Electrolytic Preparation, Structure Characterization and Electrochemical Performance of NiOOH

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Abstract   NiOOH was prepared by one-step electrolysis of spherical Ni(OH)$_2$ and the effects of electrolysis parameters were examined. The highly pure NiOOH was obtained after electrolysis at a current density of 60mA·g^{-1} and 30℃ with anodic potential controlled in the range of 1.73—1.85V (*vs.* Zn/ZnO) for 360min. The NiOOH samples were characterized by X-ray powder diffraction (XRD) and scanning electron microscope (SEM) analysis. Results indicate that the electrolysis product is spherical NiOOH doped with graphite. Charge and discharge tests show that the prepared NiOOH offers a discharge capacity of over 270mAh·g^{-1} at current density of 30mA·g^{-1} and can be directly used as cathode material of alkaline Zn/NiOOH batteries. Galvanostatic charge/discharge and cyclic voltammetry (CV) tests reveal good cycling reversibility of the NiOOH electrode.
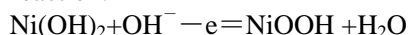**Keywords**   NiOOH, electrolysis, current density, discharge capacity, cycling reversibility
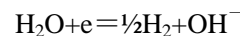
1 INTRODUCTION

To develop new batteries, electrode materials become more and more important in the field of contemporary electrochemistry[1—8]. In recent years, with increasing sorts and amount of digital code products, the alkaline Zn/NiOOH batteries have attracted much attention because of their excellent electrochemical performance under heavy load[9—12]. They have high discharge voltage platform (1.6V), and the discharge capacity is several times higher than the alkaline manganese batteries at high current density. In addition, NiOOH is also useful to Li-ion batteries because the cathode material LiNiO$_2$ can be obtained by ion exchange reaction based on the property of good proton transfer of high purity NiOOH[13—17]. Hence, how to quickly and conveniently prepare NiOOH of high purity is important not only to alkaline Zn/NiOOH batteries but also to the preparation of LiNiO$_2$ material. Recently, an improved chemical method is reported to prepare high capacity NiOOH by oxidizing spherical Ni(OH)$_2$ in strong alkali solution and the excellent performance of the alkaline Zn/NiOOH batteries constructed with the prepared NiOOH[18]. However, chemical oxidization method has disadvantages of containing too many reaction steps and consuming too much reagents after all. If an electrolysis method is applied to realize this process, it can considerably reduce consumption of raw materials except Ni(OH)$_2$. Here a method is reported to obtain highly pure NiOOH by one-step electrolysis of spherical Ni(OH)$_2$ in alkali solution.

The synthesis process for NiOOH is intrinsically the process of losing proton and electron. The electrode reactions of electrolytic preparation can be expressed as follows.

Anode reaction:

$$Ni(OH)_2 + OH^- - e = NiOOH + H_2O$$

Cathode reaction:

$$H_2O + e = ½H_2 + OH^-$$

Total reaction:

$$Ni(OH)_2 = NiOOH + ½H_2 \qquad (1)$$

The above overall reaction suggests that Ni(OH)$_2$ as raw material and NiOOH and H$_2$ as products are not pollutive to the environment. It can also be seen that the anodic reaction is to lose electron and consume OH$^-$ and highly concentrated OH$^-$ is beneficial to forming NiOOH.

In the present work, the influence of various parameters (*e.g.* electrolyte concentration, temperature, electrolysis duration, and current density) on electrolysis is investigated, and the structure and electrochemical performance of the prepared NiOOH are characterized by means of X-ray powder diffraction (XRD), scanning electron microscope (SEM), cyclic voltammetry (CV) and galvanostatic charge/discharge tests.

