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Solvothermal preparation and lithium storage properties of Fe_2O_3/C hybrid microspheres

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ABSTRACT

In this paper, we reported a one-pot method to synthesize Fe_2O_3/C hybrid microspheres via a solvothermal approach for the first time. Only peaks of Fe_2O_3 could be observed from X-ray diffractometry (XRD) patterns, indicating that the carbon in the composite was amorphous. The content of carbon in the composite was 64.2 wt% as calculated according to the elemental analysis. Field-emission scanning electron microscope (FE-SEM) and transmission electron microscopy (TEM) images showed that the surfaces of these as-prepared spheres were relatively smooth and of about 2.0 μm in diameter. Electrochemical property demonstrated that the annealed Fe_2O_3/C hybrid microspheres possessed higher reversible capacity and cycling stability than that of Fe_2O_3 nanoparticles. The annealed Fe_2O_3/C hybrid microspheres exhibited a large initial discharge capacity of 1562 mAh g^{-1}, and the stabilized capacity was as high as 889 mAh g^{-1} after 30 cycles. These improvements can be ascribed to the amorphous carbon, which can enhance the conductivity of Fe_2O_3, suppress the aggregation of active particles, and increase their structural stability during cycling.

1. Introduction

Nanostructured transition metal oxides have received great interest in lithium-ion battery [1–11]. The electrodes made of transition metal oxides (MO, where M is Co, Ni, Cu, or Fe) demonstrated high electrochemical capacities of 700 mAh g^{-1}, great capacity retention, high recharging rates, and they can offer a promising carbon alternative to negative-electrode materials in lithium-ion batteries [1,2].

Although these nanostructured transition metal oxides are so attractive because of their high capacities, their commercial use is still hindered. The most critical problem is their large specific volume change, resulting in the aggregation of small particles into larger particles in the host matrix during the insertion and deinsertion of Li [3–7]. This causes rapid anode disintegration under the induced mechanical stress and capacity fading upon cycling [8–11]. It was reported that the cycling performance of SnO_2 [12–14], CoO [15], NiO [16,17] and Fe_2O_3 [18–20] had been significantly enhanced by forming composite with carbon. The carbon can act as a barrier to suppress the aggregation of active particles and thus increase their structural stability during cycling [12–20], and also act as a buffering matrix to relax the expansion that occurred within the electrode upon lithiation/delithiation process [12–20]. Furthermore, the carbon has a high electronic conductivity and it can improve the conductance of the active materials [12–20].

In this present work, we reported a one-pot method to synthesize Fe_2O_3/C hybrid microspheres via a solvothermal approach for the first time. Field-emission scanning electron microscope and transmission electron microscopy images showed that the surfaces of these as-prepared spheres were relatively smooth and of about 2.0 μm in diameter. Electrochemical performance demonstrated that the resulting annealed Fe_2O_3/C hybrid microspheres possessed much higher reversible capacity and cycling stability than that of Fe_2O_3 nanoparticles. The first discharge capacity of the annealed Fe_2O_3/C hybrid spheres was 1562 mAh g^{-1}, which was much higher than that of the as-prepared Fe_2O_3/C hybrid spheres (1024 mAh g^{-1}) and Fe_2O_3 nanoparticles (1005 mAh g^{-1}) previously reported in the literatures [3]. The specific capacity after 30 cycles for the annealed Fe_2O_3/C hybrid spheres was 889 mAh g^{-1}, which suggesting its excellent cyclical performance. The carbon filled in the composite formed a conductive network and also increased the structural stability of active particles during cycling, thus enhancing the capacity retention properties.

2. Experimental

2.1. Material preparation

In a typical synthesis, 0.27 g $FeCl_3\cdot6H_2O$ (AR) was added to 18 mL of distilled ethanol. Then 0.198 g glucose was added to the above solution. The resulting solution was transferred to a 22-mL Teflon-lined autoclave and stored at 180 °C for 24 h, then air-cooled to room temperature. The product were washed several times with

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distilled ethanol, and finally dried at 60 °C in a vacuum-oven. The products were donated as the as-prepared Fe_2O_3/C hybrid microspheres. Subsequently, the as-prepared sample which prepared via solvothermal reaction was annealed in the tube furnace at 800 °C in a high purity nitrogen atmosphere under ambient pressure. Then the furnace was naturally air cooled to room temperature under the protection of purity nitrogen atmosphere. The final products were donated as annealed Fe_2O_3/C hybrid microspheres.

