Biomorphic combustion synthesis of hematite porous structure with enhanced Li storage properties

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ABSTRACT

Uniform porous Fe_2O_3 nanostructure was prepared by a facile and effective biomorphic combustion synthesis. Porous Fe_2O_3 nanostructure is assembled by primary nanoparticles and lots of open pores between interconnected nanoparticles. As an anode material for the lithium-ion batteries (LIBs), the resultant porous Fe_2O_3 electrode shows high specific capacity and good cycle stability (891.8 mAh g^{-1} at 200 mA g^{-1} up to 150 cycles), as well as enhanced rate capability. The excellent electrochemical performance can be attributed to 3D porous structure with the short pathway for the diffusion of Li$^+$, high interfacial contact area between the nanoparticles and electrolyte, and good accommodation of structural stress.

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1. Introduction

Recently, 3d transition metal oxides have been widely investigated as promising anodes in the field of LIBs since they were firstly proposed by Tarascon et al. [1]. They possess much higher capacities (two or three times) than that of graphite, and smaller volume change during the charge-discharge process than that of alloy anodes, which will hopefully realize the wide application of LIBs in various fields such as electric vehicles, military, and the like [2–4]. Among them, iron oxide, such as hematite (α-Fe_2O_3), has gained much attention due to its high theoretic capacity (1007 mAh g^{-1}), non-toxicity, natural abundance, and low cost. Despite its many advantages, Fe_2O_3 suffers from low electrical conductivity, large volume expansion during the conversion reaction process, thus resulting in large irreversible loss, poor electrochemical performance and limiting its wide practical application [5]. These issues can partially overcome by developing different nanostructures, which is an effective strategy to ameliorate the electrochemical capability for their large surface area, the sufficient contact between active material and electrolyte, and the short Li ion diffusion path.

In this work, we used a facile and high-efficiency biomorphic combustion synthesis to prepare porous Fe_2O_3 nanostructure with cotton as template. It should be noted that this synthetic process meets the demand of the green and sustainable modern industry and is more suitable for large-scale production. Compared to many other methods, this biomorphic combustion synthesis requires less complicated reactants and synthetic conditions, which are more attractive with respect to both cost and scalability. In the as-prepared sample, the primary Fe_2O_3 nanoparticles form a secondary structure, resulting in an organized 3D porous nanostructure. While the small dimensions of the primary nanoparticles make ionic and electronic transport much easier, the secondary porous structure can well accommodate the strain associated with Li$^+$ intercalation and the volume expansion of active materials. Thus, as the anode material for LIBs, the porous Fe_2O_3 nanostructure shows greatly enhanced electrochemical performance.

2. Experimental

Porous Fe_2O_3 structure was synthesized via a cellulose combustion method. 40.4 g $Fe(NO_3)_3 \cdot 9H_2O$ was dissolved in 100 mL of ethanol with stirring, into which clean cotton was soaked for 4 h. Then the wet cotton was directly put into a chamber furnace which was pre-heated to 500 °C in air, and treated at this temperature for 1 h to obtain the porous Fe_2O_3 structure.

The morphology and microstructure of products were characterized using X-ray diffractometer (XRD, Rigaku D/max 2550 PC, Cu K$_\alpha$), scanning electron microscope (SEM, Hitachi S-4700) and transmission electron microscope (TEM, JEM 200CX at 160 kV and Tecnai G2 F30 at 200 kV).

The electrochemical measurements were performed using a coin-type half cell (CR 2025). The slurry consisted of 85 wt% Fe_2O_3, 10 wt% acetylene black and 5 wt% polyvinylidene fluoride (PVDF)

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was pasted on copper foil. Test cells were assembled in an argon-filled glove box with the metallic lithium foil as both the reference and counter electrodes, 1 M $LiPF_6$ in ethylene carbonate (EC)-dimethyl carbonate (DME) (1:1 in volume) as the electrolyte, and a polypropylene (PP) micro-porous film (Cellgard 2300) as the separator. The galvanostatic charge-discharge tests were conducted on LAND battery program-control test system in the voltage range of 0.01–3.0 V (versus Li/Li^+) at room temperature (25 ± 1 °C). Cyclic voltammetry (CV) was performed on CHI660C electrochemical workstation.

3. Results and discussion

SEM, TEM and powder XRD were used to analyze the morphology and crystallinity of as-prepared porous Fe_2O_3 nanostructure. In Fig. 1a, the sample shows a 3D porous matrix rather than the morphology of the original cotton fibers, which is ascribed to the combustion method. Combustion synthesis involves an exothermic and self-sustaining chemical reaction, resulting in the collapse of the original fibrous structure of the cotton [6]. The relatively high-magnification SEM image is shown in Fig. 1b. Porous Fe_2O_3 nanostructure contains primary particles of about 100 nm in diameter, and these primary particles form a 3D porous matrix. The detailed morphological and structural features of the powder are also examined by TEM. Fig. 1c further confirms the 3D porous nanostructure. There are lots of open pores ranging from 20–100 nm between interconnected nanoparticles. The HRTEM image in the inset shows well-resolved atomic lattice fringes with

adjacent lattice planes of 0.25 nm, which is in good agreement with the value of the (110) plane of rhombohedral Fe_2O_3. The crystal structure of sample is analyzed by XRD analysis in Fig. 1d. All the diffraction peaks confirm that the crystal structure is in agreement with the standard values for the rhombohedral phase of Fe_2O_3 [JCPDS Card no. 33-0664].

