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Ni/Al/Co-substituted α-Ni(OH)$_2$ as electrode materials in the nickel metal hydride cell

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Abstract

It is found that the phase of the product formed after nickel is co-precipitated with both aluminium and cobalt cations is α-Ni(OH)$_2$. In this paper, its physical characteristics have been identified with scanning electron microscopy (SEM) and X-ray diffraction (XRD). It was used as an electrode material in an open Ni/MH cell and its electrochemical properties have been examined. The results show that the electrochemical properties have been improved by adding Al and Co. The electrode fabricated from the nickel hydroxide with additives of Al and Co show a better reversibility and charge–discharge capability compared with the electrode with no additive. Also a maximum capacity of 319 mAh/g was obtained for this electrode. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Electrode materials; Nickel metal hydride cell; Charge–discharge capability

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1. Introduction

Nickel hydroxide is the positive electrode material of all nickel-based alkaline secondary batteries [1]. It exists in two polymorphic forms known as α- and β-Ni(OH)$_2$, which are transformed into γ-NiOOH and β-NiOOH, respectively on charging.

Although β-Ni(OH)$_2$ is commercially used in alkaline secondary batteries and many improvements have also been made in its performance, electrochemical cycling between the α-Ni(OH)$_2$ and γ-NiOOH phases is much more advantageous than cycling between β-Ni(OH)$_2$ and β-NiOOH phases [2]. First, mechanical strains are significantly reduced because the α-Ni(OH)$_2$ and γ-NiOOH phases have similar lattice constants. Second, a larger specific capacity can be expected for the α-Ni(OH)$_2$/γ-NiOOH couple as compared with the β-Ni(OH)$_2$/β-NiOOH couple. While the β-Ni(OH)$_2$/β-NiOOH couple delivers a capacity value corresponding to a 0.8e equivalent, a capacity equivalent to 1.2e [3] can be achieved by using the α-Ni(OH)$_2$/γ-NiOOH couple.

However, the α-Ni(OH)$_2$ is unstable in strong alkaline media and transforms to the β-Ni(OH)$_2$. Much effort has been devoted to stabilising α-Ni(OH)$_2$ by doping with aluminium [4–6] and zinc [7,8] cations.

In our study, the elements aluminium and cobalt were co-precipitated with nickel cations to form α-phase hydroxides.

2. Experimental

2.1. Materials synthesis

One hundred milliliters of a mixed metal-nitrate solution (1.5 N in total metal cations concentration) containing Ni, Al and Co at a certain ratio was added dropwise (3 ml min^{-1}) to 100 ml of 1.5 N NaOH solution containing sodium carbonate (3.75 g) with constant stirring at room temperature. The resulting blue-green suspension was filtered and rinsed to neutral pH, then the precipitate was dried at 65°C for 12 h.

2.2. Physical characterization

The phase structure was identified with a Philips PW 1010 X-ray diffractometer (XRD) with Cu Kα radiation at 40 KV and 20 mA. Surface images were investigated with

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a Leica/Cambridge Stereoscan 440 scanning electron microscopy (SEM).

2.3. Electrode fabrication

The nickel hydroxide electrode was prepared by inserting an active materials paste containing 90% nickel hydroxide and 10% cobalt oxide (with 5% PVA used as binder) into a nickel foam, after drying, sandwiched with two same size nickel foam and then pressed under 20 kg/cm^2 for 1 min.

2.4. Electrochemical properties measurement

A commercial metal hydride electrode ($LaNi_5$ type) and HgO/Hg/6 M KOH were employed as counter electrode and reference electrode, respectively, in the experimental measurement, and the capacity and size of the counter electrode was twice that of the working electrode. The electrolyte used in the electrochemical test was 6 M KOH (containing LiOH).

The electrode was galvanostatically charged at 30 mA/g to 150% of the theoretical capacity, then rested for half an hour, and discharged at 60 mA/g to 1.0 V against the counter electrode.

3. Results and discussion

Fig. 1 shows the X-ray diffraction pattern of nickel hydroxides with additive aluminium and cobalt and no additive. In Fig. 1B the peaks mainly can be indexed to β-phase $Ni(OH)_2$, but a typical peak attributing to α-phase is also observed, which is identified as an interstratification of α- and β-type phases [9]. For powder A, the peaks can be indexed to the α-$Ni(OH)_2$ phase, indicating that the dopant aluminium and cobalt are incorporated in the lattice of nickel hydroxide and have substituted the position for nickel in the lattice.