2 EXPERIMENTAL

The electrode was manufactured from the mixture of cathode active material Ni(OH)$_2$ (Changsha Reaserch Institute of Mining and Metallurgy, Xiangtan Power Materials Branch. Brand No.—Zn$_{3.0}$Co$_{1.5}$; Zn$_{3.0}$Co$_{3.0}$; Zn$_{3.0}$Co$_{5.5}$) and expansive graphite (Qingdao Tianhe Graphite Co., LTD. Brand No.—Kp80, 99.2%) in a mass ratio of 80∶15 as well as 5% polytetrafluoroethylene (PTFE) as binder. This mixture was fully mixed in an agate mortar and pressed on to a porous nickel foil (2cm×2cm). Table 1 is the compositions of three kinds Ni(OH)$_2$ in accordance with the contents of cobalt: 1[#]—1.5% Co-Ni(OH)$_2$(Zn$_{3.0}$Co$_{1.5}$); 2[#]— 3.0% Co-Ni(OH)$_2$(Zn$_{3.0}$Co$_{3.0}$); 3[#]— 5.5% Co-Ni(OH)$_2$(Zn$_{3.0}$Co$_{5.5}$). The electrolysis cell consists of a pure Pt sheet as cathode, Ni(OH)$_2$ electrode as anode and KOH solution of various concentrations as electrolyte. The electrolysis was performed at various current densities and for various durations. The anodic

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Table 1 The compositions of spherical $Ni(OH)_2$ raw materials (%)

$Ni(OH)_2$	Ni	Co	Zn	Fe	Cu	Ca	Cl^-	SO_4^-	H_2O
1[#]	57.61	1.46	2.98	0.0040	0.001	0.0012	0.0039	0.18	0.60
2[#]	56.01	3.02	3.06	0.0029	0.0012	0.008	0.0035	0.25	0.58
3[#]	54.45	5.15	3.12	0.0035	0.0015	0.012	0.0029	0.28	0.55

resultant NiOOH after electrolysis was moved from the nickel foil with ultrasonic vibration. The product was washed with 1% KOH solution and distilled water, followed by vacuum drying at 60℃ for 6h.

The purity of the NiOOH was determined by the excess ferrous ion analysis method[18]. The XRD patterns were collected by means of a Rigaku D/max2500VB2+/PCX diffractometer. The morphology of the obtained NiOOH sample was examined by means of SEM (Cambridge S250MK3) observations.

The prepared NiOOH mixture ($W_{NiOOH/C/PTFE}=80:15:5$) was rolled into a thin film and pressed on to a porous nickel screen ($1cm \times 1cm$) with a force of $6 \times 10^3 kg$, thus the cathode of the testing cell was obtained. $9mol \cdot L^{-1}$ solution of KOH was used as the electrolyte, a pure nickel wire as counter electrode and a Zn/ZnO/KOH ($9mol \cdot L^{-1}$) as reference electrode (RE). The galvanostatic charge/discharge test was carried out with a LAND CT2001A cell test instrument, and an end voltage of 0.9V was set for discharge tests. The cyclic voltammetry measurement was performed by means of an EG&G Princeton Applied Research 273 Potentiostat controlled by M270 electrochemistry software. The scan rate was $0.5mV \cdot s^{-1}$ in the voltage range from 0.9V to 1.95V.

