

Synthesis and lithium electrode application of ZnO–ZnFe₂O₄ nanocomposites and porously assembled ZnFe₂O₄ nanoparticles

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ABSTRACT

The mixed metal oxide nanocomposites composed of spinel ZnFe₂O₄ and wurzite ZnO phases are prepared by the heat-treatment for Zn,Fe-layered double hydroxide (Zn,Fe-LDH) at elevated temperatures. The following selective etching of ZnO domains from the nanocomposites yields porously assembled ZnFe₂O₄ nanocrystals. The structural transformation from the brucite LDH structure to the spinel and/or wurzite structures was confirmed by X-ray diffraction and X-ray absorption spectroscopy. According to chemical analysis, electron microscopy, and N₂ adsorption–desorption isotherm measurements, not only the chemical composition of the nanocomposites but also the particle size and surface area of the etched ZnFe₂O₄ nanoparticles can be controlled by changing the Fe/Zn ratio in the precursor metal hydroxide. The calcined nanocomposites show promising functionality as negative electrode materials for lithium ion batteries, which is superior to that of uncomposited ZnFe₂O₄ or ZnO phase. The degrading of the electrode performance of the nanocomposites after the selective etching of ZnO component clearly demonstrates the positive effect of nanocomposite formation on the electrochemical activity of metal oxides.

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1. Introduction

Over the past decades, layered double hydroxide (LDH) has attracted intense research interest because of its diverse functions as absorbents, flame retardants, reservoirs/carriers for biomolecules such as DNA, amino acids, or drug [1–6]. Most of the LDH's functionalities originate from its anion-exchange capability. The exchangeable anions are introduced in the interlayer space of the LDH to compensate the positive charge of brucite-type host layers generated by the partial replacement of divalent metal ions with trivalent metal ions [7–10]. The LDH has a general chemical formula of $[A^{2+}_{1-x}B^{3+}_x(OH)_2]^{x+}[C^{n-}_{x/n}]^{x-} \cdot zH_2O$, where A²⁺, B³⁺, and Cⁿ⁻ denote divalent metal cations (e.g., Ca²⁺, Mg²⁺, Zn²⁺, Ni²⁺, Mn²⁺, Co²⁺, Fe²⁺, Cu²⁺, etc), trivalent metal cations (e.g., Fe³⁺, Al³⁺, Cr³⁺, Mn³⁺, Ga³⁺, Co³⁺, Ni³⁺, etc), and interlayer anions, respectively. To dates, many couples of divalent and trivalent metal ions are accommodated in the LDH lattice, reflecting the high structural stability of the brucite layer [7]. The heat-treatment at elevated temperatures can induce a phase transformation from metal hydroxide to mixed metal oxide nanocomposite through dehydroxylation reaction. In one instance, the nanoscale mixture of wurzite-structured ZnO and spinel-structured ZnM₂O₄ can be prepared by the post-calcination for the Zn-containing LDH (hereafter denoted it as Zn,M-LDH) [11,12]. Furthermore, since ZnO is readily soluble in aqueous media at high pH condition [11,12], the porous assembly of spinel ZnM₂O₄ nanoparticles is

easily obtained by a basic etching of the ZnO–ZnM₂O₄ nanocomposite. Considering that this etching process selectively removes ZnO domains in the nanocomposite, the particle size and surface area of the remaining ZnM₂O₄ nanocrystals are supposed to be controllable by changing the relative population of ZnO domains over ZnM₂O₄ ones in the nanocomposite. From the viewpoint of material's application, the spinel-structured ZnFe₂O₄ is applicable as negative electrode material for lithium ion batteries [13,14]. This metal oxide-based electrode material suffers from marked volume change upon lithiation–delithiation process, because this material experiences phase transformations during electrochemical cycling [13]. The resulting strain on the electrode would be relieved by the formation of nanocomposite with buffer ZnO domains, leading to the improvement of the cyclability.

