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Ultrastable α phase nickel hydroxide as energy storage materials for alkaline secondary batteries

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ABSTRACT

α Phase nickel hydroxide (α-$Ni(OH)_2$) has higher theoretical capacity than that of commercial β phase $Ni(OH)_2$. But the low stability inhibits its wide application in alkaline rechargeable batteries. Here, we propose a totally new idea to stabilize α phase $Ni(OH)_2$ by introducing large organic molecule into the interlayer spacing together with doping multivalent cobalt into the layered $Ni(OH)_2$ host. Ethylene glycol is served as neutral stabilizer in the interlayer spacing. Nickel is substituted by cobalt to increase the electrostatic attraction between layered $Ni(OH)_2$ host and anion ions in the interlayer spacing. Polyethylene glycol (PEG-200) is utilized to design a three-dimensional network structure. This prepared α-$Ni(OH)_2$-20 exhibits specific capacity as high as 334 mAh g^{-1} and good structural stability even after immersing into strong alkaline zincate solution for 20 days. $Ni(OH)_2$ electrode with a specific capacity of 35 mAh cm^{-2} is fabricated and used as positive electrode in zinc-nickel single flow batteries, which also shows good cycling stability. This result can provide an important guideline for the rational design and preparation of highly active and stable α phase $Ni(OH)_2$ for alkaline secondary battery.

1. Introduction

Alkaline rechargeable batteries have been intensely researched in the pursuit of sustainable and efficient use of electricity from portable electronics to energy storage [1]. Nickel hydroxide, as a kind of outstanding electrode materials, has been widely used in alkaline based batteries such as Ni-MH, Ni-Cd, Ni-Zn and so on [2–7]. On the basis of its crystal structure, nickel hydroxide can be divided into α and β phases, which are oxidized to β phase NiOOH and γ phase NiOOH, respectively [8]. β phase $Ni(OH)_2$ has a brucite-like structure composed of an ordered stack of well-oriented $Ni(OH)_2$ layers and a stoichiometric composition, which is extensively utilized in conventional nickel-based batteries. The redox between β phase $Ni(OH)_2$ and β phase NiOOH is one electron transfer reaction leading to a low theoretical capacity of 289 mAh g^{-1}. Moreover, γ phase NiOOH with larger interspace (0.7 ∼ 0.8 nm), is formed by over oxidating β phase $Ni(OH)_2$ (0.46 nm), which causes volume expansion and decreases the stability of nickel hydroxide electrode during repeated charge-discharge cycles[9].

α Phase $Ni(OH)_2$ has a hydrotalcite-like structure, which consists of stacked and positively charged $Ni(OH)_2$ layers with charge-balancing anions in the interlayer spacing between two $Ni(OH)_2$ layers [8]. As α phase $Ni(OH)_2$ has more defects than β phase $Ni(OH)_2$ due to its hydrotalcite-like structure, so it has higher electrochemical activity. Moreover, the oxidation product of α phase $Ni(OH)_2$ is γ phase NiOOH, which has the similar crystal structure with α phase $Ni(OH)_2$. So redox cycling stability of α phase $Ni(OH)_2$/γ phase NiOOH is very good without any mechanical failure. More importantly, the electron transfer number of α phase $Ni(OH)_2$ to γ phase NiOOH can be as high as 1.67 resulting a high theoretical capacity of 482 mAh g^{-1} [10,11]. However, α phase $Ni(OH)_2$ can easily transform into β phase $Ni(OH)_2$ by losing H atoms in $Ni(OH)_2$ layers and anions in the interspace in strong alkaline solution, which decreases the stability of α phase $Ni(OH)_2$ and hinders its application in alkaline based batteries [12]. Another problem blocking its application is the low conductivity of α phase $Ni(OH)_2$, which is firstly formed on the surface of the electrode and thereby prevent the transport of electrons from inter active materials to the reactive interface [13,14].

