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Original Research Paper

$Co_2(OH)_3Cl$ nanoparticles as new-type electrode material with high electrochemical performance for application in supercapacitor

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ABSTRACT

In this work, we report the preparation of $Co_2(OH)_3Cl$ nanoparticles with average size of ~20 nm and well-defined cubic shape at room temperature by an epoxide precipitation route. It was found that the as-prepared $Co_2(OH)_3Cl$ nanoparticles could be used as a promising new electrode material for application in redox supercapacitors due to its high electrochemical performance. It presented superior specific capacitance of 783 F g^{-1} at low current density of 2.8 A g^{-1}, while it had a high value of 604 F g^{-1} at high current density of 56.6 A g^{-1}, proving its excellent high rate performance. Its 75% capacitance retention after 10,000 cycles of charge–discharge demonstrated its long-life span. According to characterization results, the possible mechanism for the electrochemical process that $Co_2(OH)_3Cl$ nanoparticles underwent was proposed as a process of $Co_2(OH)_3Cl \rightarrow \beta\text{-}Co(OH)_2 \rightarrow CoOOH \leftrightarrow Co_3O_4$.

1. Introduction

As efficient energy conversion and storage devices, electrochemical supercapacitors are of great interest due to their promising application in peak-power and backup-power sources [1–3]. There are two general categories of supercapacitors: electrical double-layer capacitors (EDLC) and redox supercapacitors. Redox supercapacitors have significant advantages such as much higher energy density than EDLC. However, their frustrating disadvantages such as lower power density than EDLC have been issues slowing their further progress [4,5]. It seems that the electrochemical mechanism for redox supercapacitors has been well understood, but eliminating their prominent disadvantages that originate from the inherent characteristics of electrode materials is still a great challenge. Lots of works have to be done including deep investigation on electrochemical mechanism, building appropriate microstructure, and developing new electrode materials.

Redox supercapacitors utilize the fast and reversible redox reactions occurring at the interface of electrode materials and electrolyte. The valence electrons of electroactive electrode materials are transferred across the interface, resulting in potential-dependent capacitance [1–3,6]. The frequently investigated electrode materials for redox supercapacitors include oxide [7–9], hydroxides [10–12] and polymers [13,14]. Base on already known electrochemical mechanism, the research on electrode materials mainly focuses on assembly of hierarchical nanostructure or compounding with other materials such as graphene [15,16], trying to solve the issues of known materials. Great progress has been made during the past decade, however it seems that further breakthrough is rare recently, probably because of the exhausted potential for these two strategies. Maybe, developing new electrode materials for redox supercapacitors is the most possible pathway.

Transition metal hydroxides such as $Co(OH)_2$ and $Ni(OH)_2$ have layered structure and large theoretical specific capacitance, which are one category of frequently investigated electrode materials for application in redox supercapacitors [17–19]. As electrode materials, these hydroxides suffer two main disadvantages: poor electric conductivity and low charge-discharge cycle stability. These two disadvantages are the main obstacles for transition metal hydroxides to become leading electrode materials. As interesting derivatives of hydroxides, cobalt basic salts, expressed with a general formula of $Co(OH)_{2-x}(A^{n-})_x$ (A: Cl^-, NO_3^-, SO_4^{2-}, CO_3^{2-}, etc.), are considered compositionally a solid solution of $Co(OH)_2$ and Co_nA_2 and structurally associated with $Co(OH)_2$ as a hydroxyl-rich phase [20]. Due to the unique structure, cobalt basic salts present superior properties, having promising applications in various non-energy storage areas [21–23]. It was found recently that $Co_2(OH)_3Cl$, a typical cobalt basic salt, could be used as an efficient anode material for Li ion battery, exhibiting exceptional electrochemical performance due to the introduction of chlorine group in its structure [20,24–26]. In 2016, Ranganatha et al. [27] pioneered a work

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related with the application of $Co_2(OH)_3Cl$ as electrode material in redox supercapacitors, finding the faradaic capacitive behavior of $Co_2(OH)_3Cl$ in alkaline electrolyte solution. However, it is pity that the electrochemical performance of $Co_2(OH)_3Cl$ was not good enough (450 F g^{-1} at current density of 2 A g^{-1} and 145 F g^{-1} at 25 A g^{-1}). It exhibited poor electrochemical stability in alkaline electrolyte (76% capacitance retention after 1000 cycles of charge-discharge). More importantly, the electrochemical mechanism of $Co_2(OH)_3Cl$ was not well-discussed in detail.

In this work, we prepared $Co_2(OH)_3Cl$ nanoparticles with well-defined cubic shape and average size of 20 nm by an epoxide precipitation method. The electrochemical behavior of as-prepared $Co_2(OH)_3Cl$ nanoparticles in alkaline electrolyte solution was systematically investigated. It was found that the nanosized $Co_2(OH)_3Cl$ had superior electrochemical performance in the application of redox supercapacitors: high specific capacitance of 783 F g^{-1} at low current density of 2.8 A g^{-1} and excellent high rate performance (high specific capacitance of 603 F g^{-1} at high current density of 56.6 A g^{-1}). Also, this material showed high electrochemical stability in alkaline solution (75% capacitance retention after 10,000 cycles of charge-discharge). According to characterization results, a possible electrochemical mechanism for $Co_2(OH)_3Cl$ nanoparticles was given in detail.

