

Electrochemical performance of multiphase nickel hydroxide

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Abstract: The high density nano-crystalline multiphase nickel hydroxide containing at least three doping elements was synthesized and its electrochemical characteristics were studied. The electrochemical behavior of the high density spherical multiphases α -Ni(OH)₂ were also investigated. The results show that the structure of the material is a mixed phase of α -Ni(OH)₂ and β -Ni(OH)₂, which has a the same stabilized structure as α -Ni(OH)₂ during long-term charge/discharge process. High density spherical multiphases α -Ni(OH)₂ have a much better redox reversibility, a much lower oxidation potential of Ni(II) than the corresponding oxidation state in the case of β -Ni(OH)₂, and a much higher reduction potential. They exchange one electron during electrochemical reaction and have a higher proton diffusion coefficient. The mechanism of the electrode reaction is proton diffusion, and the proton diffusion coefficient is 5.67×10^{-10} cm²/s. Moreover, they reveal a higher discharge capacity than β -Ni(OH)₂/ β -NiOOH because they exchange one electron per nickel atom during charge/discharge process.

Key words: multiphase nickel hydroxide; electrochemical performance; voltammogram; exchange electron number; manganese

1 Introduction

Rechargeable batteries are critical components in exploding new technologies of portable electronics, power tools and electric vehicles. The Ni/Cd, Ni/MH, Ni/H₂ and Ni/Zn batteries belong to alkaline secondary batteries. A common feature of these batteries is electrochemical active Ni(OH)₂ electrode used as positive electrode and the Ni(OH)₂ electrode is the essential limited factor in the overall battery energy density.

There are two polymorphs about the nickel hydroxide denoted α -Ni(OH)₂ and β -Ni(OH)₂. Both form crystals in the hexagonal system with the brucite-type structure with Ni(OH)₂ layers stacked along the *c*-axis. The main difference between the β - and α -Ni(OH)₂ phase resides in the stacking of the layers along the *c*-axis. For β -Ni(OH)₂ layers are perfectly stacked along the *c*-axis with an interlamellar distance of 0.46 nm; while for α -Ni(OH)₂ layers are completely misoriented relative to each other corresponding to a turbostratic phase in the presence of water molecules and anionic

species at the van der Waals gap. The interlamellar distance for the α -Ni(OH)₂ is about 0.78 nm[1–6].

Conventional electrode reaction of β -Ni(OH)₂ is considered to be a one-electron process involving oxidation of divalent nickel hydroxide to trivalent nickel oxyhydroxide in charge and subsequent discharge of trivalent nickel oxyhydroxide to divalent nickel hydroxide. Thus, β -Ni(OH)₂ has a maximum theoretical specific capacity of 289 mA·h/g. However, it has also been reported that α -Ni(OH)₂ has better electrochemical properties than β -Ni(OH)₂[7–11]. α -Ni(OH)₂ can be oxidized to γ -NiOOH at a lower potential than the corresponding oxidation state compared with β -Ni(OH)₂, and has a higher discharge capacity than β -Ni(OH)₂/ β -NiOOH since the valence of nickel in γ -NiOOH exceeds 3, due to Ni⁴⁺ defects (3.3–3.7)[12–13].

It is also reported that α -Ni(OH)₂ is not stable in presence of the high concentrate basic electrolyte media and is transformed into β -Ni(OH)₂. Attempts to improve stability of the α -Ni(OH)₂ have a lot of reports[7–11]. In this paper, a high density multiphase α -Ni(OH)₂ with stabilized α -Ni(OH)₂/ γ -NiOOH cycle during charge/discharge process was synthesized through adding at

least three modifier elements. It can improve capacity, cycle life and electrochemical performance. And the electrochemical performances of the high density spherical multiphase α -Ni(OH)₂ were investigated.

2 Experimental

The material was synthesized by coprecipitation of several metal ions from the aqueous solution. The resulting brownish precipitate was filtered by a laboratory suction filter and washed with distilled water until it was free from neutral salts, then dried at 80 °C to produce powder. The powder was subjected to chemical and X-ray diffraction analysis. The doped metal ions are most preferably Co, Zn and Mn. For comparison all samples had the same Co and Zn contents, and only Mn content was changed.

The electrochemical behavior of the spherical multiphase nickel hydroxide in 6 mol/L KOH electrolyte was studied. A typical three-electrode one-compartment electrolysis cell was used for the experimental measurements. The working electrode was a platinum powder microelectrode with diameter of 200 μ m. Nickel sheet counter electrode was placed on the side and the working electrode was positioned at the center. A LUGGIN capillary with a salt bridge was used to connect the cell to the reference electrode. All potentials were measured and quoted with respect to a Ag/AgCl (3 mol/L NaCl) reference electrode.

