Cyclic voltammetric studies of pasted nickel hydroxide electrode microencapsulated by cobalt

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Spherical nickel hydroxide microencapsulated by cobalt has been used as the electrochemically active material in pasted-type nickel electrodes of rechargeable alkaline batteries. Cobalt coating on the surface of nickel hydroxide particles can be converted to CoOOH during charge. Well distributed CoOOH forms the conductive network on the surface of nickel hydroxide particles, thereby leading to higher utilization of active material. Cyclic voltammetric studies suggest that nickel hydroxide microencapsulated by cobalt has better reversibility of the Ni(OH)₂/NiOOH redox couple, greater discharge capacity and higher oxygen evolution overpotential than nickel hydroxide with added cobalt metal powder as a conductor. The mechanism of the electrode reaction is still found to be controlled by proton diffusion, and the proton diffusion coefficient is \(1.2 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}\).

Keywords: cyclic voltammetry, microencapsulation, nickel hydroxide electrode, oxygen evolution overpotential, proton diffusion coefficient, reversibility

1. Introduction

The electrochemical properties of the nickel hydroxide electrode has been the subject of investigation for several decades, due to its application as the positive plate in Ni-Cd, Ni-H₂ and Ni-metal hydride (MH) batteries [1–3]. The effect of cobalt hydroxide as a performance enhancing additive on the nickel hydroxide electrode has been known for some time [4]. It is generally believed that the presence of cobalt is responsible for reducing the oxygen evolution overpotential and improving the performance of the nickel hydroxide electrode [5–7].

It is known that, after initial oxidation, cobalt remains in the (III) state throughout its cycle life within a nickel hydroxide lattice and that, as a result, it does not contribute through the Co(II)/Co(III) couple to the capacity of the electrode [5]. However, cobalt, being an element of a variable valence, is considered to increase the proton conductivity of nickel hydroxide [8] thereby improving electrode performance. In general, cobalt coexists in the lattice of nickel hydroxide in the form of cobalt hydroxide by chemical impregnation or electrochemical impregnation. Nevertheless, the distribution of cobalt is nonuniform. Uneven distribution of cobalt within the active material–nickel hydroxide may play a diminished role during activation of the active material and, as a consequence, the active material cannot be fully utilized in practical electrodes. Recently, in order to further increase the energy density of Ni–Cd and Ni–MH batteries, a low cost and high performance pasted nickel electrode made from a porous foam nickel or fibrous nickel substrate has been developed. Since active material–nickel hydroxide is a low conductivity p-type semiconductor [9], there is a relatively large resistance between the nickel hydroxide particles and the current collector, thus resulting in poor electrode performance and a relatively low active material utilization. To reduce the resistance between the active material and current collector, and to maximize electrode performance, many researchers add increased quantities of cobalt to their electrodes. The addition of cobalt in relatively large amounts, however, results in a substantial decrease in the discharge potential plateau and an increase in cost.

In our previous studies, electroless cobalt on the surface of spherical nickel hydroxide particles has been developed [10, 11]. In the present study, we investigate the electrochemical characteristics of the nickel hydroxide electrode microencapsulated with cobalt by cyclic voltammetry, and the reversibility of the Ni(OH)₂/NiOOH redox reaction and the oxygen evolution overpotential. In addition, we also discuss the reasons for the high performance of nickel hydroxide electrodes microencapsulated by cobalt.

2. Experimental details

Spherical nickel hydroxide was prepared by reactive crystallization under highly controlled pH conditions using NiSO₄ and NaOH solutions in addition to aqueous ammonia as a complexing agent and CoSO₄ as an additive. The sample was \(\beta\)-Ni(OH)₂ and contained about 1.5 wt% cobalt in the form of cobalt hydroxide in its lattice as indicated by XRD measurements and chemical analysis. Electroless cobalt deposition was carried out in a solution containing cobalt sulfate, sodium citrate, ammonium sulfate and...
sodium hypophosphite [10]. Scanning electron micrographs of the spherical nickel hydroxide particles before and after electroless cobalt are shown in Fig. 1. If the SEM of a spherical particle microencapsulated by cobalt in Fig. 1(b) is enlarged, it can be distinctly seen that surface roughness of nickel hydroxide particle increases, thus indicating that the particle has a large real surface area [11].

