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Facile synthesis of core–shell porous Fe$_3$O$_4$@carbon microspheres with high lithium storage performance

Qichao Wu$^a$, Rongli Jiang$^*$,$^a$, Huaiwen Liu$^a$, Xiaojiang Li$^a$ and Dan Xie$^a$

$^a$ College of Chemical Engineering and Technology, China University of Mining and Technology, No. 1, Daxue Road, Xuzhou City 221116, Jiangsu Province, China
E-mails: wqcchemistry16@163.com (Q. Wu), ronglij@cumt.edu.cn (R. Jiang), liuhuaiwen.cn@gmail.com (H. Liu), lxjchemistry19@163.com (X. Li), xdchemistry19@163.com (D. Xie)

Abstract. Core–shell porous Fe$_3$O$_4$@C (CP-Fe$_3$O$_4$@C) microspheres were synthesized using an environmentally viable hydrothermal method. Carbonization can reduce Fe$_2$O$_3$ and provide a conductive coating simultaneously. CP-Fe$_3$O$_4$@C microspheres as an active material for Lithium-ion batteries demonstrate pseudocapacity for improved rate performance. With a distinct nanostructure and pseudocapacitive effect, the CP-Fe$_3$O$_4$@C microspheres show excellent electrochemical performance (∼785 mAh·g$^{-1}$ at 0.3 A·g$^{-1}$ after 200 cycles). Capacity measurements of CP-Fe$_3$O$_4$@C microspheres suggest near 90% pseudocapacitance at relatively low scan rates (5 mV·s$^{-1}$).

Keywords. Lithium-ion batteries, Fe$_3$O$_4$, Porous core–shell structures, Carbon.

1. Introduction

Microelectronic technology continues to advance in the 21st century, with an increase in the number of microelectronic devices and a higher consumer demand for power sources. Lithium-ion batteries (LIBs) have clear and obvious advantages and continue to dominate the market [1–4]. Transition metal oxides were considered for LIB anode materials in early 2000 due to their high capacities stemming from conversion reaction mechanisms [5–7]. Fe$_3$O$_4$ was among these early studied anode materials with a high capacity (theoretical value 926 mAh·g$^{-1}$) [8–10]. However, during cycling, Fe$_3$O$_4$ expands and breaks, causing rapid loss of capacity. Additionally, the conductivity of Fe$_3$O$_4$ is poor [11]. Carbon coating was found to help alleviate these problems, both addressing Fe$_3$O$_4$ volume expansion during cycling and preventing particle agglomeration [12–14]. More importantly, the carbon layer not only improved the conductivity of the electrode but also stabilized the solid electrolyte interface (SEI), which greatly improved the cycle life and rate capability of LIBs [15–17]. Further research in materials design pushed for Fe$_3$O$_4$ with a porous or hollow structure, which improves electrode reversibility and active material/electrolyte contact [18–20]. Recently, Wang et al. reported a novel Fe$_3$O$_4$@Carbon yolk–shell nanorod anode material by a one-pot method. The voids in the Fe$_3$O$_4$@Carbon core–shell nanorods were beneficial for volume expansion and
allowed the Fe$_3$O$_4$@Carbon-based electrode to maintain its structural integrity during repeated Li$^+$ insertion/extraction. Additionally, carbon coating on Fe$_3$O$_4$ provided a stable SEI film. The Fe$_3$O$_4$@Carbon composites exhibited high mechanical stability and excellent cycling performance (954 mAh·g$^{-1}$ 200 cycles at 0.5 A·g$^{-1}$) [21]. Liu et al. prepared micron-sized porous Fe$_3$O$_4$ spheres through the solvothermal and calcination methods. Carbon-covered Fe$_3$O$_4$ porous microspheres demonstrated an outstanding reversible capacity (747 mAh·g$^{-1}$ after 50 cycles at 0.1 A·g$^{-1}$) and good rate capacity (255 mAh·g$^{-1}$ at 1.6 A·g$^{-1}$) [22]. Zhou et al. synthesized uniform porous Fe$_3$O$_4$@Carbon microspheres by a hydrothermal method. These microspheres showed good electrochemical performance (609 mAh·g$^{-1}$ after 200 cycles at 0.2 A·g$^{-1}$) [23].

