



Rapid synthesis of Cr-doped γ -Fe₂O₃/reduced graphene oxide nanocomposites as high performance anode materials for lithium ion batteries



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ABSTRACT

Cr-doped γ -Fe₂O₃/reduced graphene oxide (rGO) nanocomposites are successfully synthesized through a rapid and environmentally friendly microwave method in just 10 min. Under the microwave heating, graphene oxide (GO) is reduced to rGO with ferrous ion (Fe²⁺) served as the reductant, and Cr-doped γ -Fe₂O₃ nanoparticles are synthesized in the meantime. It is found that Cr doping can not only affect the phase of Fe₂O₃, but also has an effect on the morphology, the electrical conductivity and the electrochemical properties. As anode material for lithium ion batteries, the 4.0 at% Cr-doped γ -Fe₂O₃/rGO nanocomposites exhibit the highest reversible capacity of 1060 mAh g⁻¹ after 100 cycles (66.9% of the initial capacity) at a current density of 100 mA g⁻¹. Furthermore, when assembled as a full cell against commercial cathode including LiCoO₂ and LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂, the battery shows promising cycling performance. The superior electrochemical performance could be attributed to the uniform nanostructure and the synergistic effect between Fe₂O₃ and rGO as well as the doping of chromium, which can reduce the size of Fe₂O₃ particles and improve the electrical conductivity.

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1. Introduction

Nowadays with the growing popularity of portable electronic devices and electric vehicles, high performance energy storage devices have been intensively pursued. Lithium ion batteries (LIBs) have drawn a large amount of attention with their high volumetric capacity, long cycle life and environmental friendliness [1–3]. However, the traditional commercialized anode graphite materials of Li-ion batteries have a limited theoretical capacity about 372 mA h g⁻¹. To overcome this issue, an enormous amount of research effort has been dedicated to develop high-performance LIBs with higher capacity, longer lifespan, and enhanced rate capability [4,5]. And it has been proved that transition metal oxides (TMOs), such as MnO₂, Co₃O₄, Fe₂O₃ and Cr₂O₃, can deliver much higher theoretical capacities as anode materials for lithium ion batteries than that of graphite [6,7]. As a typical TMO, iron oxide (Fe₂O₃) is considered as a promising candidate of anode material for lithium ion batteries due to their unique features including high

theoretical capacity (1007 mA h g⁻¹), low cost, quite high abundance of Fe and nontoxicity [8–10]. However, the electrode pulverization, which is caused by the drastic volume changes during Li⁺ insertion/extraction processes, and low conductance considerably limit the practical applications of Fe₂O₃.

To circumvent these obstacles, several feasible strategies have been devoted to improving the electrical conductivity and capacity retention stability of Fe₂O₃ [11] such as nanoscale materials, incorporation of carbon and modification by doping. First of all, reducing the size of Fe₂O₃ to nanoscale, such as nanorods, nanoshells and nanoparticles, can shorten the lithium diffusion pathways, minimize the mechanical stress during the volume changes and enlarge the electrode/electrolyte interfacial area [12,13]. Secondly, it is helpful to construct Fe₂O₃ and carbon hybrid materials which can increase the electrical conductivity, buffer the strain from the volume change and facilitate lithium storage, including Fe₂O₃/graphene, Fe₂O₃/amorphous carbon, and Fe₂O₃/carbon nanotube [14–16]. Among these, graphene has attracted widespread attention as an excellent additive material owing to its large specific surface area, superior mechanical flexibility, high electrical conductivity and high specific capacity [17,18]. Finally, it is found that Ti, Cr, and Ce have been successfully used to modify Fe₂O₃, and

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that adding some metal elements can greatly affect the morphology of Fe_2O_3 and effectively improve the electrical conductivity [19,20]. Chromium (Cr) is a promising additive for Fe_2O_3 to enhance its electrochemical performance owing to the relatively low lithium insertion potential and a high Li-storage theoretical capacity (1058 mA h g^{-1}) [21].

Currently, there are a variety of methods employed to synthesize Fe_2O_3 /graphene hybrid materials. Zhu et al. developed a two-step synthesis of Fe_2O_3 /rGO with hydrazine acted as the reductant, which exhibited discharge capacity of 1027 mA h g^{-1} after 50 cycles at 100 mA g^{-1} [22]. LEE et al. fabricated a nanocomposite comprising Fe_2O_3 nanotubes and rGO through a hydrothermal method with the specific capacitance of 128 F g^{-1} at a current density of 5 A g^{-1} after 200 cycles [23]. Zhu et al. employed microwave method to synthesize Fe_2O_3 /rGO nanocomposites by using hydrazine hydrate as a reductant, which exhibited a reversible specific capacity of 650 mA h g^{-1} after 50 cycles at a current density of 1.0 A g^{-1} [24]. However, the synthesis of Cr-doped $\gamma\text{-Fe}_2\text{O}_3$ /rGO have not been reported yet to the best of our knowledge. In this regard, it is highly desirable to develop a rapid and environmentally friendly method to synthesize Cr-doped $\gamma\text{-Fe}_2\text{O}_3$ /rGO nanocomposites as high-performance anodes for LIBs.

