Influence of Electrolytic Conditions on the Preparation of NiOOH by Catalytic Electrolysis Method

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In this paper, we propose a new method for the preparation of spherical nickle oxyhydroxide (NiOOH) by a clean catalytic electrolysis process of spherical $Ni(OH)_2$ in alkaline solution. The influence of various parameters, such as kinds of catalysts, reaction temperature and electrolysis duration on electrolysis is studied and the catalytic electrolysis mechanism is discussed. The prepared NiOOH sample is characterized by X-ray diffraction, scanning electron microscope observation and electrochemical measurements. The experimental results show that the spherical β-NiOOH powder with high capacity is obtained by electrolysis process under the conditions of a temperature of 30-35 $^{\circ}$C with addition of $KMnO_4$ for 4 h in 6-9 mol L^{-1} NaOH solution. The obtained NiOOH electrodes have superior electrochemical performance than commercial MnO_2 electrodes under different current densities. The NiOOH electrode offers 273.6 mAh g^{-1} specific capacity at 60 mA g^{-1}, which is about 20% higher than that of commercial MnO_2 electrode.

1. INTRODUCTION

With increasing sorts and amounts of the digital code products, the study of high-performance electrode material has been attracted more and more attention [1-8]. NiOOH has been considered as a new cathode material for alkaline batteries because it has high work voltage of 1.6 V, much higher than that of alkaline Zn/MnO_2 batteries (1.2 V). In addition, the discharge capacity of Zn/NiOOH battery is much higher than that of the alkaline manganese batteries under heavy load, especially pulse discharge [9-11]. Recently, NiOOH has also been a research hot due to its good electrocatalytic activity for the oxygen evolution reaction [12-17]. Though $Ni(OH)_2$ can be oxidized into NiOOH by

charge process in MH/Ni batteries, it is not easy to obtain the pure NiOOH by the separation of the mixture of NiOOH, graphite and PTFE. Usually, the high capacity NiOOH is prepared by chemical oxidizing sphere $Ni(OH)_2$ in strong alkali solution [18-22]. However, the chemical oxidization method has shortcomings of consuming much chemical reagents and containing many reaction steps, leading to the high emission of a large amount alkali chemical wastes.

In order to reduce the chemical consumption of the preparation of NiOOH, researchers have paid much attention to electro-synthesis of NiOOH. The electrolytic method can greatly reduce consumption of chemicals except the raw materials of $Ni(OH)_2$ [23-26]. Guo [27] has reported a direct oxidizing reaction of $Ni(OH)_2$ on porous nickel anode suspended in alkaline sodium potassium solution, however, only was 75% of $Ni(OH)_2$ oxidized and its electrochemical performance needs to be improved.

To solve this problem, we have proposed a new catalytic electrolysis method to prepare highly pure NiOOH by adding the $KMnO_4/K_2MnO_4$ couple as electron transport medium during the electrolysis process [28]. In this process, the discharge process of the single point to point contact of $Ni(OH)_2$-electrode surface is transformed to the process of both the single point to point contact and the overall surrounding contact of spherical $Ni(OH)_2$ with the solution through the self-redox reaction of catalyst $KMnO_4$, thus achieving a high electrolysis efficiency. In the present paper, we have systematically studied catalytic electrolysis mechanism and the catalytic electrolysis process of NiOOH, including the influences of various parameters (e.g. kinds of catalysts, reaction temperature, electrolysis duration) on electrolysis. Furthermore, the recycling of the electrolyte and its effects on the electrolysis process is also investigated in this manuscript.

2. EXPERIMENTAL

2.1 The catalysis preparation of NiOOH material

Both anode and cathode were composed of commercial foam Nickel with the thickness of 2.0 mm (Changsha Lyrun new material Co. Ltd.), and the MH/Ni battery separator paper was used as separation membrane (GC-1, Zhejiang Prime Technology Co. Ltd). Various concentrations of NaOH and 0.15 mol L^{-1} eletro-catalyst solution and a certain amount of spherical $Ni(OH)_2$ powder were added to the anode compartment. A certain amount of NaOH solution was added to the cathode chamber. After electrolyzing for a period of time under constant stirring speed of 60 rpm, the black NiOOH suspension was separatedd with a G4 sintered glass filter. Then the precipitate was washed with 30 ml 1% NaOH solution and subsequent deionization water. Finally, the NiOOH sample was obtained by drying in a vacuum oven for 6 h at 60 ^{o}C.

2.2 Structural characterization of the prepared NiOOH material

The morphology of the NiOOH samples was tested by means of scanning electron microscope (SEM) observations with a Cambridge S250MK3 instrument. The X-ray powder diffraction (XRD)

patterns were collected by a Rigaku D/max 2500VB2+/PCX diffractometer with a Cu anticathode (40 kV, 200 mA).