In this work, novel core–shell porous Fe$_3$O$_4$@C microspheres (CP-Fe$_3$O$_4$@C) were successfully designed and constructed by simple hydrothermal and carbonization methods. First, the Fe$_3$O$_4$@GU microspheres were synthesized using ferric chloride as an iron source and common chemicals glucose and urea as filler particles; the Fe$_3$O$_4$@GU composite was heat-treated in oxygen atmosphere to obtain the porous Fe$_2$O$_3$ microspheres. Second, resorcinol-formaldehyde (RF) resin was applied to porous Fe$_2$O$_3$ microspheres to obtain core–shell Fe$_2$O$_3$@RF microspheres, which were then used for the fabrication of CP-Fe$_3$O$_4$@C microspheres by one-step carbonization without a surfactant. The material synthesized through our straightforward method shows excellent performance as an anode material for LIBs.

2. Experimental section

2.1. Preparation of Fe$_3$O$_4$@GU

The Fe$_3$O$_4$@GU microspheres were prepared by a simple hydrothermal technique. Briefly, 2.13 g of ferric chloride (FeCl$_3$), 2.0 g of glucose (C$_6$H$_{12}$O$_6$) and 2.1 g of urea (CH$_4$N$_2$O) were added to 90 mL of deionized (DI) water and stirred. The resulting orange solution was placed into a 200 mL stainless steel Teflon-lined autoclave, heated at 200 °C for 6 h and then cooled to ambient temperature. The black Fe$_3$O$_4$@GU microspheres were washed with DI water thrice and dried at 60 °C for 12 h.

2.2. Preparation of porous Fe$_2$O$_3$

The Fe$_3$O$_4$@GU microspheres were heated at 500 °C in oxygen for 4 h, after which the furnace was cooled to the ambient temperature naturally. The bright orange porous Fe$_2$O$_3$ microspheres were washed with DI water thrice and dried at 60 °C for 12 h.

2.3. Preparation of CP-Fe$_3$O$_4$@C microspheres

A mixture containing 15 mL of DI water and 15 mL of ethanol was used to disperse porous Fe$_3$O$_3$ microspheres. Then, 2 mL of formaldehyde and 0.8 g of resorcinol were added, and the whole mixture was stirred for 30 min. The mixture was then transferred into a 100 mL stainless steel Teflon-lined autoclave and heated at 100 °C for 36 h. The resulting material (which was Fe$_2$O$_3$@RF composite) was calcined at 500 °C for 4 h under N$_2$ at a heating rate of 2 °C·min$^{-1}$ to produce CP-Fe$_3$O$_4$@C microspheres. A schematic of the preparation process for CP-Fe$_3$O$_4$@C microspheres is shown in Figure 1.

2.4. Material characterization

Crystalline phases were confirmed by X-ray diffraction (XRD) using Cu K$_\alpha$ radiation ($\lambda = 0.15406$ nm) by a D8 type advanced diffractometer (40 kV and 30 mA). X-ray photoelectron spectroscopy (XPS) was performed at 280 eV using ESCALAB 250Xi operated using Al K$_\alpha$ radiation as an excitation source. Morphology and microstructure were characterized by field emission scanning electron microscopy (FE-SEM, Merlin Compact) and transmission electron microscopy (TEM, G2F20). Raman spectra were recorded using the Bruker-Senterra spectrometer with 514 nm laser excitation. Sample weight losses were measured by thermo-gravimetric analysis (TGA, HCT-3). The analysis was performed in air in a range of 30 to 800 °C at a heating rate of 10 °C·min$^{-1}$. The surface area of the CP-Fe$_3$O$_4$@C composite was measured by the Brunauer–Emmett–Teller (BET) method (Autosorb-IQ). Pore sizes were obtained from the corresponding nitrogen adsorption/desorption isotherms using the Barrett–Joyner–Halenda formula.