In this study, we successfully synthesized Cr-doped $\gamma\text{-Fe}_2\text{O}_3$ /rGO nanocomposites through a rapid and environmentally friendly microwave method. Five different ratios (from 0 to 8.0 at%) of Cr to Fe_2O_3 /rGO had been synthesized by utilizing water as the solvent. GO with high surface area served as framework and oxidant. Accompanied with the assistance of microwave irradiation, GO was reduced by Fe^{2+} and chromium ions were incorporated into Fe_2O_3 , which was formed and dispersed uniformly on the GO sheets surfaces at the same time. In comparison with traditional method, microwave heating can expedite the kinetics of crystallization by accelerating rapid nucleation and growth, which can remarkably decrease the reaction time to 10 min from 10 h or even more time the conventional hydrothermal methods consuming. Therefore microwave method combines the advantages of high productivity and efficiency with low temperature, which can save a large amount of time and energy. Furthermore, comparing with other methods, microwave method is not only simple and rapid but also environment protecting, which was proceeded without toxic reductants to reduce GO to rGO, just like $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$. As anode materials of lithium ion batteries in half cell, the as-prepared Cr-doped $\gamma\text{-Fe}_2\text{O}_3$ /rGO nanocomposites exhibit excellent reversible capacity and outstanding rate performance. When assembled as full cell against commercial LiCoO_2 and $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ cathode, the 4.0 at% Cr-doped $\gamma\text{-Fe}_2\text{O}_3$ /rGO nanocomposites show promising electrochemical performance with excellent capacity and stable cycling performance.

2. Experimental section

2.1. Materials synthesis

All the chemical reagents utilized in the experiments were of analytical grade and used without further purification. GO was synthesized from graphite powder according to a modified Hummers' method. The Cr-doped Fe_2O_3 /rGO nanocomposites with different chromium doping levels from 0 to 8.0 at% were synthesized via a microwave method. In a typical procedure for the synthesis, taking 4.0 at% Cr-doped Fe_2O_3 /rGO for example, 20 mL GO aqueous suspension (2 mg mL^{-1}), $0.02 \text{ mol FeCl}_2 \cdot 4\text{H}_2\text{O}$, and 0.2 mol urea were dissolved in 100 mL distilled water. After vigorous stirring for 30 min, $0.8 \text{ mmol Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added into the above solution to form a homogeneous mixture solution. Subsequently, the mixed solution was poured into around-bottomed flask and

refluxed under ambient conditions for 10 min in a microwave heater. The resulting products were collected by centrifugation at 8000 rpm, and washed with deionized water and ethanol for several times, then drying at $70 \text{ }^\circ\text{C}$ in vacuum. To get better crystallinity and remove the impurities, all samples were calcined at $500 \text{ }^\circ\text{C}$ for 2 h in argon atmosphere. As control experiments, the products with different contents (0.0, 2.0, 6.0 and 8.0 at%) of Cr to Fe_2O_3 /rGO were prepared by varying the mass of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ using the same procedure. In addition, the samples of Cr-doped Fe_2O_3 were also prepared in the same process for comparison.

2.2. Material characterization

The composition and crystalline phase of the as-prepared Cr-doped $\gamma\text{-Fe}_2\text{O}_3$ /rGO nanocomposites were characterized by means of the powder X-ray diffraction (XRD) pattern, recorded on a Panalytical X-pert diffractometer using $\text{Cu K}\alpha$ radiation. The morphology and crystal structure of the obtained materials were examined by scanning electron microscopy (SEM, Hitachi S4800) operating at 10 kV and equipped with an energy-dispersive spectrometer (EDS). All the Fe 2p, Cr 2p, O 1s and C 1s XPS spectra were obtained by means of X-ray photoelectron spectroscopy (XPS) operating at an Al $\text{K}\alpha$ exciting radiation source. The Raman spectra of samples were obtained by conducting an ID SPEC ARcti3000 confocal Raman spectrometer. To determine the amount of rGO in Cr-doped $\gamma\text{-Fe}_2\text{O}_3$ /rGO nanocomposites, Thermogravimetric analysis (TGA) was performed using a TG209F1 Thermal Gravimetric Analyzer in air with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ from room temperature to $800 \text{ }^\circ\text{C}$.

2.3. Electrochemical measurements

To evaluate the electrochemical properties of the samples, the as-prepared Cr-doped $\gamma\text{-Fe}_2\text{O}_3$ /rGO nanocomposites electrodes were assembled into a CR2025-type coin cell. The working electrodes were fabricated by mixing 80 wt% of active materials, 10 wt% of carbon black and 10 wt% of polymer binder (Polyvinylidene Fluoride, PVDF), which were dissolved in 1-methyl-2-pyrrolidone (NMP), to form a homogeneous slurry. The well-mixed slurry was coated onto a copper foil and then dried at $80 \text{ }^\circ\text{C}$ in a vacuum oven for 12 h to remove water molecules. The mass of active material loading in each anode electrode disc is about 1.0 mg cm^{-2} . The pure lithium foils were utilized as counter and reference electrodes. The electrolyte solution was 1 M LiPF_6 in ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) (1:1:1, in weight percent). A Celgard 2400 microporous polypropylene membrane was used as the separator. The coin-type cells were assembled in a high-purity argon-filled glovebox with water and oxygen contents less than 1 ppm. The cyclic voltammetry (CV) was measured by a CHI660E electrochemical workstation between 0.01 and 3.0 V vs. Li^+/Li at a scan speed of 0.1 mV s^{-1} . The galvanostatic charge and discharge profiles of the cells were measured using a Land CT 2001 battery tester. 2025 coin-type full cells were constructed using 4.0 at% Cr-doped $\gamma\text{-Fe}_2\text{O}_3$ /rGO as anode and commercial LiCoO_2 or $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ as cathode.

3. Results and discussion

3.1. Morphological and structural characterization

The crystal structure of the as-prepared Cr-doped $\gamma\text{-Fe}_2\text{O}_3$ /rGO nanocomposites were investigated by XRD and corresponding results are presented in Fig. 1(a). As shown in the XRD diffraction patterns, all of the identified diffraction peaks of undoped Fe_2O_3 /rGO nanocomposites can be clearly indexed to the standard $\alpha\text{-Fe}_2\text{O}_3$

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