

Effect of ultrasonic on structure and electrochemical performance of α -Ni(OH)₂ electrodes

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Abstract: Al/Co co-doped α -Ni(OH)₂ samples were prepared by either ultrasonic co-precipitation method (Sample B) or co-precipitation method (Sample A). The crystal structure and particle size distribution of the prepared samples were examined by X-ray diffraction (XRD) and laser particle size analyzer, respectively. The results show that Sample B has more crystalline defects and smaller average diameter than Sample A. The cyclic voltammetry and electrochemical impedance spectroscopy measurements indicate that Sample B has better electrochemical performance than Sample A, such as better reaction reversibility, lower charge-transfer resistance and better cyclic stability. Proton diffusion coefficient of Sample B is $1.96 \times 10^{-10} \text{ cm}^2/\text{s}$, which is two times as large as that ($9.78 \times 10^{-11} \text{ cm}^2/\text{s}$) of Sample A. The charge-discharge tests show that the discharge capacity (308 mA·h/g) of Sample B is 25 mA·h/g higher than that of Sample A (283 mA·h/g).

Key words: Al/Co co-doped α -Ni(OH)₂; ultrasonic co-precipitation method; proton diffusion coefficient; charge-transfer resistance; electrochemical performance

1 Introduction

Nickel hydroxide has been extensively used as an active material of the positive electrode in rechargeable alkaline batteries. There are two phases known as α and β , which are transformed to γ -NiOOH and β -NiOOH, respectively during charging [1]. The β -Ni(OH)₂ only has a theoretical capacity of 289 mA·h/g and is easily transformed to γ -NiOOH when overcharge happens [2], the γ -NiOOH can lead to a subsequent swelling of the positive electrode. While, α -Ni(OH)₂ has been attracted much attention since the α -Ni(OH)₂ not only has a superior theoretical capacity (482 mA·h/g), but also avoids the volume expansion in the charge-discharge process due to the similar lattices of α -Ni(OH)₂ and γ -NiOOH. Unfortunately, α -Ni(OH)₂ is easily converted to β -Ni(OH)₂ in alkaline media. Many studies have been carried out through partial substitution of nickel ion by other metal ions such as Al [3], Co [4], and Zn [5] in order to improve the stability of α -Ni(OH)₂. Although the stable α phase structure can be obtained after adding metal ions in the Ni(OH)₂, the performance of Ni-MH

batteries is adversely affected, such as the capacity fading, the internal resistance increasing and cycle life decreasing during charge-discharge process.

Also, it is difficult to synthesize nano-sized α -Ni(OH)₂ because of its agglomeration. Thus, the application of α -Ni(OH)₂ is limited in Ni-MH batteries. Chemical co-precipitation is the commonly used method to prepare α -Ni(OH)₂, but the powder shows coarse aggregates. Based on the above consideration, in the present study, nano-sized α -Ni(OH)₂ was synthesized by ultrasonic co-precipitation method, which can produce discrete and uniform particles due to the dispersive action of ultrasonic.

2 Experimental

2.1 Preparation of nickel hydroxide

The Sample B was prepared as follows. A mixed solution containing NiCl₂·6H₂O, Al₂(SO₄)₃·18H₂O, Co(NO₃)₂·6H₂O (the molar ratio of Ni:Al:Co is 1:0.10:0.17) and the proper amount of sodium hydroxide aqueous solution were dropped into a mother liquid synchronously while stirring at 50 °C. Sodium hydroxide

was modulated to keep the pH value at 9.00 ± 0.10 . The agitation lasted 5 h after the dropping was finished, and ultrasonic was applied in the whole processes. The suspension was aged for 12 h, and then washed three times with distilled water and twice with anhydrous ethanol. The attained nickel hydroxide product was dried at $80\text{ }^{\circ}\text{C}$. The same procedure was carried out to synthesize Sample A except no application of ultrasonic.

