hydroxide powder are studied.

2. Experimental

2.1. Treatment of Ni(OH)₂ powder in alkali solution

The nickel hydroxide powder (from Canada, co-precipitated with 4 wt.% Zn) was mixed with 5 wt.% Co(OH)₂ + 5 wt.% Co and put into a container with an alkali solution, which were kept at constant temperature for various times under stirring. The rate of the mixed powder to solution volume is 50 g l⁻¹. After treated, the nickel hydroxide

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powder was washed with hot distilled water to neutral pH and then dried at 65°C in the air.

2.2. Deposition of $\text{Co}(\text{OH})_2$ on the surface of $\text{Ni}(\text{OH})_2$ powder

Nickel hydroxide powder was mixed with sodium hydroxide solution. A complex solution of cobalt sulphate with ammonia was dropped into the above solution to form a $\text{Co}(\text{OH})_2$ deposit on the surface of the nickel hydroxide powder at a controlled of pH = 10 and 50°C under stirring. The deposited nickel hydroxide powder was washed with hot distilled water to neutral pH and then dried at 65°C in the air. The deposited amount of $\text{Co}(\text{OH})_2$ was analyzed using ICP-AES (Leemen, USA).

2.3. Preparation of nickel hydroxide electrode

The test nickel electrodes were prepared by mixing nickel hydroxide and additives with binders (5% PTFE + 1% methylcellulose) to form a slurry which was applied to a nickel-foam substrate (20 mm × 20 mm × 1.5 mm) with an electrical nickel lead. The respective nickel electrodes were fabricated by using a mixture of unmodified nickel hydroxide powder with 5 wt.% $\text{Co}(\text{OH})_2$ + 5 wt.% Co and 5 wt.% C, a mixture of modified nickel hydroxide powder with 5 wt.% C and a mixture of deposited nickel hydroxide powder with 5 wt.% Co and 5 wt.% C. The pasted electrodes were dried at 60°C and pressed to a thickness of 0.65 mm.

2.4. Test of electrochemical properties of nickel electrodes

The electrochemical properties of the nickel electrodes were performed in a three-compartment electrochemical cell. To avoid shedding or removal of active material from the electrode during the electrochemical polarization, the test nickel electrodes were wrapped into a separator, and an MH electrode with higher capacity and with two fix plates were put on both sides (Fig. 1). An Hg/HgO electrode was used as the reference electrode. The test nickel electrodes were charged at 0.1 C for 15 h and discharged at 0.2 C to 0.1 V (versus Hg/HgO), followed by 5 cycles of charge for

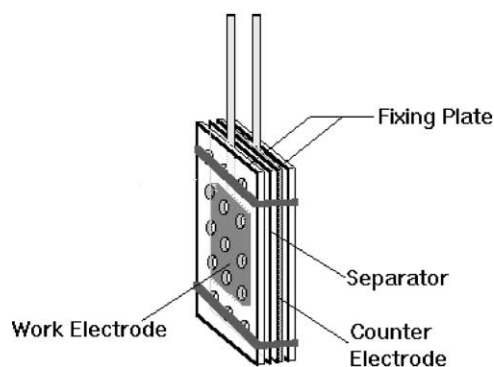


Fig. 1. Schematic diagram of splint-type electrode system.

6 h and discharge to 0.1 V both at the 0.2 C rate. The electrolyte was 6 mol l⁻¹ KOH.

2.5. Electrochemical impedance spectroscopy(EIS)

After several charge/discharge cycles at 0.2 C rate, the nickel electrodes were subjected to EIS measurements at a 20% state of charge of the electrode in order to check variation of the surface characteristics. In this charged state, the kinetics of electrode were controlled by surface charge transfer [19,20]. Thus, the states of the surface modification of the nickel hydroxide powder can be obtained by EIS data. The EIS was obtained using a 1250 frequency response analyzer connected to a Solartron SI 1287 electrochemical interface in the frequency from 10⁵ to 10⁻² Hz.