Great efforts have been focused on stabilizing the structure of α phase $Ni(OH)_2$. Obtaining positive charge in hosted $Ni(OH)_2$ layers by substituting Ni^{2+} with other two bivalent metal cations or one trivalent metal cation is a common method to stabilize α phase $Ni(OH)_2$ [8]. Cobalt is proved to be an effective element due to its multi-valent (bivalent and trivalent) and superior conductivity of its oxides and hydroxides [15,16]. Cobalt

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substituted α phase $Ni(OH)_2$ shows specific capacity as high as 300 mAh g^{-1}(Ni:Co = 2:1), which is much higher than the theoretical capacity of β phase $Ni(OH)_2$ (289 mAh g^{-1}) [17]. Although cobalt can enhance the electrostatic attraction between layered $Ni(OH)_2$ host and anions in the interlayer spacing, the transform of α phase $Ni(OH)_2$ to β phase $Ni(OH)_2$ still can not been totally prevented in concentrated alkaline solution [8,18]. Besides, structure-directing agents such as cetyltrimethylammonium bromide, sodium dodecylsulfate, tween and polyvinyl alcohol can modify the morphology, particle size, and some properties of a phase nickel hydroxides [17,19,20], but the products usually has poor structural stability. In a word, α phase $Ni(OH)_2$ with stable structure and high specific capacity for practical application has seldom been reported.

Here, we proposed a totally new method to stabilize α phase $Ni(OH)_2$ by introducing small organic molecules into the interlay spacing along with substituting nickel by cobalt. Ethylene glycol was served as neutral stabilizer in the interlayer spacing. Nickel was substituted by cobalt to increase the electrostatic attraction of between layered $Ni(OH)_2$ hosts and anion ions in the interlayer spacing, and the conductivity of α phase $Ni(OH)_2$. PEG-200 was used as structure-directing agent to design and control the transport of hydroxide ions and electrons. Prepared cobalt substituted α phase $Ni(OH)_2$, with a three-dimensional network structure, exhibits high structural and cycling stability, and high specific capacity, which is promising electrode material for alkaline based batteries.

2. Material and methods

2.1. Synthesis of cobalt substituted α phase nickel hydroxide

In a typical synthesis, 2.326 g of $Ni(NO_3)_2{\cdot}6H_2O$, 0.476 g of $CoCl_2{\cdot}6H_2O$ and 1.2 g of urea were dissolved in 50 mL deionized water. Then, PEG-200 with amount of 0 g, 0.5 g, 2.0 g or 4.0 g and ethylene glycol were added into above solutions forming 100 mL complex solution. The mixture was heated at 80 °C for 24 h, followed by filtering and washing six times with deionized water and ethanol, and finally vacuum freeze-drying for 8 h. Four samples are named as α-$Ni(OH)_2$-0, α-$Ni(OH)_2$-5, α-$Ni(OH)_2$-20 and α-$Ni(OH)_2$-40, respectively.

2.2. Sample characterization

The X-ray diffraction (XRD) pattern was conducted by a DX-2700 diffractometer (Dandong Haoyuan Instrument Co., LTD, China) with Cu Kα radiation at λ = 1.54 Å. The morphology of prepared cobalt substituted nickel hydroxide was characterized by scanning electron microscopy (FEI, Quanata 200F). Elemental mapping was carried out using scanning transmission electron microscopy (STEM) equipped with energy-dispersive X-ray spectrometry (Tecnai C2 TF20). All prepared nickel hydroxide materials were analyzed in X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi, UK). Obtained spectra is charge corrected to the adventitious C1s spectral component with binding energy of 284.6 eV. Fourier transform infrared spectroscopy (FTIR)was obtained by Jasco FTIR-4100. The quantities of nickel and cobalt were calculated by inductively coupled plasma optical emission spectrometry (ICP, Optima 2000 DV, Perkin Elmer Co., USA).