2.5. Electrochemical measurements

Anodes were prepared by mixing the active materials with conductive acetylene black and poly-vinylidene
Figure 1. Synthesis flow chart of the CP-Fe$_3$O$_4$@C composite.

fluoride (PVDF) binder at a ratio of 8:1:1. The N-methyl pyrrolidone solvent (1.0 mL) was added to prepare slurry, which was applied to a copper foil and dried at 80 °C for 12 h. Coin cells (with standard size 2032) were assembled in a glove box under Ar atmosphere. Metallic Li was used as the counter electrode. The LiPF$_6$ (1.0 M) dissolved in a 1:1 ethylene carbonate:dimethyl carbonate mixture was used as the electrolyte. Galvanostatic charge–discharge (GCD) measurements at various current densities were recorded using NEWARE CT-4008 (Shenzhen). Cyclic voltammetry (CV) was measured using an electrochemical workstation (Solartron 1287) from a potential of 0.01 to 3.00 V at a 0.1 mV·s$^{-1}$ sweep rate. Electrochemical impedance spectroscopy was conducted on the electrochemical workstation (Solartron 1287) from 0.01 Hz to 100 kHz at a perturbation of 5 mV AC.

3. Results and discussion

As-prepared Fe$_3$O$_4$@GU, Fe$_2$O$_3$ and CP-Fe$_3$O$_4$@C microspheres were characterized by XRD (Figure 2a). The strong reflections of Fe$_2$O$_3$ microspheres observed at $2\Theta = 24.2, 33.2, 35.7, 40.9, 49.5, 54.0, 62.4$ and $64.0^\circ$ correspond to the (012), (104), (110), (113), (024), (116), (214) and (330) planes of hematite (JCPDS 33-0664) [24]. The XRD of Fe$_3$O$_4$@GU and CP-Fe$_3$O$_4$@C microspheres showed several peaks that are consistent with the face-centered Fe$_3$O$_4$ phase (JCPDS 19-0624) [12,25]. In addition, no peaks of Fe$_2$O$_3$ were found in the diffraction peak of CP-Fe$_3$O$_4$@C, indicating that Fe$_2$O$_3$ was converted to Fe$_3$O$_4$. The carbon content analyses for Fe$_3$O$_4$@GU, Fe$_2$O$_3$ and CP-Fe$_3$O$_4$@C materials are shown in Figure 2b. Fe$_2$O$_3$ demonstrated almost no carbon weight loss and was corroborated by the XRD showing that only a Fe$_2$O$_3$ phase was present in this sample. There was rapid weight loss for Fe$_3$O$_4$@GU and CP-Fe$_3$O$_4$@C occurring from 200 to 400 °C, which was attributed to the decomposition of the carbon layer. With this weight loss, it was determined that the carbon content values for the Fe$_3$O$_4$@GU and CP-Fe$_3$O$_4$@C microspheres were 37.61% and 17.35%, respectively.

Raman spectra showed the presence of carbon in the CP-Fe$_3$O$_4$@C microspheres (see Supplementary Figure S1), indicated by the presence of two broad peaks at 1349 and 1587 cm$^{-1}$, which correspond to D and G bands. These bands are assigned to sp$^3$ disordered and sp$^2$ ordered graphitic carbon bonds [26]. The ratio between D and G bands ($I_D/I_G$) is often used to evaluate the degree of carbon graphitization. For the CP-Fe$_3$O$_4$@C microspheres, the ratio was 0.96, and this suggests a high degree of graphitization in the carbon coating of the Fe$_3$O$_4$ microspheres. This graphitization is beneficial for electrical conductivity of the composite [27].

The nitrogen absorption/desorption isotherms of CP-Fe$_3$O$_4$@C show a hysteresis from 0.5 to 1.0 relative pressure (see Figure 2c). The BET surface area of the CP-Fe$_3$O$_4$@C was equal to 16.8 m$^2$·g$^{-1}$. The pore size distribution curve shows a peak near 3.8 nm (see insert in Figure 2c), evincing a nanopore presence. High surface area and porosity provide good contact between the electrode material and the electrolyte. This in turn promotes Li$^+$ diffusion and allows active material to adapt to the volume expansion [28].

