NRC Publications Archive Archives des publications du CNRC

Effects of different Ni(OH)₂ precursors on the structure and electrochemical properties of NiOOH

Shangguan, Enbo; Tang, Hongwei; Chang, Zhaorong; Yuan, Xiao-Zi; Wang, Haijiang

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:

<https://doi.org/10.1016/j.ijhydene.2011.02.132>

International Journal of Hydrogen Energy, 36, 16, pp. 10057-10064, 2011-06-12

NRC Publications Record / Notice d'Archives des publications de CNRC:

<https://nrc-publications.canada.ca/eng/view/object/?id=93dfa755-1186-4e16-b11a-624484c0c603>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=93dfa755-1186-4e16-b11a-624484c0c603>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

Available at www.sciencedirect.com journal homepage: www.elsevier.com/locate/he

Effects of different Ni(OH)₂ precursors on the structure and electrochemical properties of NiOOH

Enbo Shangguan^a, Hongwei Tang^a, Zhaorong Chang^{a,b,*}, Xiao-Zi Yuan^b, Haijiang Wang^b

^a College of Chemistry and Environmental Science, Henan Normal University, Xinxiang 453007, PR China

^b Institute for Fuel Cell Innovation, National Research Council of Canada, Vancouver, BC, Canada V6T 1W5

ARTICLE INFO

Article history:

Received 2 February 2011

Received in revised form

22 February 2011

Accepted 25 February 2011

Available online 12 June 2011

Keywords:

Nickel oxyhydroxide

High tap-density

Zn–NiOOH batteries

Cathode materials

ABSTRACT

Nickel oxyhydroxide (NiOOH), an active material for alkaline Zn–NiOOH batteries, was synthesized by electrolysis oxidation of different Ni(OH)₂ precursors, which were prepared by three methods: polyacrylamide (PAM) assisted two-step drying (PTSD), conventional coprecipitation (CCP), and “controlled crystallization” (CC). The NiOOH samples were characterized and tested using X-ray diffraction (XRD), infrared spectroscopy (IR), scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) testing, laser particle size analysis, tap-density testing, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and a discharge test. The results demonstrate that the physical and electrochemical properties of NiOOH are strongly dependent on the properties of the Ni(OH)₂ precursor, such as its morphology, microstructure, tap density, and specific surface area. The results of the electrochemical studies also show that the sample prepared by the PTSD method is superior to the others in electrochemical performance. The as-prepared, high-density, non-spherical NiOOH is a promising active material for the positive electrode in Zn–NiOOH batteries.

Copyright © 2011, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

1. Introduction

As the types and amounts of digital products have increased in recent years, a new type of alkaline Zn–NiOOH battery containing NiOOH as the positive electrode material has attracted worldwide research interest because of its high practical specific energy, excellent specific power, high working voltage, and low toxicity [1–3]. β -NiOOH, which is well-known to be the oxidized or charged state of β -Ni(OH)₂, offers a high discharging voltage platform (1.6 V) and a specific capacity several times higher than alkaline manganese batteries at high current density [4–6]. In addition, β -NiOOH

doped in the positive electrode of Ni–MH batteries not only can successfully regulate the discharge reservoir of the negative electrodes to an adequate extent, but also can effectively improve the batteries' electrochemical performance [7–9]. Thus, there is substantial scientific and technological interest in the study of NiOOH synthesis due to its extensive application in the positive electrodes of alkaline batteries. It is now also becoming a promising digital battery material and has drawn considerable interest in that area [9–12].

Conventionally, owing to its high tap density and excellent electrochemical performance, β -NiOOH is synthesized by the

* Corresponding author. College of Chemistry and Environmental Science, Henan Normal University, Xinxiang 453007, PR China. Tel.: +86 373 3326335; fax: +86 373 3326336.

E-mail address: czr_56@163.com (Z. Chang).

0360-3199/\$ – see front matter Copyright © 2011, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved. doi:10.1016/j.ijhydene.2011.02.132

chemical oxidation of spherical β -Ni(OH)₂ precursor using hypochlorite salt or potassium persulfate as an oxidant in a strong alkali solution [12–15]. However, this chemical oxidation method contains many reaction steps, consumes a great deal of reagent, and generates large amounts of waste effluents. To avoid such problems, two electrolysis oxidation methods have been proposed [16,17]. The target materials have been successfully synthesized by both methods and exhibited better electrochemical characteristics. However, the products prepared by these electrolysis methods are inconvenient to filtrate and launder due to the use of a strong alkali solution.

