Novel Co(OH)$_2$ with cotton-like structure as anode material for alkaline secondary batteries

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Abstract. The cotton-like Co(OH)$_2$ (S-Co(OH)$_2$) was successfully synthesized and its electrochemical performance was systematically investigated. S-Co(OH)$_2$ was prepared through the “destruction” of the newly formed colloid Co(OH)$_2$ by the reduction using sodium borohydride. The crystal structure and surface morphology were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS). Used as an anode material for alkaline secondary batteries, S-Co(OH)$_2$ sample exhibited better cycle stability, higher electrochemical capacity, and higher rate performance than those of conventional β-Co(OH)$_2$. At a discharge current density of 100 mA/g, the initial discharge capacity of S-Co(OH)$_2$ is 549.3 mAh/g and the discharge capacity is still sustained to be 329.2 mAh/g after 100 charge-discharge cycles with a capacity retention of 59.9%.

1. Introduction

Facing the global concerns of energy crisis and environmental risk, researchers have been trying their best to find new alternative energy sources and/or optimize the energy storage and conversion devices in these years [1-3]. As a device for electrical energy storage, alkaline secondary batteries have aroused extensive attention of many researchers due to their low cost, high specific energy, large power and safety performance [4-6]. However, with the ever-increasing requirement of the energy density and power density for all kinds of electronic equipments, alkaline secondary batteries are in the face of unprecedented challenges. Therefore, it is of great urgency to develop high-performance alkaline secondary batteries.

The anode materials for alkaline secondary batteries mainly including alloys or metals are crucial for their electrochemical properties. AB$_5$-type alloys, AB$_2$-type alloys, AB-type intermetallic compounds and Mg-based alloys have been developed to be used as the negative electrode materials for nickel/metal hydride (Ni/MH) secondary batteries [2, 7-9], which is a special kind of alkaline secondary batteries. Cobalt or cobalt-based alloys have been paid much attention thanks to high theoretical electrochemical capacity (909 mAh/g) [10]. They were also used for many devices, such as lithium ion batteries [11], alkaline secondary batteries [12], and supercapacitor [13]. Among Co-based compounds, Co(OH)$_2$ has received great interest owing to its layered structure with large inter-layer spacing, which makes it a promising electrode material. For example, the amorphous Co(OH)$_2$ nanorod arrays on Ni foam exhibited high specific capacity (172 mAh/g at 2 A/g), enhanced rate
performance (83 mAh/g at 10 A/g), and superior cycling performance over 6000 cycles [14]. In addition, it can also be used as positive electrode materials in alkaline secondary batteries [14, 15]. As a negative electrode material in alkaline batteries, the electrode reaction is according to the following equation [5]:

$$\text{Co(OH)}_2 + 2e^- \leftrightarrow \text{Co} + 2\text{OH}^- \tag{1}$$

Feng et al. found that the main drawback of β-Co(OH)$_2$ was its higher discharge median voltage of 783 mV (vs. Hg/HgO) in comparison with AB$_2$-type alloy [16]. Also, the discharge capacity fluctuated during charge-discharge cycles. Toward these problems, we successfully synthesized a cotton-like β-Co(OH)$_2$ in this work. Its electrochemical properties were systematically investigated as anode materials for alkaline secondary batteries.

2. Experimental

2.1. Synthesis of β-Co(OH)$_2$

β-Co(OH)$_2$ was prepared by a simple hydrothermal method with some modification [17-19]. A typical synthesis process is as follows. 8.0 g cobalt chloride hexahydrate (CoCl$_2$·6H$_2$O) was dissolved in 30 mL ultra-pure water and 3.0 g sodium hydroxide was dissolved in 40 mL ultra-pure water. Then these two solutions were transferred into a Teflon-lined stainless autoclave and homogenously mixed to form colloidal solution. It was maintained at 50 °C for 2 h and then cooled down to room temperature naturally. Finally, the pink precipitate was collected and washed with distilled water and absolute ethanol. β-Co(OH)$_2$ was obtained through drying the precipitate in vacuum at 60 °C for 24 h.

2.2. Synthesis of S-Co(OH)$_2$

S-Co(OH)$_2$ was synthesized by the “destruction” of the newly formed Co(OH)$_2$ by the reduction of sodium borohydride. 10.0 g cobalt chloride hexahydrate (CoCl$_2$·6H$_2$O) was dissolved in 30 mL ultra-pure water and 3.4 g sodium hydroxide was dissolved in 30 mL ultra-pure water. These two kinds of solution were homogenously mixed and 30 mL sodium borohydride solution (6.9 mol/L) was slowly added at a rate of 1.5 mL/min with the assistance of ultrasonication. Finally, the gray precipitate was washed with distilled water and absolute ethyl alcohol. S-Co(OH)$_2$ was obtained through heating the precipitate under vacuum at 60 °C for 24 h.

