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Preparation of core–shell porous magnetite@carbon nanospheres through chemical vapor deposition as anode materials for lithium-ion batteries

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ABSTRACT

Monodispersed core-shell porous Fe_3O_4@C nanospheres are prepared through hydrothermal treatment and subsequent chemical vapor deposition (CVD). Specially, the magnetite reduction and carbon coating are completed via CVD simultaneously and the process is verified by X-ray diffraction, scanning electron microscope and transmission electron microscope. Fe_3O_4@C composites exhibit high reversible capacity (~1100 mA h g^{-1} at 100 mA g^{-1} after 60 cycles), excellent cyclic stability and good rate performance. The carbon coating layer serves as a highly conducting framework and provides a flexible space for buffering strain and stress, and the pores facilitate ion transport during electrochemical cycling. More importantly, the core-shell Fe_3O_4@C composite is connected by carbon to form a three-dimensional network, which contributes to the relief of inner strain and the fast transport of electrons and lithium ions.

1. Introduction

Nowadays, lithium ion batteries (LIBs) have been applied to various portable electronics such as laptops and mobile phones, and they are highly expected to meet demands of electric vehicles (EV) and smart grids [1–5]. Specifically, anode materials for LIBs play essential roles of high specific capacity, long cycling life, and good safety. As the widely commercialized LIB anode, graphite has the theoretical capacity of only 372 mA h g^{-1} [5], which is difficult to satisfy the EV need. Meanwhile, transition metal oxides (such as Fe_2O_3 [6], Co_3O_4 [7], and MnO_2 [8]) have attracted much attention because of their intriguing properties (i.e., low cost, environment friendliness, high theoretical capacity, and abundant resource) as promising LIB anode materials. In particular, various reports on Fe_2O_3 [9,10] and Fe_3O_4 [11,12] emerged successively and displayed good electrochemical performances regarding anode materials for LIBs. Compared with Fe_2O_3, magnetite (Fe_3O_4) exhibits better electrical conductivity, although it shows slightly lower theoretical capacity (928 mA h g^{-1}) than Fe_2O_3 (1007 mA h g^{-1}) [10,13,14]. In spite of its intriguing properties mentioned above, Fe_3O_4 encounters poor cycling performance and low rate capability due to large volume changes upon cycling and innate kinetic restrictions [15–18].

To solve these issues, many efforts have been made to confine volume expansion by decreasing particle size [16,19–21], controlling morphology [15,22–24] and fabricating Fe_3O_4@C core–shell nanostructures [15,25–28]. Especially synthesizing Fe_3O_4 composites with graphene and carbon coating is expected to maintain the integrity of electrodes and improve the electrical conductivity. First of all, graphene is widely utilized to enhance electrical conductivity of Fe_3O_4-based composites but the preparation processes are rather complicated [15,29]. On the other hand, the general method (hydrothermal method) for carbon coating on Fe_3O_4, conducted by using glucose as the carbon source, suffers from long-time procedures (10–27 h) including hydrothermal process and thermal treatment [24,30–35]. In general, these carbon coating processes are complicated, time-consuming and of low yield. In contrast, chemical vapor deposition (CVD) is a facile method of modifying LIB electrode materials in terms of simple and timesaving procedures [33]. Up to now, there have been only a few reports employing CVD to prepare magnetite/C composites as anode materials for LIBs. For example, Ma et al. [25] and Wang et al. [33] prepared Fe_3O_4@C nanoparticles through this method and

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these materials exhibited a reversible capacity of $<$1000 mA h g^{-1} at the 50th cycle but showed poor rate capacity. However, coating Fe_3O_4-based materials with carbon through CVD method has rarely achieved for monodipersed nanoparticles [14,36–38], which contribute to excellent contact among active materials. Despite the advances above, achieving monodispersed Fe_3O_4@C nanoparticles with fine shape control and excellent performances still remains a challenge.

In this work, we succeeded to prepare porous monodispersed Fe_3O_4@C nanospheres through the CVD of acetylene by using Fe_2O_3 as the precursor. As for Fe_2O_3, pores formed during the hydrothermal process and calcination process before carbon coating. These pores provide more active sites for lithium ion storage, facilitate the contact between active material and electrolyte, and then interconnected porous nanospheres could shorten the transport path of lithium ions and electrons. Furthermore, note that not only the CVD carbon coating process took only 1 h, but also the iron reduction and uniform carbon deposition on the surface of Fe_2O_3 nanospheres were completed simultaneously within the CVD process. The as-prepared $Fe_3O_{4@C}$ showed excellent electrochemical performances as promising anode materials for LIBs. Importantly, monodispersed nanospheres were almost fully connected by carbonaceous materials, forming the three-dimensional (3D) core-shell network-like structure. The materials displayed high reversible capacity, outstanding cycling stability and excellent high rate performance consequently.

