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Synthesis and characterization of nanostructured $CuFe_2O_4$ anode material for lithium ion battery

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ABSTRACT

A nanostructured binary transition metal oxide, copper ferrite ($CuFe_2O_4$) is synthesized via polymer-pyrolysis method. The effects of the processing temperature on the particle size and electrochemical performance of the nanostructured $CuFe_2O_4$ are investigated. The electrochemical results show that the sample synthesized at 700 °C shows the best cycling performance, retaining a specific capacity of 551.9 mAh g^{-1} beyond 100 cycles for lithium ion batteries. The electrode has a good rate capacity within the range of 0.2 *C*–4 *C*. At the highest rate of 4 *C*, the reversible capacity of $CuFe_2O_4$ is about 200 mAh g^{-1}. It is believed that the ternary transition metal oxide $CuFe_2O_4$ is quite acceptable compared with other high performance nanostructured anode materials.

1. Introduction

Transition metal oxides and binary metal oxides are promising anode electrode materials for rechargeable lithium ion batteries (LIBs). Their advantages include high theoretical capacities, safety-in-operation, environmental friendliness, and moderate prices, etc. [1-5]. Nanoscaled spinel ferrites for LIBs have been intensively developed as anode materials because of their novel Li-ion-storage mechanism. The mechanism differs from the classical Li insertion/extraction and Li alloying/dealloying processes. It involves the formation and decomposition of lithium oxide (Li_2O), accompanying the reduction and oxidation of metal nanoparticles [6-12]. The transition metal oxide MFe_2O_4 (M = Ni, Co and Zn) has been widely proved favorable for LIBs [13-16]. The initial charge capacities of these ferrite materials usually exceed 1000 mAh g^{-1}, which is about three times of those of commonly used carbon materials. However, few endeavors have been devoted to optimizing $CuFe_2O_4$ for LIBs [17,18]. In fact, $CuFe_2O_4$ can be considered as a promising anode material for LIBs, due not only to its low-cost, high abundance, and environmental benignity, but also to its high theoretical capacity (896 mAh g^{-1}). In the previous literatures, Bomio [17] had used a thermal decomposition of metal citrate precursor method to synthesize $CuFe_2O_4$. The product has demonstrated high capacities, but poor cycle life. Selvan [18] had investigated $CuFe_2O_4/SnO_2$ composites as a means to enhance the electrochemical behavior. In particular, the vital limiting factors in the applicability of $CuFe_2O_4$ are the rate of diffusion of lithium in the bulk material, very low conductivity, and the large volume expansion and contraction during the Li^+ insertion and extraction reactions. Therefore, nanomaterial design and preparation strategy are crucial to further improve the electrochemical performance of $CuFe_2O_4$ for LIBs.

The current study reports the preparation of nanoscaled copper ferrite ($CuFe_2O_4$) materials by a polymer pyrolysis method (PPM) using a polyacrylate precursor [19,20]. The Fe and Cu ions are considered as able to retain their atomic-scale homogenous distributions similar with those in the original solution. Subsequently, a simple heat treatment can lead to good homogenous particle sizes, a short production time, a good stoichiometry and an ultimately uniform particle distribution in the final production. The generated nanomaterials have been thoroughly characterized by different techniques including thermogravimetric analysis (TGA), Fourier transformed infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), cyclic voltammograms (CV), and galvanostatic charge–discharge tests. Besides, the impedance changes during the initial Li-insertion/extraction especially, at the different states of discharge (SODs) for the $CuFe_2O_4$ electrode of the first charge/discharge cycle have been systematically investigated.