2.3 Electrochemical measurements of the obtained NiOOH samples

The obtained NiOOH sample and expanded graphite were well mixed in the weight ratio of 8:2 in an agate mortar, then 5% (wt.) PTFE latex was added to the mixture followed by grinding for 20 min, and then the prepared paste was rolled on a rolling machine to form NiOOH membrane with thickness of 80 μm. The membrane was cut with the size of 1×1 cm^2 onto a same size Nickel foam as current collector and pressed under 8 MPa to form NiOOH electrodes. The commercial MnO_2 electrode which was used for comparison was fabricated according to the same method. 40% KOH (including 10 g L^{-1} ZnO) was used as an electrolyte, Ni plate (1×1 cm^2) as an auxiliary electrode, and a Zn(Hg)/ZnO as a reference electrode. The charge/discharge test was carried out with a LAND CT2001A cell test system.

3. RESULTS AND DISCUSSION

3.1 Effects of different kinds of catalyst on the synthesis of NiOOH
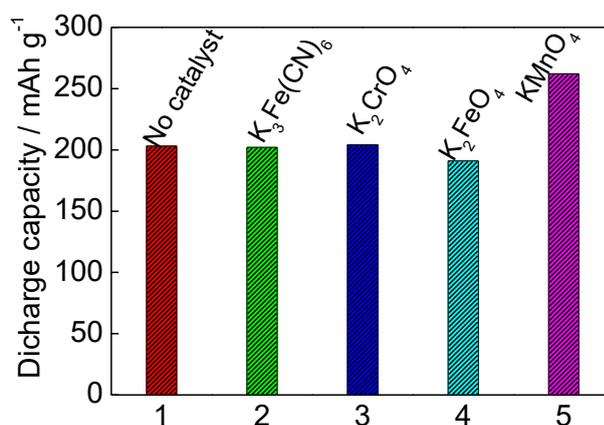
Figure 1. Influence of kinds of catalyst on the electrolysis of $Ni(OH)_2$ (1- no catalyst; 2-addition of $K_3Fe(CN)_6$; 3- addition of K_2CrO_4; 4- addition of K_2FeO_4; 5- addition of $KMnO_4$. Electrolyte: 6 mol L^{-1} NaOH, electrolysis time: 4h, electrolysis temperature: 30 ^{o}C, discharge current density: 120 mA g^{-1})

In order to select the suitable electrolytic catalyst, a series of higher-valence dissoluble transition metal salts with electron-transfer ability were searched. Considering the physical chemistry characteristics, especially dissolubility, stability, flexible valence and the potential of anode, we selected K_2CrO_4, $KMnO_4$, $K_3Fe(CN)_6$ and K_2FeO_4 as the candidates of intermediary agents to transfer electrons during the electrolysis process.

Fig. 1 demonstrates the electrolysis results when the above mentioned transition metal salts are added respectively. The result indicates that K_2CrO_4 and $K_3Fe(CN)_6$ have no facilitation to the catalytic electrolysis of NiOOH. Besides, the capacity of NiOOH produced is slightly decreased when K_2FeO_4 is added, which is probably due to that the decomposition product of K_2FeO_4 is $Fe(OH)_3$ which is hard to be separated from NiOOH, thus the purity of NiOOH is reduced and the discharge capacity is slightly decreased. However, the $KMnO_4$ remarkably facilitates the electro-synthesis of NiOOH. In the same electrolytic condition, the discharge capacity of NiOOH is increased by 28.7% when $KMnO_4$ is added. We therefore presume that MnO_4^- ion realizes the electron-transfer process between the electrolyte and the electrode of the $Ni(OH)_2$.

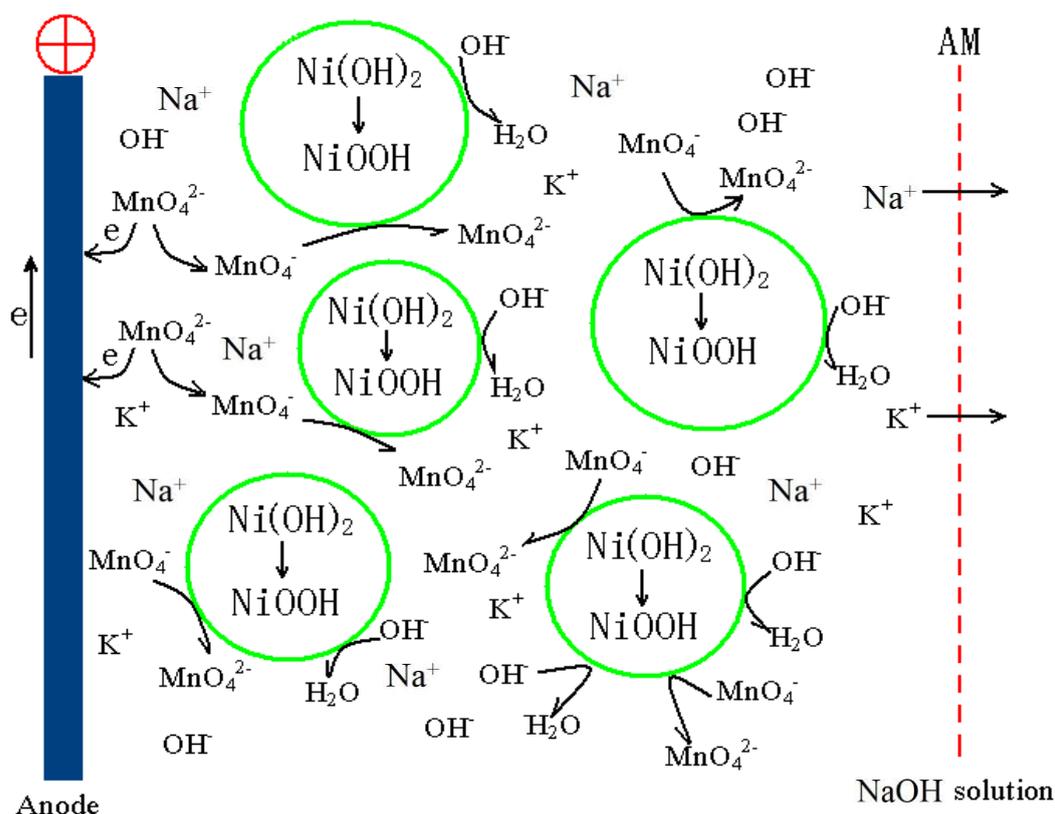*3.2 The principles of preparation of NiOOH by catalytic electrolysis with $KMnO_4$*

