

Short communication

β -CoOOH coated spherical β -NiOOH as the positive electrode material for alkaline Zn-NiOOH battery

Xian-Zhu Fu ^{a,*}, Qing-Chi Xu ^a, Rong-Zong Hu ^a, Bing-Xuan Pan ^b,
Jing-Dong Lin ^a, Dai-Wei Liao ^{a,*}

^a State Key Laboratory of Physical Chemistry on Solid Surfaces, Department of Chemistry, College of Chemistry and Chemical Engineering, Institute of Physical Chemistry, Xiamen University, Xiamen 361005, PR China

^b Xiamen Three Circles Co. Ltd., Xiamen 361000, PR China

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Abstract

β -CoOOH coated spherical β -NiOOH powders were synthesized as the positive electrode material for a new type of alkaline Zn-NiOOH battery. The scanning electron microscope (SEM), X-ray diffraction (XRD), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), storage stability and electrochemical properties of the samples were investigated. The results showed that the β -CoOOH coated spherical β -NiOOH exhibited superior electrochemical performance and storage stability than uncoated spherical β -NiOOH. AA size alkaline Zn-NiOOH batteries were assembled by directly using β -CoOOH coated spherical β -NiOOH as the positive electrode material. The discharge-charge experiments revealed that the alkaline Zn-NiOOH battery displayed longer discharge time and higher discharge voltage than the conventional alkaline Zn-MnO₂ battery under heavy load. Moreover, the Zn-NiOOH battery can be used not only conveniently as primary battery but also repeatedly as rechargeable battery.

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1. Introduction

Recently, a new type of primary alkaline Zn battery, which contained spherical β -NiOOH as the positive electrode material, has been developed to meet the high power requirement of digital code portable electronics [1–3]. Although spherical β -NiOOH has uniform morphology and high tapping density, its storage stability in alkaline electrolyte is poor, leading to serious self-discharge of battery. Moreover, the usage of primary battery is very convenient but it is a source-waste. In fact, the NiOOH electrode has excellent cycle reversibility. It is not similar to MnO₂ which has bad reversibility when discharge 100% depth and the development of rechargeable Zn-MnO₂ batteries is not easy. The conventional rechargeable Zn-Ni battery used β -Ni(OH)₂ as the positive electrode material, which represents

high specific energy and low cost, has been improved with good cycle performance [4]. Thus, the alkaline Zn-NiOOH battery with β -NiOOH as the positive electrode material could be used not only conveniently as primary battery but also repeatedly as rechargeable battery.

Though NiOOH is well known as the oxidized or charged state of Ni(OH)₂, it has gained little attention as a raw positive electrode material to directly fabricate battery in the past. In contrast, Ni(OH)₂ has been intensively studied and used in commercial alkaline rechargeable batteries [5]. In recent years, Co [6–8], Co compounds [9–11], Ni [12], Y(OH)₃ [11,13] and Lu(OH)₃ [14] coated β -Ni(OH)₂ positive electrode materials have been developed to improve the electrochemical performance of Ni(OH)₂ electrode at room and elevated temperature. The coating method might be an effective way to improve the properties of β -NiOOH as the positive electrode material for a new type of alkaline Zn-NiOOH battery.

In this work, we prepared β -CoOOH coated spherical β -NiOOH and investigated its electrochemical performance and storage stability. AA size alkaline Zn-NiOOH batteries directly

* Corresponding authors. Tel.: +86 592 218 3045; fax: +86 592 218 3043.
E-mail addresses: xzfu@xmu.edu.cn (X.-Z. Fu), dwliao@xmu.edu.cn (D.-W. Liao).

used β -CoOOH coated β -NiOOH as the positive electrode material were also assembled and studied.

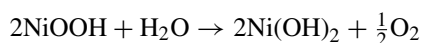
2. Experimental

The coated β -NiOOH was prepared by adding spherical β -Ni(OH)₂ powders and CoSO₄ solution into KOH and ammonia solution at 60 °C, followed by adding excess amount of K₂S₂O₈. The composition was controlled by the weight ratio of spherical β -Ni(OH)₂ and the CoSO₄. After reaction, the black product was washed and dried at 60 °C. In order to identify the phase structure of the coating, the pure coating material without spherical β -Ni(OH)₂ powders was prepared by a same process. For comparison, the uncoated β -NiOOH was prepared by adding spherical β -Ni(OH)₂ powders and excess amount of K₂S₂O₈ into KOH solution at 60 °C. The spherical β -Ni(OH)₂ were used in this work is a commercial product.