In the present study, we prepared the mixed metal oxide nanocomposites of ZnO–ZnFe₂O₄ by the post-calcination of the precursor Zn,Fe-LDH, and porously assembled ZnFe₂O₄ nanocrystals by the following selective etching of the nanocomposite. The crystal structure, surface area, and chemical composition of the pristine Zn,Fe-LDHs and their derivatives were examined using X-ray diffraction (XRD), N₂ adsorption–desorption isotherm measurement, and elemental analysis, respectively. The effects of chemical etching and post-calcination on the crystal morphology and chemical bonding nature of the pristine Zn,Fe-LDHs were investigated with field emission-scanning electron microscopy (FE-SEM), high resolution-transmission electron microscopy (HR-TEM), and X-ray absorption near-edge structure (XANES) spectroscopy, respectively. The calcined nanocomposites were applied as negative electrode for lithium ion batteries, together with their etched derivatives and non-composited metal oxides.

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2. Experimental

2.1. Synthesis

The precursor metal hydroxides with different Fe/Zn ratios were prepared by co-precipitation reaction using the aqueous solutions of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ for Zn,Fe-LDH-1 and Zn,Fe-LDH-2. The concentrations of Zn^{2+} , Fe^{2+} , and Fe^{3+} ions were controlled to be 20, 10, and 20 mM for Zn,Fe-LDH-1 and 30, 0, and 10 mM for Zn,Fe-LDH-2, respectively. After mixing the precursor solutions, the resulting mixture solution was stirred at room temperature under nitrogen atmosphere for 24 h. The pH of reactant solution was adjusted to 7 ± 1 by adding 1 M NaOH solution. After the completion of the synthesis, the precipitates were collected by centrifugation, washed with ethanol, and dried in a vacuum oven at room temperature. To prepare the nanocomposite composed of ZnO and ZnFe_2O_4 , the resulting Zn,Fe-LDH materials were heated at 400, 600, and 800 °C for 2 h in ambient atmosphere. The porous ZnFe_2O_4 nanoparticles were prepared by a selective etching of ZnO component from the nanocomposites calcined at 600 °C. The etching process was done by reacting 0.5 g of the nanocomposite with 200 mL of 1 M NaOH aqueous solution at room temperature for 5 h.

2.2. Characterization

The structural variations of the Zn,Fe-LDHs upon the post-calcination and chemical etching were probed with powder XRD analysis (Rigaku D/Max-2000/PC general X-ray diffractometer using Cu K α radiation). The crystal morphology and particle size of the samples were determined by FE-SEM (Jeol JSM-6700 F) and HR-TEM (Jeol JEM-2100 F). The chemical compositions of the Zn,Fe-LDHs were analyzed with inductively coupled plasma (ICP) spectrometry, CHNS elemental analysis, and thermogravimetric analysis (TGA). The surface area and porosity of the nanoparticles were examined by measuring volumetrically nitrogen adsorption–desorption isotherms at liquid nitrogen temperature. The calcined samples were degassed at 150 °C for 2 h under vacuum before the adsorption measurement. XANES experiments were carried out at the Fe K-edge with the extended X-ray absorption fine structure (EXAFS) facility installed at the beam line 7C at the Pohang Accelerator Laboratory (PAL) in Korea. The present XANES data were collected from the thin layer of powder samples deposited on transparent adhesive tapes in a transmission mode using gas-ionization detectors. The measurements were carried out at room temperature with a Si(111) single crystal monochromator. No focusing mirror was used. All the present spectra were carefully calibrated by measuring iron metal foil simultaneously. The electrochemical measurements were performed with the 2032 coin-type cell of Li/1 M LiPF_6 in ethylene carbonate/diethyl carbonate (50:50 v/v)/composite electrode, which was assembled in a dry-box. The composite electrode was prepared by mixing thoroughly the active material (70%) with 20% of acetylene black and 10% of PTFE (polytetrafluoroethylene). The composite electrode was dried at 120 °C overnight before use. All the experiments were carried out in a galvanostatic mode with a Maccor multichannel galvanostat/potentiostat in the voltage range of 0.005–3.0 V at a constant current density of 30 mA/g.