Figure 2. Schematic diagram of catalytic electrolysis by MnO_4^- / MnO_4^{2-}

Fig. 2 shows the schematic diagram of catalytic electrolysis. As illustrated in Fig. 2, the MnO_4^- which is dissolved in the electrolyte can oxidize $Ni(OH)_2$ to form NiOOH and is reduced to MnO_4^{2-}. The formed MnO_4^{2-} is oxidized into MnO_4^- again on the anode surface, thus the regeneration of MnO_4^- is implemented. The reaction is illustrated in ref. 27.

It is obvious that through the self-redox reaction of $KMnO_4$, the highly efficient electron-transfer process between the electrolyte and the electrode of the spherical $Ni(OH)_2$ is realized, thus resulting in a high electrolysis efficiency and short electrolysis time. In addition, the volume-

production of NiOOH can be realized by using this catalytic electrolysis method, which is completed through the electron-transfer between the electrolyte and Ni(OH)$_2$ particles instead of between the electrolyte and the solid electrode [23].
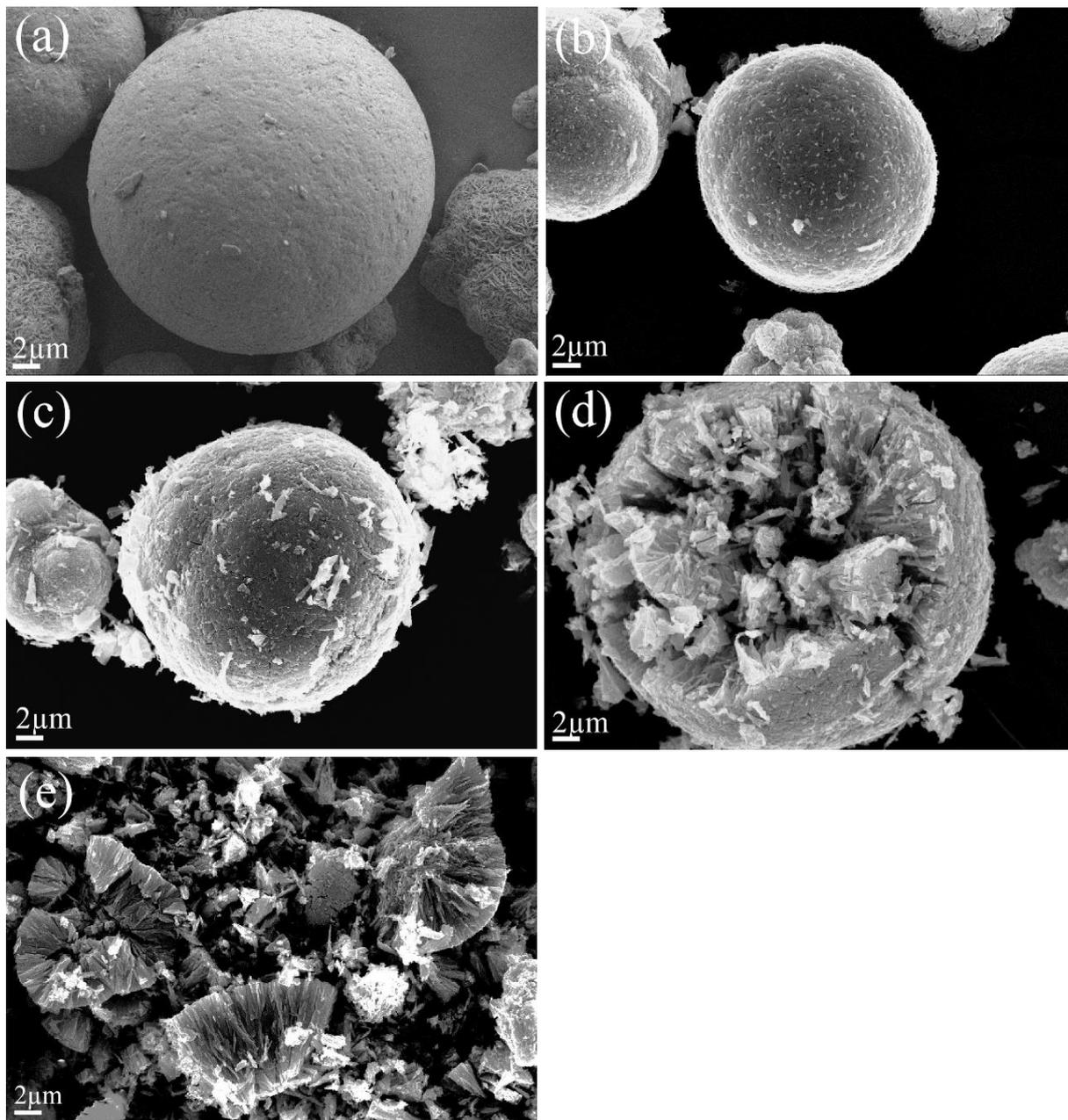
3.3 Effect of electrolysis time on the synthesis of NiOOH
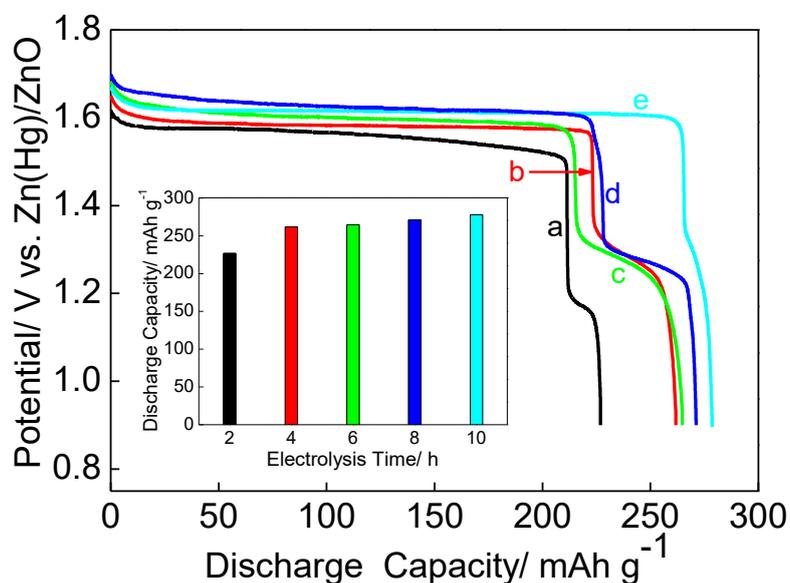
Figure 3. The capacity of NiOOH prepared by electrolyzing for different time (a- 2 h; b- 4 h; c- 6 h; d- 8 h; e-10 h. Electrocatalyst: 0.15 mol L^{-1} KMnO$_4$, electrolyte: 6 mol L^{-1} NaOH, electrolysis temperature: 30 ^{o}C, discharge current density: 120 mA g^{-1})