The XPS of CP-Fe$_3$O$_4$@C microspheres shows peaks corresponding to Fe, C and O (see Figure 2d). High-resolution scans and curve fitting show Fe peaks at 711.2 and 724.8 eV, which belong to Fe 2p$^{3/2}$
Figure 2. Sample characterization. (a) XRD pattern, (b) TGA pattern, (c) nitrogen adsorption/desorption isotherms and pore size distribution curve (inset), XPS spectra of the CP-Fe$_3$O$_4$@C (d) survey, (e) Fe 2p, (f) C 1s.

and Fe 2p$_{1/2}$, respectively (see Figure 2e), which are typical of Fe$_3$O$_4$-based materials [29,30]. Two pairs of peaks at 710.3 and 723.3 eV and at 711.9 and 725.5 eV correspond to Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$ of Fe$^{2+}$ and Fe$^{3+}$, respectively [31]. High-resolution scans of C 1s (see Figure 2f) show peaks at 284.4 (typical of sp$^2$-hybridized graphitic C), 285.0 eV (attributed to the sp$^3$-hybridized C) and at 286.3 and
289.0 eV (both of which are attributed to the carbon layer surface functional groups such as C=O and O=C=O) [32].

The SEM of Fe$_3$O$_4$@GU microspheres demonstrated particles with uniform spherical shapes with an average diameter of 250 nm (see Figure 3a). After annealing, Fe$_3$O$_4$@GU microspheres were completely converted to Fe$_2$O$_3$ microspheres (Figure 3b) as supported by XRD. The surface of the Fe$_2$O$_3$ microspheres shows strong porosity unlike Fe$_3$O$_4$@GU microspheres. Micrographs of the CP-Fe$_3$O$_4$@C microspheres obtained after carbon coating of Fe$_2$O$_3$ microspheres are shown in Figure 3c. It can be seen that the surfaces of the CP-Fe$_3$O$_4$@C microspheres are smooth compared to those of the Fe$_2$O$_3$ microspheres because the carbon layer was successfully coated. Figures 3d, e and f are TEM images of Fe$_3$O$_4$@GU, Fe$_2$O$_3$ and CP-Fe$_3$O$_4$@C microspheres, respectively. From these three figures, it can be seen that both Fe$_2$O$_3$ and CP-Fe$_3$O$_4$@C microspheres show clear porosity, while Fe$_3$O$_4$@GU microspheres exhibit almost none. The TEM image of the CP-Fe$_3$O$_4$@C microspheres shows a thin carbon outer layer approximately 20 nm thick (see Supplementary Figure S2). High-resolution TEM images of the CP-Fe$_3$O$_4$@C microspheres (Supplementary Figure S3) show distinct lattice fringes with a spacing of 0.252 nm, which corresponds to the (311) planes of cubic Fe$_3$O$_4$. The scanning TEM image of the CP-Fe$_3$O$_4$@C microspheres (Figure 3g) and the corresponding element mapping (Figure 3h–j) further establish that CP-Fe$_3$O$_4$@C microspheres were successfully carbon-coated.

Cyclic voltammetry of the CP-Fe$_3$O$_4$@C electrode displays a definite reduction peak at 0.2–0.8 V during the first discharge (Figure 4a), which corresponds to the structural transformation caused by lithium incorporation according to the chemical reaction:

$$\text{Fe}_3\text{O}_4 + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{Fe}_3\text{O}_4$$

Further conversion of Li$_x$Fe$_3$O$_4$ to Fe(0) occurs according to the reaction [5,33]:

$$\text{Li}_x\text{Fe}_3\text{O}_4 + (8-x)\text{Li}^+ + (8-x)e^- \rightarrow 4\text{Li}_2\text{O} + 3\text{Fe}$$