2.2 Preparation of nickel hydroxide electrode

The pasted nickel electrodes were prepared as follows. 8% Samples A or B, 74% commercial micro-size spherical nickel, 15% nickel powder, 2% CMC were mixed thoroughly with 1% PTFE solution. The paste obtained was incorporated into nickel foam substrates with the geometrical size of $2.5\text{ cm} \times 2.5\text{ cm}$. The pasted electrodes were dried naturally and then mechanically pressed. A slurry containing 88% AB_5 -type metal hydride powder, 2% CMC as a binder and 10% nickel powder was forced into the same nickel substrates, then dried and compressed to obtain negative electrodes.

2.3 Physical characterization

The structures of the samples were determined using X-ray diffraction (XRD) (D/max-III A X-ray diffractometer, Rigaku, Japan) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54\text{ \AA}$) operated at 36 kV and 20 mA. Particle size distribution (PSD) was analyzed using a Nanotrac 150 particle size analyzer.

2.4 Electrochemical measurements

Electrochemical tests are performed in a three-compartment electrolysis cell at ambient temperature. The cell comprised a working electrode (the positive electrode), a counter electrode (the negative electrode) and an Hg/HgO reference electrode. Electrolyte of 7 mol/L KOH and 0.05 mol/L LiOH was used. Both cyclic voltammetry (CV) and electrochemical impedance measurements (EIS) were conducted by using a Chenhua CHI7600 model electrochemical workstation. The scanning rate of CV test ranges from 0.02 V/s to 0.1 V/s and the cell potential ranges from -0.2 to 0.7 V . EIS measurements were made at open circuit potential in the frequency range of 10 kHz–100 Hz.

Negative electrodes (the cathode) and positive electrodes (the anode) were assembled with polypropylene as the separator to form simulated batteries. Galvanostatic charge-discharge tests were conducted at $0.2C$ rate to cut-off voltage of 1.0 V by using a Neware BTS-51800 battery testing system at ambient temperature.

3 Results and discussion

3.1 Characterization of nickel hydroxide samples

The particle size distribution for the prepared nickel hydroxides is shown in Fig. 1. It can be seen that the size is uniformly distributed for both samples, but the average diameter of Sample A (90 nm) is bigger than that (61 nm) of Sample B. It may be due to some degree of agglomeration without ultrasonic. This can be understood that high temperature and high pressure will be generated from the cavitation when the ultrasonic is used in the preparation of the samples. The energy provided by the ultrasonic will cause the rate of nucleation to enhance several orders [6], which results in forming ultrafine particles. The cavitation also produces a lot of tiny bubbles on the surface of solid particles, and thus greatly decreases the specific surface free energy of particles in order to constrain the growth and agglomeration of crystal nucleus. Meanwhile, ultrasonic cavitation will produce the shock-wave and internal jet, which can break the agglomerates into pieces, and lead to small particle size.

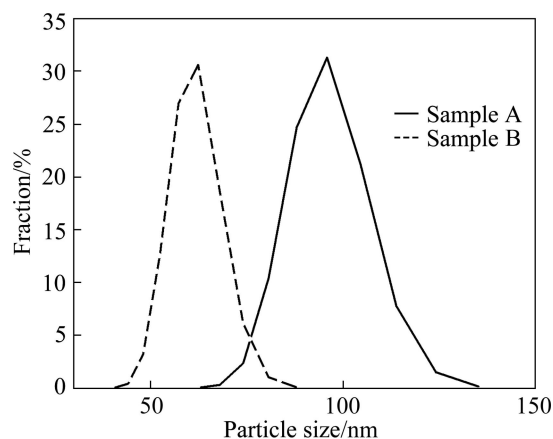


Fig. 1 Particle size distribution of Samples A and B

The XRD patterns of both samples given in Fig. 2 are similar to the standard XRD pattern of $\alpha\text{-Ni(OH)}_2 \cdot 0.75\text{H}_2\text{O}$ (JCPDS 38-0715). The asymmetric diffraction peak located in the range of 32° – 36° is the characteristic of the turbostratic disorder in $\alpha\text{-Ni(OH)}_2$ [7]. The peaks corresponding to all the reflections in the XRD patterns of Sample B are slightly broadened as compared with those in the patterns of Sample A. Moreover, the diffraction peak of Sample B corresponding to crystal reflections (015) and (018) cannot be obviously distinguished, while other peaks appear at the same positions. This illustrates that the $\alpha\text{-Ni(OH)}_2$ prepared by ultrasonic co-precipitation method has lower crystallinity and smaller particle size than those obtained by co-precipitation method, as

shown in Fig. 1. The proper broadening of reflections caused by smaller size may increase the structural defects [8–9]. Thus, more structural defects are formed in the Sample B, which is beneficial to improving the electrochemical performance for $\text{Ni}(\text{OH})_2$ due to the presence of disorders [10].