The phase structure of samples was identified by X-ray diffraction (XRD) measurements. XRD patterns were obtained using a Philips1010 X-ray diffractometer (Cu K α radiation, $\lambda = 1.540598 \text{ \AA}$) with a scan step of 0.008° (2θ) for 5 s at 40 kV and 30 mA. Morphologies of samples were observed using an Oxford Instrument LEO1530 field emission scanning electron microscope (SEM). The metal content in the NiOOH product was determined by a Thermo Electron Corporation inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

Cyclic voltammetry (CV) measurement was performed in a three-compartment electrolysis cell at 25 °C using a CHI830 electrochemical analyzer. The powder microelectrode with 100 μm diameter platinum was used as a working electrode and the nickel sheet was used as a counter electrode. The Hg/HgO/9 M KOH reference electrode was used with a Luggin capillary in the region of working electrode. The 9 M KOH solution was used as an electrolyte in the test.

The storage stability of NiOOH can be easily investigated by measuring the O₂ gas evolution in 9 M KOH solution at 60 °C with a gas meter since the deterioration of the storage stability in the alkaline electrolyte results from the following reaction [15]:



This method is similar to the investigation of AgO positive material stability in the alkaline electrolyte as previously reported [16].

AA size Zn-NiOOH alkaline batteries were constructed in an AA size Zn-MnO₂ alkaline batteries assembly line by directly using β -CoOOH coated and uncoated β -NiOOH as the positive materials, concentrated KOH solution as electrolyte and Zn powders as anode. AA size conventional Zn-MnO₂ alkaline batteries were also fabricated for comparison. After 24 h, the discharge–charge cycle tests were conducted as following processes: (I) discharged at 1000 mA constant current to a cut off voltage of 0.9 V, (II) rested for 30 min, then charged with constant 1.9 V for 10 h and 200 mA limited and (III) rested for 60 min, then discharged as (I) and cycled. Both discharge

and charge experiments were carried out by using a BS-9300R battery tester at room temperature.

3. Results and discussion

3.1. Surface morphology of coated and uncoated spherical NiOOH

Both coated and uncoated NiOOH powders have similar uniform spherical morphology in the low-magnification SEM images as shown in Fig. 1(a and c), meaning that the coated layer is very thin. The high-magnification surface image of coated spherical NiOOH in Fig. 1(b) is significantly different from that of uncoated spherical NiOOH powder in Fig. 1(d). The uncoated NiOOH surface is made up of smaller granular crystalline grains whereas the coated NiOOH surface is completely covered by a layer. This result clearly confirms the successful formation of coated layer on the surface of pristine spherical NiOOH particles.

3.2. Phase structure of coated and uncoated spherical NiOOH

The XRD patterns of the pure coating material, both coated and uncoated spherical β -NiOOH are shown in Fig. 2. It can be seen that the pure coating material is β -CoOOH (JCPDS 14-0673) and the coated NiOOH is a single phase of β -NiOOH (JCPDS 6-0141) similar to the uncoated NiOOH. The characteristic diffraction peaks of the β -CoOOH did not appear in the patterns of coated β -NiOOH. This is because that the coating amount is too small to be detected by XRD analysis, which was estimated to approximately 5 wt% by ICP-AES measurement.