2. Experimental

2.1. Preparation of porous α-Fe_2O_3 nanospheres

α-Fe_2O_3 nanospheres were prepared under hydrothermal condition followed by calcination. Firstly, 10 ml solution composed of 8 mmol iron(III) nitrate was obtained by dissolving ferric nitrate nonahydrate in acetic acid under magnetic agitation at room temperature and then 70 ml ethanol was added to the above solution under vigorous agitation. The solution was transferred into a 100 ml Teflon-lined stainless steel autoclave and was maintained at 180 °C for 20 h. After the autoclave was cooled to room temperature, the resulting deposit was washed by distilled water and ethanol several times, before it was dried under vacuum at 60 °C overnight. Finally, the dried sediments were calcined in air at 400 °C for 5 h (heating rate was 5 °C min^{-1}).

2.2. Preparation of core–shell porous Fe_3O_4@C nanospheres

Fe_3O_4@C composite was prepared through CVD as follows: the as-prepared α-Fe_2O_3 powder was heated to 520 °C (heating rate was 5 °C min^{-1}) in Ar atmosphere, and then a gas mixture (C_2H_2: Ar = 1:9, volume ratio) was infused into the furnace for 30 min continuously. Afterwards, the powder was preserved for 30 min in Ar atmosphere and was cooled to room temperature.

2.3. Materials characterization

The material was characterized by X-ray diffraction (XRD) (Rigaku MiniFlex II) by using Cu Kα radiation (λ = 1.5418 Å). X-Ray photoemission spectroscopy (XPS) was performed on a PHI5000-VersaProbe spectrometer. The morphology and size of as-prepared products were characterized by using field-emission scanning electron microscope (FESEM, JEOL Model JSM-7500F), transmission electron microscope (TEM, JEM100CXII) and high-resolution TEM (HRTEM, FEI Tecnai, Model G2F-20). Thermogravimetric analysis (TGA) was conducted under air by using PTC-10A TG-DTA analyzer from room temperature to 700 °C with a heating rate of 10 °C/min. The specific surface area and porosity of the sample were measured by N_2 adsorption–desorption technique (Quantachrome NovaWin). Raman spectra were obtained on a Renishaw inVia Raman spectrometer with laser excitation length of 514.5 nm.

2.4. Electrochemical measurements

The electrochemical performances of the prepared Fe_3O_4@C and Fe_2O_3 samples were evaluated as anode materials of lithium ion cells with galvanostatic charge/discharge technique. CR2025-type coin cells were fabricated and the working electrode was prepared by dispersing the as-prepared active material, Ketjen black and polyvinylidene difuoride (PVDF) with the weight ratio of 75:15:10 in the solvent of *N*-methyl-2-pyrrolidone (NMP) to form slurry, which was casted on a copper foil subsequently and dried in vacuum overnight. The electrolyte consisted of a solution of 1 M $LiPF_6$ in dimethyl carbonate (DMC), ethylmethyl carbonate (EMC), and ethylene carbonate (EC) (1:1:1 by volume). Celgard 2400 membrane was used as a separator. The galvanostatic discharge/charge tests were conducted in the potential range of 0.01–3 V (vs. Li/Li$^+$) by using LAND-CT2001A battery test system. Cyclic voltammetry (CV) measurements were performed on a Zahner-Elektrik IM6e electrochemical workstation with a potential range of 0.01–3 V (vs. Li/Li$^+$). Electrochemical impedance spectroscopy (EIS) was performed also on the Zahner-Elektrik IM6e electrochemical workstation in the frequency from 10^{-2} Hz to 100 kHz with a signal amplitude of 5 mV. All the above measurements were conducted at room temperature.

3. Results and discussion

3.1. Material characterization

Fig. 1 presents the XRD patterns of as-prepared samples obtained at different stages of the preparation process. All the main peaks of the Fe_2O_3 precursor prepared through the hydrothermal method could be well indexed to hematite phase (JCPDS, Card No. 89-598). After calcination, there are no obvious changes of main peaks in the XRD patterns. Moreover, all the main peaks of Fe_3O_4@C composite match with magnetite phase (JCPDS, Card No. 89-688), which proves the transformation from Fe_2O_3 to Fe_3O_4 after the CVD treatment. XPS was then used to examine the oxidation states of Fe in calcined Fe_2O_3 and Fe_3O_4@C composite. Two distinct peaks at binding energies of ~710.9 eV for Fe2p$_{3/2}$ and 724.4 eV for Fe2p$_{1/2}$ appear in the high-resolution Fe2p spectrum

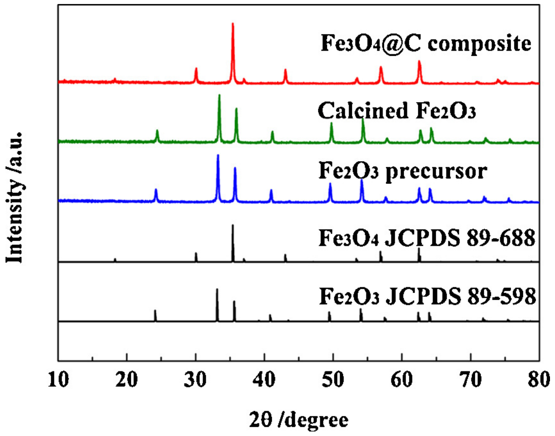

Fig. 1. XRD patterns of Fe_2O_3 precursor, Fe_2O_3 product after calcination and Fe_3O_4@C composite.