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A one-pot approach towards FeF_2–carbon core–shell composite and its application in lithium ion batteries

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ABSTRACT

Core–shell nanorod with FeF_2 as core and graphitized carbon as shell was prepared by a one-pot thermal reaction using a mixture of ferrocene and polyvinylidene fluoride as precursor. The core–shell composite had an average length of about 1 μm and diameter ranging from 100 nm to 1 μm. The shell thickness was about 10–20 nm. Its electrochemical properties were studied in the potential range between 1.3 and 4.2 V at a current density of 30 mA g^{-1} at room temperature. The core–shell composite exhibited an initial discharge capacity of 345 mA h g^{-1}. A reversible capacity of 217 mA h g^{-1} was maintained over 50 cycles with coulombic efficiency of 96% per cycle.

1. Introduction

Lithium ion batteries (LIBs) are important energy storage devices, and they are required with higher energy density for usage in electric/hybrid vehicle and grid scale storage [1]. As the commercial cathode material $LiCoO_2$ or $LiFePO_4$ has a capacity of 150 or 170 mA h g^{-1}, respectively [2–10], the key to improve the energy density of LIBs is looking for electrode materials with high energy density [11–14]. Metal fluoride can store more than one lithium per molecular through a multi-electron conversion reaction, so its theoretical capacity can be very high. Besides, metal fluoride has a high voltage potential brought by high ionicity of M–F bond. However, the high ionicity of M–F bond also leads to a large band gap, which makes metal fluoride poor in conductivity [15]. Among various metal fluoride, FeF_2 has a capacity of 571 mA h g^{-1} and a high electrochemical potential of 2.66 V [15], it is a good candidate for high energy density LIBs. But its wide band gap (3.14 eV) [16] make it suffer from poor conductivity. Fortunately, carbon coating on the particle surface is proved to be effective to enhance the electrical conductivity and buffer the volume change during charge/discharge [17–24], together with particle-size reduction in order to reduce the electronic and ionic transportation distance [25–27]. Armstrong et al. reported the deposition of an amorphous carbon layer onto the surface of FeF_2 material by using $Fe(acac)_3$ as a single source precursor [28], while it is believed that carbon layer with a high degree of crystallinity is beneficial to raise the electrical conductivity. In addition, ferrocene has been used as both an iron and carbon precursor for synthesis of C–Fe–LiF nanocomposites [29,30], and this paves a new way for the introduction of iron and carbon simultaneously.

Here we report on the in situ synthesis of a FeF_2–carbon core–shell composite by a simple procedure based on the thermal decomposition and reaction of a mixture of ferrocene and polyvinylidene fluoride (PVDF). Ferrocene not only serves as a reagent to provide the necessary iron source to form FeF_2, but also involves in the formation of highly graphitized carbon shell around FeF_2 particles. And the composite's electrochemical property as cathode electrode is tested.

2. Experiment details

Ferrocene powder (average size ∼70 mm, from Sinopharm Chemical Reagent Co. Ltd.) and PVDF powder (average polymerization degree of ∼1500, from Shanghai, China) were analytical grade reagents and used as received. First, ferrocene (1 g, 5.37 mmol) and PVDF (0.34 g) were mixed with planetary ball milling for 2 h at 500 rpm. Subsequently, the homogeneous mixture was transferred into a stainless steel reactor. Then the reactor was filled with pure argon and sealed. The detail of the reactor is demonstrated in Fig. S1 and SI-1. Then, the reactor was heated in a

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muffle furnace at a rate of 10 °C/min up to 700 °C. After pyrolysis for 3 h, the reactor was cooled to room temperature naturally. Finally, the product was collected and then subjected to structure and property characterization.

Crystal structure of the as-prepared product was characterized by X-ray diffraction (XRD) using D8 ADVANCE (3 KW) with Cu K radiation. The morphology and structure were investigated by a scanning electron microscope (SEM, JSM-7001F) and transmission electron microscopy (FEI Tecnai G^2 F30). Raman measurement was carried out on a Renishaw RM2000 Confocal Raman Spectrometer with an excitation line of 514 nm.

For electrochemical measurements, as-prepared product was mixed with PTFE in a weight ratio of 9:1 to fabricate cathode. The cell was assembled in an argon filled glovebox with lithium foil as anode and Celgard 2500 film as separator. The electrolyte is a solution of 1 M $LiPF_6$ dissolved in a mixed solvent of ethylene carbonate (EC), dimethyl carbonate (DMC), and ethylene methyl carbonate (EMC) (1:1:1 by volume). Charge–discharge experiments were performed galvanostatically with current density of 30 mA g^{-1} between 1.3 and 4.2 V on battery testers (Land CT2001A). The cells were cycled at room temperature.

3. Results and discussion

3.1. Morphology and structure of the FeF_2–carbon core–shell composite

As-prepared products are soft powder and black in color. Fig. 1 shows the XRD pattern of the as-prepared product. All peaks can be indexed to JCPDS-45-1062, indicating pure tetragonal FeF_2.