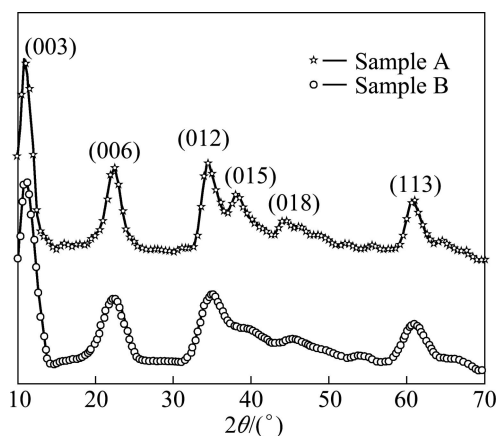


Fig. 2 XRD patterns for Samples A and B

3.2 Cyclic voltammetric behavior

Figure 3 shows the typical cyclic voltammograms of two $\text{Ni}(\text{OH})_2$ at scanning rate of 0.1 V/s. The anodic peaks are due to the oxidation of $\alpha\text{-Ni}(\text{OH})_2$ to $\gamma\text{-NiOOH}$ [11], similarly the cathodic peaks are for the reverse process. The cyclic voltammetric parameters corresponding to Fig. 3 are listed in Table 1. The $\Delta E_{\text{O,R}}$ is taken as an estimate of the reversibility of the redox reaction, the smaller $\Delta E_{\text{O,R}}$ is, the more reversible the electrochemical reaction is [12]. Compared with $\Delta E_{\text{O,R}}$ value (0.324 V) of sample A, $\Delta E_{\text{O,R}}$ value (0.301 V) of Sample B decreases, suggesting that the ultrasonic can play a positive role in improving the reversibility of electrode reaction. The oxygen evolution reaction (OER) is known as a parasitic reaction during charging of nickel hydroxide. The separation between the oxidation peak potential and the OER potential ($E_{\text{OER}} - E_{\text{O}}$) is very

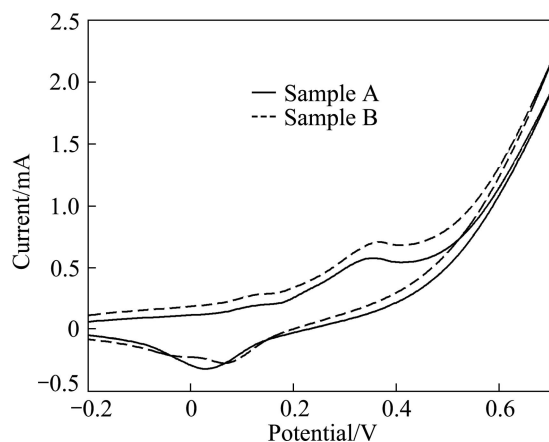


Fig. 3 Cyclic voltammograms of Samples A and B at scanning rate of 0.1 V/s

Table 1 CV results of Samples A and B

Sample	E_{O}/V	E_{R}/V	E_{OER}/V	$\Delta E_{\text{O,R}}/\text{V}$	$(E_{\text{OER}} - E_{\text{O}})/\text{V}$
A	0.356	0.028	0.407	0.324	0.051
B	0.366	0.065	0.435	0.301	0.069

E_{O} : Oxidation peak potential; E_{R} : Reduction peak potential; E_{OER} : Oxygen evolution potential; $\Delta E_{\text{O,R}}$: Difference between reduction peak potential and oxidation peak potential

important, the large value is expected [13]. From Table 1, the $E_{\text{OER}} - E_{\text{O}}$ of Sample B is larger than that of Sample A, thus more active materials can be utilized during charge and discharge, which is in accordance with the charge-discharge results.