3. Results and discussions

3.1. Effect of treatment of mixed nickel hydroxide powder in NaOH solution on the electrochemical properties of nickel electrode

Figs. 2–4 show the effect of concentration of alkali solution, temperature of alkali solution and treatment time

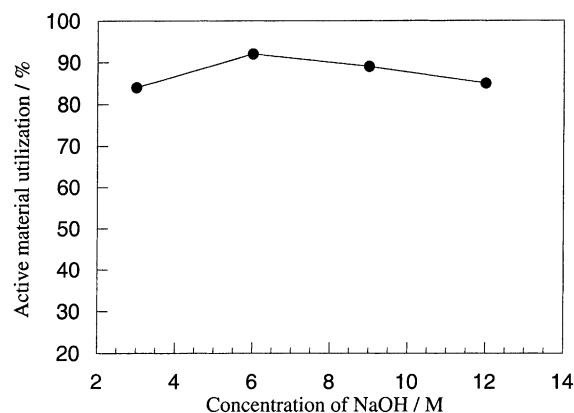


Fig. 2. Effect of treatment solution concentration on the active material utilization of nickel electrodes.

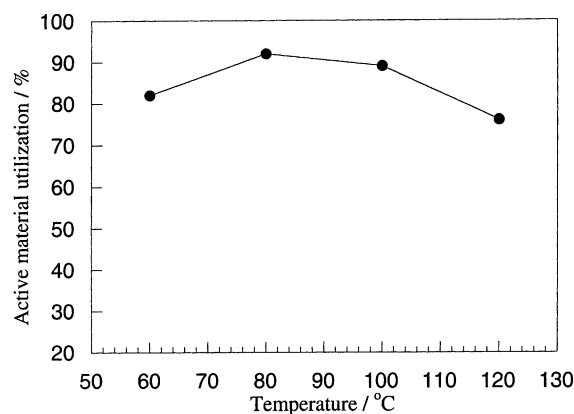


Fig. 3. Effect of treatment solution temperature on the active material utilization of the nickel electrodes.

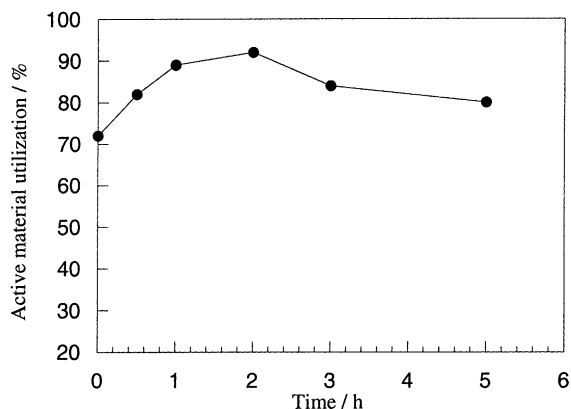


Fig. 4. Effect of treatment time on the active material utilization of the nickel electrodes.

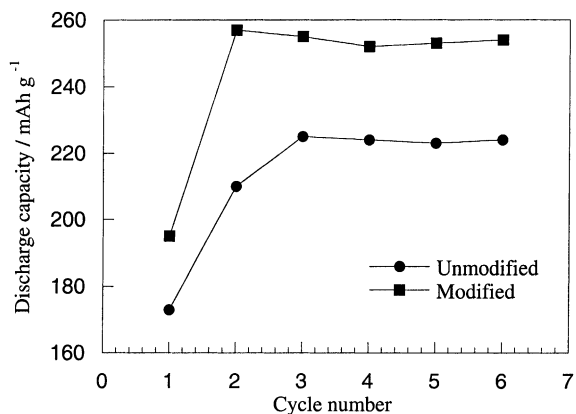


Fig. 5. Capacities of the nickel electrodes formed by using modified and unmodified nickel hydroxide powder as a function of cycle number.