Fig. 2 shows typical SEM images, TEM images and EDS spectrum of as-prepared product. SEM images (Fig. 2a and b) shows that the products are short rods with length of about 1 μm and diameter ranging from 100 nm to 1 μm. TEM observations (Fig. 2c and d) further verify that the particles are of core–shell structure. The clearly observable lattice fringes of the core, which correspond to an inter-planar (*d*) spacing of 0.327 nm, can be indexed to the (110) set of planes of tetragonal FeF_2 (JPCDS: 45-1062). The shell layer shows thickness in the range of 10–20 nm. Besides, the interlayer spacing is ~0.34 nm, which is similar to that of graphite. The EDS spectrum (Fig 2e) shows that the core–shell nanoparticles consist of Fe, F and C elements, and the atomic content is 12.8, 25.0 and 62.2 at.%, respectively. To further clarify the structure and chemical composition of the shell layer, its surface was characterized with XPS. The XPS full spectrum, as well as high resolution spectra of Fe 2p and F 1s of the composite (see Fig. S2), shows that the shell is composed of C element (no Fe or F element). Combining with TEM observation, the shell layer is determined to be graphitized carbon.

Raman spectroscopy is also used to further characterize the structure of the composite. The Raman spectrum of the composite shown in Fig. 3 is characteristic of pyrolytic and carbonized carbon shell [31–34]. Two bands locating at 1353 and 1599 cm^{-1} are assigned to the in-plane sp^2 vibration (G-band) and a disorder-induced phonon mode (D-band) of carbon, respectively [35]. The I_D/I_G ratio of the composite is about 0.69. it is well known that a low I_D/I_G ratio means a high sp^2/sp^3 and a high quality carbon [35]. Therefore, such a carbon shell with a good structure is expected useful for enhancing the electronic conductivity and electrochemical performance of the composite. It has been reported that ferrocene decomposes above 400 °C to release iron [36]. And iron nanoparticles can act as catalysts to assist the conversion of amorphous carbon to graphitic structure [37,38]. So it is speculated that the good graphitization of the carbon shell origins from the catalysis effect of iron derived from ferrocene's decomposition.

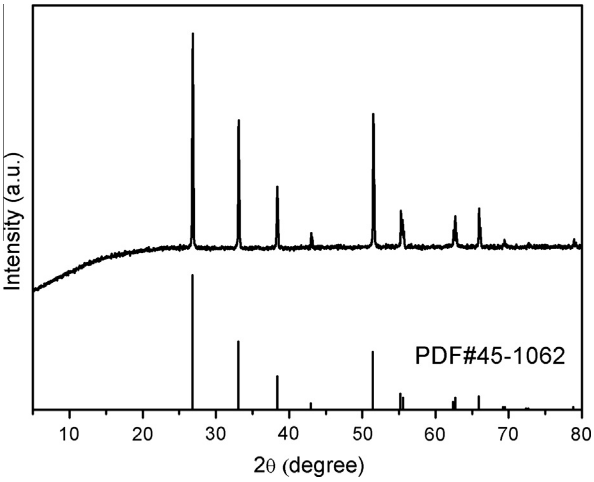

Fig. 1. XRD profile of FeF_2–carbon core–shell composite. The bar makers indicate the standard pattern of FeF_2 (PDF: 45-1062).

3.2. Growth mechanism of the FeF_2–carbon core–shell composite

The core–shell composite was synthesized by a simple one-pot thermal reaction, and the growth process is proposed, as schematically shown in Fig. 4. It can be described as follows: (1) when the temperature increased, ferrocene sublimes and decomposes into Fe, carbon and H_2. Meanwhile, PVDF gradually decomposes to release HF along with the rise of temperature, as studies showed that dehydrofluorination is a typical degradation process of PVDF [39,40], (2) the fresh Fe derived from the thermolysis of ferrocene reacts with HF to form FeF_2 nucleus. At the same time carbon clusters derived from the decomposition of ferrocene and PVDF are adsorbed onto the surface of FeF_2 nucleus, and (3) FeF_2 nucleus gradually grows to large particles, and carbon clusters covers thoroughly around the particles to form carbon shell. During this process, as stated above, Fe can catalyze the graphitization of carbon shell. Thus the FeF_2–carbon core–shell particles are resultantly formed. The H_2 gas leaks out of the reactor when the temperature decreases (see SI-1). In the synthesis, by replacing PVDF with ammonium fluoride (NH_4F) or ammonium hydrogen difluoride (NH_4HF_2), core–shell nanoparticles with spherical morphology can be obtained. In addition, by replacing ferrocene with nickelcene or cobaltcene, NiF_2–carbon or CoF_2–carbon core–shell composites can be synthesized. The related detailed studies are underway.

3.3. Electrochemical performances of the FeF_2–carbon core–shell composite

The electrochemical performance of the FeF_2–carbon core–shell composite as cathode was evaluated. Fig. 5a shows the discharge–charge curves of the composite in the voltage range of 1.3–4.2 V at a current density of 30 mA g^{-1}. During the first cycle, the composite delivers a specific discharge capacity of 345 mA h g^{-1}. The reversible specific charge capacity is 314 mA h g^{-1}, corresponding to an initial coulombic efficiency of 91.1%. The first discharge process can be subdivided into two specific capacity/voltage regions. In the first region, the voltage decreases from open circuit voltage to 1.9 V, corresponding to a specific capacity of 60 mA h g^{-1}. The second region corresponds to a voltage plateau from 1.9 V to 1.3 V. The first region in the initial discharge curve is presumably attributed to the insertion of Li into FeF_2, which occurres in a high potential window of 3.0–2.0 V and involves the formation of $Li_xFe_{1-x}F_2$ [41]. The second region involves the conversion reaction, accompanied by the formation of Fe and LiF. In the following cycles, the plateaus are almost the same except the over potential increasing, which may be attributed to the improvement on conductivity due to generation of iron nanoparticles in the conversion reaction [42]. The voltage platform is lower than the theoretical voltage (2.66 V). The possible reasons are as follows. The thick carbon layer presents a longer diffusion length, thus limiting Li ion