3.3. Storage stability of coated and uncoated spherical NiOOH

NiOOH may self-decompose to Ni(OH)₂ and give out O₂ gas in the alkaline electrolyte, deteriorating the storage stability of NiOOH and decrease the battery discharge capacity as mentioned in Section 1. Fig. 3 shows the released O₂ gas volume of the coated and the uncoated β -NiOOH during soaking in 9 M KOH electrolyte at 60 °C. This condition is very strict in practical usage of batteries for the storage stability. It demonstrates that the O₂ gas evolution of uncoated spherical β -NiOOH is much faster than that of coated spherical β -NiOOH. After 15 days, the total released O₂ gas volume of coated spherical β -NiOOH is only 0.15 ml g⁻¹, whereas that of spherical β -NiOOH is 3.35 ml g⁻¹. Therefore, the coated spherical β -NiOOH has remarkably better storage stability than the uncoated spherical β -NiOOH in alkaline electrolyte. This may be due to the β -CoOOH coating layer hinders the self-reduction of β -NiOOH in the core by insulating the β -NiOOH directly contacted with KOH electrolyte. Moreover, the β -CoOOH is harder reduced than β -NiOOH, which can be deduced from the previous report that CoOOH still exists in the electrode when the β -NiOOH discharged to β -Ni(OH)₂ [17]. Thus, CoOOH coating is an effec-

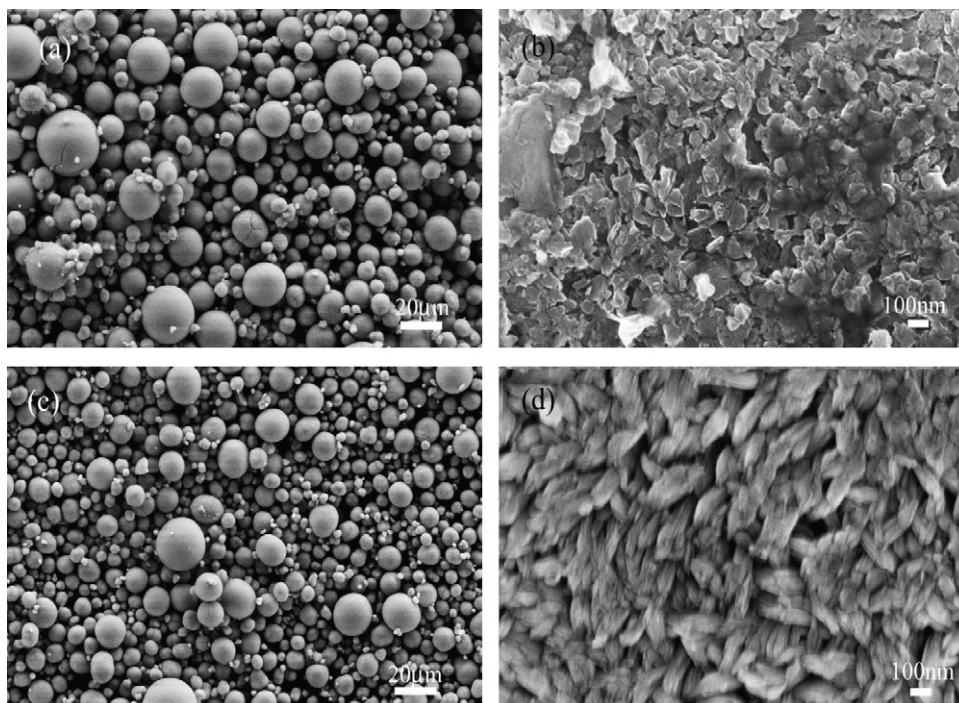


Fig. 1. SEM images of: (a) low-magnification and (b) high-magnification of CoOOH coated NiOOH particles and (c) low-magnification and (d) high-magnification of surface of uncoated NiOOH particles.

tive way to improve the storage ability of β -NiOOH in alkaline electrolyte.

3.4. Cyclic voltammetric studies of coated and uncoated spherical NiOOH electrodes

The cyclic voltammograms in the fifth cycle of the β -CoOOH coated and the uncoated β -NiOOH electrodes are shown in Fig. 4. The reversibility of electrode can be evaluated by the difference between oxidation potential (E_O) and reduction potential (E_R) [9]. The result shows that the β -CoOOH coated β -NiOOH

has a less value of $E_O - E_R$ (0.20 V) comparing to the uncoated β -NiOOH (0.23 V). It indicates that the β -CoOOH coated β -NiOOH has better reversibility than the uncoated one. This attributes to β -CoOOH with higher conductivity than β -NiOOH [9–11,17,18].

