

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

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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.^(1, 2) 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 Electrodes based on Fe₃O₄ with a conductive coating usually exhibit greatly enhanced rate performance. In fact, the intimate conductive coating may destroyed 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 Fe_3O_4 microspheres from aggregation during cycling. Fig. 1d shows the XRD patterns of the bare Fe_3O_4 microspheres and the Fe_3O_4 @graphene. All diffraction peaks are assignable to the standard profiles of magnetite (Fe_3O_4 -JCPDS no. 19-0629), indicating a high purity of the obtained product.

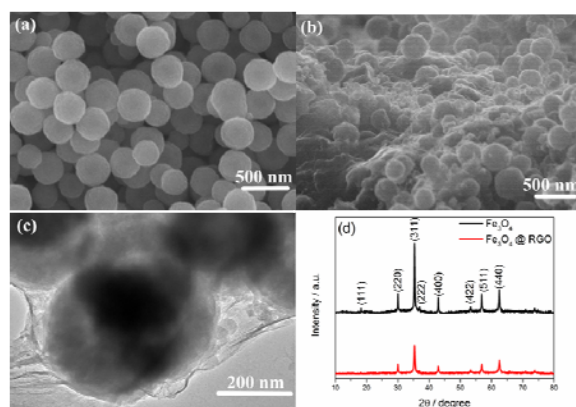


Figure 1. (a) SEM image of the bare Fe_3O_4 , (b) SEM image of the Fe_3O_4 @graphene, (c) TEM image of the Fe_3O_4 @graphene, (d) XRD spectra of the bare Fe_3O_4 , the Fe_3O_4 @graphene.

To identify the lithium ion storage behaviours in the Fe_3O_4 @graphene, its cyclic voltammograms (CVs) was measured. Fig. 2a shows that the CVs of the Fe_3O_4 @graphene exhibit typical electrochemical characteristics of the Fe_3O_4 based material. The peak at ~ 0.1 V 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 electrolyte, and further reduction of $\text{Fe}^{3+}/\text{Fe}^{2+}$ to Fe^0 . In the subsequent cycles, the appearance of a new cathodic peak at ~ 0.95 V could be attributed to the electrochemical reduction reaction of Fe_3O_4 to Fe^0 , while the peak at ~ 1.65 V and ~ 1.85 V is ascribable to the electrochemical oxidation reaction of Fe^0 to Fe_3O_4 .

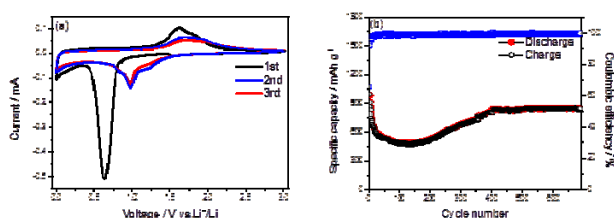


Figure 2. (a) CVs of the Fe_3O_4 @graphene anode at scan rate of 0.1 mV s⁻¹, (b) cycle performance and coulombic efficiency of Fe_3O_4 @graphene anode at a current density of 1.0 A g⁻¹.

Fig. 2b shows the galvanostatic discharge/charge curves of the Fe_3O_4 @graphene at a current rate of 1.0 A g⁻¹. The first discharging and charging capacities of the Fe_3O_4 @graphene are 1514.8 and 991.6 mAh g⁻¹, respectively. The discharge and charge capacities of

the Fe_3O_4 @graphene in the subsequent discharge/charge cycles are greatly reduced, due to the formation of the solid electrolyte interphase (SEI) layer on the surface of the electrode and the decomposition of the electrolyte, as shown in Fig. 2b. Further increase of the cycle number would lead to an increase in the discharging and charging capacities of the Fe_3O_4 @graphene. Fig. 2b shows that the Fe_3O_4 @graphene can still deliver reversible discharge/charge capacity of 845.5 mAh g⁻¹ after 686 cycles at the current density of 1.0 A g⁻¹, indicating a high capacity retention of the Fe_3O_4 @graphene with the cycling. The coulombic efficiency of the Fe_3O_4 @graphene has increased to $\sim 100.0\%$ after the initial several cycles from 65.5% in the first cycle, indicated an improved reversibility of Li^+ ion insertion and extraction. This could also be demonstrated by the CV profiles shows in Fig. 2a. The results shown above make us believe that the Fe_3O_4 @graphene could be used as a promising anode material for the LIBs

