Enhanced cycling performance of Fe₃O₄–graphene nanocomposite as an anode material for lithium-ion batteries

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1. Introduction

Lithium-ion batteries have been widely utilized as power sources for portable electronic devices and viewed as the promising power source of electric vehicle. Their energy density and power density mainly depend on the physical and chemical properties of both cathode and anode materials [1]. Graphite is the widely commercial anode material for lithium-ion batteries because of its high columbic efficiency and excellent cycle performance. However, the theoretical specific capacity of graphite is only 372 mAh g⁻¹ (by forming intercalation compounds (LiC₆)) [1]. Because of the capacity limit of graphite, the energy density of lithium-ion batteries cannot satisfy needs for portable electronic devices and recently developed electric vehicles. To meet the increasing demands for lithium-ion batteries with both high energy and power density, many new anode materials have been explored for lithium-ion batteries [2–8]. Among them, Fe₃O₄ has been widely concerned as one of the most promising anode materials for lithium-ion batteries due to the following reasons. Firstly, based on a novel conversion mechanism, Fe₃O₄ + 8Li⁺ + 8e⁻ = 3Fe⁺₀ + 4Li₂O, its theoretical specific capacity is 924 mAh g⁻¹, which is much higher than that of the already-commercialized graphite (372 mAh g⁻¹) [9–12]. Secondly, the potential of the Fe₃O₄ anode is higher than that of graphite, which reduces the potential safety problems with metallic lithium deposition on the host anode during rapid charge [1,12]. Furthermore, the Fe₃O₄ has advantages over other carbon alternatives in terms of high electronic conductivity, low cost and eco-friendliness [5,11–14]. However, its application in practical lithium-ion batteries is still hindered by the poor cycling performance arising from the severe aggregation and huge volume change of Fe₃O₄ particles during Li insertion/extraction process [11–14]. To circumvent these problems, many approaches have been used, such as carbon-coating [11,15], nanocomposite [9,12,14] and nanostructure [5,10,13,16]. Although remarkable progress has been made, it is still a great challenge to explore Fe₃O₄ electrode material with large reversible specific capacity, high columbic efficiency and long cycling life as well as good rate capability.

Graphene, a single-atom-thick sheet of honeycomb carbon lattice, exhibits many unique physical and chemical properties [17,18]. Since its discovery in 2004, much effort has been devoted to investigating the technological applications of graphene materials [18]. Graphene sheets as an anode material for lithium-ion batteries have been investigated and exhibit a large reversible specific capacity (540–1264 mAh g⁻¹) [19–23]. Unfortunately, they all suffer from large irreversible capacity, low initial coulombic efficiency and fast capacity fading [19–23]. Recently, it has been reported that graphene can be used in nanocomposites (like SnO₂–graphene, Sn–graphene, Si–graphene, Co₃O₄–graphene, Co(OH)₂–graphene) to improve the electrochemical performances of these materials [24–32]. However, to the best of our knowledge, there were fewer reports on the Fe₃O₄–graphene nanocomposite as an anode material for lithium-ion batteries so far. The Fe₃O₄ nanoparti-
cles combined with porous graphene sheets could exhibit several advantages. Firstly, the ultrathin graphene sheets can act as a barrier to prevent the aggregation of Fe₃O₄ nanoparticles and enhances the cycle performance [28–30,32]. Secondly, the porous graphene sheets can provide a void space against the volume changes of the Fe₃O₄ particles during lithium ion insertion/extraction process [23,24,28], which can improve the cycling performance. Thirdly, the graphene sheets itself is an active material for additional Li⁺ storage [19–24,29,32], which is of great benefit to the reversible specific capacity. Finally, the Fe₃O₄ nanoparticles are anchored on the surface of the curled graphene sheets, which may lead to a high rate performance due to the high electronic conductivity of graphene sheets and short path length for Li⁺ transport of Fe₃O₄ nanoparticles [25,26,32]. Therefore, it is believed that such Fe₃O₄–graphene nanocomposite can possess large reversible specific capacity, long cycling life and good rate capability. Herein, such Fe₃O₄–graphene nanocomposite was synthesized and its electrochemical performances were evaluated. The experimental results indicate that the Fe₃O₄–graphene nanocomposite can indeed deliver a very high reversible specific capacity together with excellent cycle performance.