During subsequent cycles, lithium insertion at the cathode occurred mainly between 0.58 and 1.15 V, and lithium extraction at the anode mainly occurred between 1.38 and 2.11 V. It is worth noting that the 2nd, 3rd, and 10th cycles of CV almost coincide, indicating that the electrode cycling process has a minimal impact on subsequent cycles. Figure 4b shows the GCD of the CP-Fe$_3$O$_4$@C electrode after the 1st, 2nd, 3rd, 50th, 100th and 200th cycles at 0.3 A g$^{-1}$ between 0.01 and 3.0 V. The initial discharge curve showed a plateau between 0.21 and 0.66 V. The second and subsequent discharge voltages increased to 0.62–1.10 V, which is consistent with CV. The initial discharge and charge capacity of the CP-Fe$_3$O$_4$@C electrode were 1291 and 914 mAh g$^{-1}$. These drastic differences in capacity usually stem from the formation of the SEI and often occur during the first cycle. The stability and capacity of the CP-Fe$_3$O$_4$@C electrode were compared to those of the Fe$_3$O$_4$@GU and Fe$_2$O$_3$ electrodes (see Figure 4c). After 200 cycles at 0.3 A g$^{-1}$, the reversible capacities of the CP-Fe$_3$O$_4$@C, Fe$_3$O$_4$@GU and Fe$_2$O$_3$ electrodes were 785, 508 and 203 mAh g$^{-1}$, respectively. It is clear that the porous core–shell structure of the CP-Fe$_3$O$_4$@C electrode plays a critical role in the electrochemical performance. Experimentally obtained electrochemical characteristics of different Fe$_3$O$_4$@carbon electrodes with respect to their corresponding Li storage capacity are shown in Supplementary Table S1. The rate capability of the CP-Fe$_3$O$_4$@C electrode is shown in Figure 4d. The stable discharge capacities of the CP-Fe$_3$O$_4$@C electrode at 0.3, 0.8, 1.6, 3 and 6 A g$^{-1}$ were ~791, 648, 471, 312, and 130 mAh g$^{-1}$, respectively. Additionally, the discharge capacity value returned to 723 mAh g$^{-1}$ after the current density was reduced back to 0.3 A g$^{-1}$. These results demonstrate that the CP-Fe$_3$O$_4$@C electrode has outstanding rate capability, high reversibility, and stability for LIBs. Figure 4e shows the charge–discharge curves of the anodes containing CP-Fe$_3$O$_4$@C microspheres as the active material at various current densities. The charge–discharge voltage plateau gradually sloped as the current density was increased, but even at a current density of 6 A g$^{-1}$, the charge–discharge voltage plateaus still persisted.

The electrochemical impedance behavior of the CP-Fe$_3$O$_4$@C electrode under different current cycles at the same current density was studied using Nyquist plots (see Figure 4f). All plots exhibit semicircles in the high- and intermediate-frequency regions and oblique curves at low frequencies. Additionally, equivalent circuit modeling (top right insets,
Figure 3. SEM images of (a) Fe\(_3\)O\(_4\)@GU, (b) Fe\(_2\)O\(_3\) and (c) CP-Fe\(_3\)O\(_4\)@C composites. TEM images of (d) Fe\(_3\)O\(_4\)@GU, (e) Fe\(_2\)O\(_3\) and (f) CP-Fe\(_3\)O\(_4\)@C composites. EDX elemental mapping of (g–j) CP-Fe\(_3\)O\(_4\)@C composite.

Figure 4f) was carried out using Z-VIEW software to obtain kinetic parameters of three composites. According to the equivalent circuit diagram, the intercept of the high-frequency semicircle with the x-axis corresponds to the electrolyte resistance (\(R_e\)), while \(R_f\) and \(R_{ct}\) correspond to SEI film and charge transfer resistances, respectively [27,34]. The slope at low frequencies corresponds to the Warburg impedance (\(Z_w\)) of the Li\(^+\) diffusion; CPE1 and CPE2 are the SEI film and double layer capacitances, respectively [35, 36]. CP-Fe\(_3\)O\(_4\)@C-based anodes exhibited lower \(R_{ct}\) values (which were equal to 16.5 \(\Omega\)) after the first cycle, especially when compared to \(R_{ct}\) values of the fresh cycle (which was equal to 395.7 \(\Omega\)). This difference is mainly due to the wetting of the electrode and proper SEI formation during the first cycle. The \(R_{ct}\) value after the 200th cycle differs only slightly from the \(R_{ct}\) value after the 100th cycle, again pointing to an excellent electrode structural stability. Resistance values of electrodes based on Fe\(_3\)O\(_4\)@GU and Fe\(_2\)O\(_3\) active materials were higher than the total resistance of the CP-Fe\(_3\)O\(_4\)@C-based electrodes for all cycles tested in this work (see Supplementary Figures S4a and S4b).