2.3. Sample characterization

The crystal structure and surface morphology of the as-prepared samples were characterized by a Bruker D8 Advance diffractometer with Cu Kα radiation and scanning electron microscopy (SEM, QUANTA FEG450). In addition, the chemical composition of the samples was characterized by the energy dispersive spectrometer (EDS, X-Max20). The BET specific surface area was determined using a Quantachrome Autosorb-iQ2 sorptometer.

2.4. Electrochemical tests

The as-prepared Co(OH)$_2$ samples were used as negative electrode materials for alkaline secondary batteries. The working electrodes were fabricated according to our previous papers [5, 6, 20]. Typically, the as-prepared samples and Ni powder as conductive agent in a mass ratio of 1:3 were homogeneously mixed and then pressed into a wafer with a diameter of 13 mm under a pressure of 30 MPa. Each side of the wafer was coated with a rounded foam nickel sheet whose diameter is about 25 mm. Then the sandwich-like electrode was pressed under 6 MPa and spot-weld at the edge of foam nickel tightly. Finally, a nickel wire was attached to this pressed foam nickel sheet by spot welding. The charge/discharge cycles and high rate discharge-ability (HRD) were tested on an automatic instrument (LAND-CT2001A). The current density is 300 mA/g for charge and 100 mA/g for discharge in galvanostatic charge-discharge test. For HRD test, the charge current density is 300 mA/g and the discharge current density is 300, 600, and 900 mA/g. The electrochemical impedance spectroscopy (EIS) with an alternate current oscillation of 5 mV from 0.005 Hz to 10 kHz and anodic
polarization (AP) at a scan rate of 1 mV/s from 0 to 0.5 V were measured on a Zahner Elektrik IM6e electrochemical workstation. All electrochemical tests were conducted in a three-electrode cell containing a Ni(OH)\(_2\)/NiOOH counter electrode, a Hg/HgO reference electrode, and a fabricated working electrode in 6 M KOH electrolyte. The testing temperature was set at 25 °C.

3. Results and Discussion

3.1. Sample structure
As can be seen from XRD patterns shown in figure 1, the diffraction peaks of two Co(OH)\(_2\) samples match well with those of hexagonal phase Co(OH)\(_2\) (JCPDS 74-1057) in space group P-3m1 with the unit cell parameters of \(a = 0.3183\) nm, \(c = 0.4652\) nm, \(c/a = 1.461\) for \(\beta\)-Co(OH)\(_2\) and \(a = 0.3182\) nm, \(c = 0.4656\) nm, \(c/a = 1.463\) for S-Co(OH)\(_2\). There are no diffraction peaks for \(\alpha\)-Co(OH)\(_2\) at 22.22° [16] or any other impurity in the XRD patterns, suggesting high purity of the as-prepared samples. However, it is obvious that the peak intensity for S-Co(OH)\(_2\) is decreased compared to that of \(\beta\)-Co(OH)\(_2\), which may be attributed to the destruction of the crystallization process of Co(OH)\(_2\) by NaBH\(_4\). Specially, the destruction of crystallization process of the newly-formed colloid Co(OH)\(_2\) resulting from NaBH\(_4\) reduction may give rise to a low crystallite size. In addition, the effect of ultrasonication may exacerbate this destruction to the further formation of cotton-like structure [21, 22]. This is supported by crystallite size determined from Rietveld refinement. The crystallite size of S-Co(OH)\(_2\) was decreased to be 23 nm from 68 nm for \(\beta\)-Co(OH)\(_2\), which will be beneficial to the electrochemical reaction such as electron transport.

