Fe₃O₄/reduced graphene oxide nanocomposite as high performance anode for lithium ion batteries

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ABSTRACT

Fe₃O₄/reduced graphene oxide (Fe₃O₄/RGO) nanocomposite was prepared by a facile interface reaction and subsequent in situ reduction process. The electrochemical performances of the as-prepared Fe₃O₄/RGO nanocomposite were evaluated in coin-type cells. It delivers high reversible capacity of 1025 mAh g⁻¹ at 100 mA g⁻¹ after 50 cycles and outstanding cycle stability. Even after 800 cycles at various rates from 100 to 4000 mA g⁻¹, the capacity still retains 959.4 mAh g⁻¹ at 100 mA g⁻¹. A transmission electron microscopy image has shown the flexible interleaved structure of nanocomposite, and the interface reaction is also benefit to ensure strong interfacial interaction between Fe₃O₄ nanoparticles (50 nm) and RGO nanosheets. The designed structure plays key role in improving electrochemical performance. The Fe₃O₄/RGO nanocomposite with super long cycling life will be an ideal candidate of anode material for lithium ion batteries.

1. Introduction

With the development of lithium ion batteries as promising power source for electrical/hybrid vehicles, the high capacity anode materials with less resistance and higher safety play important role in improving power and energy density for lithium ion batteries [1–3]. Instead of graphite many materials including metal oxide, metal, nonmetal and their composites have been explored. [4,5]. The transition metal oxides (NiO [6], Fe₃O₄ [7–9], Fe₂O₃ [10–12], SnO₂ [13], Co₃O₄ [14], CuO [15], MnO [16,17], TiO₂ [18]) with high theoretical capacity have been widely utilized in various fields, especially lithium ion batteries [19]. But the electrode polarization and the decreased surface area are observed due to the large volume expansion/contraction and the severe aggregation of the nanoparticles during the Li⁺ insertion/extraction process, resulting in capacity fade and poor cycle performance [1,20,21], which limits their application for storage energy system.

Reduced graphene oxide (RGO) nanosheets are very popular anode material due to good chemical stability, excellent electronic conductivity, large specific surface area, and good structural flexibility [3,4,21–23]. But the restacking of RGO is generally caused by a strong van der Waals, leading to loss of their high surface area and intrinsic chemical and physical properties [24,25]. The large irreversible capacity, low initial coulombic efficiency and fast capacity

fading [20] make it not suitable as high performance anode for lithium ion batteries.

More recently, based on relative high theoretical capacity of transition metal oxides and excellent intrinsic chemical and physical properties of RGO nanosheets, transition metal oxides/graphene nanocomposite as anode materials for lithium ion batteries have been widely reported [1–3,20–39]. During the Li⁺ insertion/extraction process, it is not difficult to find that the introduction of RGO can not only mitigate large volume change but also improve the conductivity, and the as-formed transition metal oxides nanoparticles disperse between RGO nanosheets as spacers to prohibit nanosheets restacking. Amongst all transition metal oxides, Fe₃O₄ exhibits good application prospect as anode for lithium ion batteries because of its high abundance, low cost, environmental benignity and relative high electronic conductivity [1,5,20,21]. Then more and more Fe₃O₄/graphene nanocomposite and some relative promising results had been reported previously [1,19–22,26,35–39,27]. However, to meet the requirements of future energy storage systems, achieving high reversible capacity and super long cycling life of Fe₃O₄/graphene electrode material still remains a great challenge.

This paper reports that the Fe₃O₄/RGO nanocomposite is synthesized by a facile interface reaction and subsequent in situ reduction process. Fig. 1 shows the forming mechanism of Fe₃O₄/RGO nanocomposite. The optimized Fe₃O₄/RGO nanocomposite, with uniform morphologies and structures, high crystallography and few impurities, are observed by TEM, XRD, FT-IR, and Raman. The strong interfacial interaction between Fe₃O₄ nanopaticles (50 nm) and RGO nanosheets can protect the whole electrode structure

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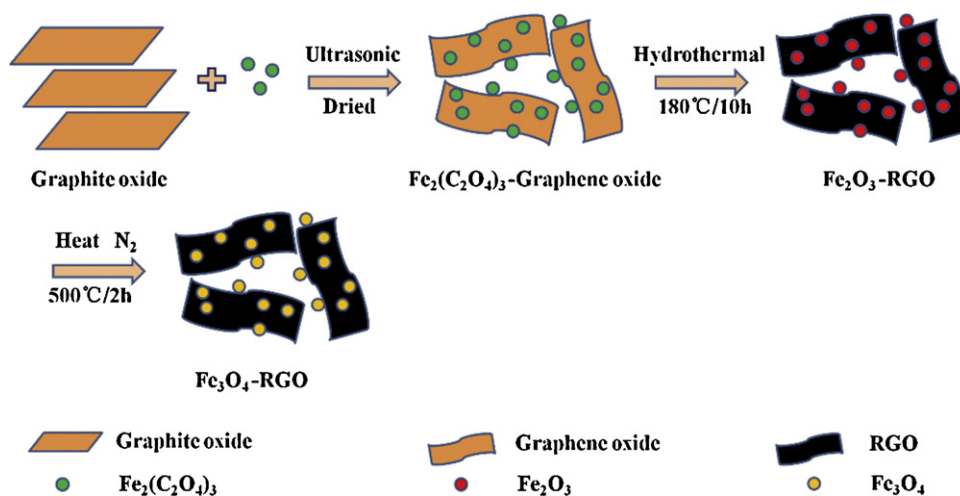 *E-mail address:* jiamq@mail.buct.edu.cn (M. Jia).