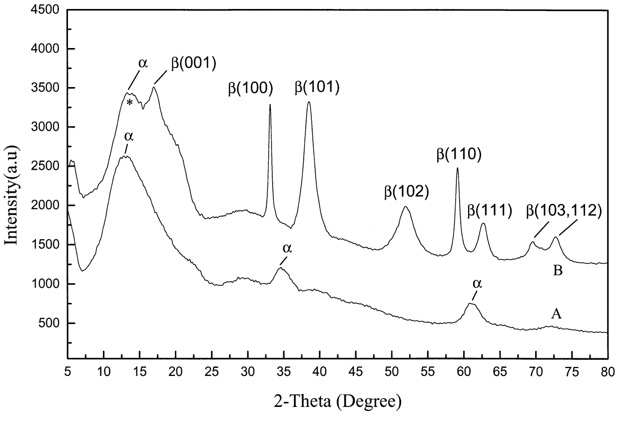


Fig. 1. XRD patterns of nickel hydroxides (A: Al, Co-subsituted α-$Ni(OH)_2$; B: no additive).

The surface images of the nickel hydroxide powder with additive Al and Co and no additive were analysed by SEM and are shown in Fig. 2. At the lower magnification (2000×) they all consist of irregular particles. At higher magnification (5000×), the Al, Co-substituted α-$Ni(OH)_2$ is much more like a crystalline structure.

Cyclic voltammograms for the electrodes are shown in Fig. 3. It can be seen that the cathodic peak corresponding to nickel hydroxide reduction of electrode A (with additive Al and Co) shifts to more positive position compared with electrode B (with no additive). The experimental data obtained from the cyclic voltammetric study are summarised in Table 1. E_a and E_c are employed as the symbol of the potential of anode and cathodic peak, respectively. $\Delta E_{a,c}$, the difference between the anodic and cathodic peak position, is taken as an estimate of the reversibility of the redox reaction, which is an important parameter to judge the electrochemical properties of the electrodes. The smaller is $\Delta E_{a,c}$, the more reversible is the electrochemical reaction [10,11].

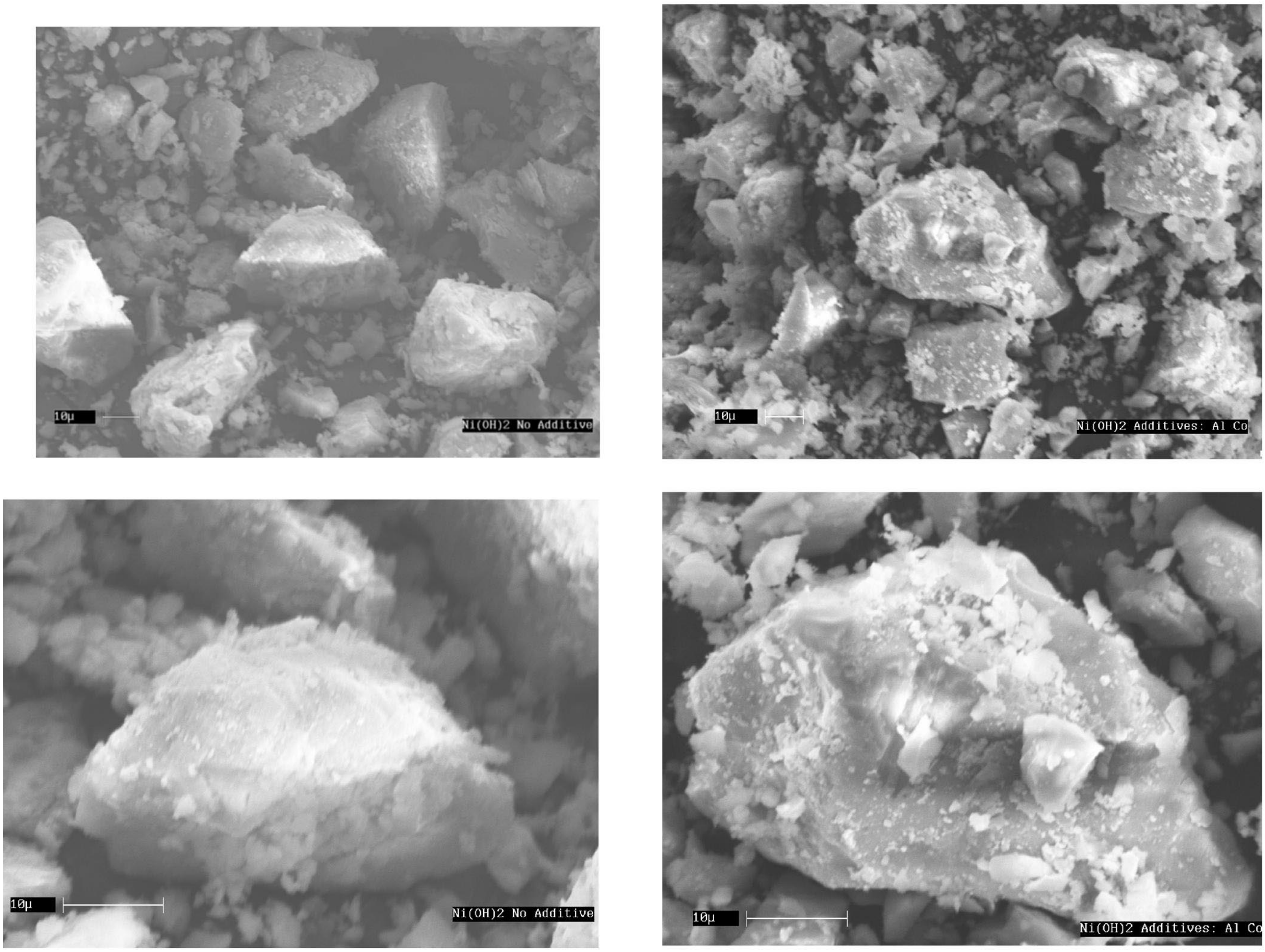
The results in Table 1 show that $\Delta E_{a,c}$ is 158 mV for the electrode with additive Al and Co, while $\Delta E_{a,c}$ is found to be 168 mV for the electrode with no additive. It indicates that the reversibility for electrochemical redox reaction has been improved by adding Al and Co. It also shows that the charge-discharge process for the nickel electrode is easier and more reversible for the electrode with additives of Al and Co compared with the electrode with no additive. This will certainly improve the electrochemical properties if used in the Ni/MH battery.