Cyclic voltammetric experiments were performed using EG & G PAR Mode 273A potentiostat/galvanostat, and a computer interface for experimental control and automatic data acquisition was used.

3 Results and discussion

Fig.1 shows the typical cyclic voltammograms for multiphase nickel hydroxide microelectrode with various Mn contents, which was activated by 15 cyclic voltammograms at a rate of 5 mV/s. In the range of scanning potentials employed, an anode oxidation peak for the electrode with various Mn contents, appearing between 0.34 and 0.38 V, was recorded prior to oxygen evolution. One oxyhydroxide reduction peak at about 0.162–0.177 V was observed on the reverse sweep. As shown in Fig.1, the potential of oxidation peak that corresponds to the formation of higher-valence nickel species apparently decreases with the increase of Mn content in nickel hydroxide, while the potential of reduction peak changes a little. Similar voltammogram is also observed (Fig.1(a)) for the electrode without Mn. The anodic oxidation peak corresponding to Ni(II)

oxidation reaction shifts to more positive potentials, and cathodic peak potential corresponding to nickel hydroxide reduction reaction shifts to less positive compared to the characteristics of the above results. The cyclic voltammetric results in Fig.1 are listed in Table 1. To compare the effect of multiphase α -Ni(OH)₂ on oxygen evolution reaction, the difference between the oxidation peak potential and the oxygen evolution potential(DOP) on the reverse sweep required to produce 50 μ A of anodic current is also estimated from voltammograms.

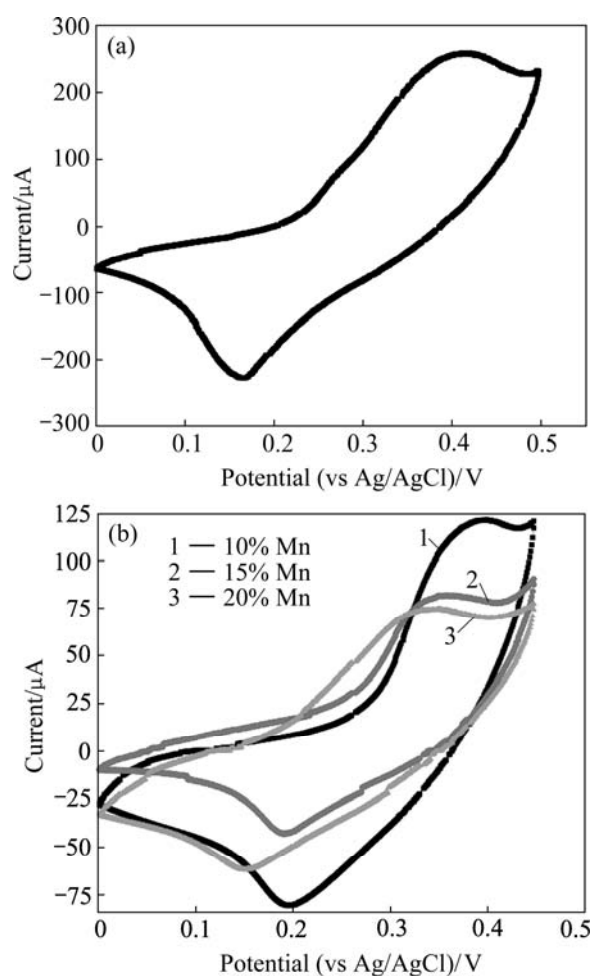


Fig.1 Cyclic voltammograms of multiphase nickel hydroxide with various mass fractions of Mn at 15th charge/discharge cycle: (a) Without Mn; (b) 10 % Mn, 15 % Mn and 20% Mn

The results in Fig.1 and Table 1 illustrate that multiphase α -Ni(OH)₂ allows the electrode to charge at a significantly less positive potential (387, 352 and 346 mV) instead of 412 mV. In addition, the charge process occurs more reversibly (ΔE_{ac} is 210, 168 and 184 mV instead of 254 mV). Moreover, their oxygen evolution overpotentials have nearly the same values. Thus, these results clearly indicate that multiphase α -Ni(OH)₂

Table 1 Parameters for nickel hydroxide electrode with various mass fraction of Mn

