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Energy materials



The facile preparation of hollow Fe₃O₄/C/CNT microspheres assisted by the spray drying method as an anode material for lithium-ion batteries

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ABSTRACT

We have designed a facile process to synthesize the hollow $Fe_3O_4/C/CNT$ microspheres through a spray drying method. The composite has both the high theoretical capacity of Fe_3O_4 and the great electronic conductivity of carbon nanotubes (CNTs). And the hollow structure built by spray drying is beneficial to relieve the volume change during conversion reaction. With the combination of Fe_3O_4 and carbon materials, the $Fe_3O_4/C/CNT$ microspheres show a great electrochemical performance. It has maintained a high reversible capacity of 1200 mA h g⁻¹ after 100 cycles at the current density of 200 mA g⁻¹ and a specific capacity of 750 mA h g⁻¹ after 300 cycles at the current density of 1 A g⁻¹. The composite also shows a high initial coulombic efficiency of 75.7% at 200 mA g⁻¹. Hence, the high-performance hollow $Fe_3O_4/C/CNT$ s microsphere is a promising substitute for anode material of lithium-ion batteries (LIBs). Furthermore, the spray draying method is widely used in industrial manufacture. Therefore, this composite has greater potential for a practical application.

Introduction

In contemporary society, the need of portable electronic devices has been growing with the accelerated pace of life [1–3]. Although there is no doubt that commercial lithium-ion batteries (LIBs) fit the bill of various portable electronic devices in recent years, we still expect batteries to possess higher energy density to meet the requirement of prolonged use [4–6]. The graphite anode material plays a major role in the commercial anode materials of LIBs because of its fine cycle performance and abundant reserves. However, the theoretical capacity of graphite is only 372 mA h g⁻¹, which restricts the development of high-capacity batteries. Therefore, the search for a proper substitute has been an urgent business [2, 7, 8].

In those potential substitutes, Fe₃O₄ has been researched extensively for its ultra-high theoretical

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capacity of 924 mA h g^{-1} and low cost [9]. Despite the advantages of Fe_3O_4 , there are still several intrinsic problems obstructing its practical application. For example, the electrical conductivity of Fe₃O₄ is low, and Fe₃O₄ is a kind of transition metal oxides following a conversion reaction mechanism during charge–discharge process [10, 11]. The conversion reaction is accompanied with big volume change, resulting in the structural destruction of anode [12]. Hence, the capacity of pristine Fe₃O₄ anode fades rapidly in the first several cycles [2, 13]. To solve these problems, many approaches have been attempted. The most effective method is to fabricate a composite of Fe_3O_4 and carbon materials [7]. Carbon materials can improve the electrical conductivity of the composite, and they can also form a framework for the Fe₃O₄ composite. Those particular designed structures improve the stability of anode greatly, and they can also relieve the pressure of volume change during cycling. Therefore, it is a promising modification method for Fe₃O₄.

Many strategies have been devoted to fabricating carbon composites of Fe₃O₄, for example fabricating carbon-coated Fe₃O₄ nanospindles [14], wrapping Fe_3O_4 particles with graphene nanosheets [15], embedding Fe₃O₄ nanoparticles in interconnected SWNTs net [16] and synthesizing hollow Fe₃O₄ beads [17]. Although these reported Fe_3O_4/C composites show an obvious promotion in capacity and cycling stability, most of their preparation processes are based on a high-pressure hydrothermal method, which is hazardous and not suitable for practical application. It is necessary to find a convenient and practical technology to synthesize the Fe₃O₄/C composite. As we know, the spray drying method is a widely used technology in an industrial manufacture, it can help the formation of spherical particles of a composite, and its operation process is simple and efficient [18]. Hence, it is a good choice for the synthesis of Fe_3O_4/C composite.