4 Conclusions

In summary, the Fe_3O_4 @graphene has been fabricated by a simple procedure. When tested in a LIB, the Fe_3O_4 @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 Fe_3O_4 reported in the literatures. This, along with its better cycling performance and higher rate capacity make the Fe_3O_4 @graphene particularly attractive as the anode material for LIBs.

References

- [1] Z. Jiang, B. Pei, A. Manthiram, J. Mater. Chem. A 26 (2013) 7775.
- [2] Z. Wu, W. Ren, L. Xu, F. Li, H. Cheng, ACS Nano 7 (2011) 5463-5471.
- [3] L. Zhan, S. Yang, Y. Wang, Y. Wang, L. Ling, X. Feng, Advanced Materials Interfaces 4 (2014) n/a-n/a.
- [4] S. Liu, R. Wang, M. Liu, J. Luo, X. Jin, J. Sun, L. Gao, J. Mater. Chem. A 13 (2014) 4598.
- [5] H. Zhu, X. Qin, X. Sun, W. Yan, J. Yang, Y. Xie, Scientific Reports (2013).
- [6] R. Wang, C. Xu, J. Sun, L. Gao, C. Lin, J. Mater. Chem. A 5 (2013) 1794.
- [7] Y. Jiang, Z.-J. Jiang, L. Yang, S. Cheng and M. Liu, J. Mater. Chem. A, 2015, 3, 11847-11856. Online
- [8] S. Sun, C. Wei, Z. Zhu, Y. Hou, S. S. Venkatraman, Z. Xu, Chinese Physics B 3 (2014) 37503.
- [9] L. Li, T. Wang, L. Zhang, Z. Su, C. Wang, R. Wang, Chemistry - A European Journal 36 (2012) 11417-11422.
- [10] L. Shen, J. Bao, D. Wang, Y. Wang, Z. Chen, L. Ren, X. Zhou, X. Ke, M. Chen, A. Yang, Nanoscale 5 (2013) 2133.
- [11] J. Xu, Y. Zhu, F. Chen, J. Solid State Chem. (2013) 204-211.

- [12] J. Xu, Y. Zhu, J. Colloid Interf. Sci. 1 (2012) 58-65.
- [13] P. L. S. G. Poizot, Nature 407 (2000) 496-499.
- [14] P. L. Taberna, S. Mitra, P. Poizot, P. Simon, J. M. Tarascon, Nat. Mater. 5 (2006) 567-573.
- [15] Q. Q. Xiong, J. P. Tu, Y. Lu, J. Chen, Y. X. Yu, Y. Q. Qiao, X. L. Wang, C. D. Gu, The Journal of Physical Chemistry C 10 (2012) 6495-6502.
- [16] S. Ito, K. Nakaoka, M. Kawamura, K. Ui, K. Fujimoto, N. Koura, J. Power Sources 1-2 (2005) 319-322.
- [17] S. M. Yuan, J. X. Li, L. T. Yang, L. W. Su, L. Liu, Z. Zhou, ACS Applied Materials & Interfaces 3 (2011) 705-709.
- [18] T. Zhu, J. S. Chen, X. W. D. Lou, The Journal of Physical Chemistry C 19 (2011) 9814-9820.
- [19] T. Muraliganth, A. V. Murugan, A. Manthiram, Chem. Commun. 47 (2009) 7360.
- [20] G. Lee, J. Park, Y. Sung, K. Y. Chung, W. I. Cho, D. Kim, Nanotechnology 29 (2009) 295205.
- [21] H. Sun, X. Sun, T. Hu, M. Yu, F. Lu, J. Lian, The Journal of Physical Chemistry C 5 (2014) 2263-2272.
- [22] Y. Jiang, Z.-J. Jiang, S. Cheng and M. Liu, Electrochimica Acta, 2014, 146, 437-446.