To solve these problems we recently employed a novel electrolysis method to prepare high-purity β -NiOOH powders by oxidizing spherical β -Ni(OH)₂ in a dilute alkaline solution [18]. The new method has greater electrolytic efficiency and is environmentally friendly, simple, and economical for industrial manufacturing. Moreover, the obtained spherical β -NiOOH sample not only exhibits excellent electrochemical activity but also has a high tap density. Nevertheless, although the spherical precursor can be used to obtain higher pile density and superior electrode performance, the preparation procedures for these spherical powders are complex and rather time consuming, product quality is not easily guaranteed, and the production costs are high. Therefore, a simpler and more economical method of synthesizing Ni(OH)₂ precursor is required.

In a previous study we succeeded in synthesizing high-density non-spherical β -Ni(OH)₂ as a cathode material for Ni–MH batteries using a simple polyacrylamide (PAM) assisted two-step drying (PTSD) method [19]. The procedures are much simpler than those for spherical powders, are more economical because there is no hydroxide-forming step, and are more environmentally friendly because no ammonium is involved. However, to the best of our knowledge non-spherical β -NiOOH has attracted little attention as a raw material for the positive electrode in alkaline Zn–NiOOH batteries because non-spherical powders always show a lower tap density, which results in a low volumetric specific capacity, thus seriously limiting the energy density of Zn–NiOOH batteries. Few reports exist on the synthesis and characterization of high-density non-spherical NiOOH. Hence, the objective of the present work is to use non-spherical β -Ni(OH)₂ as a precursor to prepare high-density NiOOH, compare this with NiOOH prepared using a spherical precursor, and thereby explore the effect of different precursors on the microstructure and electrochemical properties of the resulting NiOOH.

In the present study, following upon our previous work [18,19], we report the synthesis of NiOOH cathode materials using electrolysis oxidation of different Ni(OH)₂ precursors, which are prepared by three methods: PAM-assisted two-step drying (PTSD), conventional co-precipitation (CCP), and “controlled crystallization” (CC). The physical and electrochemical properties of the prepared NiOOH are investigated with X-ray diffraction (XRD), infrared spectroscopy (IR), scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) testing, laser particle size analysis, tap-density testing, and electrochemical techniques. The effects of different precursors on the microstructure and electrochemical properties of NiOOH are discussed in detail.

2. Experimental

2.1. Preparation of precursors and NiOOH powders

The β -Ni(OH)₂ precursors and β -NiOOH samples obtained are denoted as follows—sample A: PTSD method, sample B: CCP method, and sample C: CC method.

Synthesis of non-spherical precursor (A) using the PTSD method was carried out as described previously [19]. Stoichiometric amounts of NiSO₄·6H₂O, CoSO₄·7H₂O, and ZnSO₄·7H₂O (molar ratio of Ni:Co:Zn, 100:2.5:5) were dissolved in distilled water to create a concentration of 1.7 mol l^{−1}. The aqueous solution was precipitated by adding a NaOH solution of 4 mol l^{−1} with continuous stirring at 50 °C. The co-precipitation mixtures were stirred continuously after the reaction ceased, then coagulated by adding PAM (10 ml PAM (0.6%) per 200 ml solution), filtrated (under 20 MPa pressure), dried (at 120 °C for 2 h), ground, washed, and dried again (at 120 °C for 2 h) to obtain precursor (A).

Non-spherical precursor (B) was synthesized by the CCP method. The starting materials and proportions were the same as used in the PTSD method. The aqueous solution was precipitated by adding a NaOH solution of 4 mol l^{−1} with continuous stirring at 50 °C. The co-precipitation mixtures were stirred continuously after the reaction ceased, then filtrated, washed, and dried at 120 °C for 2 h in a vacuum drying oven to obtain precursor (B).

