Research Article

Facile Synthesis of Fe_2O_3 Nanomaterials from MIL-101(Fe) Template and Its Application in Lithium Ion Batteries

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Sponge-like porous Fe_2O_3 nanomaterials were obtained through the calcination process of the iron-based metal organic framework (MIL-101). As anode materials for lithium-ion batteries, thus, obtained products show a good electrochemical performance with a high specific capacity (1358 mA h g^{-1} at 100 mA g^{-1} in the initial cycle) and a relatively stable cycle performance (750 mA h g^{-1} after 80 charge/discharge cycles). The superior cycling performance may be attributed to their special structure, which facilitates charge transfer and Li^+ diffusion.

1. Introduction

The concept of promoting environmental protection and energy conservation becomes a hot topic, and renewable clean energy has attained global attentions. Lithium-ion batteries (LIBs), as one of the prominent energy storage systems, have been extensively studied and broadly utilized in many electronic devices owing to their high energy density and long cycling life [1, 2]. The low cost, chemically stable, and highly conductive graphite carbon is recognized as the leading electrode material for the anodes of commercial LIBs. However, the low capability of charge storage (theoretical capacity is only 372 mA h g^{-1}) limits further applications of graphite carbon in LIBs [3]. In order to meet the demands of ever-growing performance, developing new alternative anode materials has become an urgent task in building next-generation LIBs. Transition metal oxides (M_xO_y , $\text{M} = \text{Fe}, \text{Co}, \text{Zn}, \text{Mn}, \text{Mo}$, etc.) have been extensively investigated in a diverse range of applications in energy, environment, catalysis, and electronics fields [4]. Among the available alternative anode materials, iron oxides have attracted people's attention because of nontoxicity, high corrosion resistance, and higher capacity as well as low processing cost [5–9]. However, high intrinsic resistance and the slow kinetics for ionic diffusion and charge transfer induce performance decay

especially at high current densities, which seriously limited the application of Fe_2O_3 in Li-ion batteries. It has shown that Fe_2O_3 with nanostructures not only promotes ion diffusion and electron transfer but also effectively accommodates the large changes in volume that occurs during lithiation and delithiation to prevent the electrode disintegration. So far, a lot of attempts have been made to resolve the above issues by fabricating iron oxide nanostructure materials with optimized particle shapes, sizes, and component compositions [10–12]. MOF (metal-organic framework) as a novel class of organic-inorganic porous materials formed by strong bonds between organic ligands and metal ions has been used as precursors or templates for the synthesis of metal oxides by simple thermal decomposition. The MOF-derived nanomaterials exhibit relatively porous or hollow structures [13–15]. A rational design of MOF precursors with novel structures is highly desirable for the synthesis of high-performance electrode materials. For instance, Prussian blue (PB) microcubes were used as templates to prepare hollow Fe_2O_3 microboxes, which exhibited excellent cycling performance [16, 17].

Here, we present a simple and general MOF-assisted method for the fabrication of sponge-like Fe_2O_3 as anodes for LIBs. Firstly, MIL-101(Fe) nanopolyhedrons were formed by a one-pot hydrothermal method. Then,

these nanopolyhedrons could be further converted to porous sponge-like nanoparticles through a subsequent annealing treatment in air. These nanoparticles exhibit good electrochemical performance when used as anodes for LIBs. The remarkable electrochemical properties may attribute to the porous structure which not only facilitate electron transport but also efficiently relieve the volume change caused by insertion/extraction of Li^+ . Therefore, the present study provides a simple way for the preparation of high-performance electrode materials for LIBs. And the method for the synthesis of Fe_2O_3 nanomaterials can be extended to the preparation of various MOF-derived functional nanocomposites for various energy-related applications.

2. Experimental Section

2.1. Preparation of the Electrode Materials. Dimethylformamide (DMF), ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), terephthalic acid (TPA), and ethyl alcohol (EtOH) were obtained from Shanghai Chemical Reagent Co. Ltd. (P. R. China) and used without further treatment. Doubly distilled water was used for preparing solutions.

2.1.1. Synthesis of MIL-101(Fe). MIL-101(Fe) nanopolyhedrons were prepared by a hydrothermal method based on the reported procedure with some modifications [18]. Specifically, 0.675 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (2.5 mmol) and 0.21 g TPA (1.25 mmol) were mixed in 20 mL DMF, and the mixture was ultrasonicated for 20 min to make the solid full suspension. Next, the reaction mixture was loaded into a 50 mL Teflon-lined stainless steel autoclave and placed under static conditions at 110°C in an oven for 24 h. After naturally cooling down to room temperature, orange mud was obtained. Then, it was separated by centrifugation and washing with absolute DMF and EtOH to remove the raw materials. The product was vacuum-dried at 80°C for 120 min.

2.1.2. Synthesis of Fe_2O_3 Nanoparticles. The as-formed composite was placed in a ceramic boat and heated to 380°C in the muffle furnace for about 1 h under an ambient atmosphere at a ramp rate of $10^\circ\text{C min}^{-1}$. Upon naturally cooling down, red-brown powders of Fe_2O_3 were collected.