It is well known that the proton diffusion process controls the rate of battery reaction [14]. Therefore, it is of great importance to study the proton diffusion coefficient. In case of semi-infinite diffusion, at 25 °C, the peak current may be expressed by the classical Randle-Sevick equation [15]:

$$I_p = 2.69 \times 10^5 \times n^{3/2} \times S \times (D\nu)^{1/2} \times C_0 \quad (1)$$

where I_p is the anodic peak current; n is the electronic number of reaction (the value is about 1 for $\text{Ni}(\text{OH})_2$); S is the real surface area of the electrode; D is the diffusion coefficient; ν is the scanning rate; C_0 is the initial concentration of active material. For nickel hydroxide electrode:

$$C_0 = \frac{\rho}{M} \times x \quad (2)$$

where ρ is the theoretical density of $\text{Ni}(\text{OH})_2$ (2.82 g/cm³); M is the mole mass of $\text{Ni}(\text{OH})_2$ (92.7 g/mol); x is the molar fraction of sample powders in composite electrode.

Cyclic voltammograms for Samples A and B under various scanning rates are presented in Fig. 4. As the scanning rate increases, the anodic peak potential shifts to more positive direction, while the cathodic peak only has a slight movement toward the negative direction. This result is similar to that reported previously [16–18]. The linear relationship between I_p and $\nu^{1/2}$ for both samples can be founded, as shown in Fig. 5. From the slope of the fitted line in Fig. 5 and Eq. (1) we can get the proton diffusion coefficient D . Proton diffusion coefficient of sample A is $9.78 \times 10^{-11} \text{ cm}^2/\text{s}$, and that of Sample B is $1.96 \times 10^{-10} \text{ cm}^2/\text{s}$. This can be explained by the fact that the sample B has a smaller particle size and large specific surface area, which not only provides more chances for the particles to contact the electrolyte solution, but also shortens the diffusion distance in solid-state. Moreover, the intercalation and release of protons into and from the nickel hydroxide host lattice can be enhanced by crystal imperfection.

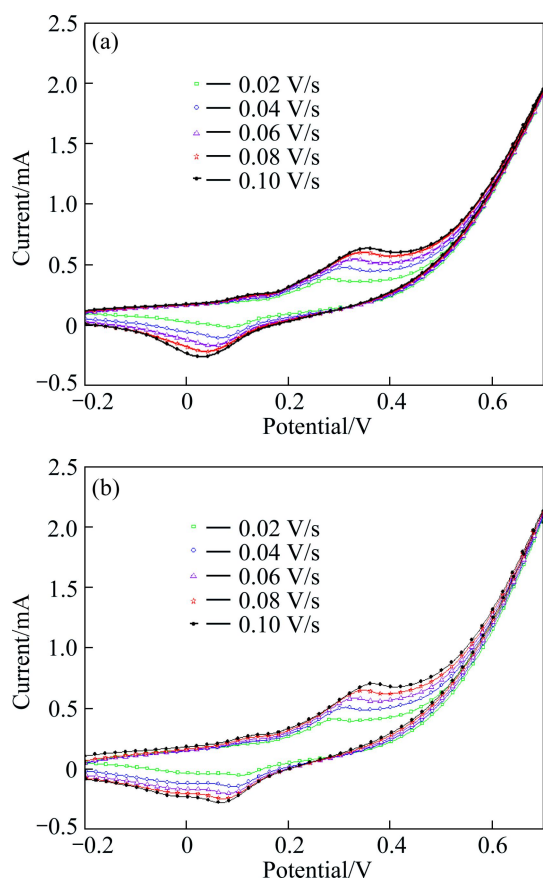


Fig. 4 Cyclic voltammograms for Samples A (a) and B (b) under different scanning rates