2. Experimental

Nanocrystalline spinel ferrite $CuFe_2O_4$ materials were prepared by PPM using the polyacrylate of Cu and Fe nitrates as the precursor compounds (Fig. 1). The polymeric precursor was produced by the in situ polymerization of the mixed an aqueous acrylic acid solution of acrylic acid in the presence of $Cu(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$, with $(NH_4)_2S_2O_8$ as the initiator. The molar Cu/Fe ratio was fixed at 1:2. First, $Cu(NO_3)_2 \cdot 6H_2O$ (0.01 mol) and $Fe(NO_3)_3 \cdot 9H_2O$ (0.02 mol) were dissolved in 10 g of acrylic acid aqueous solution (acrylic acid:

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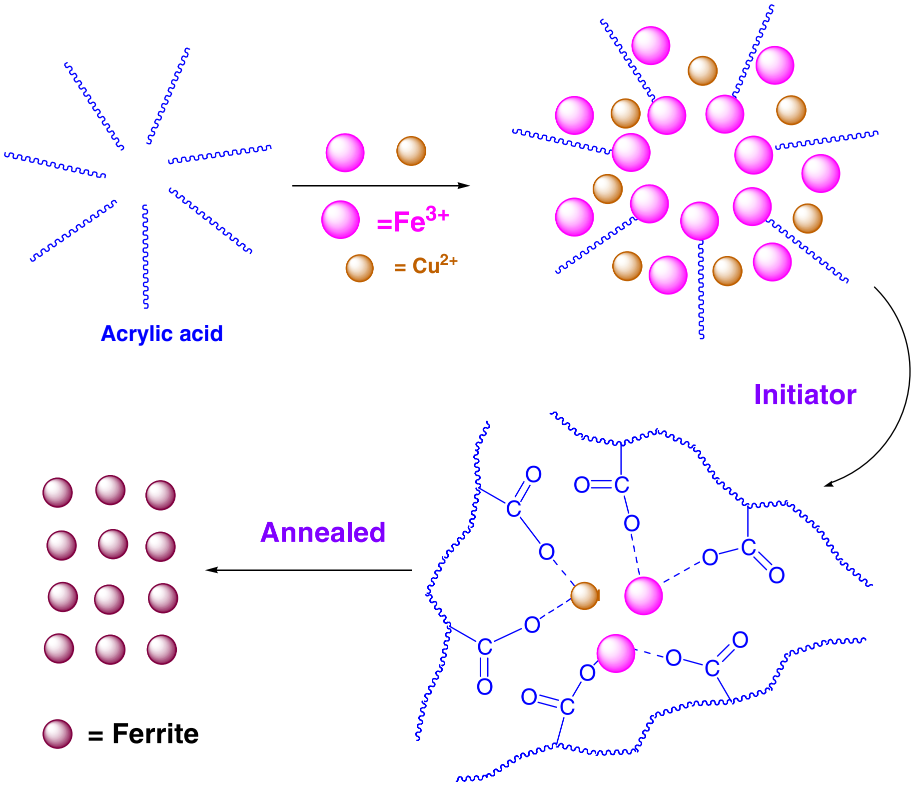


Fig. 1. Schematic representation of polymeric chain of the co-polymeric precursor of Cu–Fe polyacrylates.

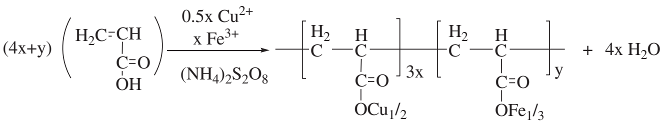
$H_2O = 70{:}30$ wt.%) under stirring. Afterwards, a small amount (1 mL) of 5% $(NH_4)_2S_2O_8$ aqueous solution as the initiator was added to the mixed acrylic acid solution to promote the polymerization. After heating at 80 °C for 2 h, the mixture was dried to form the well-distributed polyacrylate salt, which was further dried at 120 °C for 12 h. Annealing at different temperatures (500, 600, 700, and 800 °C) for 4 h in air yielded the desired integrated crystalline samples (CuFe-500, CuFe-600, CuFe-700, and CuFe-800, respectively).