Fig. 3 shows the influence of electrolysis time on the discharge capacity of NiOOH, and the current density is 120 mA g^{-1}. It can be seen that the discharge capacity rapidly amounts to 225 mAh g^1 within 2 h through the catalysis of KMnO$_4$. As electrolytic time extends to 10 h, the discharge capacity increases to 282 mAh g^{-1}, which is close to the theoretical value of 291mAh g^{-1}. After the electrolysis time exceeds 4 h, the discharge capacity of NiOOH tends towards stability gradually. The phenomenon indicates that through the catalytic function of KMnO$_4$, a high capacity of NiOOH from Ni(OH)$_2$ within a shorter electrolytic time is achieved, thus greatly improving current efficiency.

Fig. 4 is the SEM photo of the NiOOH sample obtained at different electrolysis time. It is obviously seen that when electrolysis time is within 2-4 h, NiOOH basically retains the initial spherical structure and the NiOOH sphere is composed of regular crystal form, but some NiOOH spheres begin to deform when electrolysis time rises to 6 h. When electrolysis time is over 8 h, most spherical NiOOH breaks and dissociates into pieces. Therefore, ideal shapes and crystal forms of NiOOH samples can be obtained by controlling electrolysis time. Considering the results of discharge test and SEM, it can be seen that the ideal electrolysis time is about 4 h.

Figure 4. Scanning electron micrographs of NiOOH by electrolyzing for different time (a-0 h; b-2 h; c-4 h; d-6 h; e-8 h. Electrocatalyst: 0.15 mol L^{-1} KMnO$_4$, electrolyte: 6 mol L^{-1} NaOH, electrolysis temperature: 30 ^{o}C).