In this study, we have synthesized the hollow $Fe_3O_4/C/CNT$ microspheres through a facile spray drying method. Through the combination of Fe_3O_4 and CNTs, a stable spherical framework of the composite is fabricated. And carbon nanotubes (CNTs) are widely used in various carbon composites for their superb electronic conductivity and tensile strength [19, 20]. The formation of three-dimensional frame of CNTs can relieve the volume change effectively in cycling. The hollow microsphere structure

provides a buffer zone for the volume change and improves the stability of the composite [21, 22]. Compared with the contrast anode prepared by pristine commercial Fe₃O₄ nanoparticles, the composite anode shows excellent electrochemical performance. The Fe₃O₄/C/CNT electrodes show a high capacity of 1200 mA h g⁻¹ at 0.2 A g⁻¹ after 100 cycles, while the commercial Fe₃O₄ electrodes fade to about 200 mA h g⁻¹ rapidly. And the 75.7% coulombic efficiency of the first cycle is also attained. Meanwhile, the Fe₃O₄/C/CNT electrodes show great rate performance, and a capacity of 502 mA h g⁻¹ is achieved at 5 A g⁻¹. And in a long cycling process of 1 A g⁻¹, the composite electrodes maintain a capacity of 750 mA h g⁻¹ after 300 cycles.

Experimental section

Materials

Glucose (AR) and $Fe(NO_3)_3 \cdot 9H_2O$ (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. The CNTs suspension (10 wt%) was purchased from Chengdu Organic Chemicals Co., Ltd. Fe₃O₄ nanoparticles (NPs) were purchased from Alfa Aesar (China) Chemicals Co., Ltd. All reagents were used without further purification.

Preparation of the hollow Fe₃O₄/C/CNT microspheres

A spray drying method was used to obtain the precursor of hollow Fe₃O₄/C/CNT microspheres. Typi-4.04 g $Fe(NO_3)_3 \cdot 9H_2O_7$ 1.50 g cally, **CNTs** suspension (10 wt%) and 0.5 g glucose were dispersed in 100 mL H₂O. After stirring for 3 h, the suspension was introduced to a spray dryer (BUCHI Mini Spray Dryer B-290). The inlet temperature of spray dryer was set at 205 °C, and the pump speed was 10%. The precursor was collected and annealed at 600 °C for 10 h in the atmosphere of argon. Then, we get the final product of hollow Fe₃O₄/C/CNT microspheres.

Material characterization

The morphologies of the sample were observed by the field-emission scanning electron microscopy (FESEM, HITACHI, S-4800) and the high-resolution transmission electron microscopy (HRTEM, JEOL, JEM-2100). The X-ray diffraction (XRD) tests were operated by Rigaku Miniflex 600 X-ray diffractometer from 10° to 90°. The X-ray photoelectron spectroscopy (XPS) measurements were taken by the PHI Quantum 2000. Thermogravimetric analysis (TGA) was conducted on the SDT-Q600 from room temperature to 800 °C in air atmosphere. N₂ adsorption–desorption measurement was taken by Micromeritics ASAP 2020. The powder electronic conductivity measurements were taken by the Power Resistivity Meter SZT-D (Suzhou Jingge Electronics Co., Ltd.).

Electrochemical measurements

To measure the electrochemical properties of hollow Fe₃O₄/C/CNT microspheres and commercial Fe₃O₄ nanoparticles, the electrodes were prepared by mixing the active material, acetylene black and LA132 binder at a weight ratio of 70:20:10 in water. Then, the slurries were coated onto copper foil and dried in a vacuum oven at 80 °C overnight. The CR2016 coin cells were assembled in an argon-filled glovebox with lithium foil as the counter electrodes. The electrolyte was composed of 1 M LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1, in volume), and the separator was chosen Celgard 2400. The galvanostatic charge/discharge tests were performed on LAND CT2001A battery test system from 0.01 to 3.00 V (vs. Li⁺/Li), and the electrochemical impedance spectra (EIS) were carried on Solartron 1260/1287 with a frequency range from 0.01 to 100 kHz. The cyclic voltammogram test was operated on CHI 1030C from 0.01 to 3.00 V (vs. Li^+/Li) at 0.2 mV s^{-1} . The calculation of specific capacity of the $Fe_3O_4/C/CNTs$ electrode is based on the total weight of $Fe_3O_4/C/CNTs$ composite.

Results and discussion

As the process shown in Fig. 1, a suspension of $Fe(NO_3)_3$, CNTs and glucose is prepared firstly, and then followed by a spray drying process, the water of liquid droplets is evaporated fast which helps the formation of hollow microsphere structure, and finally by an annealing process, we get the hollow $Fe_3O_4/C/CNT$ microspheres material. As we have seen, the overall process is simple and convenient. And through the adjustment of the spray drying

temperature and the concentration of suspension, we can control the synthesis of hollow spherical structure.