2. Experimental

2.1. Synthesis of Fe₃O₄–graphene nanocomposite and Fe₃O₄ nanoparticles

Graphene sheets were prepared via a thermal exfoliation route involving graphite oxidation, following by rapid thermal expansion under nitrogen atmosphere. Detailed preparation procedure can be found in our previous paper [23]. Fe₃O₄–graphene nanocomposite and Fe₃O₄ nanoparticles were prepared by a gas/liquid interfacial reaction, as shown in Fig. 1. Briefly, in a 20-mL beaker, 0.8080 g of Fe(NO₃)₃·9H₂O was dissolved in 10 mL of ethylene glycol (EG), and then 0.0450 or 0.0218 g of graphene sheets were added and sonicated for 6 h to yield a homogeneous suspension. Then the beaker was placed into a 100-mL Teflon-lined autoclave that contained 14 mL of ammonia solution. Then the autoclave was sealed and placed in a drying oven preheated to 180 °C and kept at that temperature for 12 h. During this process, the Fe₃O₄ nanoparticles were in situ deposited onto the graphene sheets. Briefly, at the elevated reaction temperature (180 °C), evaporated ammonia reacted with Fe³⁺ at the gas/liquid interface to produce Fe(OH)₃, which could be quickly decomposed to Fe₂O₃ and further reduced to Fe₃O₄ by EG [33]. After cooling and centrifugation, washing with ethanol for several times, then the black solid product was dried at 100 °C in vacuum to obtain the desired Fe₃O₄–graphene nanocomposite. The Fe₃O₄ nanoparticles were synthesized under the same condition without the addition of graphene sheets for comparison.

Fig. 1. (a) Schematic illustration for the reaction system and (b) synthesis process of Fe₃O₄–graphene nanocomposite.

Fig. 2. XRD patterns of the as-synthesized (a) Fe₃O₄–22.7 wt.% graphene nanocomposite and (b) Fe₃O₄ nanoparticles, they are identified as face-centered Fe₃O₄ (JCPDS File Card No. 88-0315). Inset shows the XRD patterns of graphite and graphene sheets.
2.2. Characterization of Fe₃O₄–graphene nanocomposite and Fe₃O₄ nanoparticles

The structure and morphology of the as-prepared Fe₃O₄–graphene nanocomposite and Fe₃O₄ nanoparticles were characterized by X-ray diffraction (XRD, Bruker D8 Advance), scanning electron microscopy (SEM, Quanta 200F) and high-resolution transmission electron microscopy (HRTEM, FEI, Tecnai G² F30 S-Twin). N₂ adsorption/desorption isotherms were measured using a Micromeritics ASAP 2010 (USA) analyzer at liquid nitrogen temperature. Elemental analysis was carried out on vario EL III elementar (Germany) by burning the Fe₃O₄–graphene nanocomposite to form carbon dioxide. The content of carbon (i.e., graphene sheets) in Fe₃O₄–graphene nanocomposite was calculated accord-
ing to the mass of carbon dioxide. The content of graphene in Fe₃O₄–graphene nanocomposites prepared by adding different graphene sheets amounts (0.0450 or 0.0218 g) was determined to be 22.7 wt.% and 12.4 wt.%, respectively.