The rate performance of CP-Fe\(_3\)O\(_4\)@C-based LIB anodes as well as their reaction kinetics was analyzed.
Figure 4. (a) CV curves at 0.1 mV·s$^{-1}$ and (b) GCD curves at 0.3 A·g$^{-1}$ of the CP-Fe$_3$O$_4$@C electrode. (c) Cyclic performance at 0.3 A·g$^{-1}$ of the Fe$_2$O$_3$, Fe$_3$O$_4$@GU and CP-Fe$_3$O$_4$@C electrodes. (d) Rate performance at different current densities. (e) Representative discharge–charge voltage profiles at various rates. (f) Nyquist plots of the CP-Fe$_3$O$_4$@C electrode (top right insets show the equivalent circuit model).

by CV. The contribution of capacitance is calculated and identified using gradually increasing sweep rates during CV as shown in Figure 5a. Using the method of Dunn [37,38], the total current response ($i$) at con-
Figure 5. (a) CV curves at different scan rates from 0.1 to 5 mV·s⁻¹. (b) The fitted lines of \( i(V)/v^{1/2} \) versus \( v^{1/2} \) at different voltages. (c) CV curves with capacitive contribution at 0.4 mV·s⁻¹. (d) Separation of contributions from capacitive effects and diffusion-controlled capacities at different scan rates.

The constant potential \( (V) \) can be represented as a combination of surface capacitive effects and diffusion-controlled insertion processes (see (1) and (2)):

\[
i(V) = K_1 v + K_2 v^{1/2}, \tag{1}\\
i(V)/v^{1/2} = K_1 v^{1/2} + K_2, \tag{2}
\]

where \( K_1 v \) and \( K_2 v^{1/2} \) are the contributions of the total surface capacitive and diffusion-controlled insertion processes, respectively. Comparing CV results at different sweeps, the values of \( K_1 \) and \( K_2 \) can be determined by fitting \( i(V)/v^{1/2} \) versus \( v^{1/2} \) as a linear function according to (2) as shown in Figure 5b. Subsequently, \( K_1 \) and \( K_2 \) are replaced by their values in (1), partitioning the contribution of Faradic capacitance from the contribution of pseudocapacitance in the total stored charge. Figure 5c shows a separation of capacitance and diffusion currents at a scan rate of 0.4 mV·s⁻¹. Brown areas represent capacitance effect, and blank areas represent diffusion-controlled capabilities. As can be seen from Figure 5d, at 0.1, 0.4, 1.2, 2.4 and 5 mV·s⁻¹, pseudocapacitance accounts for 19%, 29%, 41%, 57% and 91%, respectively, of the total capacity, indicating significant pseudocapacitance behavior during the cycling of CP-Fe₃O₄@C-based anodes at high rates. Thus, CP-Fe₃O₄@C-based electrodes demonstrated higher pseudocapacitance contribution at almost all current densities, which is indicative of an excellent rate performance.
The morphology of the CP-Fe$_3$O$_4$@C-based electrode was tested before cycling and also after 10 and 60 cycles (Figure 6). Fe$_3$O$_4$ microspheres in prepared CP-Fe$_3$O$_4$@C electrode material are uniformly wrapped by a carbon layer (see Figure 6a). The carbon coating on the CP-Fe$_3$O$_4$@C electrode after the 10th cycle is still intact, and the carbon layer is mostly unchanged (see Figure 6b). After the 60th cycle, Fe$_3$O$_4$ structurally deteriorates into smaller microspheres, but Fe$_3$O$_4$ remains well coated with carbon layers (see Figure 6c).

4. Conclusions

In summary, the core–shell CP-Fe$_3$O$_4$@C microspheres were synthesized by simple methods using common inexpensive and easily removable chemicals as filler particles. The unique structural characteristics of the CP-Fe$_3$O$_4$@C microspheres yielded electrodes with capacities equal to 785 mAh·g$^{-1}$ (at 0.3 A·g$^{-1}$ after 200 cycles). In addition, it was further shown that the CP-Fe$_3$O$_4$@C electrode has excellent rate performance through reaction kinetics. These experimental results show that the CP-Fe$_3$O$_4$@C composite prepared by this simple method has strong prospects as an active anode material for high-performance LIBs.

Conflicts of interest

The authors declare no conflict of interest.

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Supplementary data

Supporting information for this article is available on the journal’s website under https://doi.org/10.5802/crchim.18 or from the author.

References