3.4 Effect of temperature on the synthesis of NiOOH

Fig. 5 demonstrates the influence of temperature on the electrolysis. As shown in the figure, when temperature is between 10 ^{o}C and 15 ^{o}C, the current efficiency of NiOOH rises with increasing electrolyte temperature and reaches the peak when temperature is within 25-35 ^{o}C. When temperature reaches 35-40 ^{o}C, the current efficiency begins to decline gradually and the decrease becomes fast at above 45 ^{o}C. In consideration of the oxygen bulb appearance in the solution during the electrolysis, the

above phenomenon can be attributed to the competition between the oxidation of $KMnO_4$ and the reduction of electrolyte viscosity. In the range of lower temperature, the rise in temperature reduces the electrolyte viscosity greatly, enabling $KMnO_4$ to function well in the electron-transfer process. When temperature is within 25-35 ^oC, the advantage of viscosity reduction parallels the effect of self-resolving of $KMnO_4$, causing current efficiency to remain stable. While the temperature exceeds 45 ^oC, the merit of viscosity decrease cannot catch up with the effect of self-resolving of $KMnO_4$, leading to current efficiency declining consequently.
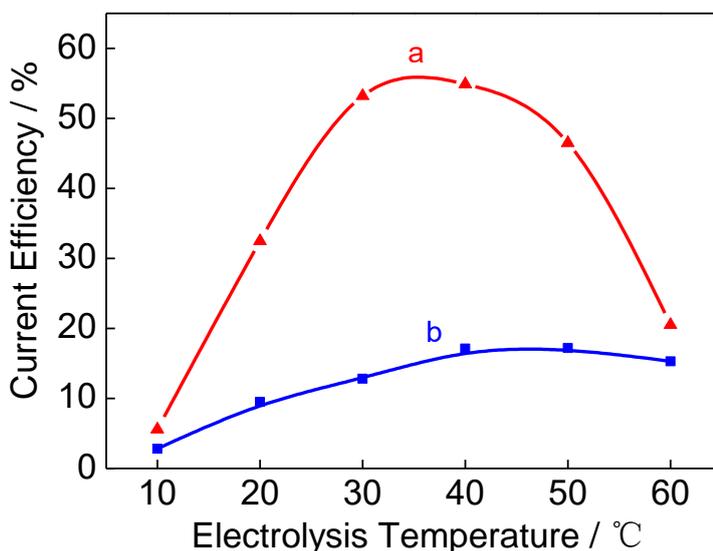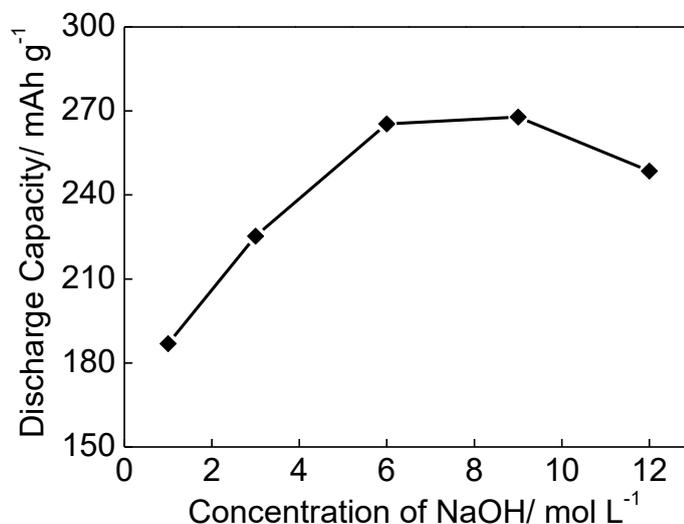

Figure 5. Influence of temperature on current efficiency of electro-synthesis of NiOOH (a- Catalytic electrolysis; b- Electrolysis without catalyst. Electrocatalyst: 0.15 mol L^{-1} $KMnO_4$, electrolyte: 6 mol L^{-1} NaOH, electrolysis time: 4 h)

In addition, Fig. 5 also indicates catalytic electrolysis preparation of NiOOH has a high current efficiency compared to the electrolytic preparation without $KMnO_4$, for which the current efficiency is only about 17%. However, the highest efficiency of catalytic electrolysis preparation with $KMnO_4$ can reach above 55%, indicating the great contribution of $KMnO_4$ during the electrolytic process. Therefore, the optimal temperature for the catalytic electrolysis preparation of NiOOH should be controlled within 30-35 ^oC.