### 2.3. Electrochemical testing of Fe₃O₄–graphene nanocomposite and Fe₃O₄ nanoparticles

The electrochemical experiments were carried out using the coin-type cells [23]. The working electrode was prepared by mixing active material (Fe₃O₄ nanoparticles or Fe₃O₄–graphene nanocomposite) with poly(vinylidene fluoride) (PVDF) and Super P carbon at a weight ratio of 75:10:15 in N-methyl-2-pyrrolidone (NMP) to form slurry. Then, the resultant slurry was uniformly pasted on Cu foil with a blade, dried at 120 °C in a vacuum oven and pressed under a pressure of 20 MPa. The active material loading density of the electrode is ca. 1.0 mg cm⁻². The Celgard 2325 microporous membrane was used as separator. The electrolyte was 1 mol L⁻¹ LiPF₆ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume). The lithium sheet was used as both counter and reference electrode. CR2025-type coin cells were assembled in an argon-filled glove box and lithium metal as the anode. The electrolyte was 1 mol L⁻¹ LiPF₆ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume). The lithium sheet was used as both counter and reference electrode. Cyclic voltammograms (CVs) measurements were carried out on an electrochemical workstation (Zahner IM6ex) over the potential range 0.01–3.0 V versus Li/Li⁺ at a scanning rate of 0.2 mV s⁻¹.

### 3. Results and discussion

#### 3.1. Microstructural characterization

Fig. 2 shows XRD patterns of as-prepared Fe₃O₄–graphene nanocomposite and Fe₃O₄ nanoparticles. The XRD patterns of Fe₃O₄–graphene nanocomposite and Fe₃O₄ nanoparticles match well with that of magnetite (JCPDS File Card No. 88-0315). All peaks in the XRD pattern of Fe₃O₄ nanoparticles are also in good agreement with those reported in the literature [33]. The broad diffraction peaks suggest that the nanoparticles are very small in size. Furthermore, no obvious diffraction peak attributed to graphite was observed, which indicates that the stacking of graphene sheets in the Fe₃O₄–graphene nanocomposite is disordered. The disordered stacking of graphene sheets in the Fe₃O₄–graphene nanocomposite can also be confirmed by the SEM observation.

The SEM and HRTEM micrographs of Fe₃O₄ nanoparticles, graphene sheets and Fe₃O₄–graphene nanocomposite are shown in Fig. 3. As shown in Fig. 3a, the Fe₃O₄ nanoparticles are aggregated to larger particles, which would lead to the poor cycling performance as an anode material for lithium-ion batteries based on a conversion mechanism [5,12,29,32,35]. Fig. 3b show the SEM images of graphene sheets, a curled morphology, which the graphene intrinsically owns [34], with wavy structures can be observed from the SEM picture. Fig. 3e indicates that ultrathin graphene sheets have been successfully prepared via a thermal exfoliation route. The thickness of the graphene sheets is approximately 2.1 nm [23]. From Fig. 3c, it can be observed that the graphene sheets are distributed between the loosely packed Fe₃O₄ nanoparticles and the nanoporous composite with large amount of void spaces was formed. Such porous nanocomposite with large amount of void spaces could result in an enhanced cycling performance as an anode material for lithium-ion batteries [12,24,28]. Moreover, the graphene sheets distributed between the Fe₃O₄ nanoparticles can prevent the aggregation of Fe₃O₄ nanoparticles to a certain extent, which can be of great benefit to cycle life. It should be pointed out that the random hybridization between Fe₃O₄ nanoparticles and ultrathin graphene sheets can form 3-dimensionally porous structure of the Fe₃O₄–graphene nanocomposite, which is beneficial for achieving high rate performance [25,29]. The formed 3D electronic conduction network and reduced lithium ion diffusion length in Fe₃O₄–graphene nanocomposite can facilitate electron and lithium ion transport [25,29,32]. The HRTEM images (Fig. 3d and f) revealed that the average particle size of Fe₃O₄ nanoparticles in the Fe₃O₄–graphene nanocomposite is comparable to that of bare Fe₃O₄ nanoparticles, which is about 12.5 nm. More importantly, even after a long time of sonication during the preparation of the TEM specimen, the Fe₃O₄ nanoparticles were still strongly anchored on the surface of graphene sheets with a high density (shown in Fig. 3f), implying the strong interaction between Fe₃O₄ nanoparticles and graphene sheets [32].