Figure 2a shows the XRD patterns of the hollow $Fe_3O_4/C/CNT$ microspheres and commercial Fe_3O_4 NPs. All the peaks of two samples are consistent with Fe₃O₄ PDF standard card (JCPDS: 01-072-2303). And the weak peak of Fe₃O₄/C/CNTs around 26.2° belongs to the CNTs [23]. In the annealing process at 600 °C in an argon atmosphere, $Fe(NO_3)_3$ is decomposed and converted to Fe₃O₄ under the reduction of glucose and CNTs. The glucose is also decomposed to amorphous carbon [24]. The XRD results prove the formation of the Fe₃O₄/C/CNTs composite preliminarily. To further explore the content of carbon material in this composite, the TGA is conducted. As shown in Fig. 2b, the weight loss of the composite is 14.9%. In this process, the carbon material is burnt out and Fe₃O₄ is also oxidized to Fe₂O₃. There is an obvious increase between 250 and 400 °C in the TGA curve, and the increase ratio of weight is about 1.5%. This phenomenon results from the oxidation of Fe₃O₄ before the burning of most carbon. The 1.5% weight increase is less than the theoretical weight increase in the oxidation of Fe_3O_4 (2.9%), so the appearance of this phenomenon is reasonable and consistent with previous reports [25, 26]. Hence, the calculated content of carbon material of $Fe_3O_4/C/CNTs$ composite is 17.7%. To characterize the porous structure of Fe₃O₄/C/CNTs composite, the N₂ adsorption-desorption test is performed (Fig. 2c, d). From the N₂ adsorption-desorption isotherm (Fig. 2c), we can see that it shows a type IV isotherm and it means the Fe₃O₄/C/CNTs composite has a mesoporous structure. And analyzed by the Brunauer-Emmett-Teller (BET) method, the surface area of the composite is 23.3 m² g⁻¹ and the pore volume is 0.13 cm³ g⁻¹. This big specific surface area means more active sites to the conversion reaction, and it brings better rate performance. From the pore size distribution (Fig. 2d) calculated by the Barrett–Joyner–Halenda (BJH) method, the mesoporous size of composite presents a distribution of 3.5 and 34 nm. This hybrid mesoporous structure of Fe₃O₄/C/CNTs composite can help the immersion of electrolyte and the quick migration of Li⁺, and the big pore volume can also relieve the volume change of Fe₃O₄ during the cycling process [27, 28].

The XPS measurements are taken to further analyze the surface composition of $Fe_3O_4/C/CNTs$



Figure 1 Schematic synthesis process of the hollow Fe₃O₄/C/CNT microspheres.



Figure 2 a XRD patterns of $Fe_3O_4/C/CNTs$ composite and commercial Fe_3O_4 NPs. b TGA curve of the $Fe_3O_4/C/CNTs$ composite in air atmosphere. c N_2 adsorption–desorption isotherm and d pore size distribution of $Fe_3O_4/C/CNTs$ composite.

composite. From the wide-scan spectra (Fig. 3a, c) of $Fe_3O_4/C/CNTs$ composite and commercial Fe_3O_4 nanoparticles, we can see that there are prominent peaks of Fe 2p, O 1s and C 1s in the spectrum of the $Fe_3O_4/C/CNTs$ composite, but the C 1s peak of commercial Fe_3O_4 nanoparticles is weak for lack of carbon material itself. The appearance of weak C 1s

peak is attributed to the pollution of environmental carbon. To confirm that pure Fe₃O₄ has been synthesized, the high-resolution XPS spectra (Fig. 3b, d) of Fe 2p are performed. There are prominent peaks of Fe $2p_{1/2}$ and Fe $2p_{3/2}$ in both spectra. The fitting curves of Fe $2p_{3/2}$ spectrum belong to the peaks of Fe²⁺ and Fe³⁺. The Fe $2p_{3/2}$ spectrum of Fe₃O₄/C/



Figure 3 XPS spectra of **a**, **b** $Fe_3O_4/C/CNTs$ composite and **c**, **d** commercial Fe_3O_4 nanoparticles: **a**, **c** wide-scan spectra and **b**, **d** $Fe_2p_3O_4/C/CNTs$ composite and commercial Fe_3O_4 nanoparticles, respectively.