*3.5 Effect of electrolyte compositions on the synthesis of NiOOH*

Fig. 6 shows the influence of different concentration of electrolyte on the discharge capacity of NiOOH prepared by catalytic electrolysis. The discharge current density is 120 mA g^{-1}. In consideration of the low dissolubility of $KMnO_4$ in the KOH solution due to common ion effect, NaOH solution is adopted as the electrolyte with concentrations from 1 mol L^{-1} to 12 mol L^{-1}. The curve indicates that high concentration of NaOH solution is favorable to the formation of NiOOH. The

discharge capacity of NiOOH arrives at the highest in the range of 6-9 mol L^{-1}, but when the concentration exceeds 9 mol L^{-1}, the capacity decreases instead. This is perhaps due to the high electrolyte viscosity caused by extra high concentration of alkaline solution, which is disadvantageous to the transfer and diffusion of the electrons. Therefore, we conclude that 6-9 mol L^{-1} NaOH is favorable to our synthesis process.

Figure 6. Influence of NaOH concentration on electro-synthesis of NiOOH (Electrocatalyst: 0.15 mol L^{-1} KMnO$_4$, electrolysis temperature: 30 ^{o}C, electrolysis time: 4 h, discharge current density: 120 mA g^{-1})

3.6 The recycle of the electrolyte
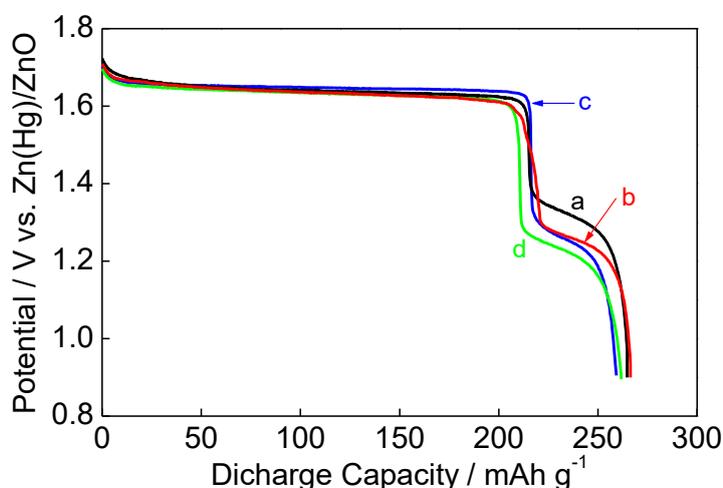
**Figure 7.** The discharge curves of NiOOH prepared in recycled electrolyte (Cycling for different times: a- initial; b-1st time; c- 2nd time; d-3rd time. Electrocatalyst: 0.15 mol L^{-1} KMnO$_4$, electrolyte: 6 mol L^{-1} NaOH, electrolysis temperature: 30 ^{o}C, electrolysis time: 4 h, discharge current density: 120 mA g^{-1})

From the reaction formula of Ni (OH)$_2$ electrolysis, it is obvious that only electric power and Ni(OH)$_2$ are consumed in the NiOOH synthesis process. NaOH electrolyte and KMnO$_4$ play the role of conductance and electrolytic catalyst, respectively, in this process and keep intact after reaction [29]. Therefore, we can conclude that the catalysts and electrolyte can be recycled for the electrolytic production of NiOOH. Fig. 7 shows the discharge curves of the NiOOH sample prepared with the electrolyte recycled for the first three times. It is observed that four discharge curves are very close to each other, indicating that the recycle of electrolyte has no obvious influence on the electrolysis of NiOOH.

The concentration of NaOH and KMnO$_4$ was monitored by the chemical titration analysis process. Through the measurement of electrolyte recycled for three times, it is found that when the concentration of NaOH solution rose from 6 mol L^{-1} to 6.6 mol L^{-1}, the concentration of KMnO$_4$ dropped from the original 0.15 mol L^{-1} to 0.14 mol L^{-1}. The inference can be explained thus: the increase in concentration of NaOH during recycling electrolyte process is partly due to the volatilization of water under 35 ^{o}C, and partly attributed to the side-reaction of water dissociation. On the other hand, the slight reduction of KMnO$_4$ concentration probably comes from the washing process of the products. Therefore, it is necessary to supplement proper amount of water and KMnO$_4$ in accordance with the quantity of NaOH and KMnO$_4$ in the solution to resume the compositions of the original electrolyte.

3.7 The XRD characterization of the prepared NiOOH sample
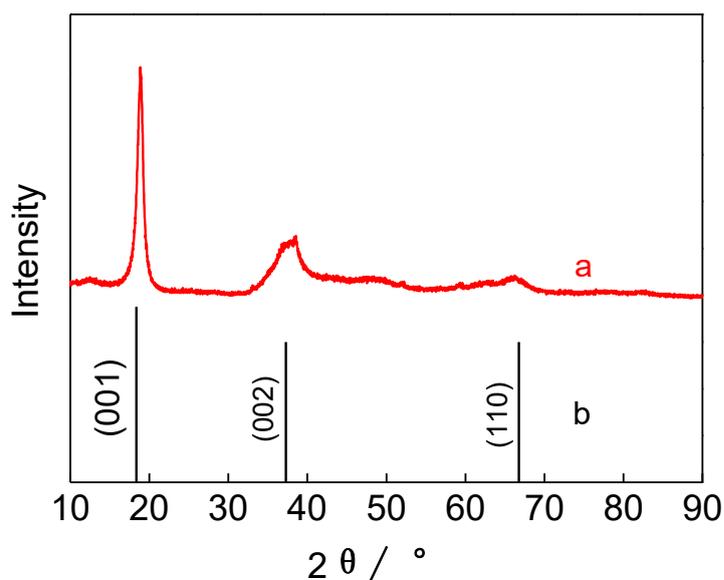
Figure 8. The XRD plots of the samples (a-the electro-synthesized NiOOH sample; b- the JCPDS card of β-NiOOH. Electrocatalyst: 0.15 mol L^{-1} KMnO$_4$, electrolyte: 6 mol L^{-1} NaOH, electrolysis temperature: 30 ^{o}C, electrolysis time: 4 h)