2.2. Material characterization

X-ray diffraction (XRD) patterns of the products were recorded on a X-ray diffractometer (MAC Science Co. Ltd. MXP 18 AHF) with monochromatized Cu Kα radiation (λ = 1.5406 Å). Field-emission scanning electron microscope (FE-SEM, JSM-5600) was used to characterize the morphology of microspheres. Transmission electron microscopy (TEM) was performed on a transmission electron microscopy (Philip CM 120) unit at an accelerating voltage of 120 kV. The samples for TEM were prepared by dispersing the final powders in ethanol; the dispersion was then dropped on carbon-copper grids. Thermogravimetric measurement was conducted on a TGA 2050 analyzer under an air-flow of 100 mL/min with a heating rate of 10 °C/min from room temperature to 800 °C.

2.3. Electrochemical measurements

Electrodes were prepared by coating a copper foil substrate with the slurry of the Fe_2O_3/C hybrid microspheres (80 wt%), carbon black (10 wt%), and poly (vinylidene fluoride) (10 wt%) dissolved in cyclopentanone. After coating, the slurry was dried at 100 °C for 12 h and then pressed between two stainless steel plates at 1 MPa. Prior to cell assembling, the electrodes with area of 0.64 cm^2 were dried at 120 °C for 4 h under vacuum. The testing cells had a typical three-electrode construction using lithium foils as both counter electrode and reference electrode, and 1 M $LiPF_6$ dissolved in ethylene carbonate (EC), dimethyl carbonate (DMC) and ethylene methyl carbonate (EMC) (1:1:1, v/v/v) as the electrolyte. The cells were assembled in an argon-filled glove box. Charge–discharge tests were carried out at a constant current density of 50 mA g^{-1} in a range of 3.0–0.01 V versus Li/Li^+. All the tests were performed at room temperature.

3. Results and discussion

Fig. 1 shows thermogravimetric curve of the as-prepared Fe_2O_3/C hybrid microspheres prepared via the solvothermal reaction. From TGA measurements, it is seen that the final products decomposes in two steps. The first step occurs between 100 and 250 °C in the TGA curve, the weight loss in this step was 4.7%. The weight loss could be attributed to the evaporation of physically absorbed water and residual solvent in the samples. In the second step, a gradual continuous mass loss takes place from 250 to 800 °C, the weight loss in this step was 47.5%, duo to the more water molecule was released, the iron hydroxide decomposed into iron oxide and water, and the oxidation of amorphous carbon.

The crystal structures of the resulting products were examined by X-ray diffractometry (XRD). Fig. 2 shows the typical XRD patterns of as-prepared and annealed Fe_2O_3/C hybrid microspheres. Fig. 2a reveals the amorphous nature of the as-prepared sample. This amorphous sample could be transferred into crystalline materials after annealing in nitrogen atmosphere. Obviously, annealing temperature affected the samples crystallization. Higher the annealing temperature resulted in higher the crystallinity of iron oxide in the annealed sample. After thermally treated at 800 °C in N_2 atmosphere, the crystallinity of the resulting sample has been improved significantly (Fig. 2b). The diffraction peaks of the annealed sample can be indexed to Fe_2O_3 (JCPDS File No. 2-915). The diffraction patterns were observed at 2θ = 33.2, 35.7, 40.8, 49.5, 54.2, 62.4, and 64.2° and were assigned as (1 0 4), (1 1 0), (1 1 3), (0 2 4), (1 1 6), (2 1 4), (3 0 0) reflections. Some peak intensity of the samples are weak, indicating there are impurities in the samples, because Fe_2O_3 can be easily reduced to Fe_3O_4 in the presence of carbon at high temperatures. Only peaks of Fe_2O_3 could be observed, indicating that the carbon in the composite was amorphous. EDS analysis of the as-prepared sample confirmed the existence of carbon, the substrate of test is conductive adhesive. The content of carbon in the composite was 64.2 wt% as calculated according to the elemental analysis.

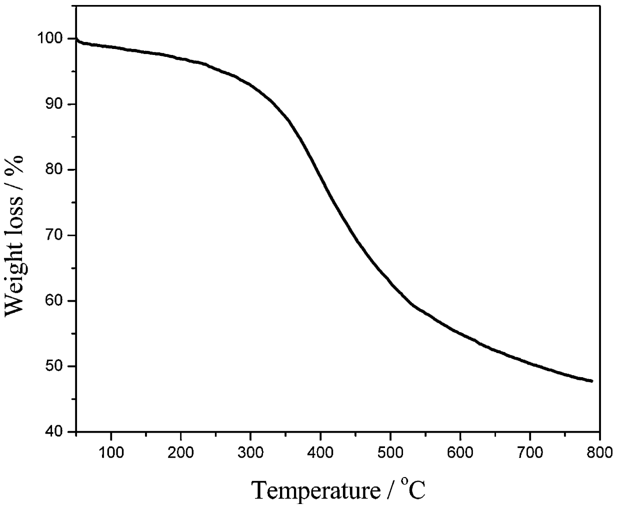

Fig. 1. Thermogravimetric curve of the as-prepared Fe_2O_3/C hybrid spheres.