CNTs composite is separated to Fe^{2+} (710.8 eV) and Fe^{3+} (712.5 eV) corresponding to the distribution of commercial Fe₃O₄ nanoparticles (Fe²⁺ (710.5 eV) and Fe³⁺ (712.2 eV)). And there is none satellite peak between Fe 2p_{1/2} and 2p_{3/2} in the spectrum of Fe₃O₄/C/CNTs composite. It is an essential basis to judge the existence of Fe₂O₃ [29, 30]. Hence, it confirms that there is none Fe₂O₃ in the composite, and we get the pure Fe₃O₄/C/CNTs composite.

The morphologies of Fe₃O₄/C/CNTs composite are observed by SEM and TEM. The composite presents a series of spheres in a relatively uniform size distribution, with the diameter of 2–4 μ m (Fig. 4a). And there are some smaller particles around microspheres, and these particles fill the voids and connect the electrical conductivity network further. A clearer image of Fe₃O₄/C/CNTs microsphere (Fig. 4b) indicates that the surface of microsphere is covered with CNTs, and the space among crossed CNTs is filled by Fe₃O₄ particles. In this composite structure, CNTs build the frame of microspheres, and CNTs and Fe₃O₄ particles are cross-linked tightly. CNTs improve the electrical conductivity and the structure stability of the composite. To demonstrate the hollow structure of the microspheres, the TEM images are shown. It is obvious that the center area of the $Fe_3O_4/$ C/CNTs microsphere is much brighter than the edge part (Fig. 4c), confirming the microsphere is hollow. The inner space of microspheres enlarges the contact area of anode and electrolyte. And it also provides buffer space for the volume change of Fe₃O₄. As for the high-resolution image (Fig. 4d) of $Fe_3O_4/C/$ CNTs, the interplanar distance of the obvious lattice plane is 0.49 nm, corresponding to the (111) plane of Fe₃O₄. And the curved lattices can be assigned to CNTs. The elemental mapping images (Fig. 4e-h) show a homogeneous distribution of C, O and Fe elements. It means that CNTs and Fe₃O₄ are well mixed through spray drying process, and it is beneficial to the stability of hollow Fe₃O₄/C/CNT microspheres.

To prove whether the addition of CNTs and amorphous carbon improves the electrical conductivity of the composite, the powder electronic



Figure 4 a, b SEM images, c, d TEM images and e-h elemental mapping of the hollow Fe₃O₄/C/CNT microspheres.

conductivity of two samples is measured. As shown in Table 1, the electronic conductivity of the hollow $Fe_3O_4/C/CNT$ microspheres is 3.413 S cm⁻¹, while the commercial Fe₃O₄ nanoparticles are $5.028 \times 10^{-6} \text{ S cm}^{-1}$. The carbon materials show a great improvement in the electrical conductivity of the composite, and the CNTs fabricate a three-dimensional conductive network, which is in favor of the fast transportation of electrons during dischargecharge process of the electrodes. Therefore, the Fe₃O₄/C/CNT electrodes are expected to show better electrochemical performance.

Table 1 Powder electronic conductivity of $Fe_3O_4/C/CNT$ and commercial Fe_3O_4 nanoparticle samples measured at the pressure of 4 MPa

Samples	Conductivity (S cm^{-1})
Samples	
Fe ₃ O ₄ /C/CNTs	3.413
commercial Fe ₃ O ₄ nanoparticles	5.028×10^{-6}

To investigate the electrochemical performances of the hollow microspheres, the galvanostatic charge/ discharge tests are performed with $Fe_3O_4/C/CNT$ electrodes and commercial Fe_3O_4 electrodes in a voltage range from 0.01 to 3.00 V at 200 mA g⁻¹. The discharge/charge profiles are shown in Fig. 5a and b. Figure 5a shows that $Fe_3O_4/C/CNT$ electrodes deliver an initial discharge capacity of 1193 mA h g^{-1} with a coulombic efficiency of 75.7%. Though the commercial Fe₃O₄ electrodes exhibit a higher initial discharge capacity of 1537 mA h g^{-1} , the capacity fades rapidly in the following cycles, while the Fe₃O₄/C/CNT electrodes show a stable cycling capacity. In the initial discharge step of $Fe_3O_4/C/$ CNT electrodes, a long voltage plateau of about 0.8 V can be found, which corresponds to the conversion reaction process $Fe_3O_4 + 8Li^+ + 8e^- \rightarrow 3Fe + 4Li_2O$ [31]. This plateau can also be observed in the step of commercial Fe₃O₄ electrodes. The extra plateau around 1-0.8 V (Fig. 5b) of commercial Fe₃O₄ electrodes is assigned to the part intercalation process of $Fe_3O_4 + xLi^+ + xe^- \rightarrow Li_xFe_3O_4$ [32]. The unusual large capacity of the first discharge process of two electrodes is attributed to the formation of solid electrolyte interface (SEI) film, and the following discharge curves become sloping. It means that some irreversible reactions have happened in the first cycle [33].