Fig. 4 illustrates the charge-discharge curves of nickel hydroxides. It is found that for the electrode A with additives of Al and Co has a lower charge voltage and much higher discharge voltage compared with the electrode B with no additive. The higher is the discharge voltage, the higher is the utility of the electrode, especially when discharging at high rate. Also a much higher capacity, 319 mAh/g is obtained for the electrode with additives, while the capacity for the electrode with no additive is only 220 mAh/g. The results show that the electrode with additives of Al and Co has better charge–discharge capability, which conforms with the result from the cyclic voltammetry study.

4. Conclusion

It is found that the peaks in the X-ray diffraction pattern for nickel hydroxide with additive Al and Co can be indexed to α-$Ni(OH)_2$. This indicates that the elements Al and Co have been incorporated into the lattice of nickel hydroxide.

In the cyclic voltammetry study, $\Delta E_{a,c}$, an important



(a) (b)

Fig. 2. SEM images of nickel hydroxides (a, no additive; b, additives Al and Co).

parameter to judge the reversibility of electrode redox reaction, is found to be 158 mV for the electrode fabricated by nickel hydroxide with additive Al and Co, which is smaller than 168 mV for the electrode with no additive. This shows that the charge-discharge process is easier and more reversible for the electrode with additives of Al and Co.

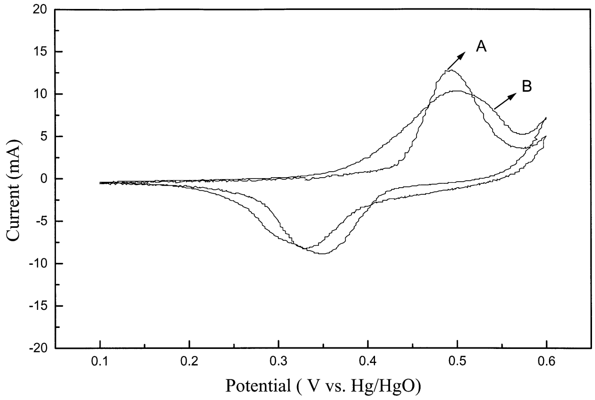


Fig. 3. Cyclic voltammograms of nickel hydroxides (Scan rate : 0.1 m V/s). (A: Al, Co-substituted α-$Ni(OH)_2$; B: no additive).

By analysing the charge–discharge curve, the conclusion can be made that the electrochemical properties of the electrode have been improved by adding Al and Co. The electrode has a lower charge voltage, a much higher discharge voltage and also a much higher discharge capacity.

All the results show that the Al/Co-substituted α-$Ni(OH)_2$ is promising as an active material in the Ni/MH battery.

Table 1
Data obtained from the cyclic voltammetry measurement

Electrode	E_a (mV)	E_c (mV)	$\Delta E_{a,c}$ (mV)
A*	495	327	168
B*	510	352	158

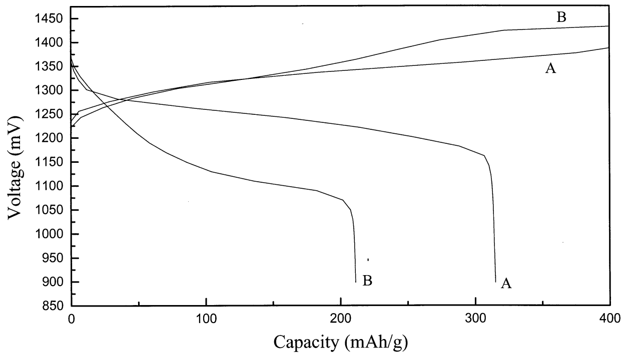


Fig. 4. Charge–discharge curve of nickel hydroxide electrodes in an open cell (A: Al, Co-subsituted α-$Ni(OH)_2$; B: no additive).

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