![Figure 1. Rietveld refinement of XRD patterns for the as-prepared samples.](image)

Figure 2 shows the SEM micrographs of the as-prepared Co(OH)\(_2\) samples. Clearly, \(\beta\)-Co(OH)\(_2\) shown in figure 2 (a) is observed to be consisting of agglomeration of nanosheets. As can be seen from magnified image in figure 2 (b), these sheets are in hexagonal shape with a thickness in the range of 50 ~ 200 nm. In contrast, S-Co(OH)\(_2\) shown in figure 2 (c and d) has a cotton-like structure, which endows it a higher specific surface area of 42.3 m\(^2\)/g than \(\beta\)-Co(OH)\(_2\) (18.2 m\(^2\)/g). The special structure may be attributed to the destruction of the newly prepared colloid Co(OH)\(_2\). When NaBH\(_4\) was added into the resultant solution, volume of newly formed colloid Co(OH)\(_2\) was destructed by removing some oxygen atoms in its lattice during the reduction [23]. Meanwhile, both the bubbles produced from the reduction reaction of NaBH\(_4\) and the effect of ultrasonication could exacerbate the self-assembled process of cotton-like structure [21, 22]. EDS analysis of S-Co(OH)\(_2\) in figure 2 (e) shows that there is trace of boron element in this sample, which may come from the reduction of the newly formed Co(OH)\(_2\) by NaBH\(_4\). Upon the addition of NaBH\(_4\), the newly formed colloid Co(OH)\(_2\) may partly transform into Co and B with the induction of ultrasonication [21, 22]. Therefore, amorphous CoB alloy was suggested to be included into S-Co(OH)\(_2\). However, the diffraction peak of amorphous
CoB alloy generally appearing at $\theta = 40\text{-}50$ [5] was not observed, which is probably due to its smaller amount and/or stronger diffraction peaks of Co(OH)$_2$ in the XRD pattern.

Figure 2. SEM micrographs: (a) and (b) for $\beta$-Co(OH)$_2$, (c) and (d) for S-Co(OH)$_2$. (e) Elemental distribution mappings of S-Co(OH)$_2$.

3.2. Electrochemical performance

For $\beta$-Co(OH)$_2$ electrode material, it is well accepted that the electron reaction can be expressed as equation (1) [16]. To determine their electrochemical properties as anode materials for alkaline secondary batteries, the charge-discharge capacities of these two samples were investigated and the related electrochemical properties were summarized in Table 1. The galvanostatic charge-discharge curves in Figure 3 (a) show that there is no activation process for both samples. Moreover, the maximum discharge capacity of S-Co(OH)$_2$ is 549.3 mAh/g, which is higher than that of $\beta$-Co(OH)$_2$. It is important to highlight that the discharge capacity of S-Co(OH)$_2$ is obviously higher than that of $\beta$-Co(OH)$_2$ at the 100th charge-discharge cycle. After 100 cycles, the discharge capacity of S-Co(OH)$_2$ is still sustained to be 329.2 mAh/g, which increased by about 4% than $\beta$-Co(OH)$_2$. Unlike the fluctuation in the curves of cycle life [16], they are very smooth in our case. As shown in Figure 3 (b), the discharge voltage plateau for both Co(OH)$_2$ samples is almost the same at about 800 mV, which coincides with those observed in previous literatures [6, 23]. Note that it is higher than $\beta$-Co(OH)$_2$ (about 780 mV) synthesized by solid-state chemical reaction [16]. On the contrary, the charging
voltage plateau of S-Co(OH)₂ sample is a little higher than that of β-Co(OH)₂, which indicates that the polarization of β-Co(OH)₂ electrode is more serious than S-Co(OH)₂. It is generally believed that the polarization has a negative effect on the electrochemical properties of the alloy electrodes [24], which is responsible for the improvement of electrochemical properties for S-Co(OH)₂. Figure 3 (c) shows the HRD of as-prepared Co(OH)₂ samples at 298 K. At a current density of 300, 600, and 900 mA/g, HRD of S-Co(OH)₂ and β-Co(OH)₂ are all higher than reported Co or Co-based alloys [12, 20, 24], which may be attributed to the high specific surface areas [24, 25].

| Samples      | Activation number | C_{max} (mAh/g) | C_{100} (mAh/g) | C_{100}/C_{max} (%) | HRD_{900} (%) |
|--------------|-------------------|-----------------|-----------------|---------------------|---------------|
| β-Co(OH)₂    | 1                 | 533.1           | 316.6           | 59.4                | 96.6          |
| S-Co(OH)₂    | 1                 | 549.3           | 329.2           | 59.9                | 97.4          |

In order to deeply investigate the kinetic characteristics, we conducted the EIS and AP tests for both samples at the discharge depth of 50% after full activation of the electrodes, which are shown in figure 4. According to a previous report [24], there are a semicircle and a straight line in each EIS spectrum, and the semicircle is corresponding to the charge-transfer reaction resistance in the surface of alloy electrode. The big radius of the semicircle means higher charge-transfer resistance, which enhance the difficulty of charge-discharge process. That is to say, the bigger radius of the semicircle represents the higher charge-transfer reaction resistance of the electrode. In AP curves, the peak is related to the limiting current density I_L representing the diffusion rate in Co(OH)₂ electrode. The bigger the I_L is, the quicker the diffusion in the alloy electrode is [12, 20, 24]. Clearly we can see that S-Co(OH)₂ has a smaller radius of the semicircle in EIS curve and a higher peak in AP curve, which indicates that S-Co(OH)₂ sample exhibits better electrode reaction kinetic performance than β-Co(OH)₂ from the other point of view.