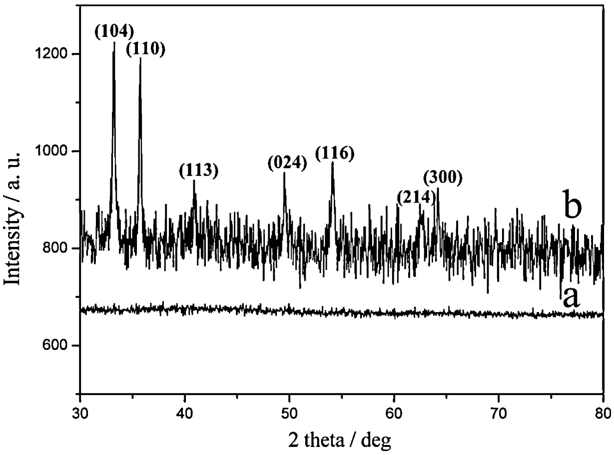

Fig. 2. XRD patterns of the as-prepared (a) and annealed (b) Fe_2O_3/C hybrid spheres.

The morphologies of the resulting samples were investigated by field-emission scanning electron microscope and transmission electron microscopy. We found the as-prepared sample consisted of spherical particles (Fig. 3a). The sizes of these spheres were relatively uniform. Their diameters were in the range of 1.2–2.8 μm. The surfaces of these spheres were relatively smooth. A typical TEM image (Fig. 3b) further confirms the spherical morphology of the as-prepared sample. Fig. 4 shows the FE-SEM and TEM images of Fe_2O_3/C hybrid microspheres after annealing in nitrogen atmosphere at 800 °C. The spherical morphology and the diameter were kept well after being annealed at 800 °C (Fig. 4a). However, their surfaces became rough. Fig. 4b further confirms the spherical morphology of the annealed Fe_2O_3/C hybrid materials. It is different from the previous study reported by Sun [21], they have obtained oxides@C core–shell structures with carbonaceous polysaccharide shells and oxides cores via one-pot hydrothermal method. But in our study, the core–shell structures were not observed on the basis of TEM, suggesting that Fe_2O_3 nanoparticles were homogeneously distributed in the carbon spherical matrix [15].

It is well known that Fe_2O_3 and hard carbon from glucose are all lithium storage materials. The iron oxide nanoparticles have a theoretical specific capacity of 1005 mAh g^{-1} [3], which was much higher than that of already-commercialized graphite (about 350 mAh g^{-1}) [19]. The mechanism of the reaction with lithium of transition-metal oxides differs from the classical mechanisms, which are based either on reversible insertion/deinsertion

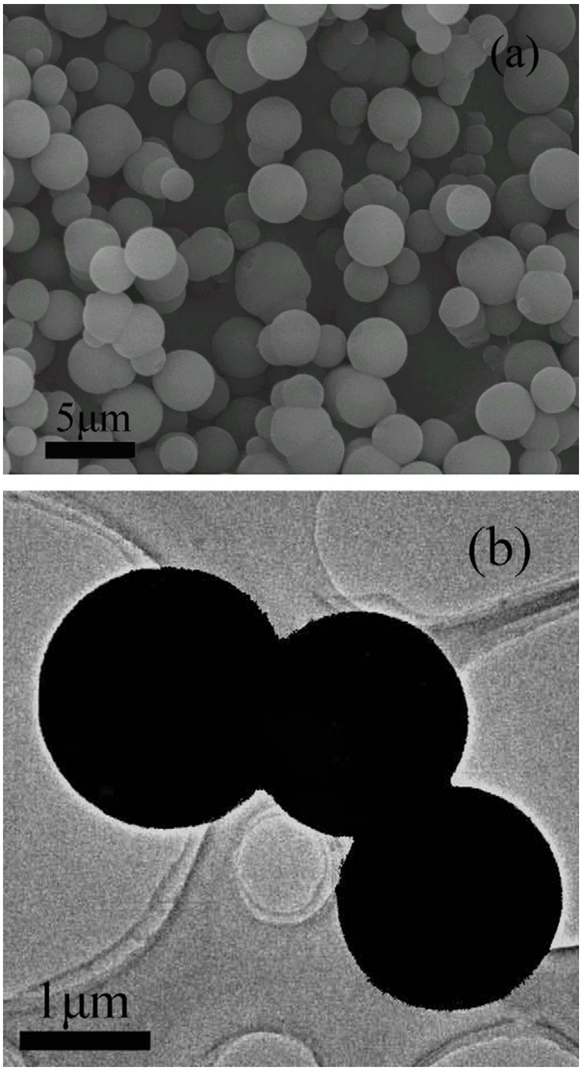

Fig. 3. FE-SEM (a) and TEM (b) images of the as-prepared Fe_2O_3/C hybrid microspheres.