The Li storage capability of porous Fe_2O_3 nanostructure is fully characterized to demonstrate its potential use as anode for LIBs. The CV collected at a scan rate of 0.1 mV s^{-1} is shown in Fig. 2a. During the first discharge process, there is one large cathodic peak located at 0.71 V, along with a very small peak centered at 1.5 V. The small peak indicates the intercalation of Li into the crystal structure of the Fe_2O_3 nanostructure. The strong peak at 0.71 V can be attributed to the complete reduction of Fe^{3+} to Fe^0 and the irreversible decomposition reaction of electrolyte. During the anodic polarization process, two peaks are present at 1.63 and 1.84 V, corresponding to the oxidation of Fe^0 to Fe^{2+} and further oxidation to Fe^{3+}. During the second cycle, the full lithiation voltage shifts to 0.92 V, which is higher than that in the first cycle (about 0.71 V). It is probably due to the reduced polarization of the porous Fe_2O_3 electrode resulting from a microstructural alteration after the first lithiation [7]. Fig. 2b shows typical discharge and charge voltage profiles of the first two cycles at 200 mA g^{-1}. During first discharging process, a poorly defined plateau (1.2–0.9 V) and a perfect one at about 0.85 V are observed, which are in agreement with the CV results. The two plateaus are followed by a continuous sloping curve down to the cut voltage of 0.01 V. The first discharge capacity of porous Fe_2O_3 electrode is 1195.5 mAh g^{-1}, whereas the first charge capacity is
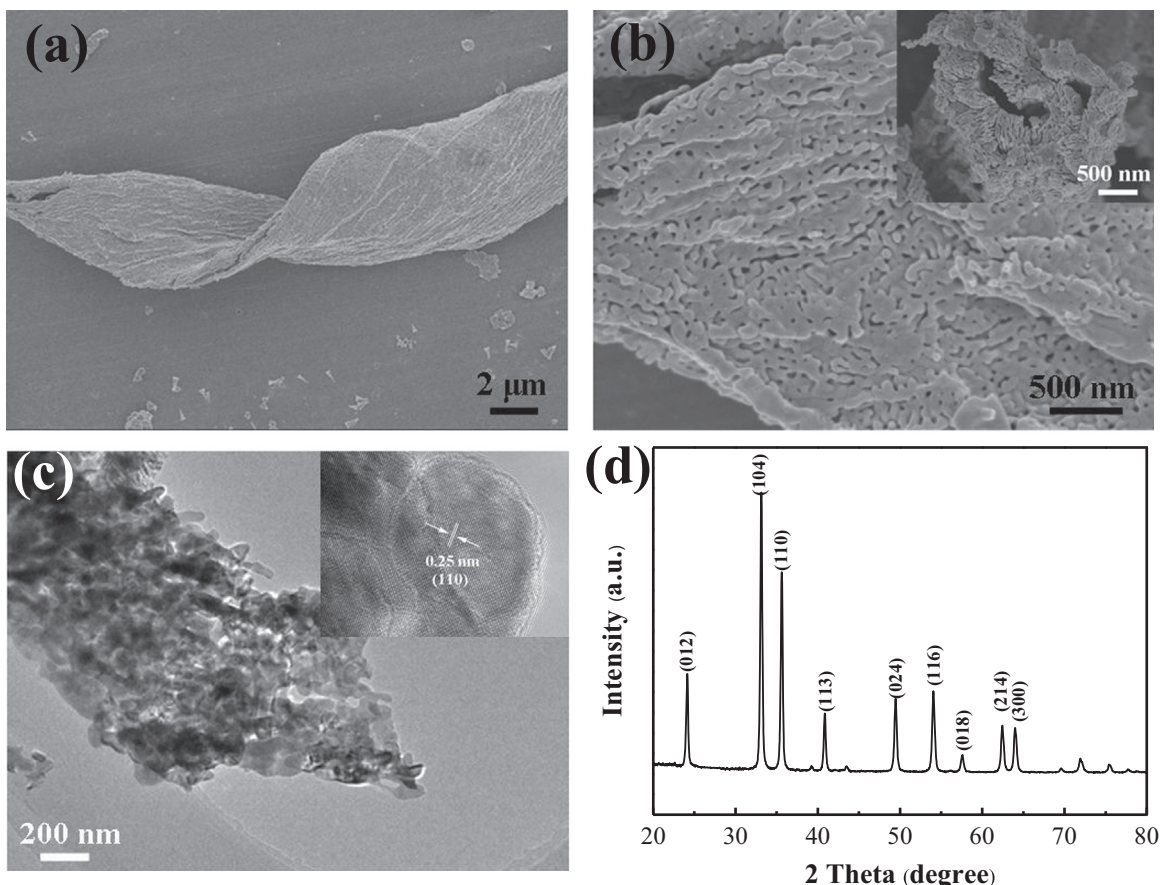

Fig. 1. Morphology and crystallinity characterization of porous Fe_2O_3 nanoparticles: (a,b) SEM images; (c) TEM image, with HRTEM image (inset); (d) XRD pattern.