2.3. Electrochemical measurements

The nickel hydroxide electrodes were prepared as follows: cobalt substituted α phase $Ni(OH)_2$, carbon (Super P) and PTFE were mixed at the ratio of 80 wt.%, 15 wt.% and 5 wt.% into ethanol solution forming a slurry. Then, the slurry was coated on nickel foam (1.0 cm × 1.0 cm for three-electrode system, 3.0 cm × 3.0 cm for battery test), followed by drying at 80 °C for 10 h and mechanically pressing under 10 MPa for 2 min. Electrolytes used in all electrochemical measurements were 8 mol L^{-1} KOH and 0.4 mol L^{-1} ZnO aqueous solutions. A conventional three-electrode system was conducted by electrochemical workstation (CHI 760D, CH instrument Inc, China) with the prepared nickel hydroxide electrode (1.0 cm × 1.0 cm) as working electrode, a platinum plate as counter electrode and a Hg/HgO as reference electrode. The cyclic voltammetry (CV) was carried out in the potential range of 0 V–0.6 V (vs. Hg/HgO) at the scan rate of 1 mV s^{-1} . Electrochemical impedance spectra was measured at equilibrium potential with 5 mV amplitude over a frequency range of 100 kHz–0.01 Hz. Galvanostatic charge–discharge tests were performed at the current densities of 0.1 A g^{-1}, 0.2 A g^{-1}, 0.5 A g^{-1} and 1.0 A g^{-1} by Arbin BT-2000 (Arbin Instruments, America).Two-electrode battery (Zinc-nickel single flow battery) was assembled in a self-designed installation using prepared nickel hydroxide electrode as positive electrode, nickel sheet as negative electrode [12]. The battery was charged to 35 mAh cm^{-2} and discharged to 0.8 V at the current density of 20 mA cm^{-2}, 40 mA cm^{-2} and 80 mA cm^{-2}, respectively. Coulombic efficiency (CE) was defined as the ratio of discharging capacity to charging capacity. Voltage efficiency (VE) was calculated by divided average discharging voltage by average charging voltage. Energy efficiency (EE) was the ratio of discharging energy to charging energy.

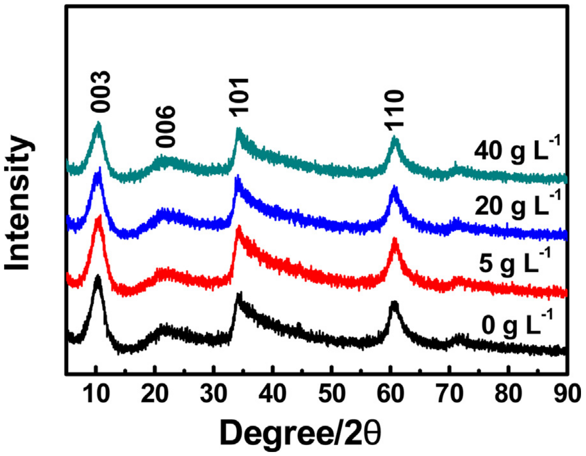

Fig. 1. XRD patterns of α-$Ni(OH)_2$-0, α-$Ni(OH)_2$-5, α-$Ni(OH)_2$-20 and α-$Ni(OH)_2$-40.

3. Results and discussion

Cobalt substituted α phase $Ni(OH)_2$ were synthesised by homogeneous deposition with various concentrations of PEG-200 from 0 g L^{-1} to 40 g L^{-1}, which are named as α-$Ni(OH)_2$-0, α-$Ni(OH)_2$-5, α-$Ni(OH)_2$-20 And α-$Ni(OH)_2$-40, respectively. In the synthesizing process, urea firstly hydrolyzed at 80 °C and formed a basic solution, then Ni $^{2+}$ and Co $^{2+}$ reacted with OH^- producing nickel and cobalt hybrid hydroxide. Meanwhile, PEG-200 was used to direct the grown and assembly of monomers to larger particles by selecting adsorption on $Ni(OH)_2$ crystal during the nuclei and growth processes, and ethylene glycol inserted into the interlayer spacing acting as neutral stabilizer. The physical structures of four prepared materials were investigated via the X-ray diffraction (XRD). Typical XRD patterns of these prepared materials are displayed in Fig. 1. The four prepared materials all contain four characteristic peaks at 10.8°, 22.4°, 34.3° and 60.5° corresponding to the (003), (006), (101) and (110) planes of α phase $Ni(OH)_2$ with hydrotalcite-like structure (JCPDS 38-0715), respectively.[2,21]. Generally, the broader the diffraction peak in XRD patterns is, the smaller of the crystal