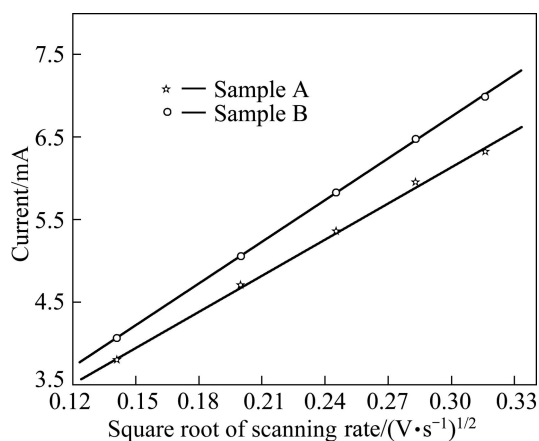


Fig. 5 Relationship between anodic peak current and square root of scanning rate for Samples A and B

3.3 Electrochemical impedance spectroscopy measurement

Figure 6 shows the Nyquist plots for both electrodes at steady state. The corresponding equivalent circuit for impedance analysis is displayed as the inset of Fig. 6, where R_L is the resistance of the solution; R_{ct} is the charge-transfer resistance; Z_W is the Warburg resistance; and Q_C is the constant phase element for the double layer capacitance. For both electrodes at high frequencies (HF),

the semicircle is characteristic of the charge-transfer resistance acting in parallel with the double layer capacitance [19]. At low frequencies (LF), a straight line having an angle of 45° with the real axis indicates a linear Warburg portion, being characteristic of the semi-infinite diffusion. It is worth noting that the line having a slope higher than 45° is not discovered at LF, which may result from the disappearance of finite diffusion effects and is related to the finite length [20]. Generally, the electrode reaction occurring at nickel hydroxide is controlled by charge transfer and proton diffusion. The simulated values of the elements for the equivalent circuits are listed in Table 2. From Table 2, Sample B has smaller R_{ct} than Sample A, but the values of Q_C are converse, which may be due to the fact that the Sample B has a large efficient active specific surface area for the electrochemical reactions because of the smaller sized crystals and incorporating with relatively more foreign ions and water molecules [21]. The results illustrate that the Sample B exhibits a lower resistance to charge-transfer and higher efficient proton diffusion than that of Sample A during the electrochemical reaction.

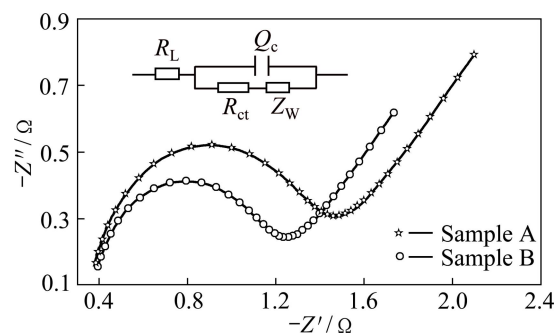


Fig. 6 Nyquist plots and equivalent circuit of Samples A and B

Table 2 Impedance parameters for Samples A and B

Sample	R_L/Ω	R_{ct}/Ω	Q_C/F
A	0.332 8	0.979 2	9.881×10^{-6}
B	0.359 7	0.777 3	1.174×10^{-5}

3.4 Galvanostatic charge-discharge measurement

Figure 7 shows the charge-discharge curves of two electrodes at $0.2C$ rate. It can be seen that the discharge capacity of Sample B is $308 \text{ mA}\cdot\text{h/g}$, which is $25 \text{ mA}\cdot\text{h/g}$ higher than that ($283 \text{ mA}\cdot\text{h/g}$) of Sample A. Moreover, Sample B has a lower charge potential and higher discharge potential compared with Sample A, which is in good agreement with the CV tests. The cyclic behavior of the two electrodes at $0.2C$ rate is illustrated in Fig. 8. Two curves show that discharge capacity increases firstly, then it reduces after reaching the maximum value. However, the discharge capacity of sample A decreases sharply after 10 cycles, and just has a slight decrease for

Sample B. The deterioration rates R_d [22] for Samples A and B are 4% and 23%, respectively. This indicates that Sample B has much better cyclic stability than sample A during the cycle process.