3 RESULTS AND DISCUSSION
3.1 Effect of electrolysis parameters on the synthesis of NiOOH

It is found at the beginning that the NiOOH generated by one-step electrolysis could only offer a discharge capacity of $276mAh \cdot g^{-1}$ (equivalent to the purity of 94.5%), lower than the theoretical capacity of $292mAh \cdot g^{-1}$ (equivalent to the purity of 100%), even if the electrolysis duration was fully prolonged. So the effect of numbers of times for electrolytic formation on the purity of NiOOH had to be studied before the electrolysis conditions were optimized. The influence of electrolysis formation times on the synthesis of NiOOH at medium current density of $60mA \cdot g^{-1}$ is shown in Fig.1. Under the same electrolysis condition, the discharge capacity is $261mAh \cdot g^{-1}$ (the first formation), $273mAh \cdot g^{-1}$ (the second), $278mAh \cdot g^{-1}$ (the third) and $281mAh \cdot g^{-1}$ (the fourth). It is seen that with increasing times of electrolysis formation, the purity of NiOOH increases and trends to be stabilized. The results of the traditional chemical titration analysis indicate that there occurs a good linear relationship between the discharge capacity and the purity (titration result) of the prepared NiOOH, showing the higher the purity, the higher the discharge capacity. The appropriate times of electrolysis formation are 2,3 for NiOOH synthesis of higher purity, but the higher
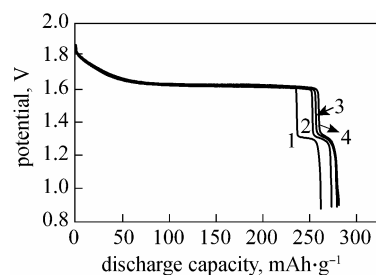

Figure 1 Effect of electrolytic formation times on the electrolysis [3[#] $Ni(OH)_2$, 35% KOH, 30℃, $60mA \cdot g^{-1}$ and 6h for each formation]

the electrolytic formation times, the longer experimental time is needed. The aim of this work is to synthesize highly pure NiOOH by electrolysis only once through optimizing electrolytic technology.

NaOH and KOH solutions of different concentration were used as electrolyte in order to study the influence of electrolyte on the electrochemical synthesis of NiOOH. The result is shown in Fig.2. Under the condition of the same concentration, it is easier to synthesize highly pure NiOOH in KOH than in NaOH because KOH is beneficial to decreasing the polarization of electrolysis due to its higher conductivity and lower viscosity so that the interlayer transfer of protons in $Ni(OH)_2$ is facilitated. From Fig.2, it can also be seen that an increase in concentration improves the purity of the electrolyzed NiOOH when concentration of KOH is below 40%. However, the purity of NiOOH begins to decrease if the concentration of KOH is over 40% probably because excessively concentrated KOH with high viscosity ($\eta_{40\%}=2.98mPa \cdot s$ and $\eta_{45\%}=3.82mPa \cdot s$ at 25℃[19]) makes transmission of reactant particles difficult and impedes the reaction. The oxygen covering the electrode surface would decrease the real electrolysis area and increase the localized current density. Taking all aspects into accounts, 35% KOH solution is considered the best.
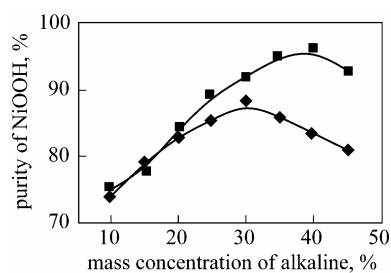

Figure 2 Influence of electrolyte concentration on the synthesis of NiOOH [1[#] $Ni(OH)_2$, 30℃, $60mA \cdot g^{-1}$, electrolysis for 6h]
■ KOH solution; ◆ NaOH solution

The influence of electrolysis duration on the purity of NiOOH in 35% KOH at current density of $60mA \cdot g^{-1}$ is shown in Fig.3. The purity of NiOOH increases sharply with increasing the time of electrolysis at the beginning of electrolysis. It is because that the $Ni(OH)_2$ electrode contains concentrated protons and the surface $Ni(OH)_2$ is easily oxidized *via* diffusion of protons at early stage of electrolysis. When the electrolysis duration is over 300min, the increase in NiOOH purity tends to be moderate and many bubbles on the electrode surface are observed. The reason is that the side reaction of oxygen evolution consumes most of anode current at the end of the electrolysis and reduces the current efficiency. So the optimal electrolysis duration is 360min at a current density of $60mA \cdot g^{-1}$.
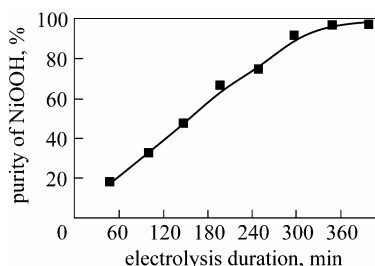