Figure 5c exhibits the cycle performance of the two electrodes at 200 mA g^{-1} . The capacity of Fe₃O₄/C/ CNT electrodes is rising gradually during cycling and maintains at almost 1200 mA h g^{-1} after 100 cycles. Generally, it is assigned to the reversible process of a polymeric gel-like film on Fe₃O₄/C/CNT electrodes [34-36]. However, the capacity of commercial Fe₃O₄ electrodes fades rapidly in the first several cycles. It fades to nearly 160 mA h g^{-1} in first 50 cycles and rises to around 200 mA h g^{-1} in the following cycles. The striking contrast shows the importance of carbon composite frame in keeping the stability of anode [37]. With the combination of Fe_3O_4 and CNTs, the frame fabricated by CNTs can improve the stability of composite effectively and the hollow sphere structure relieves the volume change during conversion reaction. In contrast, the commercial Fe₃O₄ electrodes face to the damage of structure and exfoliation of active material caused by big volume expansion during discharge-charge process. And to analyze the capacity contribution of C/CNTs in the $Fe_3O_4/C/CNTs$ composite, the composite is prepared C/CNTs under same



Figure 5 Discharge/charge profiles of a $Fe_3O_4/C/CNT$ electrodes and b commercial Fe_3O_4 electrodes at 200 mA g^{-1} . c The cycling performance of two electrodes at 200 mA g^{-1} . d The rate capability of $Fe_3O_4/C/CNT$ electrodes at various current densities.



conditions without the addition of $Fe(NO_3)_3 \cdot 9H_2O$. As shown in Fig. S1, the C/CNTs electrode shows a capacity of 256 mA h g^{-1} at 200 mA g^{-1} . And the content of carbon material in Fe₃O₄/C/CNTs composite is 17.7%; then, the capacity of 45.3 mA h g^{-1} is attributed to C/CNTs in the 1200 mA h g^{-1} of the composite. Therefore, the capacity contribution of C/CNTs is mainly neglectable. The rate capability of Fe₃O₄/C/CNT electrodes at different current densities from 0.2 to 5.0 A g^{-1} is shown in Fig. 5d. The electrodes maintain the specific capacities of 866, 770, 712 and 631 mA h g^{-1} at current densities of 0.2, 0.5, 1 and 2 A g^{-1} , respectively. Even when the current density comes to 5 A g^{-1} , there is still a capacity of 502 mA h g^{-1} . And when the current density comes back to 0.2 Ag^{-1} , the capacity recovers to 875 mA h g^{-1} . The results indicate that the Fe₃O₄/C/ CNT electrodes have a good rate performance and reversible capacity. Since the importance of volumetric capacity of electrode as an evaluation of anode electrochemical performance, the volumetric capacity of $Fe_3O_4/C/CNTs$ electrode is calculated. The $Fe_3O_4/C/CNTs$ C/CNT electrodes show a density of about 1.1 g cm^{-3} and a high volumetric capacity of 947.5 mA h cm⁻³ (Table S1), which is much higher than the 357.3 mA h cm $^{-3}$ of the contrastive graphite electrode (Table S2).

The cyclic voltammogram is carried from 0.01 to 3 V in a scan rate of 0.2 mV s⁻¹ to illustrate the electrochemical process of Fe₃O₄/C/CNTs electrode during cycling (Fig. S2). At the cathodic process of the first cycle, there is an obvious peak at 0.54 V, which is associated with the reduction in Fe₃O₄ to Fe and the formation of SEI, corresponding to the anodic peak at 1.70 V [38]. The following cycles show obvious peaks shift, which indicates that irreversible reaction has happened. The second cycle shows expansion of peaks. And in the third cycle, there are two cathodic peaks at 0.92 and 0.78 V, which are attributed to the reduction in Fe²⁺/Fe³⁺ to Fe, corresponding to the two reversible anodic peaks at 1.77 and 1.92 V [39, 40].