Nickel foam (1 cm × 1 cm) was used as the nickel electrode substrate. Two kinds of pasted-type electrodes were prepared as follows:

Electrode A: The spherical nickel hydroxide particles microencapsulated by 5 wt% cobalt were mixed with an appropriate amount of 1 wt% polytetrafluoroethylene (PTFE) aqueous suspension (60%) and kneaded to obtain paste. The paste was incorporated into the nickel foam substrate using a spatula, dried at 60°C for 1 h, and then pressed at 20 MPa for 1 min. to assure good electrical contact between the substrate and the active material.

Electrode B: The spherical nickel hydroxide particles and cobalt metal particles which was 5% of the total weight of the active material, were uniformly mixed in an agate mortar. Then appropriate amount of 1 wt% PTFE aqueous suspension was added and kneaded to obtain a paste. Subsequent procedures were the same as for Electrode A.

All cyclic voltammetric studies were performed in a three-compartment electrolysis cell at 25°C using an EG&G PARC model 273 potentiostat/galvanostat and M270 electrochemical analysing system with a personal computer. The electrolyte consisted of 6 M KOH + 0.6 M LiOH. Two nickel sheet counterelectrodes were placed at the side and the working electrode was positioned in the center. A Hg/HgO reference electrode was used with a luggin capillary in the region of the working electrode. The working electrodes were activated by charge/discharge cycling prior to the experiments.

3. Results and discussion

Figure 2 shows the cyclic voltammograms of electrodes A and B. Only one anodic oxidation peak for Electrode A, appearing at about 500 mV, was recorded prior to oxygen evolution. Similarly, only one oxyhydroxide reduction peak at about 240 mV was observed on the reverse sweep. Similar voltammograms were also observed for electrode B, with added cobalt metal powder, but the anodic peak corresponding to nickel hydroxide oxidation shifts to a more positive potential, and the cathodic peak potential corresponding to nickel oxyhydroxide reduction shifts to a less positive potential, compared to that of electrode A. This is in agreement with other researchers [1, 2, 5, 7] who incorporated Co into the lattice of nickel hydroxide in the form of Co(OH)₂.

It may also be noted from Fig. 2 that no detectable oxidation peak for cobalt was observed although 5 wt% cobalt had been microencapsulated on the surface of the nickel hydroxide particles (electrode A) and 5 wt% cobalt metal powder had been added as a conductor (electrode B). The absence of an oxidation peak for cobalt in the voltammograms of nickel hydroxide has been previously reported [1, 5, 10]. In the present study the probable cause of this phenomenon is the fact that the cobalt coating or cobalt metal powder is oxidized to cobalt oxyhydroxide when initial activation is carried out using constant current charge/discharge cycling prior to the experiments, while this oxidation reaction is irreversible [5].

To compare the characteristics of the electrodes, the results of the cyclic voltammetric study in Fig. 2 are tabulated in Table 1. The average peak potential, \( \Delta E_{\text{rev}} \), is taken as an estimate of the reversible potential and the difference in the anodic and cathodic positions, \( \Delta E_{\text{a,c}} \), is taken as an estimate of the reversibility of the redox reaction [7, 12]. Oxygen evolution is a parasitic reaction during charging of nickel battery electrodes. McKubre [13] showed that the reversible potential for oxygen evolution is more negative than that for Ni(OH)₂/NiOOH. To compare the effects of two kinds of electrode on the oxygen evolution.

Fig. 1. SEM photographs of spherical nickel hydroxide: (a) before microencapsulated cobalt; (b) after microencapsulated cobalt.