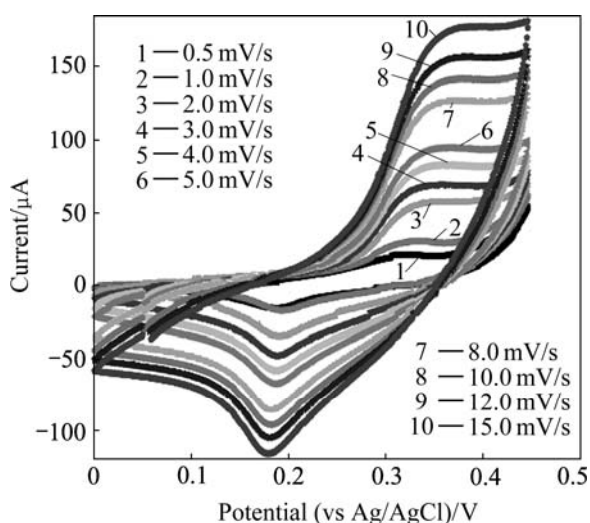
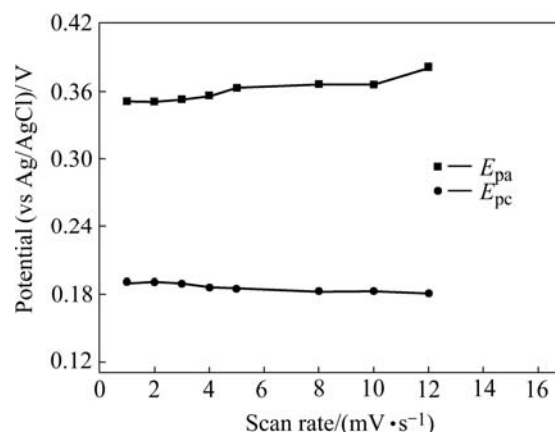
$w(\text{Mn})/\%$	$E_{\text{pa}}(\text{vs Ag/AgCl})/\text{V}$	$E_{\text{pc}}(\text{vs Ag/AgCl})/\text{V}$	$\Delta E_{\text{ac}}(\text{vs Ag/AgCl})/\text{V}$	$E_{\text{O}_2}(\text{vs Ag/AgCl})/\text{V}$
0	0.412	0.158	0.254	0.423
10	0.387	0.177	0.210	0.422
15	0.352	0.184	0.168	0.423
20	0.346	0.162	0.184	0.426

electrodes make the charge process perform more easily and more reversibly, suggesting that much more active materials can be utilized during charge.

From Figs.1–3, it can be seen that the nickel hydroxide microelectrodes with different Mn contents, which were activated by 15 cyclic voltammograms at a rate of 5 mV/s, have a single diffusion-limited peak vs Ag/AgCl. Theoretically, potential difference of peak to peak on a voltammogram for a reversible electrode reaction should be equal to $59 \text{ mV}/n$, however the values in Table 1 are markedly higher than the theoretical value. Therefore, electrode reaction of nickel hydroxide is usually considered as a quasi-reversible electrode reaction[12–14]. The dependence of E_{pa} and $E_{\text{pa}/2}$ can be expressed using Nicholson and Shain equation (Eqn.(1))[15] and can be used to calculate the number of electrons (n) participating in the rate determining stages:

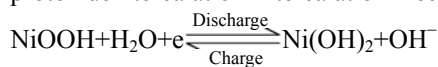
$$E_{\text{pa}} - E_{\text{pa}/2} = 1.857RT/(\alpha nF) \quad (1)$$

where $E_{\text{pa}/2}$ is the potential of half peak height, R is gas constant, T is absolute temperature, α is transfer coefficient and F is faraday constant. According to Fig.1 and Eqn.(1), the number of electrons participating in electrode reaction for nickel hydroxide microelectrode can be calculated, and the results are listed in Table 2. In addition, since oxygen evolution is a parasitic reaction

**Fig.2** Cyclic voltammograms of 15% Mn electrode at various sweep rates**Fig.3** Effect of sweep rate on anodic and cathodic potentials for 15% Mn electrode

during charge of nickel electrode, it will obscure the basic line of reduction peak current. Fig.4 shows that the anodic peak current (I_{pa}) in Fig.2 depends linearly on the square root of the potential sweep rate. As seen in Fig.4, there exists a linear relationship between the peak current and the potential sweep rate square root.