N₂ adsorption/desorption isotherms were employed to investigate the pore structures of the Fe₃O₄ nanoparticles and Fe₃O₄–graphene nanocomposite, as shown in Fig. 4. The Barrett–Joyner–Halenda (BJH) pore size distribution indicates that there is almost no micropore exiting in both of the Fe₃O₄ nanoparticles and Fe₃O₄–graphene nanocomposite, however, the Fe₃O₄–graphene nanocomposite possesses a much better porosity than Fe₃O₄ nanoparticles. The total pore volume of
Fig. 5. (a) First two discharge/charge profiles of Fe₃O₄–22.7 wt.% graphene nanocomposite and Fe₃O₄ nanoparticles at a current density of 100 mA g⁻¹. (b) Capacities versus cycle number between 0.01 and 3 V at the current density of 100 mA g⁻¹. (c) Cycling performance of Fe₃O₄–22.7 wt.% graphene nanocomposite at various current densities (the same cell after cycled for 40 cycles shown in b).

Fe₃O₄–graphene nanocomposite (0.63 cm³ g⁻¹) is much larger than that of the Fe₃O₄ nanoparticles (0.43 cm³ g⁻¹). The increased pore volume could arise primarily from the formation of secondary pores between the Fe₃O₄ nanoparticles and graphene sheets as well as the close stacking of graphene sheets distributed between the Fe₃O₄ nanoparticles. The nanopores in Fe₃O₄–graphene nanocomposite could act as buffering spaces against the volume changes of Fe₃O₄ nanoparticles during lithium ion insertion/extraction process [12], which would lead to enhanced cycling stability as an anode material for lithium-ion batteries.

3.2. Electrochemical properties of Fe₃O₄–graphene nanocomposite and Fe₃O₄ nanoparticles

The electrochemical properties of the Fe₃O₄–graphene nanocomposite and the Fe₃O₄ nanoparticles were investigated using coin-type cells. The first two discharge/charge cycles were tested at a current density of 100 mA g⁻¹, and the corresponding discharge/charge curves are shown in Fig. 5a. The first discharge voltage profile of the Fe₃O₄–graphene nanocomposite is very similar to that of Fe₃O₄ nanoparticles. Both of them present a steep voltage drop from about 2.0 to 0.85 V, which can be attributed to the reaction Fe₃O₄ + xLi⁺ + xe⁻ ↔ LiₓFe₃O₄ [9], then a long voltage plateau at about 0.85 V versus Li⁺/Li corresponding to the conversion reaction LiₓFe₃O₄ + (8−x)Li⁺ + (8−x)e⁻ ↔ 4Li₂O + 3Fe⁰ [10], followed by a sloping curve down to the cutoff voltage of 0.01 V, indicating typical characteristics of voltage trends for Fe₃O₄ electrode [5,12,13,35]. The voltage plateau is very close to that described in the literatures (about 0.8 V) for carbon coated Fe₃O₄ nanospindles and magnetite/carbon core–shell nanorods [11,15]. The sloping curve of the Fe₃O₄–graphene nanocomposite from about 0.85 to 0.01 V could be attributed to the formation of a solid electrolyte interface (SEI) film and the reversible reaction between lithium and graphene sheets 2C + Li⁺ + e⁻ ↔ LiC₂ [10,20,23]. The second discharge curves of the Fe₃O₄–graphene nanocomposite and the Fe₃O₄ nanoparticles are both different from the first, suggesting drastic, lithium-driven, structural or textural modifications [3]. Furthermore, the charge voltage plateaus of both Fe₃O₄–graphene nanocomposite and Fe₃O₄ nanoparticles are higher than the discharge. The large polarization (i.e., voltage hysteresis between charge and discharge) could be due to the poor conversion reaction kinetics (limited lithium diffusion kinetics during the intercalation/de-intercalation process, for example) of Fe₃O₄ nanoparticles in Fe₃O₄–graphene nanocomposite [5,35], since the conversion-type reaction is heterogeneous, enlisting the reactivity of three solid-state components (Fe₃O₄, Fe⁰, and Li₂O in this case). In fact, the phenomenon of polarization has been widely observed in a number of other Fe₃O₄–C composites [9–13,15]. Unfortunately, the large polarization strongly penalizes the energy efficiency of lithium-ion batteries. Therefore, it is very important to reduce the polarization of Fe₃O₄–graphene nanocomposite in the future work by improving the conversion reaction kinetics, such as reducing the particle size of Fe₃O₄ nanoparticles in Fe₃O₄–graphene nanocomposite.
The cycling performances of Fe₃O₄ nanoparticles and Fe₃O₄–graphene nanocomposites with various content of graphene were evaluated between 0.01 and 3.0 V at the current density of 100 mA g⁻¹ up to 40 cycles, as shown in Fig. 5b. The first reversible specific capacity of the Fe₃O₄ nanoparticles is as high as 832 mAh g⁻¹. However, the reversible specific capacity quickly fades and only 226 mAh g⁻¹ remains at the 34th cycle, indicating a poor cycling performance. In contrast, the reversible specific capacities of Fe₃O₄–22.7 wt.% graphene and Fe₃O₄–12.4 wt.% graphene nanocomposites are as high as 1045 and 540 mAh g⁻¹ at the 40th cycle, respectively. Both of them exhibit enhanced cycle performance as expected. Especially the reversible specific capacity of Fe₃O₄–22.7 wt.% graphene nanocomposite is constantly above 1000 mAh g⁻¹ during the forty cycles, exhibiting excellent cycling stability.