The spherical precursor (C) was synthesized by the CC method. The starting materials and proportions were also the same as used in the above methods. The aqueous solution was precipitated by adding a NaOH solution (aq.) of 5 mol l^{−1} and a certain amount of NH₄OH solution (aq.), stirring continuously. The solution was maintained at 50 °C for 30 h and the pH value was controlled at approximately 11.5–12. The desired spherical precursor was then obtained after filtering, washing, and drying at 120 °C for 2 h.

Synthesis of the β -NiOOH samples was conducted using the new electrolysis method described previously [18].

2.2. Characterization

Characterization of the crystalline structure of the obtained powders was performed using an X-ray diffractometer (D8 X) with Cu K α radiation, utilizing a working voltage of 40 kV, a working current of 40 mA, a scanning speed of 0.026° s^{−1}, and a step time of 3 s. The scanning range was 15–70°. The sample morphologies were observed using a scanning electron microscope (SEM-6701F, JEOL, Japan), and the Fourier transform infrared (FTIR) spectra of the prepared samples were recorded by a Fourier infrared spectrometer (FIRS; Bio-Rad FTS-40, USA) using the KBr pellet method. To determine the tap density of the sample, a JZ-1 tap-density tester (Chendu Powder Test Equipment Co. Ltd., China) was used. The measurement error was less than 1%. The purity of the produced NiOOH was determined by iodometry and ethylenediamine tetraacetic acid (EDTA) complexometric titration. The specific surface area was evaluated by the BET nitrogen adsorption method using a 3H-2000 surface area analyzer (China). The particle size distribution of the powder samples

Table 1 – Physical properties of Ni(OH)₂ precursors and NiOOH samples A–C prepared by different methods.

Sample	BET surface area/m ² g ^{−1}		Mean diameter/μm		Tap density/g cm ^{−3}	
	Precursor	NiOOH	Precursor	NiOOH	Precursor	NiOOH
A (non-spherical)	75.52	78.65	27.82	27.22	2.31	2.65
B (non-spherical)	103.02	108.10	21.03	20.58	1.65	1.93
C (spherical)	10.21	11.12	9.41	9.26	2.20	2.44

was obtained using an OMEC LS-POP(III) particle size analyzer (China).

2.3. Preparation of nickel electrode and measurements

The nickel electrode was prepared by mixing the prepared powder with 10 wt.% nickel powder, 5 wt.% cobalt powder, and 5 wt.% PTFE binder in relation to the total electrode mass. The mixture was then pressed into nickel foam (2 cm × 2 cm), which served as a current collector. Subsequently, the pasted electrode was dried in a 60 °C vacuum environment and pressed to a thickness of 0.5 mm.

The electrochemical properties of the nickel electrodes were performed in a three-compartment electrolysis cell at ambient temperature using a Solartron SI 1260 impedance analyzer with a 1287 potentiostat interface. Solution of 6 M KOH was used as the electrolyte, a pure nickel plate as counter electrode and an Hg/HgO (6 M KOH) as reference electrode. Cyclic voltammetry (CV) measurements were carried out between 0 V and 0.8 V (vs. Hg/HgO). The EIS experiments were performed with a superimposed 5 mV sinusoidal voltage in the frequency range of 10 kHz–1 mHz. The EIS obtained experimentally were analyzed based on the CNLS method of Boukamp using Zview 2 software (Scribner Associates).

Discharge measurements were conducted using a Land CT2001A battery performance testing instrument (Wuhan Jinnuo Electronics Co. Ltd., China). Test cells were assembled using the prepared nickel oxyhydroxide electrode as the

cathode, a Zn negative electrode as the anode, and polypropylene to separate the cathode and anode. The Zn electrode was used with a capacity far in excess of the NiOOH positive electrode, and 9 M KOH solution was used as the electrolyte. The batteries were separately discharged at respective current rates of 0.2, 0.4, 1, and 2 C. The cut-off voltage was 1.3 V.