2.2. Characterization and Electrochemical Test of the Synthesized Materials. Characterization of these synthesized products by X-ray diffraction (XRD) using a DX-2700 X-ray diffractometer was equipped with a $\text{Cu K}\alpha$ -sealed tube ($\lambda = 1.5406 \text{ \AA}$) and scanned in a range between 10° and 80° . Scanning electron microscopy (SEM) images were obtained by using a Hitachi S4800 scanning electron microscope operated at 10 kV. The transmission electron microscopy (TEM) images were carried out on JEM model 100SX electron microscopes (Japan Electron Co., Ltd.). Nitrogen adsorption-desorption isotherms were carried out with a Micromeritics TriStar II 3020 adsorption analyzer at 77 K. The electrochemical analysis was obtained with CR2016 coin-type half cells that were assembled in an Ar-filled glove box. The working electrode was fabricated in N-

methyl-2-pyrrolidinone (NMP) by medley active materials, acetylene black, and polyvinylidene fluoride (PVDF) in a ratio of 8:1:1 ($w/w/w$). Copper foil, metallic lithium, and polyethylene film (Celgard, 2400) were employed as the collector, counter electrode, and separator, respectively. LiPF_6 (1 M) in the mixed solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in volume ratio) was used as the electrolyte. The galvanostatic charge and discharge were performed on a battery testing system (CT-3008 W-5 V 10 mA, Neware Technology Co., Ltd., P. R. China) at various current densities between 0.01 and 3.0 V (vs. Li^+/Li).

3. Results and Discussion

3.1. Morphologies and Structures of the Samples. As seen in the XRD patterns (Figure 1(a)), the MIL-101(Fe) composites exhibit the diffraction peaks located at $2\theta = 2.7^\circ, 5.0^\circ, 8.9^\circ, 9.5^\circ, 10.6^\circ$, and 16.3° were observed, which was resembled with the existing researches [19]. This indicated that the synthesized powder is high-purity crystal. Figure 2(b) displays the XRD pattern of the calcined product; all the dominated diffraction peaks could be assigned to the hematite Fe_2O_3 (JCPDS No. 33-0664); besides, some weak diffraction peaks are indexed to Fe_3O_4 (JCPDS No. 65-3107) [10, 20].

As shown in the SEM and TEM images in Figure 2(a), MIL-101(Fe) exhibited a regular octahedron shape with a rough surface, and the average size is about 600 nm. After being annealed under an ambient atmosphere, sponge-like porous Fe_2O_3 nanomaterials with a diameter of ~600 nm were obtained, shown in Figure 2(b).

The porosities of the nanocomposites were further calculated by N_2 adsorption-desorption isotherms at 77 K shown in Figure 3. The sample shows a type IV isotherm, suggesting microporous material with mesoporous formed by close-packed nanoparticles. The Brunauer-Emmett-Teller (BET) pore volume and surface area of the product were calculated to be $0.288 \text{ cm}^3 \text{ g}^{-1}$ and $99.8 \text{ m}^2 \text{ g}^{-1}$, respectively. Furthermore, the pore size is around 8 nm by using the Barrett-Joyner-Halenda (BJH) method.

3.2. Electrochemical Performance. Subsequently, we evaluated the lithium storage properties of the prepared samples as anode materials in LIBs (Figure 4). The electrode exhibits good performance, giving capacities of 1358 mA h g^{-1} in the first cycle at a current density of 100 mA g^{-1} , and shows very stable capacity retention of 750 mA h g^{-1} for over 80 cycles. What is more, from the second cycle onwards, the coulombic efficiency remains nearly 100%, which indicates an excellent reversible capacity of this electrode material. The good cycling stability may be attributed to the nanosized structure and presence of the porous architecture, which lead to an increase in the electrode/electrolyte contact area and help to accommodate the strain of Li^+ insertion/extraction [21].

4. Conclusions

In summary, porous sponge-like Fe_2O_3 nanomaterials have been successfully fabricated by a facile method. The as-

FIGURE 1: XRD patterns for (a) as-prepared MIL-101(Fe) and (b) the calcined product.

FIGURE 2: (a) SEM and TEM image of MIL-101(Fe). (b) SEM image of the calcined product.

FIGURE 3: N_2 adsorption-desorption isotherms of the calcined product at 77 K.

prepared products demonstrate superior lithium storage properties (1358 mA h g^{-1} at 100 mA g^{-1} in the initial cycle and 750 mA h g^{-1} after 80 charge/discharge cycles) mostly

due to the nanosized and porous structure, which substantially facilitate electronic/ionic transport and afford good structural stability upon cycling. This work provides a cost-

FIGURE 4: Cycling performance and corresponding coulombic efficiency at a current density of 100 mA g^{-1} .

effective route for the synthesis of porous materials; we hope it can also be expanded to other materials in a wider field.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Authors' Contributions

Chunyan Zhang and Nianqiao Qin contributed equally to this work.

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