The theoretical specific capacity of the Fe₃O₄–22.7 wt.% graphene nanocomposite is 968 mAh g⁻¹ calculated based on the theoretical specific capacity of Fe₃O₄ (924 mAh g⁻¹) and graphene sheets (1116 mAh g⁻¹) [20,23]. The first reversible specific capacity of Fe₃O₄–22.7 wt.% graphene nanocomposite is as high as 1060 mAh g⁻¹, which is slightly higher than the theoretical specific capacity. The extra capacity may be attributed to the synergistic effect between the Fe₃O₄ nanoparticles and graphene sheets in the nanocomposite, such as the formed secondary pores could store some lithium [19,23,24]. The initial coulombic efficiency of the Fe₃O₄–22.7 wt.% graphene nanocomposite is 78%, which is slightly lower than 82% of the Fe₃O₄ nanoparticles, indicating an increase of the irreversible capacity loss due to the increase of specific surface area [20]. The irreversible capacity loss in the first cycle can be attributed to electrolyte decomposition and formation of solid electrolyte interface (SEI) film [12,13]. Nevertheless, after two cycles the coulombic efficiency of the Fe₃O₄–22.7 wt.% graphene nanocomposite increases to above 93% in the subsequent cycles.

After 40 cycles, the same cell was further evaluated for rate capability as shown in Fig. 5c. When the same cell was tested at various current densities from 100 to 1000 mA g⁻¹, the rationally designed nanocomposite exhibits an excellent high rate capability. At the high current densities of 300, 500 and 1000 mA g⁻¹, the Fe₃O₄–22.7 wt.% graphene nanocomposite can still deliver high reversible specific capacity of 740, 600 and 410 mAh g⁻¹, respectively. All of these values are higher than the theoretical specific capacity of the commonly used graphite anode material (372 mAh g⁻¹). Remarkably, when the current density returns to the initial 100 mA g⁻¹ after more than 85 cycles, a stable high reversible specific capacity of 1048 mAh g⁻¹ can be recovered. A rough comparison indicates that the reversible specific capacity (1048 mAh g⁻¹) of the Fe₃O₄–graphene nanocomposite is much larger than those previously reported, such as carbon-coated magnetite (Fe₃O₄) core–shell nanorods (394 mAh g⁻¹ after 100 cycles) [25], carbon coated Fe₃O₄ nanospindles (530 mAh g⁻¹ after 85 cycles) [11], Fe₀–Fe₃O₄ nanocomposite (~540 mAh g⁻¹ after 100 cycles) [14] and Fe₃O₄–carbon nanotube composites (656 mAh g⁻¹ after 145 cycles) [12]. The initial coulombic efficiency (78%) is not prominent, but still higher than those of Fe₃O₄–carbon nanotube composites (67%) [12], Fe₃O₄ submicron spheroids (70%) [10] and carbon-decorated single-crystalline Fe₃O₄ nanowires (73%) [13]. It is important that more than 93% of coulombic efficiency was observed after two cycles, indicating high charge/discharge reversibility of the Fe₃O₄–22.7 wt.% graphene nanocomposite.