Electrochemical characterizations were performed using CR2016 coin cells with a Land BT2000 battery tester (Wuhan, China). The anode used in this work with a geometrical area of 2 cm^2 consisted of 70 wt% $CuFe_2O_4$ powder (as the active material), with 20 wt% acetylene black and 10 wt% polytetrafluoroethylene (PTFE). The use of acetylene black was intended to improve the electronic conductivity, while the polymer was added to enhance the mechanical properties and ensure the adherence of the material on the stainless steel mesh. The electrode was prepared by mixing the $CuFe_2O_4$ powders, acetylene black, and PTFE emulsion to form an electrode paste, and then was rolled into a 0.1-mm-thick film, and finally the electrode film pressed into a piece of 1-cm-diameter stainless steel mesh. The electrode was dried at 120 °C and 7 mbar for 4 h and pressed under a 1 ton pressure to ensure a uniform surface. The test cells were assembled in an argon-filled glove box with 1 mol L^{-1} solution of $LiPF_6$ in ethylene carbonate/dimethyl carbonate (EC:DMC = 1:1 v/v) as the electrolyte. The counter electrode was fresh Li foil. The separator was Celgard 2300. The cell was galvanostatically cycled between 0.01 and 3.0 V (vs. Li^+/Li) unless otherwise specified. A 3-electrode cell with Li foils as the counter and reference electrodes was used for CV and the electrochemical impedance spectroscopy (EIS) analyses. A CHI 660B Electrochemical Workstation (Chenghua, Shanghai, China) was used at a scan rate of 0.1 mV s^{-1} between 0.01 and 3.0 V. In the EIS measurements, the oscillation voltage applied to the cells was 5 mV, and the frequency range was 100 kHz to 0.1 Hz.

The FT-IR features of the precursor and final product were analyzed by a Nicolet 380 spectrometer within 4000–400 cm^{-1}. All the samples were prepared as KBr pellets. To determine the exact decomposition temperature of the precursor, the thermogravimetry and differential thermogravimetry (TG-DTG) analyses were performed with a simultaneous SDT Q600 thermal analyzer. The conditions were 10 °C min^{-1} from room temperature to 600 °C, at 20 mL min^{-1} air flow rate. The structures of the samples were analyzed by X-ray powder diffraction (XRD) using a Shimadzu XRD-6000 diffractometer, in the 2θ range of 10.00°–80.00°, with the scan rate 2° min^{-1}. The morphologies of the samples were examined using scanning electron microscopy (SEM, JSM-6700F scanning electron microscope) and transmission electron microscope (TEM, Tecnai G20 Philip transmission electron microscope) at an accelerating voltage of 200 kV.

3. Results and discussion

At the first step of the ferrite synthesis, an aqueous solution of acrylic acid is mixed with the appropriate amount of Cu and Fe nitrate salts. This affords a composition which has the predetermined ratio of Cu to Fe to be compatible with the final product ($CuFe_2O_4$) according to the following formula [21]:



$$(4x+y)\left(\begin{array}{c}H_2C{=}CH\\ \;\;|\\ \;\;C{=}O\\ \;\;|\\ \;\;OH\end{array}\right)\xrightarrow[(NH_4)_2S_2O_8]{\substack{0.5x\,Cu^{2+}\\ x\,Fe^{3+}}}\left[\overset{H_2}{C}-\overset{H}{\underset{\substack{|\\ C=O\\ |\\ OCu_1/_2}}{C}}\right]_{3x}\left[\overset{H_2}{C}-\overset{H}{\underset{\substack{|\\ C=O\\ |\\ OFe_1/_3}}{C}}\right]_{y}+\ 4x\,H_2O$$

In the formula, x and y represent the polymerization degrees. Cu^{2+} and Fe^{3+} ions are bound by the strong ionic bonds between the metallic ions and carboxylate ions in a polymeric chain or between the polymeric chains.

The TG/DTG curves of the precursor are shown in Fig. 2. The weight loss of the precursor occurred in one discrete step and was terminated near 460 °C. One exothermic peak was observed within 250–460 °C, corresponding to one step of weight loss. The total weight loss was