Fig. 8 is the XRD plots of the NiOOH sample prepared by catalytic electrolysis for 4 h. It is obviously seen that the diffraction peak appears at 2θ =18.1$^{°}$, 37.4$^{°}$ and 66.6$^{°}$ respectively. Referring to

the Joint Committee of Powder Diffraction Standard (JCPDS) card (PDF#06-0141), the three diffraction peaks correspond to (001), (002) and (110) crystal lines of β-NiOOH, respectively, indicating the product is pure β-NiOOH.

3.8 Electrochemical performance of NiOOH samples
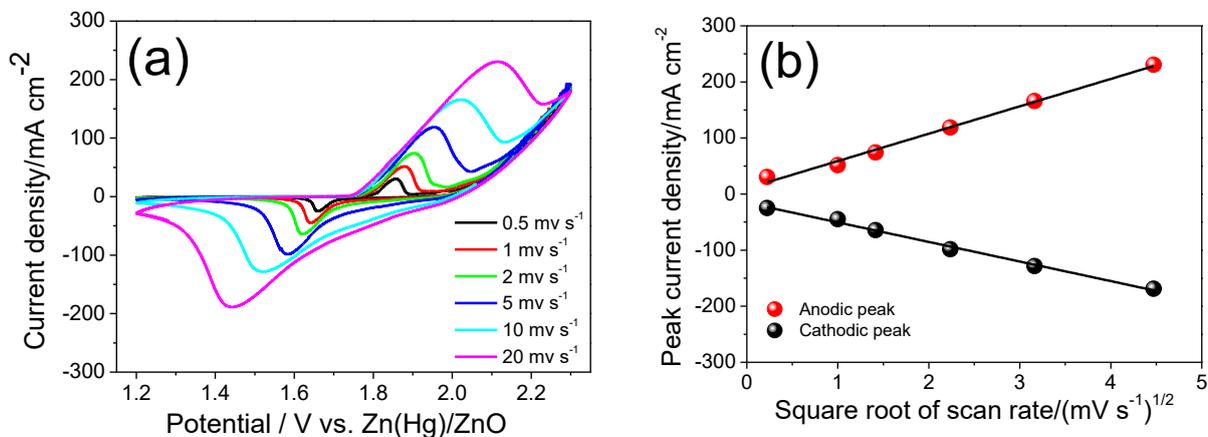
Figure 9. a-CV curves of the prepared NiOOH electrode at different scan rates from 0.5 to 20 mV s^{-1} in 6.0 mol L^{-1} KOH electrolyte at room temperature; b-the relationship between peak current and the square root of scan rate (Electrocatalyst: 0.15 mol L^{-1} KMnO$_4$, electrolyte: 6 mol L^{-1} NaOH, electrolysis temperature: 30 $^{\circ}$C, electrolysis time: 4 h)
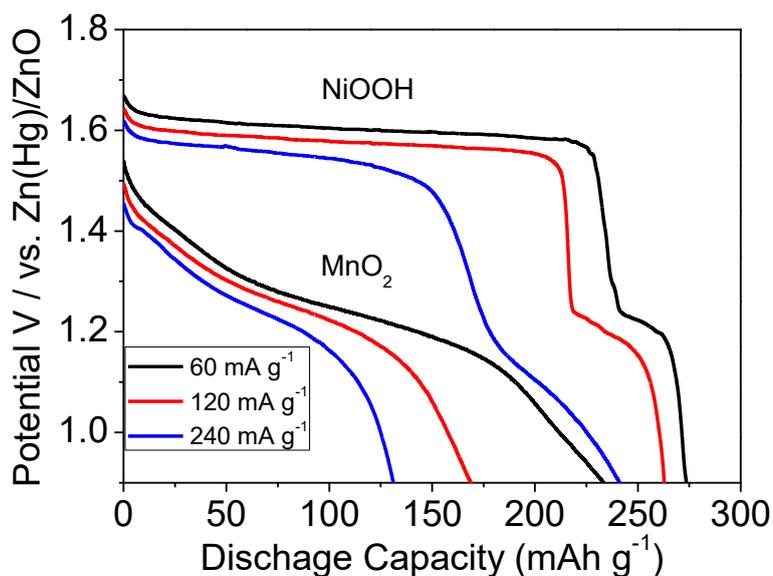
Figure 10. Discharge curves of the obtained NiOOH and commercial MnO$_2$ under different current densities (Electrocatalyst: 0.15 mol L^{-1} KMnO$_4$, electrolyte: 6 mol L^{-1} NaOH, electrolysis temperature: 30 $^{\circ}$C, electrolysis time: 4 h)