on the active material utilization of nickel electrodes, respectively. The active material utilization of the nickel electrode initially increases and then decreases as the concentration of the solution increase, showing an optimum concentration of 6 M. The temperature and the time have a similar influence on the active material utilization of the nickel electrode. From the results, an optimum condition of

treatment is obtained: 6 M NaOH, 80°C and 2 h. During the immersion process in alkali solution, the surface of the nickel hydroxide powder can be changed due to the dissolution/re-precipitation of nickel hydroxide and dissolution/re-precipitation of the additives (cobalt compounds), which improves the surface conductivity and electrochemical activity of the nickel hydroxide powder. In the case of

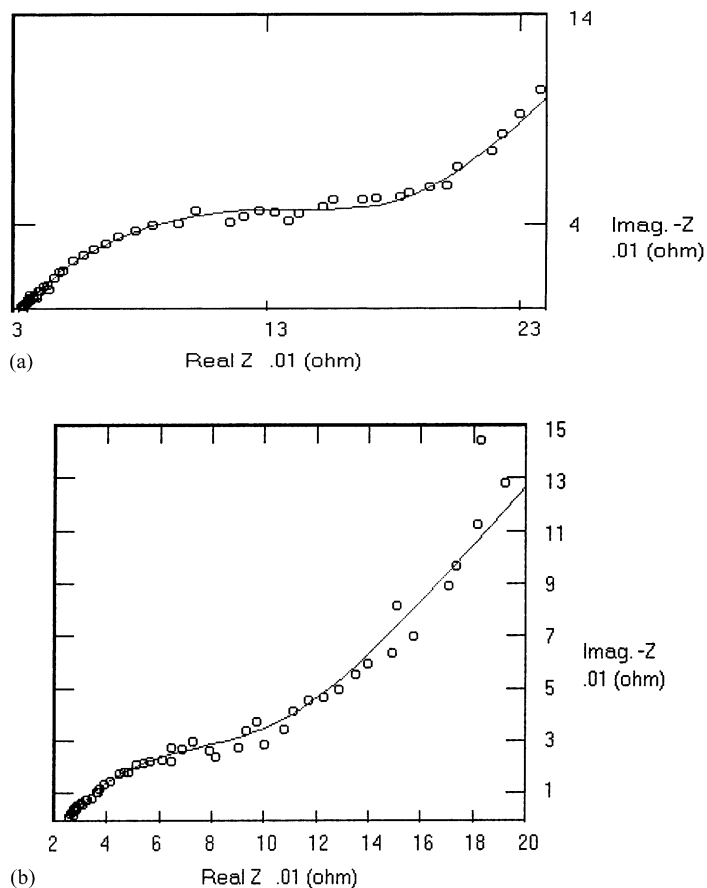


Fig. 6. The EIS of nickel electrodes prepared with unmodified nickel hydroxide (a) and with modified nickel hydroxide in alkali solution (b). Symbol for experimental data and line for fitted curve.

low concentration or low temperature or short time, the reason for low active material utilization of the nickel electrode is due to the fact that the degree of dissolution of additives ($\text{Co}(\text{OH})_2$) and re-precipitation on the surface of the nickel hydroxide powder is limited. In the case of high concentration or high temperature of the alkali solution, a non-uniform deposit layer of $\text{Co}(\text{OH})_2$ was formed on the surface of the nickel hydroxide powder, and thus, decreasing the efficiency of the surface treatment. In addition, the crystal morphology of the nickel hydroxide is easily changed in high temperature, which will also influence the active material utilization of nickel electrode. The low active material utilization for long treatment time may be related to that the high amount of $\text{Co}(\text{OH})_2$ hinders diffusion of interior proton at the nickel hydroxide particle.