3.5. Performances of AA size alkaline Zn-NiOOH batteries

The 1000 mA constant current initial discharge curves of the AA size alkaline Zn-uncoated NiOOH, the Zn-coated NiOOH and the conventional Zn-MnO₂ batteries are shown in Fig. 5.

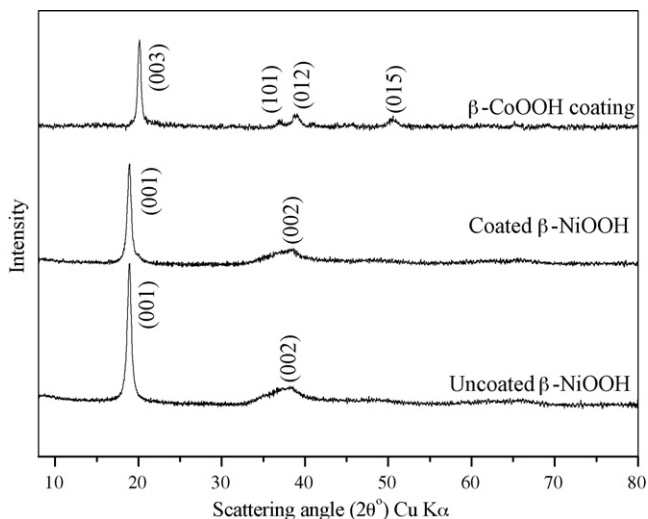


Fig. 2. XRD patterns of pure β -CoOOH coating, coated and uncoated β -NiOOH.

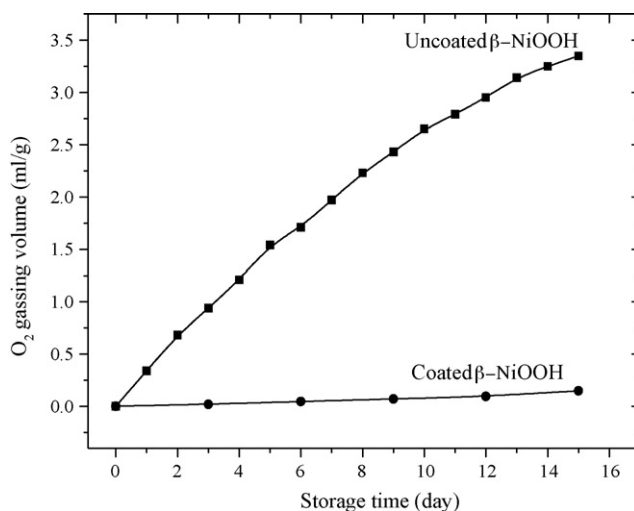


Fig. 3. O₂ gassing volume of coated and uncoated β -NiOOH in 9M KOH solution at 60 °C.

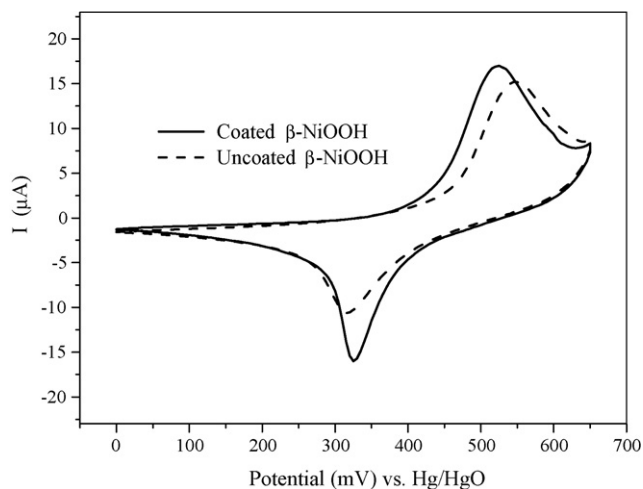


Fig. 4. Cyclic voltammograms of coated and uncoated β -NiOOH at a scan rate of 5 mV s^{-1} .