Figure 3 **Effect of electrolysis duration on the purity of NiOOH** [1# $Ni(OH)_2$, 35% KOH, 30℃, $60mA \cdot g^{-1}$]

Figure 4 shows the effect of temperature on the synthesis of NiOOH and the appropriate temperature ranges from 25℃ to 40℃. During electrolysis there are three parallel reactions: the main reaction of generating NiOOH and the two side reactions of NiOOH decomposition and oxygen evolution. At low temperature, the main and side reactions all proceed slowly, leading to the low current efficiency. With increasing temperature, the current efficiency and purity of NiOOH increase. When temperature is over 40℃, the energy barrier of NiOOH decomposition and oxygen evolution is greatly reduced and the side reactions become dominant. That results in the reduction of the purity of NiOOH.
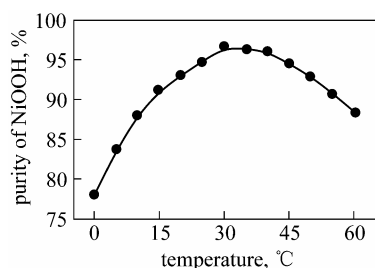

Figure 4 **Influence of temperature on the purity of NiOOH** [1# $Ni(OH)_2$, 35% KOH, $60mA \cdot g^{-1}$, 6h electrolysis]

Current density and efficiency are the two important parameters relevant to the purity and space-time yield of the electrolysis product. Fig.5 shows the effect of current density on the current efficiency at 30℃ in 35% KOH. The current efficiency
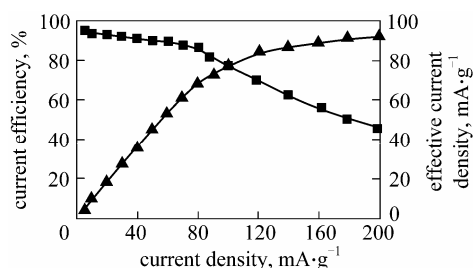

Figure 5 **Effect of current density on the current efficiency** [1# $Ni(OH)_2$, 35% KOH, 30℃, electrolysis for 6h] ■ current efficiency; ▲ effective current density

remains stable with the increase in current density when the current density is below $70mA \cdot g^{-1}$. It can be explained by that at low current density, most of the anodic product is NiOOH because the anode potential of $Ni(OH)_2$ electrode at the platform of 1.85V (*vs.* Zn/ZnO) is lower than the potential of oxygen evolution (1.9V). With increasing current density to above $70mA \cdot g^{-1}$, the current efficiency drops rapidly. It is because the anode potential rises to 1.95V, leading to obvious oxygen evolution.

In order to explain the relation between space-time yield and current density, the concept of effective current density is more useful, which is the product of actual current density and current efficiency. It can be seen in Fig.5 that with increasing actual current density, effective current density increases and trends to be stable. In combination of current efficiency and effective current density, the optimum current density is 60—$90mA \cdot g^{-1}$ (in Fig.5).

Figure 6 shows the influence of contents of Co on the electrolysis. It can be seen that the discharge property of 5.5% Co-$Ni(OH)_2$ cathode is superior to other $Ni(OH)_2$ cathodes. The sample has a high charge/discharge platform of 1.5—1.7V and an initial capacity of $273mAh \cdot g^{-1}$ based on an end discharge voltage of 1.0V and a charge/discharge rate of $30mA \cdot g^{-1}$. The result indicates that with increasing Co contents, the discharge voltage increases remarkably and the discharge capacity of NiOOH cathode also increases. It is because the increase in Co content can reduce the cathodic polarization, improve the electrochemical activity of NiOOH cathode and increase the discharge voltage[20,21]. Due to the high price of Co, 5.5% Co content is considered the optimum. That is not only
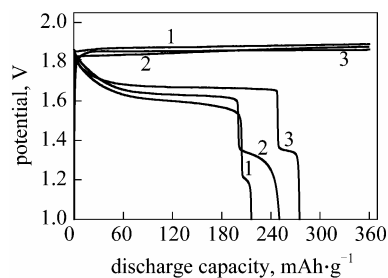