Fig. 5 shows the capacities of nickel electrodes formed by using modified nickel hydroxide powder as a function of cycle number, in comparison with that of electrodes formed by using unmodified nickel hydroxide powders. The capacities of the electrodes greatly increase by treatment in alkali solution. Surface change of the nickel hydroxide powder may be related to this improvement of the electrode. In order to check the surface change, EIS was performed on each electrode after 6 cycles. Fig. 6 shows Nyquist plots of treated and untreated nickel electrodes. The Nyquist plots show a semicircle due to the interaction effect of charge-transfer in high frequency regions and a line due to Warburg impedance of proton diffusion in low frequency regions. This system can be depicted by an equivalent circuit shown in Fig. 7, where, R_s is the solution resistance, R_t the charge-transfer resistance, Z_w the Warburg impedance and C_c the interface capacitance. Table 1 lists the parameters (R_t and C_c) related to the surface of active material powder obtained by fitting the experimental data according to the equivalent circuit. Decrease in R_t and increase in C_c indicate that the alkaline treatment improves the surface state of the active material.

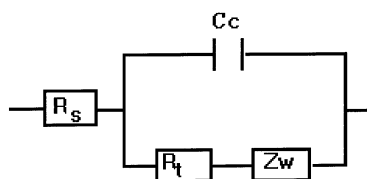


Fig. 7. Equivalent circuit for the nickel electrode.

Table 1
Impedance parameters for various nickel electrodes with unmodified and modified nickel hydroxide in alkali solution

	R_t (Ω)	C_c (F)
Unmodified electrode	0.158	2.3
Modified electrode	0.0931	3.08

Table 2
Charge/discharge data and impedance parameters for various nickel electrodes with different depositions of $\text{Co}(\text{OH})_2$ ^a

	Active material utilization (%)	E_{re} (V)	R_c (Ω)	C_c (F)
Untreated electrode	72	0.325	0.158	2.3
4% $\text{Co}(\text{OH})_2$ electrode	95	0.314	0.087	4.2
8% $\text{Co}(\text{OH})_2$ electrode	89	0.318	0.094	2.8

^a E_{re} : the recovery potential after discharge at 0.1 C rate.

3.2. Electrochemical properties of nickel hydroxide deposited with $\text{Co}(\text{OH})_2$

By controlling treatment time, nickel hydroxides with various amount of deposited $\text{Co}(\text{OH})_2$ were obtained. Using the same experimental procedures as above, the electrochemical properties of the nickel hydroxide deposited with $\text{Co}(\text{OH})_2$ were obtained. Data are listed in Table 2. Like the immersion in alkali solution, the chemical deposition improves the surface characteristics of the nickel hydroxide. Thus, the active material utilization greatly increases. It can also be seen from Table 2 that high amount of $\text{Co}(\text{OH})_2$ on the surface of the nickel hydroxide lowers the active material utilization of the nickel electrode. This is due to the fact that the thick deposition layer not only has small specific area, but also hinders the diffusion of protons from the surface to the interior of the nickel particles. The recovery-potential of the electrode after discharge shows us the full-discharge ability of the nickel electrode since the reversible potential of the nickel electrode is variable with the state of charge [21]. The nickel electrode with high deposition of $\text{Co}(\text{OH})_2$ shows a high recovery-potential as comparing with that with low deposition of $\text{Co}(\text{OH})_2$, indicating that the thick deposition hinders the diffusion of proton and thus lowers the discharge depth of the nickel electrode. The C_c of the electrode with high $\text{Co}(\text{OH})_2$ deposition is lower than that of electrode with low $\text{Co}(\text{OH})_2$ deposition, indicating that the thick deposition layer has small specific area.

4. Conclusions

The surface of nickel hydroxide powder was modified by immersing the mixture of nickel hydroxide powder with cobalt compounds in an alkali solution or by chemical deposition. The pasted nickel electrodes fabricated by modified $\text{Ni}(\text{OH})_2$ powder show high active material utilization, which is due to the uniform distribution of a $\text{Co}(\text{OH})_2$ layer on the surface of the nickel hydroxide powder. This results in the improvement of the electrochemical activity and conductivity of the nickel hydroxide powder. The EIS results show that a $\text{Co}(\text{OH})_2$ layer decreases the charge-transfer resistance and increases the active area of the nickel electrode.

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