3. Results and discussion

3.1. Characterization of the as-synthesized samples

3.1.1. Physical properties

The physical properties of the precursors and NiOOH samples A–C prepared by different methods are listed in Table 1. As shown there, the tap density of NiOOH is highest for A (2.65 g cm^{−3}), whereas for B it is 1.93 g cm^{−3} and for C 2.44 g cm^{−3}. The mean diameters of samples A, B, and C are 27.22, 20.58, and 9.26 μm, and the BET surface areas are 78.65, 108.10, and 11.12 m² g^{−1}. It is also clear that all these NiOOH samples possess smaller mean diameter, larger surface area, and higher tap density in comparison with the as-prepared precursors, which indicates that although electrolysis synthesis of NiOOH is only a process of losing protons and electrons [16,18], the physical properties of the resulting NiOOH are greatly affected by the precursor.

It is notable that the tap density of the synthesized NiOOH samples is significantly higher than that of the precursors, which may be attributable to the particle volume's contraction from 39.0 Å³, β-Ni(OH)₂ (JCPDS 14-0117), to 33.1 Å³, β-NiOOH

Fig. 1 – X-ray diffraction patterns of Ni(OH)₂ precursors and NiOOH samples: (a) PTSD, (b) CCP, (c) CC.

Fig. 2 – IR spectra of NiOOH samples a, b, and c.

Fig. 3 – SEM images of NiOOH samples a, b, and c.

(JCPDS 6-0141) during the oxidation process [13,18]. Moreover, the tap density of the NiOOH powders is directly related to that of the hydroxide precursors (Table 1). The higher the tap density of the precursor, the higher the tap density of the NiOOH powder.

In addition, the specific surface area of the non-spherical powders is seven times larger than that of the spherical samples, which is attributable to the irregular particle shape [19]. Higher specific surface area can provide high active site density and thereby promote intimate interactions between the active material and the surrounding electrolyte.

Fig. 4 – Discharge curves of electrodes prepared with NiOOH samples a, b, and c at different current rates.

3.1.2. XRD

The XRD patterns of the Ni(OH)₂ precursors and NiOOH samples a–c are presented in Fig. 1. For Ni(OH)₂ precursors a–c, the characteristic diffraction peaks at (0 0 1), (1 0 0), (1 0 1), (1 0 2), (1 1 0), and (1 1 1) show that all these precursors exhibit XRD characteristics of the β-Ni(OH)₂ phase with a brucite-type structure, but the widths of the peaks are different. For NiOOH samples a–c, reference to the Joint Committee on Powder Diffraction Standards (JCPDS 6-0141) indicates that the diffraction peaks at 19° and 37° are the typical characteristic

Table 2 – Results of discharge test for different electrodes at different current rates.

Electrode	Specific capacity/mAh g ⁻¹				Specific volume capacity/mAh cm ⁻³			
	0.2 °C	0.4 °C	1 °C	2 °C	0.2 °C	0.4 °C	1 °C	2 °C
A (non-spherical)	260.5	247.6	232.1	222.9	690.3	656.1	615.1	590.7
B (non-spherical)	216.7	195.3	179.3	160.7	418.2	376.9	346.0	310.2
C (spherical)	252.3	235.7	215.6	208.5	615.6	575.1	526.1	508.7

diffraction peaks of NiOOH, which correspond to the (0 0 1) and (0 0 2) crystal faces of NiOOH [19], indicating that all these samples are β -NiOOH and there is no other phase peak, but the widths of the peaks differ.

As previously shown [13,14,18], when spherical β -NiOOH is synthesized, increasing oxidation time leads to gradual subsidence of the Ni(OH)₂ diffraction peak. It was also reported [14] that a change in the Ni(OH)₂ characteristic peak at (0 0 1) can be regarded as indicating the synthesis of spherical NiOOH. As is evident in Fig. 1, this conclusion is also applicable for the synthesis of non-spherical NiOOH.

It is obvious that the peak width for a NiOOH powder is directly related to that of its hydroxide precursor. The broader the width of the Ni(OH)₂ precursor peak, the broader the width of the NiOOH powder peak. Generally, the broadening of peaks (0 0 1) and (1 0 1) in Ni(OH)₂ XRD patterns has often been correlated with the electrochemical activity of the Ni(OH)₂ product [19–22]. The broader the width of the peaks, the more active the electrochemical reaction [20,21]. Structural disorder plays a very important role in explaining this broadening. The full width at half maximum values of the (1 0 1) diffraction lines of precursors A, B, and C are 1.055, 1.604 and 0.791, respectively, which indicates that all these precursors possess a different density of structural disorder. Structural disorder in Ni(OH)₂ can provide a better path for the diffusion of protons within the NiO layers and can help lower the free energy by increasing the entropy contribution, which can in turn increase the electrochemical reaction rate [23]. Therefore, it can be concluded that such significant differences in the width of peaks (0 0 1) and (0 0 2) for these NiOOH powders can be explained by the different structural disorder resulting from the three types of precursors, which should significantly affect the electrochemical activity of the final compound.