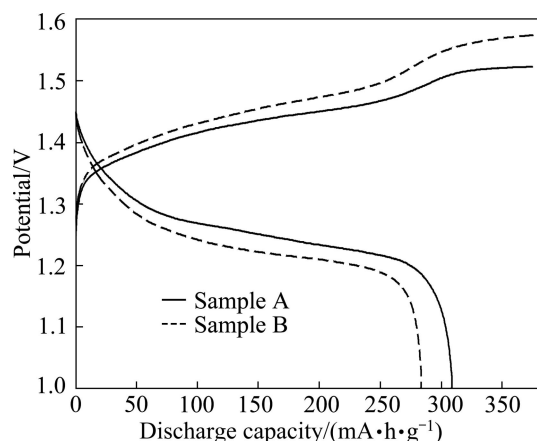


Fig. 7 Charge-discharge curves of Samples A and B at 0.2C rate

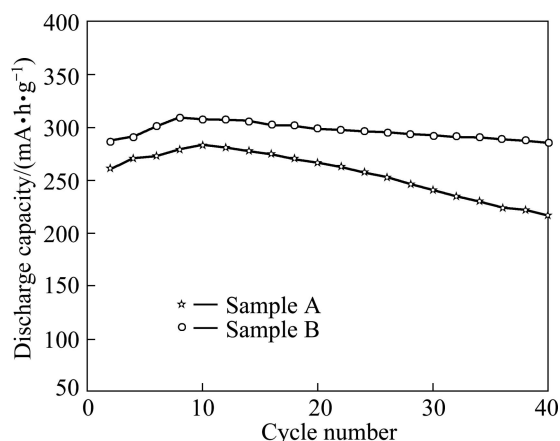


Fig. 8 Cyclic performance of Samples A and B at 0.2C rate

4 Conclusions

1) Al/Co co-doped α -Ni(OH)₂ prepared by ultrasonic co-precipitation method have smaller grain size and more crystalline defects than the Al/Co co-doped α -Ni(OH)₂ prepared by co-precipitation method.

2) Due to the utilization of ultrasonic, sample B has a relatively higher proton conductivity. The electrode reaction is found to be controlled by proton diffusion and the proton diffusion coefficient is $1.96 \times 10^{-10} \text{ cm}^2/\text{s}$ for Sample B and $9.78 \times 10^{-11} \text{ cm}^2/\text{s}$ for Sample A.

3) Electrochemical impedance spectroscopy measurements show that the sample prepared by ultrasonic co-precipitation method has a lower resistance and higher double layer capacitance than the sample prepared by co-precipitation method.

4) The galvanostatic charge-discharge experiment results show that the discharge capacity of Sample B

reaches 308 mA·h/g, while that of Sample A is 283 mA·h/g. The utilization of ultrasonic can increase the discharge potential and decrease the charge potential. The cycle stability of Sample B is obviously improved compared with that of Sample A.

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超声波对 α -Ni(OH)₂ 电极结构及电化学性能的影响

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摘要: 分别采用共沉淀法和超声波共沉淀法制备 Al/Co 复合掺杂 α -Ni(OH)₂ 样品 A 和 B, 用 XRD 和激光粒度仪表征样品的晶相结构和粒度分布。结果表明, 样品 B 比样品 A 具有较多的晶格缺陷和较小的平均粒径。循环伏安特性及电化学阻抗谱测试显示, 样品 B 比样品 A 具有更好的电化学性能: 较好的反应可逆性、较低的电荷转移电阻和较高的循环寿命等。样品 B 的质子扩散系数为 $1.96 \times 10^{-10} \text{cm}^2/\text{s}$, 约为样品 A ($9.78 \times 10^{-11} \text{cm}^2/\text{s}$) 的 2 倍。充放电测试显示, 样品 B 的放电比容量达到 308 mA·h/g, 比样品 A 的放电比容量高 25 mA·h/g。

关键词: Al/Co 复合掺杂 α -Ni(OH)₂; 超声波共沉淀法; 质子扩散系数; 电荷转移电阻; 电化学性能

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