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# Ammonia-treatment assisted fully encapsulation of $Fe_2O_3$ nanoparticles in mesoporous carbons as stable anodes for lithium ion batteries

Fei Han, Wen-Cui Li, Duo Li, An-Hui Lu\*

State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Faculty of Chemical, Environmental and Biological Science and Technology, Dalian University of Technology, Dalian 116024, Liaoning, China

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#### Abstract

To improve the initial coulombic efficiency and bulk density of ordered mesoporous carbons, active  $Fe_2O_3$  nanoparticles were introduced into tubular mesopore channels of CMK-5 carbon, which possesses high specific surface area (>1700 m<sup>2</sup>·g<sup>-1</sup>) and large pore volume (>1.8 cm<sup>3</sup>·g<sup>-1</sup>). Fine Fe<sub>2</sub>O<sub>3</sub> nanoparticles with sizes in the range of 5–7 nm were highly and homogenously encapsulated into CMK-5 matrix through ammonia-treatment and subsequent pyrolysis method. The Fe<sub>2</sub>O<sub>3</sub> loading was carefully tailored and designed to warrant a high Fe<sub>2</sub>O<sub>3</sub> content and adequate buffer space for improving the electrochemical performance. In particular, such Fe<sub>2</sub>O<sub>3</sub> and mesoporous carbon composite with 47 wt% loading exhibits a considerably stable cycle performance (683 mAh·g<sup>-1</sup> after 100 cycles, 99% capacity retention against that of the second cycle) as well as good rate capability. The fabrication strategy can effectively solve the drawback of single material, and achieve a high-performance lithium electrode material.

## Key words

ordered mesoporous carbon; Fe<sub>2</sub>O<sub>3</sub> nanoparticle; cycle stability; lithium-ion anode

# 1. Introduction

To meet the ever-increasing energy demands of portable electronics and practical electric vehicles, many researchers pay attention to rechargeable lithium-ion batteries (LIBs), which are attractive energy storage devices because of their relatively high energy density and power density as well as safety [1–3]. The low theoretical capacity (372 mAh·g<sup>-1</sup>) and poor rate capability of conventional commercialized graphite anode materials cannot match up with these demands of high performance battery systems [4-6]. With the rapid growth of nanotechnology, continual research has focused on designing new carbon-based anodes with high performances by virtue of their favorable physical and chemical stability and outstanding kinetics. Up to date, enormous novel carbon-based electrode materials with various morphologies and structures have been investigated, such as carbon nanobeads [7], nanotubes [8,9], nanofibers [6], nanospheres [10,11], graphenes [12,13], ordered mesoporous carbons (OMCs) [14], hierarchically porous carbons [5,15], and their composites [3,4]. In particular, OMCs have received much attention as anode materials on account of controllable pore structure and chemical composition as well as high surface area, excellent electrical conductivity and chemical stability [16,17].

Nonetheless, there are still a number of problems to be overcome prior to any large-scale application of such attractive OMCs. Firstly, it is an enormous challenge to simultaneously possess a high initial coulombic efficiency (>50%) and high reversible capacity  $(>450 \text{ mAh} \cdot \text{g}^{-1})$ [18,19]. OMCs usually exhibit a relatively high reversible capacity of  $400-800 \text{ mAh} \cdot \text{g}^{-1}$  due to their high surface area with more Li<sup>+</sup> storage active sites, but high exposed surface area causes the formation of more solid electrolyte interface (SEI) films from the irreversible reaction of Li-ions, thus leading to low initial coulombic efficiency even lower than 40% [14,20]. Secondly, the energy density of portable electronic devices was strictly limited by the small battery pack size, however, porous OMCs always possess loose macroscopic structure, resulting in low bulk density, which reduces the volumetric energy density and restricts the application of smallscale cell packs. To break through the bottleneck of electrochemical performance of OMCs, loading of some particles

<sup>\*</sup> Corresponding author. Tel: +86-411-84986112; Fax: +86-411-84986112; E-mail: anhuilu@dlut.edu.cn

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into the pore channels of OMCs is a heart-stirring strategy, which can integrate the advantages of each component for the preparation of high-performance LIBs [4,21]. Various metal oxides or alloys (such as Si [22], SnO<sub>2</sub> [4], MnO<sub>2</sub> [23]) and OMCs composite materials have been proposed as alternative anode materials. All of the above attempts have brought significant improvements of the electrochemical performance of OMCs-based anode materials.