3.1.3. IR spectra

Fig. 2 presents the infrared spectra of the as-prepared samples a–c. Obviously, all three samples display similar characteristics. The strong, sharp band centered at 567 cm⁻¹ corresponds to the motion of hydrogen-bonded linkages Ni–O–H and to Ni³⁺–O stretching vibrations, which constitute the typical IR spectra of nickel oxyhydroxide [24,25]. The absence of a band at 3640 cm⁻¹ indicates that few OH groups were present [26]. The broad band at 3450 cm⁻¹ is characteristic of the stretching vibration of the hydroxyl group extensively hydrogen bonded to water molecules, and the band at 1650 cm⁻¹ corresponds to the bending vibration of water molecules, which indicates the presence of a certain amount of water molecules adsorbed on the NiOOH [27]. The low band at about 1380 cm⁻¹ in the IR spectra can be assigned to interference from the vibration of carbonate ions [28] due to the open system used for synthesis. Notably, the typical IR spectra characteristic of PAM are not

found in the IR spectra of sample A (PTSD), indicating that PAM has been removed in the washing and drying process and does not affect the quality of the products.

3.1.4. SEM

Fig. 3 displays SEM photographs of samples a–c obtained with different precursors.

Previous studies have shown that the integral structure and morphology of spherical NiOOH generally remain unchanged in comparison with its spherical precursors [13,14]. In the case of sample C, it is obvious that the prepared NiOOH retains a comparatively intact spherical structure. In contrast to non-spherical particles studied previously [19], the obtained non-spherical NiOOH samples retain a non-spherical morphology similar to their precursors'. This result is attributable to the fact that the synthesis of NiOOH essentially occurs via the transfer of protons and loss of electrons from layered Ni(OH)₂. Samples A and B both appear to be aggregates of irregular tabular shapes, which leads to a higher specific surface area, as already shown above (see Table 1). Thus, it is anticipated that a higher specific surface area can effectively enhance the electrochemical performance of non-spherical NiOOH.

3.2. Electrochemical investigation of β -NiOOH

3.2.1. Discharge tests of nickel electrodes

Fig. 4 shows the discharge curves of nickel electrodes a–c at rates of 0.2, 0.4, 1, and 2 C. The experimental results are given in Table 2. It can be seen that the specific discharge capacity of sample A (PTSD) is higher than that of sample B (CCP) or C (CC). It is especially notable that at a rate of 0.2 C, sample A

Fig. 5 – Cyclic voltammograms of NiOOH samples a, b, and c at various scan rates.

Table 3 – Parameters from CV and EIS measurements for different NiOOH electrodes.

Sample	E_a/mV	E_c/mV	$\Delta E_{a-c}/\text{mV}$	$R_c/\Omega\text{cm}^2$	$W/\Omega\text{cm}^2$	CPE/Fcm^2
A (non-spherical)	261	472	211	0.1472	0.4923	0.002738
B (non-spherical)	243	567	324	0.2415	0.5872	0.002506
C (spherical)	246	512	266	0.4015	0.7120	0.002235

(non-spherical) shows a discharge capacity of 260.5 mAh g^{-1} and a volume capacity of $690.3 \text{ mAh cm}^{-3}$, which are higher than the 252.3 mAh g^{-1} and $615.6 \text{ mAh cm}^{-3}$ for sample C (spherical). Moreover, at a 2 C rate, sample A shows a higher discharge capacity of 222.9 mAh g^{-1} , whereas the values for samples B and C are 160.7 mAh g^{-1} and $208.5 \text{ mAh cm}^{-3}$, respectively, indicating that sample A exhibits much better high-rate performance. All the results suggest that sample A demonstrates excellent electrochemical performance. This is attributable to the more compact structure, high structural disorder density, and high specific surface area of the precursor synthesized by the PTSD method, as discussed in [19], which may result in better reaction reversibility and lower electrochemical impedance, leading to lower polarization and higher discharge capacitance. The results clearly show that the electrochemical performance of NiOOH prepared by electrolysis oxidation is directly related to the electrochemical activity of the precursor. To further confirm the effect of different precursors on the electrochemical performance of NiOOH electrodes, the electrochemical performance of all three electrodes was investigated using CV and EIS.