Figure 6 **Influence of contents of Co on the electrolysis** (35%KOH, 30℃, 6h electrolysis) 1—1.5%Co-$Ni(OH)_2$; 2—3.0%Co-$Ni(OH)_2$; 3—5.5%Co-$Ni(OH)_2$

beneficial to synthesizing highly pure NiOOH but to reducing the electrode cost.

Figure 7 is the curve of anodic polarization in 35% KOH. It can be seen that two current inflection points occur at 1.73V (point c) and 1.85V (point d) respectively. The anode current increases linearly according to logarithmic relation with increasing anode potential in the range of 1.73—1.85V. That expresses the electrolytic process is electrochemical control and the optimal electrolytic potential is 1.73—1.85V. When potential increases to over 1.85V, the anodic current decreases probably due to the formation of nickel dioxide. When potential is over 1.95V, anodic current increases again because of evolution of oxygen.
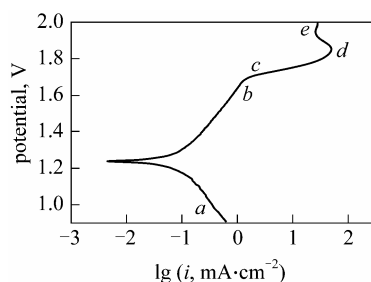

Figure 7   Anodic polarization curve of NiOOH in 35% KOH solution (scan rate: $0.5 \text{mV} \cdot \text{s}^{-1}$)

3.2   Structure characterization of prepared NiOOH

Scanning electron micrographs of samples before and after reaction are presented in Figs.8(a) and 8(b). It is shown that the morphology of NiOOH does not change obviously and keeps the spherical shape with uniform size as the raw material Ni(OH)$_2$. A few
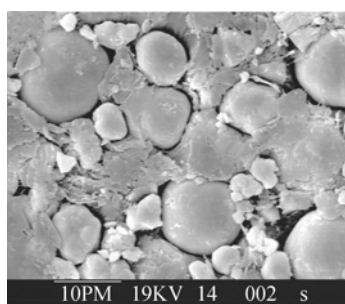
(a) Before reaction, $1^{\#}$ Ni(OH)$_2$
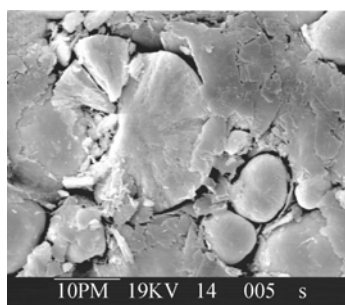
(b) After reaction, NiOOH prepared by electrolyzing $1^{\#}$ Ni(OH)$_2$ in 35% KOH at 30℃ for 360min

Figure 8   Scanning electron micrographs of samples before and after reaction

cracked fragments might be caused by swelling stress coming from oxygen evolution.

Figure 9 is the XRD plot before and after the electrolytic reaction. Referring to the standard XRD JCPDS card (PDF#06-0075), strong diffraction peaks appear at 12.560, 25.379 and 54.659 in respect to 003, 006 and 108 crystal line of NiOOH crystalline, inferring that the resultant is NiOOH. The diffraction peak at 26.540 of carbon is also observed, resulting from the graphite addition for better electrode conductance.
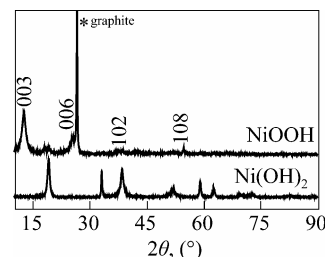