The cyclic voltammograms (CVs) of the as-prepared Fe₃O₄–22.7 wt.% graphene nanocomposite is shown in Fig. 6a. In the cathodic polarization process of the first cycle, two obvious peaks were observed at 0.59 and 0.02 V, which should be attributed to the reaction Fe₃O₄ + 8Li⁺ + 8e⁻ ⇌ 3Fe₀ + 4Li₂O and 2C + Li⁺ + e⁻ ⇌ LiC₂ respectively [12,15,23,32]. Meanwhile, in the anodic polarization process, two peaks were recorded at about 1.67 and 1.89 V, corresponding to the oxidation of Fe₀ to Fe₃O₄ [12,15]. The peak at 0.59 V matches well with the first discharge voltage plateau during the discharge/charge tests. But due to the hysteresis in the CV technique, the cathodic peak negatively shifted, and the anodic peak positively shifted compared to the discharge/charge voltage plateaus [15]. After the first cycle, the CV curves of the Fe₃O₄–22.7 wt.% graphene nanocomposite in the subsequent three cycles almost overlap, revealing an excellent reversibility. On the opposite side, as shown in Fig. 6b, the peak intensity and integral areas of the CV curves during all the four cycles were obviously decreased for Fe₃O₄ nanoparticles, implying poor capacity retention. The results are well consistent with those of galvanostatically discharged and charged tests. Moreover, after the first cycle, the cathodic peaks of both Fe₃O₄–22.7 wt.% graphene nanocomposite and Fe₃O₄ nanoparticles positively shifted, indicating structural modifications during the first cycle. This is also in good agreement with that the second discharge curves differ considerably from the first. All the results above indicate that the Fe₃O₄–graphene nanocomposite is a promising anode material for lithium-ion batteries with both high reversible specific capacity and excellent cycling stability.

4. Conclusions

In summary, Fe₃O₄–graphene nanocomposite was synthesized by a gas/liquid interface reaction. It was demonstrated that the graphene sheets distributed between the disorderly stacked Fe₃O₄ nanoparticles improve the cycling performance in two ways,
including: (i) preventing the direct contact among the adjacent Fe$_3$O$_4$ nanoparticles and thereby minimizing the aggregation of the Fe$_3$O$_4$ nanoparticles during discharge/charge cycling, (ii) providing buffering spaces against the volume changes of Fe$_3$O$_4$ nanoparticles during the Li insertion/extraction processes. As a result, the Fe$_3$O$_4$–22.7 wt.% graphene nanocomposite maintains a high reversible specific capacity of 1048 mAh g$^{-1}$ up to 90 cycles, exhibiting significantly enhanced cycling performance in comparison with that of Fe$_3$O$_4$ nanoparticles (only 226 mAh g$^{-1}$ remains after 34 cycles). The results give the clear evidence that the graphene sheets can improve the electrochemical performances of nanostructured transition metal oxides as anode materials for lithium-ion batteries.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 20936001) and the Fundamental Research Funds for the Central Universities, SCUT (2009220038).

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