3.2.2. Cyclic voltammetry

Fig. 5 presents typical CV curves for samples a–c at a scan rate of 1 mV s^{-1} and 25°C . The features of the voltammograms are summarized in Table 3. Clearly, all the voltammograms present similar trends; a unique couple of anodic (oxidation) and cathodic (reduction) peaks are evident for each electrode. E_a and E_c symbolize the potential of the anodic and cathodic peaks, respectively. $\Delta E_{a,c}$ defined as the potential difference between the anodic and cathodic peaks, is an estimate of the reversibility of the redox reaction, which is an important parameter for estimating the electrochemical properties of the electrodes [23,29,30]. The smaller the $\Delta E_{a,c}$, the more reversible the electrochemical reaction and the better the proton diffusion efficiency [23]. The results in Table 3 show that the redox reactions are quasi-reversible for all these NiOOH electrodes, as indicated by the relatively large $\Delta E_{a,c}$. Furthermore, it can be seen that the $\Delta E_{a,c}$ of electrode A is only 211 mV, which is much smaller than the values for electrodes B and C, indicating better reversibility of the electrochemical redox reaction for the non-spherical particles obtained using precursor A (PTSD).

3.2.3. Electrochemical impedance spectroscopy (EIS)

The results of electrochemical impedance spectroscopy measurements are shown in Fig. 6. All display a depressed semicircle resulting from charge transfer resistance in the high-frequency region, and a slope related to Warburg impedance in the low-frequency region [31,32]. Simplified equivalent circuit models (inset in Fig. 6) have been constructed to analyze the impedance spectra. In the models, R_s is the ohmic resistance of the alkali electrolyte, CPE is the

constant phase element related to the double layer capacity, R_c is the charge-transfer resistance, and W is the Warburg impedance (Z_w). The EIS fitting results according to the equivalent circuit are listed in Table 3. A smaller charge-transfer resistance means that the electrochemical reaction at the nickel electrode occurs more easily, which results in a decrease in the electrochemical polarization of the electrode and an increase in the utilization of the active material. Evidently, the charge transfer resistance of electrode A is the smallest, which implies that the electrochemical reaction on electrode A proceeds more easily than on electrodes B and C. Electrode C with its spherical particles displays the highest charge transfer resistance, meaning that the electrochemical reaction on this electrode proceeds less effectively. In addition, the CPE values of the non-spherical particles are larger than those of the spherical particles, which may be because the as-prepared non-spherical product has a larger effective active surface area for the electrochemical reactions. The results indicate that sample A (PTSD) exhibits a lower resistance than samples B (CCP) and C (CC) during the electrochemical reactions, which is in agreement with the results of the discharge and CV tests.

Based on these facts, we conclude that the electrochemical performance of NiOOH is strongly dependent on its precursor's properties, such as morphology, microstructure, tap density, and specific surface area. In other words, when the same electrolysis oxidation method is used, improving the precursor is a key factor in improving electrochemical performance, such as specific discharge capacity, volume discharge capacity, and high-rate discharge ability. The results also illustrate that the non-spherical precursor prepared by the PTSD method is more suitable for synthesizing NiOOH that has improved electrochemical performance and enhanced tap density.

Fig. 6 – Electrochemical impedance spectra of samples a, b, and c.