![Figure 3](image1.png)  
**Figure 3.** (a) Cycling performance curves, (b) Potential-capacity curves and (c) High rate dischargeability (HRD) curves of the as-prepared samples.

![Figure 4](image2.png)  
**Figure 4.** (a) EIS and (b) AP of the as-prepared samples.
4. Conclusions
In summary, the cotton-like Co(OH)$_2$ was successfully synthesized by a simple precipitation reaction by the destruction of the newly formed Co(OH)$_2$. As an anode material in alkaline secondary batteries, S-Co(OH)$_2$ sample has an improved electrochemical performance. After 100 charge/discharge cycles, it still has a discharge capacity of 329.2 mAh/g with a capacity retention of 59.93%, which are better than those of β-Co(OH)$_2$. Moreover, it has a higher rate dischargeability of $HRD_{90} = 97.49\%$ thanks to its improved electrochemical kinetic characteristics.

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Reference
[1] Chu S, Cui Y and Liu N 2016 Nat. Mater. 16(1) 16
[2] Liu Y, Cao Y, Huang L, Gao M and Pan H 2011 J. Alloys Compd. 509(3) 675
[3] Reddy M, Subba Rao G and Chowdari B 2013 Chem. Rev. 113 5364
[4] Taniguchi A, Fujioka N, Ikoma M and Ohta A 2001 J. Power Sources 100(1-2) 117
[5] Zhao W, Liao Y, Huang J, Chu H, Qiu S, Zou Y, Xiang C, Xu F and Sun L 2017 Key Eng. Mater. 727 751
[6] Qiu S, Huang J, Chu H, Zou Y, Xiang C, Yan E, Xu F and Sun L 2016 Metals 6(11) 269
[7] Sun L, Wang D, Lin J, Liang F, Wu Y, Zheng W, Cao Z and Wang L 2016 Diamond Relat. Mater. 66 10
[8] Zhang Y, Hou Z, Cai Y, Hu F, Qi Y and Zhao D 2016 Int. J. Mater. Res. 107(9) 1
[9] Qiu S, Huang J, Chu H, Zou Y, Xiang C, Zhang H, Xu F, Sun L and Zhou H 2015 J. Alloys Compd. 648 320
[10] Lv D 2009 Doctoral thesis from South China University of Technology 1-13
[11] Nithyadharseni P, Reddy M, Nalini B and Chowdari B 2015 Mater. Lett. 150 24
[12] Qiu S J and et al. 2016 Int. J. Hydrogen Energy 41(36) 16142
[13] Cao L, Xu F, Liang Y and Li H 2004 Adv. Mater. 16(20) 1853
[14] Meng X and Deng D 2017 ACS Appl. Mater. Interfaces 9(6) 5244
[15] Tronel F, Guerfou-Demourgues L, Goubault L, Bernard P and Delmas C 2008 J. Power Sources 179(2) 837
[16] Feng Z, Han S, Li Y, Xu G and Liu Y 2008 J. Yanshan Univ. 32 521
[17] Hou Y, Kondoh H, Shimojo M, Kogure T and Ohta T 2005 J. Phys. Chem. B 109(41) 19094
[18] Xu Z and Zeng H 2000 Int. J. Inorg. Mater. 2(2-3) 187
[19] Yao W, Yang J and Cheng H 2010 Sci. China Chem. 40 1598
[20] Huang J L and et al. 2015 Int. J. Hydrogen Energy 40(41) 14173
[21] Li H, Li H, Zhang J, Dai W and Qiao M 2007 J. Catal. 246(2) 301
[22] Wang C, Li H, Chen S and Li H 2007 J. Mol. Catal. (China) 21(3) 205
[23] Lee D, Kang M, Paek S and Jung H 2016 Electrochim. Acta 217 132
[24] Qiu S J and et al. 2016 Int. J. Hydrogen Energy 41(6) 3955
[25] Humana R, Thomas J, Ruiz F, Real S, Castro E and Visintin A 2012 Int. J. Hydrogen Energy 37(19) 14966