Figure 9   The XRD plots of $1^{\#}$ Ni(OH)$_2$ and NiOOH (prepared by electrolyzing $1^{\#}$Ni(OH)$_2$ in 35% KOH at 30℃ for 360min)

3.3   Electrochemical performances of NiOOH

The electrolysis-generated NiOOH was used to make a cathode and its discharge property was investigated. The discharge curves of NiOOH electrode at 30, 60, 120 and $240 \text{mA} \cdot \text{g}^{-1}$ are shown in Fig.10. Based on the terminal discharge voltage of 1.0V, the NiOOH cathode offers a discharge capacity of $273.7 \text{mAh} \cdot \text{g}^{-1}$ at $30 \text{mA} \cdot \text{g}^{-1}$. As compared with the theoretical discharge capacity ($291 \text{mAh} \cdot \text{g}^{-1}$), the purity of $>93.7\%$ can be estimated. That is close to the analytical result (96.9%) by redox titration. It is also seen that with increasing current density from $30 \text{mA} \cdot \text{g}^{-1}$ to $120 \text{mA} \cdot \text{g}^{-1}$, the discharge capacity decreases from $273.7 \text{mAh} \cdot \text{g}^{-1}$ to $205.8 \text{mAh} \cdot \text{g}^{-1}$, only 75.2% capacity remained.
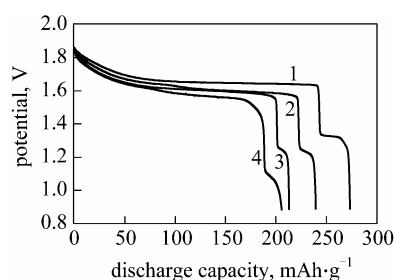
Figure 10   The discharge curves of the electrolyzed NiOOH electrode at 25℃
1—$30 \text{mA} \cdot \text{g}^{-1}$; 2—$60 \text{mA} \cdot \text{g}^{-1}$; 3—$120 \text{mA} \cdot \text{g}^{-1}$; 4—$240 \text{mA} \cdot \text{g}^{-1}$

Figure 11 is the charge/discharge curves of the first 45 cycles at 0.2C of the NiOOH cathode, which was prepared by electrolyzing $2^{\#}$ Ni(OH)$_2$ in 35% KOH at 30℃ for 360min. It shows that the sample has typical charge/discharge platforms and stable cycling capacity. It can be seen that after the first charge, the discharge capacity increases from $250.9 \text{mAh} \cdot \text{g}^{-1}$ (1st) to $273.9 \text{mAh} \cdot \text{g}^{-1}$ (5th) and becomes gradually stabilized. It can also be seen that the increase in discharge
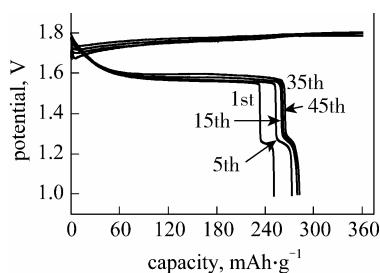
Figure 11   The first 45 cycles of charge/discharge curves of NiOOH cathode (prepared by electrolyzing $2^{\#}$ Ni(OH)$_2$ in 35% KOH at 30℃ for 360min)

capacity is obvious at high voltage of 1.5—1.6V. The capacity increase at high discharge platform is because that the synthesized NiOOH by electrochemical oxidation has superior proton path to decrease ohmic polarization on the one hand and a little NiO$_2$ is formed during the charging process on the other hand, both leading to an increase of discharge capacity. Fig.12 expresses cycling capacity of NiOOH *versus* number of cycles, showing that the discharge capacity increases to a certain extant and tends to be stabilized after 5 cycles. The specific discharge capacity of the material does not decay even after 45 cycles, indicating that the electrolysis-generated NiOOH exhibits good cycling performance.
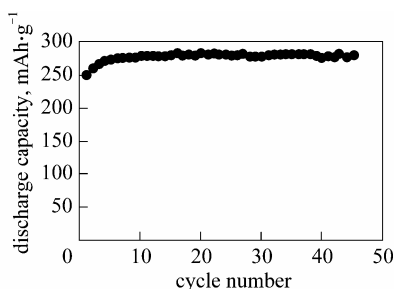