Fig. 9a shows the CV curves of the prepared NiOOH electrode at different scan rates from 0.5 to 20 mV s^{-1}. As shown in the figure, the redox peak current increases with the increase of scanning speed. It can also be seen that with increasing the scan rate, the oxidation peak shifts positively, the reduction peak shifts negatively and the potential difference becomes larger, indicating that the reaction on the NiOOH electrode surface is a quasi-reversible reaction [30,31]. Figure 9b displays that the peak current (*i*) and the square root of the scan rate (v1/2) show a good linear relationship, which indicates that the chemical reaction mechanism of NiOOH electrode is diffusion control.

Fig. 10 shows discharge curves of the obtained NiOOH and commercial MnO_2 under different current densities (60, 120 and 240 mA g^{-1}). It can be seen that the obtained NiOOH electrode has better electrochemical performance than commercial MnO_2 electrode. As compared with commercial MnO_2 electrode, the NiOOH electrode has typical discharge platforms. The discharge capacity of NiOOH electrode is much higher than that of MnO_2 electrode at each current density. For example, at 60 mA g^1, the NiOOH electrode offers specific capacity of 273.6 mAh g^{-1}, which is about 20% higher than that of commercial MnO_2 electrode. At high current density of 240 mA g^{-1}, the discharge capacity of NiOOH electrode is 240.7 mAh g^{-1}, which is about twice higher than that of MnO_2 electrode. In addition, the average discharge voltage of NiOOH electrode is about 1.6 V, which is 0.3 V higher than that of commercial MnO_2. However, the discharge capacity and discharge voltage of both NiOOH and commercial MnO_2 electrodes decrease with increasing the current densities. The reason is might be that increasing current density will lead to the increase in polarization of the electrodes.

Table 1. Comparison between the properties of our work and the previously reported methods

Preparation Methods	Consumed raw material	Atomic economy	Temperature	electrolyzer voltage /V	Capacity/ mAh g^{-1}	Ref.
Catalytic Electrolysis	$Ni(OH)_2$	100 %	30~35 ^{o}C	1.9	273.6 at 60 mA g^{-1}	This work
Chemical oxidation	$KOH+K_2S_2O_8+Ni(OH)_2$	28.6%	60 ^{o}C	No	110 at 100 mA g^{-1}	Ref. 9
Chemical oxidation	$Ni(OH)_2+Cl_2+NaOH$	61.5%	20 ^{o}C	No	267 at 60 mA g^{-1}	Ref. 10
Chemical oxidation	$KOH+K_2S_2O_8+Ni(OH)_2$	28.6%	60 ^{o}C	No	269.7 at 30 mA g^{-1}	Ref. 11
Chemical oxidation	$KOH+K_2S_2O_8+Ni(OH)_2$	28.6%	60 ^{o}C	No	257.5 at 30 mA g^{-1}	Ref. 19
Electrolysis	Graphite $+Ni(OH)_2+KOH$	100 %	30 ^{o}C	1.85	270 at 30 mA g^{-1}	Ref. 23
Direct electrolysis method	β-$Ni(OH)_2+KCl+NaOH$	Not present	10-40 ^{o}C	10	256.5 at 60 mA g^{-1}	Ref. 25

Recently, several papers all from prestigious journals have reported the electrolysis preparation of NiOOH and its electrochemical properties. The electrochemical properties of these materials and the as-prepared NiOOH in this study are compared in Table 1. Table 1 is the comparison between the properties of the previously reported methods [9-11, 19, 23, 25] and our work. It can be seen from Table 1 that the prepared NiOOH sample has excellent electrochemical activities, providing the discharge capacity of 275 mAh g^{-1} at 60 mA g^{-1}. Furthermore, the electrolysis method has high atomic utilization (100%) and low energy consumption in our work.

4. CONCLUSIONS

The high purity NiOOH powders with high specific capacity have been synthesized by catalytic electrolysis of spherical $Ni(OH)_2$ in concentrated alkaline solution. By adding the catalyst ($KMnO_4$) as the medium of electron transfer, the discharge process of the single point to point contact is transformed to the process of both the point to point contact and the overall surrounding contact of spherical $Ni(OH)_2$, which greatly improves the current efficiency. Experimental results indicate that the optimum electrolytic conditions are temperature of 30-35 ^{o}C, solution of 6-9 mol L^{-1} NaOH plus $KMnO_4$ and electrolysis time of 4 h. The FSEM and XRD results show that spherical β-NiOOH can be obtained by catalytic electrolysis for 4 h. The obtained NiOOH electrode shows better electrochemical performance than commercial MnO_2 electrode.

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