The charge-discharge process of the nickel hydroxide in alkaline solution can be described as a proton deintercalation-intercalation mechanism:



$$(E^0 \text{ (vs Ag/AgCl)} = 0.291 \text{ V}) \quad (2)$$

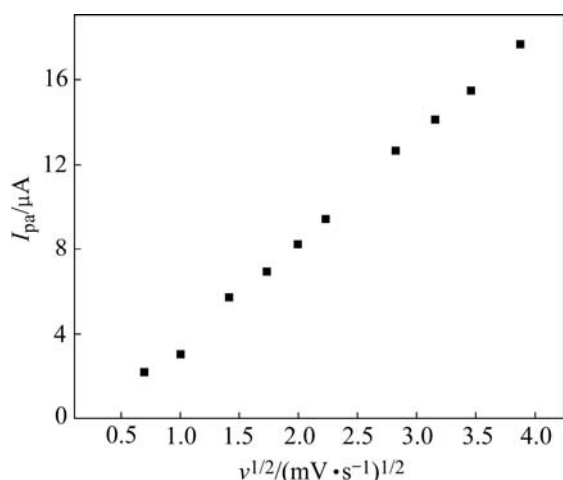
As a stationary electrode, a linear relationship between peak current and the square root of potential sweep rate ($v^{1/2}$) over the range of sweep rate in Fig.2 can be expressed as

$$I_p = 2.99 \times 10^5 n(\alpha n)^{1/2} A D_0^{1/2} C_0^0 v^{1/2} \quad (3)$$

where D_0 is the proton diffusion coefficient in nickel hydroxide, C_0^0 is the concentration of hydrogen in the solid (assuming the density of Ni(OH)_2 is 3.5 g/cm^3 and thus the maximum concentration of electrochemically active material hydrogen in the lattice, C_0^0 , is 0.038 mol/cm^3 [16]), and A is the area of electrode. According to Fig.2, Fig.4, Table 2 and Eqn.(3), diffusion coefficient of H^+ for 15% Mn multiphase nickel hydroxide is found

Table 2 Diffusion coefficients of H^+ for nickel hydroxide electrode with various mass fractions of Mn

$w(\text{Mn})/\%$	$E_{\text{pa}}(\text{vs Ag/AgCl})/\text{V}$	$E_{\text{pa}/2}(\text{vs Ag/AgCl})/\text{V}$	$I_{\text{pa}}/\mu\text{A}$	n	Diffusion coefficient, $D_0/(\text{cm}^2\cdot\text{s}^{-1})$
0	0.412	0.307	282.0	0.900	3.21×10^{-11}
10	0.387	0.301	134.0	1.255	4.47×10^{-11}
15	0.352	0.286	94.0	1.440	6.67×10^{-10}
20	0.346	0.258	89.9	1.080	9.94×10^{-11}

**Fig.4** Dependence of anodic peak current on square root of potential sweep rate for 15% Mn electrode

to be $6.67 \times 10^{-10} \text{ cm}^2/\text{s}$. Similarly, the others can also be calculated, the results are listed in Table 2.

In Table 2, the proton diffusion coefficients in the multiphase nickel hydroxide exhibit higher values, which are higher than those in Al-substituted $\alpha\text{-Ni}(\text{OH})_2$, $3.6 \times 10^{-11} \text{ cm}^2/\text{s}$ reported in Refs.[6–7].

As seen from Fig.1, Tables 1 and 2, the multiphase $\alpha\text{-Ni}(\text{OH})_2$ doped with different amounts of Mn reveals much better electrochemical performance than Mn-undoped $\beta\text{-Ni}(\text{OH})_2$, such as much lower oxidation potential of nickel (II), much higher electrochemical reversibility, and much more exchange electron number, thus the material has greater discharge capacity and higher utilization of active material.

The anions strongly anchor the positive charged brucite layers and stabilize the structure under a variety of stressful conditions. However, sample with lower anion content, namely that with 5% Mn is less stable in alkali media. As seen from Fig.1 and Table 2, the multiphase nickel hydroxide electrode that consists of 15% Mn has much better electrochemical performance, much more exchange electron number, and thus the electrode has greater discharge capacity than the theoretical capacity of $\beta\text{-Ni}(\text{OH})_2$ (289 mA·h/g). As a consequence, it can be concluded that $\alpha\text{-Ni}(\text{OH})_2$ doped with 15% Mn is an excellent positive active material for

alkaline rechargeable batteries.

4 Conclusions

1) Nickel hydroxide active materials internally containing at least three modifier elements, have a modified proton diffusion coefficient, excellent electrochemical performance and wider use of the available storage sites through improved proton transport.

2) The nickel hydroxide doped with 15% Mn has much lower oxidation peak potential and much higher reduction peak potential. The presence of Mn in nickel hydroxide lattice can increase electronic conductivity and protonic conductivity of nickel hydroxide, thus improving the performance of nickel hydroxide electrode, such as greater discharging capacity and better reversibility of $\text{Ni}(\text{II})/\text{Ni}(\text{III})$ redox reaction.

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