Fig. 1. Scheme of Fe_3O_4/RGO nanocomposite forming mechanism.

stability and electrochemical active [27,34]. Then the as-prepared Fe_3O_4/RGO nanocomposite shows high reversible capacity of 1025 mAh g^{-1} and outstanding cycle stability, and will be a potential high-performance anode material for lithium ion batteries.

2. Experimental

2.1. Synthesis of materials

All chemicals were of analytical grade and used as received, without further purification. As shown in Fig. 1, the preparation of Fe_3O_4/RGO nanocomposite could be divided into three steps: first, GO was prepared from natural graphite power by a modified Hummer's method [40], and the obtained GO colloidal suspension could keep a long time at room temperature. Second, in a 100 mL beaker, 40 mL GO (0.2 g) suspension and 50 mL $Fe_2(C_2O_4)_3 \cdot 5H_2O$ (2.33 g, Sinopharm Chemical Reagent Co., Ltd.) solution were put in an ultrasonic bath for 2 h, and the beaker was placed into a 500 mL Teflon-lined autoclave that contained 14 mL of ammonia solution. After hydrothermal treated at 180 °C for 10 h followed by furnace cooling, the 100 mL beaker was directly placed in an oven to dry at 90 °C. Finally, the dried products were calcined in a quartz tube at 500 °C for 2 h under a nitrogen atmosphere to remove the oxygen-containing functional groups of RGO [23,41] and obtain high crystallography Fe_3O_4 nanoparticles. For comparison, free Fe_3O_4 nanoparticles and RGO sheets were prepared directly by $Fe_2(C_2O_4)_3 \cdot 5H_2O$ and GO in a quartz tube at 500 °C for 2 h under a nitrogen atmosphere.

2.2. Characterization

X-ray diffraction (XRD) measurements were conducted on a Rigaku D/max-2500B2+/PCX system using Cu Kα radiation ($\lambda = 1.54056$ Å). Fourier transform infrared spectra (FT-IR, Nicolet Nexus 670) were recorded using pressed KBr pellets to test the chemical bonding of products from 400 to 3200 cm^{-1}. The TGA (TGA/DSC 1/1100 SF) analysis was carried out under an oxygen atmosphere with a heating rate of 10 °C/min, ramping between 25 °C and 1000 °C. The morphologies and structures of samples were characterized by scanning electron microscopy (SEM, SUPRA 55), transmission electron microscopy (TEM, HITACHI H-800) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-3010). In addition, the other information of products was observed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250) and Raman spectra (JY HR800).

2.3. Electrochemical testing

The electrochemical performances of Fe_3O_4/RGO nanocomposite, free Fe_3O_4 nanoparticles, and RGO sheets were tested using CR2032 (0.01–3.00 V) coin-type cell with metallic lithium as counter electrode. The mix of the active mass, acetylene black, and poly (vinylidene difluoride) with a weight ratio of 80:10:10 was dispersed in N-methylpyrrolidone (NMP) solution, and the resultant slurry was then uniformly pasted on a Ni foil current collector. The electrolyte used was a one molar LiPF$_6$ solution in ethylene carbonate/dimethyl carbonate (1:1 v/v). The cells were assembled in an Ar-filled grove box, and tested at various current densities in the voltage range from 0.01 to 3.0 V. Cyclic voltammetry (0.1 mV s^{-1}, 0.01–3.0 V) and AC impedance (5 mV, 100 kHz–0.01 Hz) measurements were carried out on the same electrochemical workstation (CS310).

3. Results and discussion

Fig. 2a shows that the XRD patterns of GO, RGO, Fe_2O_3/RGO nanocomposite and Fe_3O_4/RGO nanocomposite. For pure GO and RGO, the peak at 10.880° disappear after reduction of GO, and the weak and broad reflection peak at 25.6° is corresponding to restacking of RGO sheets, leading to loss of their high surface area and intrinsic chemical and physical properties [24,25]. All characteristic peaks of the Fe_2O_3/RGO nanocomposite are good agreement with Fe_2O_3 crystal (JCPDS File Card No. 33-0664). The Fe_2O_3 nanoparticles can be in situ reduced into Fe_3O_4 crystals due to the emission of CO and the reducibility of carbon material during the heat treatment process [30]. All peaks and intensity of Fe_3O_4/RGO nanocomposite are consistent with face-centered cubic crystal Fe_3O_4 (JCPDS File Card No. 65-3107), and show good crystallinity. In Fig 2b, there are two peaks at 711.3 and 724.3 eV, corresponding to the Fe2p3/2 and Fe2p1/2 spin–orbit peaks of Fe_3O_4, Which indicates the formation of Fe_3O_4 nanoparticles [1,19]. In addition, the RGO (0 0 2) peak in the XRD pattern of Fe_3O_4/RGO nearly vanishes, which suggests that Fe_3O_4 nanoparticles can act as spacer to keep RGO layers separated and form disordered structure [30,31], ensuring large active surface to improve electrochemical performance.

The FT-IR spectra of graphite, GO and Fe_3O_4/RGO nanocomposite are shown in Fig. 3a. For GO, the presence of oxygen-containing functional groups, such as C—O epoxy groups, tertiary C—OH groups, and C=O stretching of carbonyl and carboxyl groups, is due to oxidation of nature graphite. After interface reaction and in situ