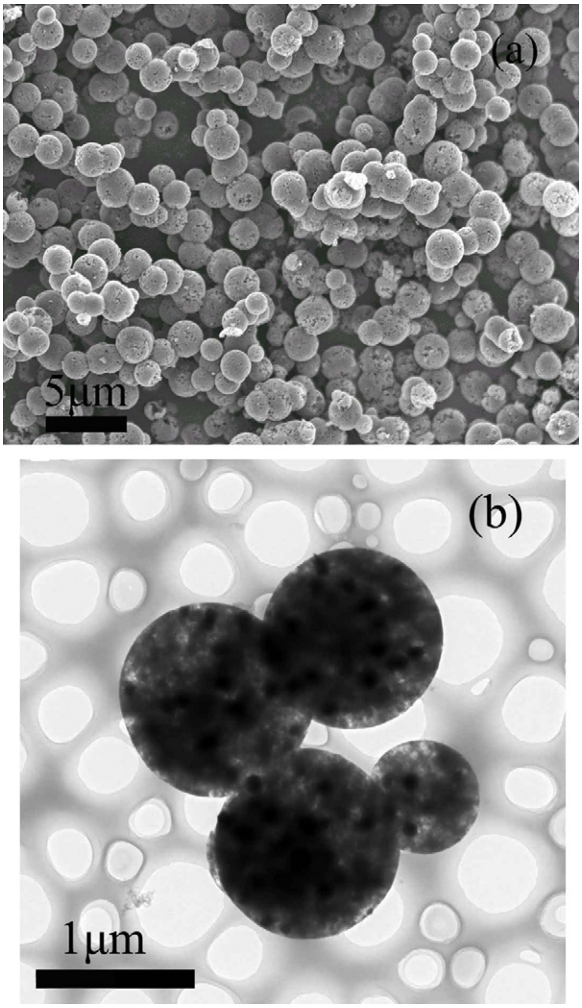

Fig. 4. FE-SEM (a) and TEM (b) images of the annealed Fe_2O_3/C hybrid spheres.

of lithium into host structures or on lithium alloying reactions. This difference lies in the fact that most of these materials crystallize in a rock-salt structure that does not contain any available empty sites for Li ions [15]. The electrochemical reaction mechanism of Li with iron oxide in lithium-ion batteries can be described as follows [19]:

$$Fe_2O_3 + 6Li^+ + 6e^- \leftrightarrow 3Li_2O + 2Fe$$

This implies the reversible formation and decomposition of Li_2O. The utility of the electroactive material Fe_2O_3 would be restricted by its low electric conductivity. The carbonaceous matrix from glucose and the addition of carbon black used as the conducting agent could promote the conductivity of the electrode and the utility of the electroactive material.

The initial discharge–charge curve of the as-prepared and annealed Fe_2O_3/C hybrid microspheres at the current density of 50 mA g^{-1} is shown in Fig. 5. In the first cycle, the discharge and charge capacity of the annealed Fe_2O_3/C hybrid spheres were 1562 and 925 mAh g^{-1}, the coulombic efficiency was 59.2%. The discharge and charge capacity of the as-prepared Fe_2O_3/C hybrid spheres for the first cycle were 1024 and 659 mAh g^{-1}, respectively. The discharge capacity of the annealed Fe_2O_3/C hybrid spheres (1562 mAh g^{-1}) was much higher than that of the as-prepared Fe_2O_3/C hybrid spheres (1024 mAh g^{-1}) and Fe_2O_3 nanoparticles (about 1005 mAh g^{-1}) previously reported in the literatures [3]. The large irreversible capacity (637 mAh g^{-1}) of the annealed Fe_2O_3/C hybrid spheres in the first cycle may be caused by the decomposition of the electrolyte on the surface of the active materials to form a passivation layer on the electrode. This assumption