3. Results and discussion

3.1. Powder XRD, elemental analysis, and TGA

The powder XRD patterns of the precursor metal hydroxides with different Fe/Zn ratios are plotted in Fig. 1, together with those of their calcined and etched derivatives. Both the precursor materials display a series of (00l) Bragg reflections at low angle region, suggesting the formation of layered LDH structure [12,15,16]. Due to the high Zn content of Zn,Fe-LDH-2, this sample contains additional $\text{Zn}_4\text{O}_3(\text{SO}_4) \cdot x\text{H}_2\text{O}$ phase

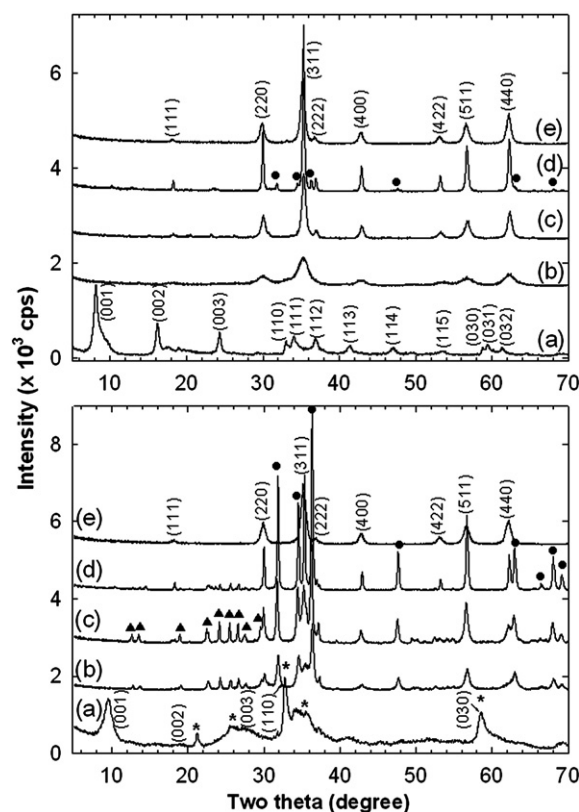


Fig. 1. Powder XRD patterns of (a) the pristine LDH and the derivatives calcined at (b) 400, (c) 600, and (d) 800 °C, and (e) the chemically etched derivative of 600 °C-calcined material. The top and bottom panels represent the data of the materials related to the precursors of Zn,Fe-LDH-1 and Zn,Fe-LDH-2, respectively. The indexed peaks correspond to the Bragg reflections of Zn,Fe-LDH in (a) or those of spinel-structured ZnFe_2O_4 in (e). The circles represent the Bragg reflections of ZnO, the triangles those of $\text{Zn}_3\text{O}(\text{SO}_4)_2$, and the asterisks those of $\text{Zn}_4\text{O}_3(\text{SO}_4) \cdot x\text{H}_2\text{O}$.

(JC-PDF No. 03-0797) as well as the LDH phase. This secondary phase is believed to act as a buffer domain for electrochemically active ZnFe_2O_4 domain after the formation of nanocomposite. According to the least-squares fitting calculation, the Zn,Fe-LDH-1 shows the basal spacing of ~ 10.8 Å, which is larger than that of the Zn,Fe-LDH-2 (~ 9.5 Å). This can be attributed to a higher Fe/Zn ratio of the former compound, resulting in the incorporation of a larger amount of guest species into the interlayer space caused by the increased positive charge of brucite layer. The ICP analysis clearly demonstrates that the Fe/Zn ratio of the obtained Zn,Fe-LDHs is dependent on the reactant ratio of iron sulfate/zinc sulfate; the Zn,Fe-LDH-1 has a higher Fe/Zn ratio of 1.24 compared with the Zn,Fe-LDH-2 material having the Fe/Zn ratio of 0.20. The CHNS elemental analysis reveals that both the LDH compounds contain sulfate anions in the interlayer space to compensate the positive charge of brucite layer. According to the results of TGA (See Supporting Information), both the pristine LDH materials show a similar mass loss of 9.2% corresponding to the evaporation of water molecules.

3.2. Structural variations upon heat-treatment and chemical etching

To synthesize mixed metal oxide nanocomposites, the pristine Zn,Fe-LDH materials were heated at 400–800 °C. As presented in Fig. 1, XRD analysis demonstrates that, after the heat-treatment, both the precursor materials are commonly transformed into the mixture of wurzite-structured ZnO and spinel-structured ZnFe_2O_4 [12]. The relative intensities of ZnO-related peaks over the ZnFe_2O_4 -related ones grow stronger with the increase of Zn/Fe ratio in the precursors. This finding clearly demonstrates that the ratio of ZnO/ ZnFe_2O_4 in the calcined nanocomposites can be controlled by changing the chemical

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