4. Conclusions

This paper describes the effects of different precursors on the microstructure and electrochemical performance of NiOOH. High-density, non-spherical NiOOH was successfully synthesized using electrolysis oxidation of a precursor generated by the PTSD method. The tap density of the powder thus obtained is 2.65 g cm^{-3} , which is the highest value yet known. Compared with spherical NiOOH, the as-prepared non-spherical particles exhibit excellent electrochemical performance that is markedly superior to the performance of spherical NiOOH, including higher specific capacity, higher volume capacity, and better high-rate discharge ability. The discharge capacity of the sample reaches 260.5 mAh g^{-1} at 0.2 C and about 222.9 mAh g^{-1} at 2 C . The CV and EIS tests reveal that the as-prepared non-spherical particles also have better reaction reversibility and lower charge-transfer resistance, and these properties contribute to the excellent electrochemical performance. The results show that the properties of the precursor, such as its morphology, microstructure, tap density, and specific surface area, have significant effects on the physical and electrochemical performance of NiOOH. The results also suggest that this high-density, non-spherical NiOOH can be considered a new positive electrode material for Zn-NiOOH batteries.

Acknowledgements

This work is financially supported by the Natural Science Foundation of China under approval No. 21071046, and Henan Provincial Department of Science and Technology Key Research Project under approval No. 080102270013.