2. Experimental

2.1. Materials

Cobalt chloride ($CoCl_2{\cdot}6H_2O$, ≥98%), propylene oxide (C_3H_6O, ≥99.5%), ethanol (C_2H_5OH, ≥99.5%) were obtained from Aladdin and used as received.

2.2. Preparation of $Co_2(OH)_3Cl$ nanoparticles

$Co_2(OH)_3Cl$ nanoparticles were prepared by an epoxide precipitation route based on our previous work [28]. In a typical procedure, a certain amount of propylene oxide as precipitant was added to a 0.6 M ethanolic solution of $CoCl_2{\cdot}6H_2O$ (the mole ratio of propylene oxide to metal ions was 10). After 24 h's reaction under stirring, the produced precipitate was separated and washed by water with centrifugation. Then, the precipitate was dried at 80 °C in an oven.

2.3. Characterizations

The crystalline phase of samples was measured with a Shimadzu LabX XRD-6100 diffractometer using Cu Kα radiation (λ = 1.5406 Å). The Fourier transform infrared (FTIR) spectra of samples were recorded in a Shimadzu IRAffinity-1S spectrometer using KBr pellet technique. The morphology of samples was observed using a JEOL JEM-1400 transmission electron microscope (TEM). The TEM samples were prepared by the dispersing of a little amount of powder sample in ethanol under ultrasonification and the following drying of one drop suspension on a 400-mesh carbon-coated copper grid.

2.4. Preparation of working electrodes and electrochemical measurement

The electrochemical measurements were carried out using an IVIUMSTAT electrochemical workstation in a three-electrode cell equipped with a working electrode, a platinum plate counter electrode and an Hg/HgO reference electrode. The working electrode was prepared by inserting a paste into a nickel foam substrate. The paste was formed by adding a few drops of ethanol to a mixture of 80 wt% $Co_2(OH)_3Cl$ nanoparticles and 20 wt% acetylene black. After brief evaporation of ethanol, the paste was pressed at 10 MPa to the nickel foam with a nickel wire for electrical connection. The obtained electrode was dried in air for 3 h at 80 °C. Each electrode contained ~2 mg electroactive materials and had a geometric surface area of 1 cm^2. After drying, the electrode was activated by 100 cycles of cyclic voltammetry from 0 to 0.5 V versus Hg/HgO at 100 mV s^{-1} in 3 M KOH aqueous solution and then used as a working electrode. The electrochemical tests on the electrodes including cyclic voltammetry (CV) and galvanostatic charge–discharge measurements were performed in 3 M KOH aqueous solution. The calculation about the specific capacitance was based on the description in literature [29].

3. Results and discussion

$Co_2(OH)_3Cl$ nanoparticles were prepared by an epoxide precipitation route utilizing the hydrolysis reactions between $[Co(H_2O)_6]^{2+}$ and propylene oxide [28]. XRD pattern of the sample prepared in ethanolic solution of $CoCl_2{\cdot}6H_2O$ is shown in Fig. 1a. The diffraction lines of sample are well indexed to the rhombohedral phase of $Co_2(OH)_3Cl$ (JCPDS 73-2134). In TEM image (Fig. 1b), $Co_2(-$

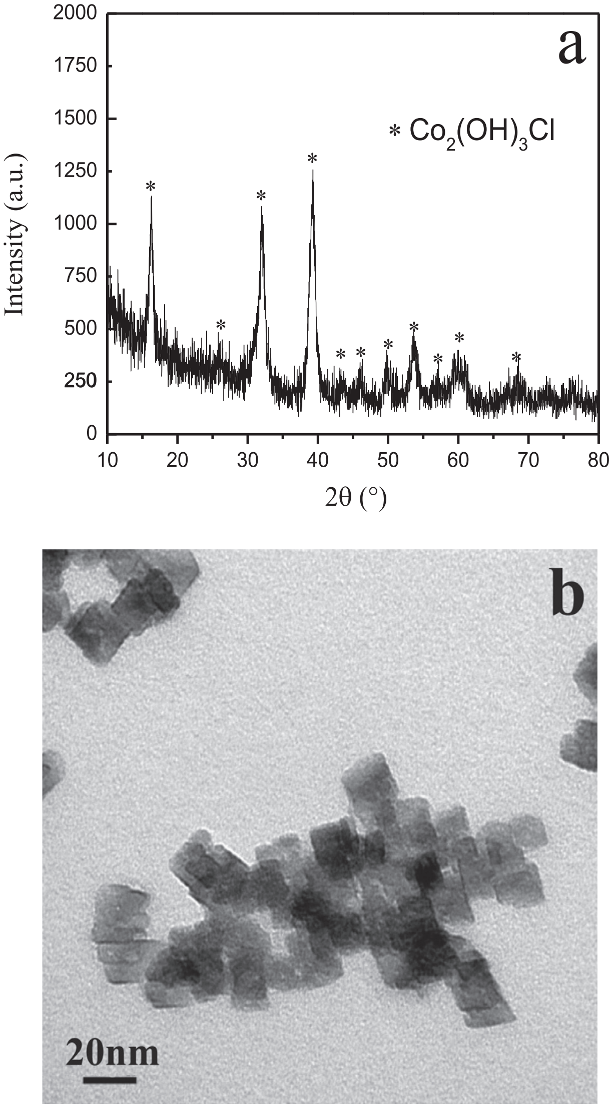

Fig. 1. XRD pattern (a) and TEM image (b) of the sample prepared in ethanolic solution of $CoCl_2{\cdot}6H_2O$.