Graphene-Wrapped Fe₃O₄ Anode Material for High-Performance Lithium Ion Batteries

Yu Jiang¹, Zhong-Jie Jiang¹* and Meilin Liu¹,2,*

¹New Energy Research Institute, College of Environment and Energy, South China University of Technology, Guangzhou 510006, Guangdong, China.
²School of Materials Science & Engineering, GA Institute of Technology, Atlanta, GA 30332, USA

Abstract. The encapsulation of Fe₃O₄ particles in a graphene shell to form a core-shell structure is a promising way to improve the electrochemical performance of lithium ion batteries (LIBs). The continuous graphene shell may enhance the electrical conductivity of the electrodes, facilitating current collection and charge transfer associated with lithium storage. The unique shell structure may suppress the aggregation of the core Fe₃O₄ nanoparticles. The electrochemical results show that the graphene encapsulated Fe₃O₄ could exhibit significantly higher electrochemical performance and better cycling stability when used as the anode material for lithium ion batteries.

1 Introduction

With growing demands in the energy supply, a great deal of attention has been drawn into the development of high energy and power density lithium ion batteries (LIBs). Specifically, the performance of a LIB is largely determined by the physical and chemical properties of the electrode material.⁶⁻¹¹ Fe₃O₄ is a promising candidate as an anode material for LIBs, with advantages of the high theoretical capacity of 922 mAh g⁻¹, environment benignity, excellent electronic conductivity and nature abundance.⁶⁻¹¹ However, the practical utilization of the Fe₃O₄-based anode materials in the LIBs has been limited by their poor cycling performance and low rate capacities, resulting from large specific volumetric changes during lithium ion insertion/extraction.¹²⁻¹³

To improve the electrochemical performance of the Fe₃O₄-based anode materials, extensive work has been devoted to the coating of Fe₃O₄ with electrically conducting materials, such as carbon,¹⁶⁻¹⁹ polyaniline,²⁰⁻²¹ and other materials.²² Electrod based on Fe₃O₄ with a conductive coating usually exhibit greatly enhanced rate performance. In fact, the intimate conductive coating may destroy upon lithiation/delithiation due to the rigidity of the conducting material and large volume change during cycling, leading to crumbling and cracking of the electrodes and loss of electrical connection with current collector. A possible solution to this could be to encapsulate Fe₃O₄ into continuous and highly pliable conducting material shell to form a composite with a core-shell structure.

2 Experimental

2.1 Fabrication of the Fe₃O₄ microspheres

2.7 g FeCl₃·6H₂O, 7.2 g sodium acetate and 2.0 g polyethylene glycol were dissolved in 80 mL ethylene glycol under vigorous stirring to form a homogeneous solution. The obtained yellow solution was placed into a 100 mL Teflon-lined stainless steel autoclave and heated to 200°C for 12 h. After cooling, the product was subject to centrifugation and washed with ethanol for several times, followed by drying at 50°C under vacuum.

2.2 Synthesis of Fe₃O₄@graphene core/shell nanocomposite spheres

The Fe₃O₄@graphene core-shell structure was achieved by a two-step procedure: (1) 80 mg as-prepared Fe₃O₄ microspheres were dispersed in ethanol (64 mL) and DI water (16 mL) by using an ultrasonic water bath. 0.1 mL (3-Aminopropyl) triethoxysilane (APTES) was then added. The resulting solution was stirred for 5 h and the product was subject to centrifugation and washed with de-ionized water for several times to remove the residual reactants. The obtained solid was dissolved in 20 mL de-ionized water. The obtained solution was adjusted to pH=2.5 by adding drops of 1.0 M HCl solution for further uses. (2) 20 mL of the above solution was added to 1.0 mg mL⁻¹ negatively charged graphene oxide (GO) suspension (50 mL). After 12 h, the mixture was placed into a 100 mL Teflon-lined stainless steel autoclave and heated at 180°C for 12 h. After cooling, the resulting suspension was subject to centrifugation and washed with de-ionized water for several times until pH = ~7, and then freeze-dried.

3 Results and discussion

The SEM image in Fig. 1a shows that the Fe₃O₄ microspheres synthesized from ferric chloride are spherical and monodisperse with an average diameter of ~350 nm. To facilitate the coating of graphene, the surface of the prepared Fe₃O₄ microspheres were modified by APTES. The APTES-modified Fe₃O₄ particles are positively charged, making them readily adsorbed onto the negatively charged GO (the presence of carboxyl, hydroxyl, and epoxy oxygen groups makes the GO negatively charged) through electrostatic interaction. After the reduction of GO through the hydrothermal process, the Fe₃O₄@graphene was fabricated successfully. Fig. 1b and c shows that graphene cannot only deposit on the surface of the Fe₃O₄ microspheres, but also interconnect neighbouring spheres,
The specific core-shell structure could reinforce the mechanical stability of the electrode material and prevent the Fe₃O₄ microspheres from aggregation during cycling. Fig. 1d shows the XRD patterns of the bare Fe₃O₄ microspheres and the Fe₃O₄@graphene. All diffraction peaks are assignable to the standard profiles of magnetite (Fe₃O₄-ICPDS no. 19-0629), indicating a high purity of the obtained product.

To identify the lithium ion storage behaviours in the Fe₃O₄@graphene, its cyclic voltammograms (CVs) was measured. Fig. 2a shows that the CVs of the Fe₃O₄@graphene exhibit typical electrochemical characteristics of the Fe₃O₄ based material. The peak at ~0.1 in the first scan could be attributed to the initial lithium insertion into graphite. The peak at ~0.59 V could be assigned to the superposition of the solid electrolyte interphase (SEI) layer formation on the surface of the electrode, the decomposition of the electrolyte, and further reduction of Fe³⁺/Fe²⁺ to Fe⁰. In the subsequent cycles, the appearance of a new cathodic peak at ~0.95 V could be attributed to the electrochemical reaction of Fe⁰ to Fe₂, while the peak at ~1.65 V and ~1.85 V is ascribable to the electrochemical oxidation reaction of Fe⁰ to Fe₃O₄.

In summary, the Fe₃O₄@graphene has been fabricated by a simple procedure. When tested in a LIB, the Fe₃O₄@graphene exhibits a reversible capacity of 848.3 mAh g⁻¹ after 686 cycles at the current density of 1.0 A g⁻¹, which is much higher than those of other forms of Fe₃O₄ reported in the literatures. This, along with its better cycling performance and higher rate capacity make the Fe₃O₄@graphene particularly attractive as the anode material for LIBs.