REFERENCES

- [1] Geng M, Northwood DO. Development of advanced rechargeable Ni/MH and Ni/Zn batteries. *Int J Hydrogen Energy* 2003;28:633–6.
- [2] Bardé F, Palacín MR, Beaudoin B, Tarascon JM. Ozonation: a unique route to prepare nickel oxyhydroxides. Synthesis optimization and reaction mechanism study. *Chem Mater* 2005;17:470–6.
- [3] Yuan YF, Tu JP, Wu HM, Yang YZ, Shi DQ, Zhao XB. Electrochemical performance and morphology evolution of nanosized ZnO as anode material of Ni–Zn batteries. *Electrochim Acta* 2006;51:3632–6.
- [4] Pan JQ, Sun YZ, Wan PY, Wang ZH, Liu XG. Synthesis, characterization and electrochemical performance of battery grade NiOOH. *Electrochem Commun* 2005;7:857–62.
- [5] Bardé F, Palacín MR, Beaudoin B, Christian PA, Tarascon JM. Cationic substitution in γ -type nickel (oxi)hydroxides as a means to prevent self-discharge in Ni/Zn primary batteries. *J Power Sources* 2006;160:733–43.
- [6] Skipworth Ewen, Donne Scott W. Role of graphite in self-discharge of nickel(III) oxyhydroxide. *J Power Sources* 2007;174:186–90.
- [7] Yu T, Liu Y, Zhai YC, Yan YH. Performance of Ni/MH batteries with NiOOH-doped nickel positive electrode. *Chin J Northeastern Univ (Natural Science)* 2005;26(7):660–2.
- [8] Chang ZR, Shangguan EB, Di Cheng, Xu YJ. Study on regulation of the discharge storage capacity of anode in Ni/MH battery by NiOOH. *Chin Battery Bimonthly* 2007;37(5):367–9.
- [9] Yuan GX, Huang KL, Liu SQ, Li YJ, Wang HY. Synthesis and characterization of spherical nonstoichiometric $\text{Ni}(\text{OH})_x$ ($x = 2.03\text{--}2.10$) as electrode materials. *J Power Sources* 2010;195:5094–100.
- [10] Pan JQ, Sun YZ, Wang ZH, Wan PY, Yang YS, Fan MH. Nano-NiOOH prepared by splitting method as super high-speed charge/discharge cathode material for rechargeable alkaline batteries. *J Power Sources* 2009;188:308–12.
- [11] Ramesh TN, Kamath PV. Nickel oxyhydroxide/manganese dioxide composite as a candidate electrode material for alkaline secondary cells. *J Power Sources* 2008;175(1):625–9.
- [12] Liu LP, Zhou ZT, Peng CH. Sonochemical intercalation synthesis of nano γ -nickel oxyhydroxide: structure and electrochemical properties. *Electrochim Acta* 2008;54:434–41.
- [13] Fu XZ, Zhu YJ, Xu QC, Li J, Pan JH, Xu JQ, et al. Nickel oxyhydroxides with various oxidation states prepared by chemical oxidation of spherical β -Ni(OH)₂. *Solid State Ionics* 2007;178:987–93.
- [14] Pan JQ, Du JJ, Sun YZ, Wan PY, Liu XG, Yang YS. The change of structure and electrochemical property in the synthesis process of spherical NiOOH. *Electrochim Acta* 2009;54:3812–8.
- [15] Fu XZ, Xu QC, Hu RZ, Pan BX, Lin JD, Liao DW. β -CoOOH coated spherical β -NiOOH as the positive electrode material for alkaline Zn-NiOOH battery. *J Power Sources* 2007;164:916–20.
- [16] Sun YZ, Pan JQ, Wan PY, Xu CC, Liu XG. Electrolytic preparation, structure characterization and electrochemical performance of NiOOH. *Chin J Chem Eng* 2007;15:262–7.
- [17] Sun YZ, Pan JQ, Wan PY, Liu XG. Study on preparation of NiOOH by a new catalytic electrolysis method. *Mater Res Bull* 2009;44:943–6.
- [18] Shangguan EB, Chang ZR, Tang HW, Yuan XZ, Wang HJ. Preparation of nickel oxyhydroxide by a new electrolysis method using spherical β -Ni(OH)₂. *Int J Hydrogen Energy* 2010;35(8):3214–20.
- [19] Shangguan EB, Chang ZR, Tang HW, Yuan XZ, Wang HJ. Synthesis and characterization of high-density non-spherical $\text{Ni}(\text{OH})_2$ cathode material for Ni-MH batteries. *Int J Hydrogen Energy* 2010;35(18):9716–24.
- [20] Bernard MC, Cortes R, Keddad M, Takenouti H, Bernard P, Senyari S. Structural defects and electrochemical reactivity of β -Ni(OH)₂. *J Power Sources* 1996;63(2):247–54.
- [21] Deabate S, Fourgeot F, Henn F. X-ray diffraction and micro-Raman spectroscopy analysis of new nickel hydroxide obtained by electrodialysis. *J Power Sources* 2000;87:125–36.
- [22] Köhler U, Antonius C, Bäuerlein P. Advances in alkaline batteries. *J Power Sources* 2004;127:45–52.
- [23] Zhang WG, Jiang WQ, Yu LM, Fu ZZ, Xia W, Yang ML. Effect of nickel hydroxide composition on the electrochemical performance of spherical $\text{Ni}(\text{OH})_2$ positive materials for Ni-MH batteries. *Int J Hydrogen Energy* 2009;34(1):473–80.
- [24] Kober FP. Infrared spectroscopic investigation of charged nickel hydroxide electrodes. *J Electrochem Soc* 1967;114:215–8.
- [25] Rajamathi M, Kamath PV, Seshadri R. Polymorphism in nickel hydroxide: role of interstratification. *J Mater Chem* 2000;10:503–6.
- [26] McEwen RS. Crystallographic studies on nickel hydroxide and the higher nickel oxides. *J Phys Chem* 1971;76:1782–9.
- [27] Zhao YL, Wang JM, Chen H, Pan T, Zhang JQ, Cao CN. Al substituted α -nickel hydroxide prepared by homogeneous precipitation method with urea. *Int J Hydrogen Energy* 2004;29(8):889–96.
- [28] Jeevanandam P, Koltypin Y, Gedanken A. Synthesis of nanosized α -nickel hydroxide by a sonochemical method. *Nano Lett* 2001;1(5):263–6.

-
- [29] Zhu WH, Ke JJ, Yu HM, Zhang DJ. A study of the electrochemistry of nickel hydroxide electrodes with various additives. *J Power Sources* 1995;56:75–9.
- [30] Wang CY, Zhong S, Bradhurst DH, Liu HK, Dou SX. Ni/Al/Co-substituted α -Ni(OH)₂ as electrode materials in the nickel metal hydride cell. *J Alloys Compd* 2002;330–332:802–5.
- [31] Liu B, Yuan HT, Zhang YS. Impedance of Al-substituted α -nickel hydroxide electrodes. *Int J Hydrogen Energy* 2004;29:453–8.
- [32] Li YW, Yao JH, Liu CJ, Zhao WM, Deng WX, Zhong SK. Effect of interlayer anions on the electrochemical performance of Al-substituted α -type nickel hydroxide electrodes. *Int J Hydrogen Energy* 2010;35:2539–45.