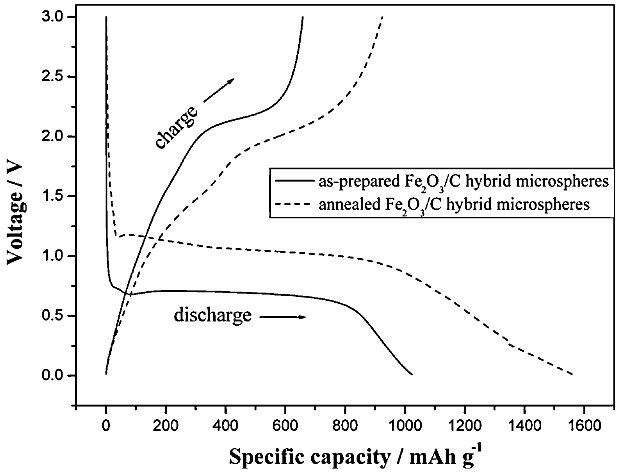

Fig. 5. The initial discharge–charge curve of the as-prepared and annealed Fe_2O_3/C hybrid microspheres at the current density of 50 mA g^{-1}.

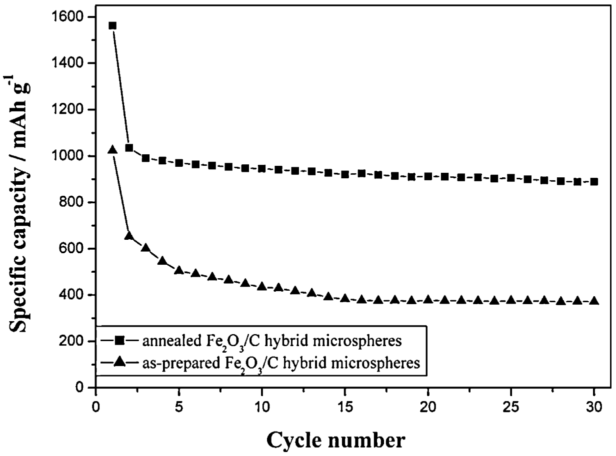

Fig. 6. The cyclic performance of the as-prepared and annealed Fe_2O_3/C hybrid microspheres at the current density of 50 mA g^{-1}.

has already been confirmed in the previous work [14,15]. The cyclic performance of the as-prepared and annealed Fe_2O_3/C hybrid microspheres electrodes is shown in Fig. 6. From Fig. 6, we can see that the annealed Fe_2O_3/C hybrid spheres exhibited much better cyclical performance than that of the as-prepared Fe_2O_3/C hybrid spheres. The specific capacity after 30 cycles for the annealed Fe_2O_3/C hybrid spheres electrode was 889 mAh g^{-1}. This value was much higher than that of the as-prepared Fe_2O_3/C hybrid spheres electrode (372 mAh g^{-1}) and Fe_2O_3 nanoparticles (405 mAh g^{-1}) previously reported in the literatures [22]. There are several reasons accounting for the better cycling performance of the annealed Fe_2O_3/C hybrid spheres. First, the annealed Fe_2O_3/C hybrid spheres have a high crystallization, resulting in the reduction of the lattice defects, which facilitates the lithium ions insertion and extraction [23]. Second, the amorphous carbon in the composites can act as a barrier to suppress the aggregation and pulverization of the active particles during cycling, thus increasing their structural stability [12,24]. In addition, the Fe_2O_3 itself is poor conductive and a poor conductive SEI film will also form during the cycling. The SEI film is a gel-like polymer, which contains LiF, Li_2CO_3, and lithium alkyl carbonate ($ROCO_2Li$) [25], so more SEI will lead to poorer conductivity. The carbon itself has a high electronic conductivity and it can improve the conductivity of the Fe_2O_3 nanoparticles [16–20]. Furthermore, the carbon with high electronic conductivity coated on the shell of the spheres, is able to keep the Fe_2O_3 particles in the spheres electrically connected and thus facilitate the charge transfer in the interface and in the inner of the spheres.

4. Conclusions

In this study, we reported a one-pot synthesis of Fe_2O_3/C hybrid microspheres via a solvothermal approach for the first time. Only peaks of Fe_2O_3 could be observed from X-ray diffractometry patterns, indicating that the carbon in the composite was amorphous. Field-emission scanning electron microscope and transmission electron microscopy images showed that the surfaces of these as-prepared spheres were relatively smooth and of about 2.0 μm in diameter. Electrochemical performance revealed that the annealed Fe_2O_3/C hybrid spheres exhibited much higher reversible capacity and better cycling performance than that of Fe_2O_3 nanoparticles. These improvements are attributed to the carbon, which can enhance the conductivity of Fe_2O_3, suppress the aggregation of active particles, and increase their structural stability during cycling. The excellent electrochemical performances make the annealed Fe_2O_3/C hybrid spheres a promising an anode material for high-power lithium-ion batteries.

Acknowledgements

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