The long-term cycling performance of $Fe_3O_4/C/$ CNT electrodes at a current density of 1 A g⁻¹ is shown in Fig. 6. The electrode is cycled at a current density of 0.2 A g⁻¹ in the first 5 cycles to activate the composite material and followed with a current density of 1 A g⁻¹ in 300 cycles. The capacity shows a slow decrease in the first 80 cycles and drops to 635 mA h g⁻¹, but in the following cycling, the



Figure 6 Long-term cycling performance of $Fe_3O_4/C/CNT$ electrodes at a current density of 1 A g^{-1} .

capacity of $Fe_3O_4/C/CNTs$ electrode increases gradually and keeps at about 750 mA h g⁻¹ after 300 cycles. The decrease in capacity in the first 80 cycles is attributed to the structure damage of $Fe_3O_4/C/CNTs$ composite caused by cycling in a big current density of 1 A g⁻¹, and the increase in capacity in the subsequent cycles is assigned to the generation of a reversible polymeric SEI layer on the surface of electrodes [41, 42].

Though we have tested the powder electronic conductivity of the $Fe_3O_4/C/CNTs$ composite and proved the promoted electrical conductivity than that of pure Fe_3O_4 particles, the practical electrochemical performances of electrodes in batteries are needed to be investigated. The EIS are carried out to test the electrical conductivity of $Fe_3O_4/C/CNT$ electrodes (Fig. 7). The $Fe_3O_4/C/CNT$ electrodes and



Figure 7 Nyquist curves and the fitting curves of $Fe_3O_4/C/CNT$ electrodes and commercial Fe_3O_4 nanoparticle electrodes, and the equivalent circuit model.

commercial Fe₃O₄ nanoparticle electrodes fabricated in coin cells are tested without cycling in the frequency range from 0.01 Hz to 100 kHz. The Nyquist curves of two electrodes are formed by the semicircle part in high-frequency region and the sloping line part in low-frequency region. And fitted with the equivalent circuit model shown in Fig. 7, the semicircle part in high-frequency area presents R_s (solution resistance), R_{ct} (charge transfer resistance) and CPE (constant phase element) of batteries, and the inclined line in low-frequency area presents W_{0} (Warburg impedance) related to the diffusion of Li⁺ [43]. The R_{ct} presents the electrical conductivity directly, and there is a positive correlation between $R_{\rm ct}$ and the diameter of the semicircle. It is distinct that the semicircle of Fe₃O₄/C/CNTs electrode is much smaller than the commercial Fe₃O₄ electrode. The fitting results show that the R_{ct} of Fe₃O₄/C/CNT electrodes is 145.1 Ω , while the R_{ct} of commercial Fe₃O₄ electrodes is 230.3 Ω . The Fe₃O₄/C/CNT electrodes have a smaller charge transfer resistance than commercial Fe₃O₄ nanoparticle electrodes. Hence, it is veritable that the amorphous carbon and CNTs enhance the electrical conductivity of the $Fe_3O_4/C/$ CNT electrodes.

Conclusions

In summary, a facile spray drying method is used to prepare the hollow $Fe_3O_4/C/CNT$ microspheres as LIBs anode material. Both the combination of Fe_3O_4 and carbon material and the hollow microsphere structure contribute to the improvement of cycling stability for the Fe₃O₄/C/CNT electrodes. The hollow space can relieve the pressure of volume change during conversion reaction process, and the CNTs crossing net can consolidate the structure of composite. Therefore, the $Fe_3O_4/C/CNT$ electrodes show greater electrochemical performances than that of the pristine Fe₃O₄ electrodes. The reversible capacities of about 1200 mA h g^{-1} after 100 cycles at 200 mA g^{-1} and 750 mA h g^{-1} at 1 A g^{-1} have been attained. The $Fe_3O_4/C/CNTs$ composite is a promising anode substitute for the LIBs and worth for further exploration, since the composite has a good cycling stability and reversible capacity, and the spray drying method is facile and widely used in industrial manufacture.

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Compliance with ethical standards

Conflict of interest The authors declare no conflicts of interest.

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