Figure 12   Curves of cycling number *versus* discharge capacity of NiOOH (prepared by electrolyzing $2^{\#}$ Ni(OH)$_2$ in 35% KOH at 30℃ for 360min)

Figure 13 is the cyclic voltammetry curves of the samples before and after electrolysis. For Ni(OH)$_2$ electrode [Fig.13(a)], it is seen that the peak current increases gradually and becomes stable after 3 cycles; the potential difference between anodic (E_aP) and cathodic (E_cP) peaks does not increase too much. That indicates the reversibility of Ni(OH)$_2$ electrode is improved because the electrolysis-generated NiOOH enhances the electrode conductivity as electrolysis goes on. For NiOOH electrode [Fig.13(b)], the peak current neither decreases obviously nor increases. That means the NiOOH is in the active range and there is no need of an activation period which the Ni(OH)$_2$ electrode needs. Besides, the electrode has good stability during the cycling process. Therefore, if the synthesized NiOOH is used as positive electrode material of a Ni/MH battery, the formation process could be negligible. From Fig.13(b), it can also be seen that a strong oxidation peak appears at 1.851V
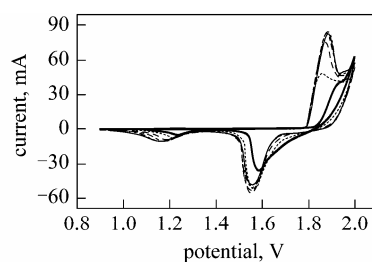
(a) Before reaction, $1^{\#}$ Ni(OH)$_2$
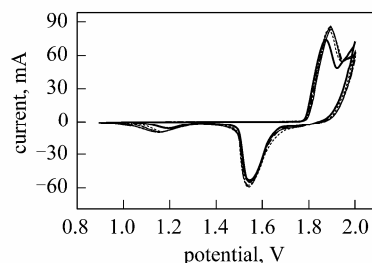
(b) After reaction, NiOOH (counter electrode Ni, reference electrode Zn/ZnO, electrolyte 9 mol·L^{-1} KOH)

Figure 13   The cyclic voltammetry curves of the samples before and after reaction
——1; - - - - - 2; - - - - 3; - - - - - 4; - - - - - 5; —— 6

corresponding to the oxidation of Ni(OH)$_2$. The small peak at 1.91V probably comes from oxygen evolution in side reaction. A strong reduction peak occurs at 1.552V corresponding to the reduction of NiOOH. The minor reduction peak at 1.15V is probably caused by ohmic polarization of Ni(OH)$_2$. The potential difference between anodic (E_aP) and cathodic (E_cP) peaks is 325mV, greater than 59mV, indicating significant polarization during electrolysis, but the areas surrounded by both oxidation and reduction peak profiles are approximately equal. In combination of both aspects, the cycling process of NiOOH is considered a sub-reversible process.

4   CONCLUSIONS

The NiOOH powder with purity of 96% has been prepared by one-step electrolysis of spherical 5.5% Co-Ni(OH)$_2$ in concentrated alkali solution. The optimum conditions are the temperature of 30℃, current density of 60mA·g^{-1}, anodic potential of 1.73—1.85V (*vs.* Zn/ZnO) and electrolysis duration of 360min. The electrolysis-generated NiOOH has high electrochemical activity and provides discharge capacity of over 270mAh·g^{-1} at current density of 30mA·g^{-1}. The cyclic voltammetry test indicates that the cycling process of NiOOH is a sub-reversible process. Our future study will be focused on increasing the reversibility of NiOOH electrode.

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