Both the alkaline Zn coated and uncoated NiOOH batteries have higher discharge plateau than the alkaline Zn-MnO₂ battery, meaning that the Zn-NiOOH batteries have higher working voltage than Zn-MnO₂ battery. In addition, the Zn-NiOOH batteries have much longer discharge time relative to alkaline Zn-MnO₂ battery, especially at high cut off voltage. For example, as a cut off voltage of 1.1 V, the discharge time of Zn-coated NiOOH battery is about five times than that of Zn-MnO₂ alkaline battery. This indicates that alkaline Zn-NiOOH battery has very good heavy current discharge performance and higher power density. It is also seen that the Zn-coated NiOOH battery has slightly larger discharge time and voltage than Zn-uncoated NiOOH battery. This is due to the fact that the β -CoOOH coating layer has a higher conductivity than β -NiOOH resulting in a higher utilization of active material [9–11,17,18]. From Fig. 5, we can furthermore infer that the new type of alkaline Zn-NiOOH battery can be directly used after fabrication as conveniently as primary batteries since the oxidized (charged) state NiOOH active material is employed. However, the conventional Zn-Ni

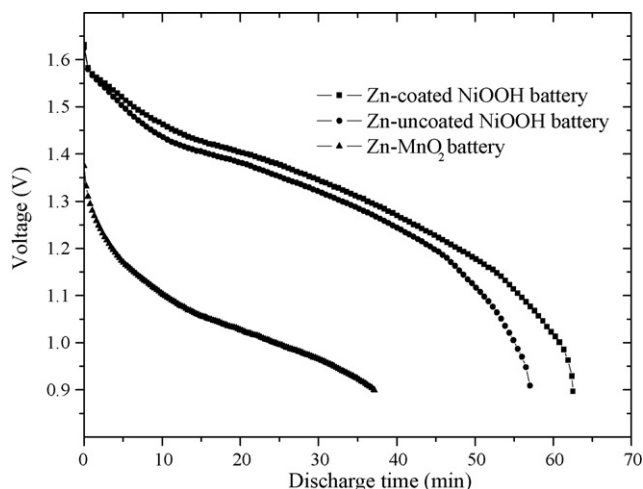


Fig. 5. Discharge curves of AA size alkaline Zn-NiOOH and Zn-MnO₂ batteries at 1000 mA constant current.

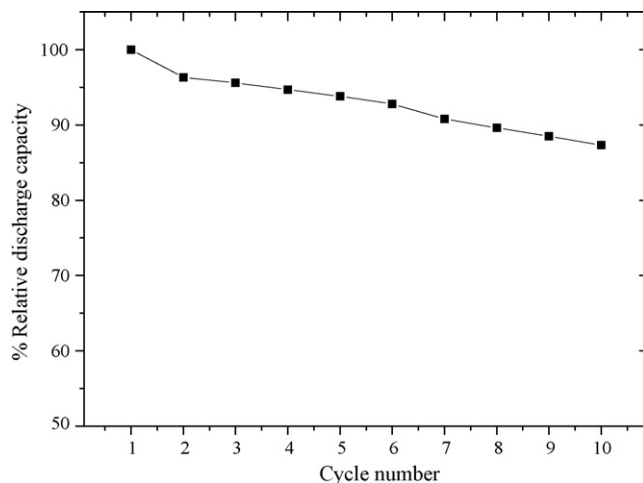


Fig. 6. Relative discharge capacity of AA size alkaline Zn-coated NiOOH battery.

battery with Ni(OH)₂ as the positive electrode material cannot be used as primary battery. The cycle performance of alkaline Zn-NiOOH battery is shown in Fig. 6, demonstrating that the capacity retention is still 87% after 10 cycles. Therefore, the new type of alkaline Zn-NiOOH battery can also be used repeatedly as rechargeable batteries.

4. Conclusions

The β -CoOOH coated spherical β -NiOOH powders were successfully prepared and it had superior electrochemical performance and storage stability than the uncoated spherical β -NiOOH. The AA size alkaline Zn-NiOOH batteries using β -CoOOH coated spherical β -NiOOH as the positive electrode material have much longer discharge time and higher voltage than the conventional Zn-MnO₂ batteries under heavy load. The new type of alkaline Zn-NiOOH battery can be used not only conveniently as primary battery but also repeatedly as rechargeable battery.

Acknowledgements

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