In recent years, Fe<sub>2</sub>O<sub>3</sub> has been widely studied as promising anode material because of its high theoretical capacity (1007 mAh·g<sup>-1</sup>), large inherent densities (5.24 g·cm<sup>-3</sup> vs. 2.16  $g \cdot cm^{-3}$  for graphite) and environmental friendliness [24,25]. Therefore, fabrication of OMCs encapsulated Fe<sub>2</sub>O<sub>3</sub> composite is considered to be an effective approach to improve the reversible capacity, bulk density and initial coulombic efficiency. Due to the poor cycle stability of Fe<sub>2</sub>O<sub>3</sub> anode derived from unstable SEI films and large volume expansion, it is extremely necessary to highly and uniformly encapsulate Fe<sub>2</sub>O<sub>3</sub> nanoparticles (NPs) into the mesopore channels for reducing the electrolyte contact area [4,20,26]. Meanwhile, adequate buffer space for volume expansion of Fe<sub>2</sub>O<sub>3</sub> should be reserved in the composites to maintain the structure integrity. Therefore, it is necessary to develop a mesoporous carbon matrix with uniform pore sizes and large pore volume. CMK-5, ordered nanostructure carbon with a dual mesopore system, possesses high specific surface area  $(>1700 \text{ m}^2 \cdot \text{g}^{-1})$ and large pore volume (>1.8 cm<sup>3</sup>·g<sup>-1</sup>) with a defined narrow pore size distribution and tunable pore sizes [4,27,28]. Consequently, highly dispersed Fe<sub>2</sub>O<sub>3</sub> NPs can be produced in a confining environment of CMK-5 as lithium-ion anodes with low electrolyte contact interface and adequate buffer space to maintain the structure stability. Recently, we have reported a polypyrrole-coated Fe<sub>2</sub>O<sub>3</sub>@CMK-5 multifunctional composite as lithium-ion anode with high volumetric capacity and excellent cycle stability [21]. It has been shown that the loading of Fe<sub>2</sub>O<sub>3</sub> NPs and the contact area between Fe<sub>2</sub>O<sub>3</sub> and electrolyte play key roles in the high performance of LIBs.

To further understand these requirements, in this study we report a new method to prepare CMK-5 and ultrafine Fe<sub>2</sub>O<sub>3</sub> composites with accurately optimized loading of Fe<sub>2</sub>O<sub>3</sub> NPs to achieve a high capacity and improved cycle stability. The as-prepared Fe<sub>2</sub>O<sub>3</sub>@C composite can overcome the challenges of conversion reaction to a large degree, and exhibit stable, high reversible capacity with good rate capability and coulombic efficiency. Its excellent electrochemical performance is attributed to the spatial confinement in the pores and low contact interface between Fe<sub>2</sub>O<sub>3</sub> NPs and electrolyte due to the protection of carbon matrix. Meanwhile, adequate buffer space in the Fe<sub>2</sub>O<sub>3</sub>@C composite can accommodate properly the huge volume expansion of Fe<sub>2</sub>O<sub>3</sub> NPs, preventing pulverization and aggregation.

## 2. Experimental

#### 2.1. Preparation of material

CMK-5, tubular mesoporous carbon, was synthesized via

nanocasting approach using SBA-15 template as described in our previous works [29,30]. The Fe<sub>2</sub>O<sub>3</sub>@C composites were prepared using in-situ ammonia treatment and then pyrolysis of Fe(NO<sub>3</sub>)<sub>3</sub> precursor in CMK-5. Firstly, 2.33 M Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O containing a drop of HCl (37%) was impregnated into the pore space of CMK-5. After drying at 50 °C for 3 h, the powder was put into a teflon bottle containing 14 wt% ammonia solution (4 mL), without direct contact to the ammonia solution. After sealing, the bottle was heated in an oven at 50 °C for 3 h to hydrolyze the metal precursor in-situ. The product was then washed several times with deionized water and ethanol, and dried at 50 °C. The impregnation and conversion steps were repeated for several times in order to control the Fe<sub>2</sub>O<sub>3</sub> loading. The dried product was further pyrolyzed to 400 °C with a heating rate of 2 °C·min<sup>-1</sup> for 4 h under an argon atmosphere to obtain the final composites, denoted as C-Fe-N-x, where x stands for the Fe<sub>2</sub>O<sub>3</sub> loading measured by TG analyses.

### 2.2. Characterization

Thermogravimetric (TG) analysis was measured using a STA449 F3 Jupiter thermogravimetric analyzer (NETZSCH) from room temperature to 800 °C in air with a heating rate of 10 °C·min<sup>-1</sup>. Powder X-ray diffraction (XRD) patterns were recorded on a D/Max-2400 diffract meter using a Cu  $K_{\alpha}$  X-ray radiation, with a voltage of 45 kV and current of 40 mA. Nitrogen adsorption was performed with a Micromeritics Tristar 3000 instrument at liquid nitrogen temperature to determine the surface area and porosity. High resolution transmission electron microscopy (HRTEM) investigations were carried out with a Hitachi HF2000 microscope equipped with a cold field emission gun at beam energy of 200 kV. Samples were prepared by dropping an ethanol droplet of the products on carbon-coated copper grids and drying at room temperature.

# 2.3. Electrochemical characterization

Electrochemical performances of the samples were evaluated using 2025 coin-type cells. The working electrodes were comprised of active material, conductive carbon black, and commercial LA133 binder at a weight ratio of 8:1:1. Lithium metal was used as the counter electrode and the reference electrode. The electrolyte was 1 M LiPF<sub>6</sub> dissolved in a mixture (1:1:1, weight ratio) of ethylene carbonate (EC), ethylene methyl carbonate (EMC), and dimethyl carbonate (DMC). Celgard 2400 was used as a separator. Charge-discharge measurements of the cells were performed at different current densities between the potentials of 0.005-3 V (vs Li<sup>+</sup>/Li) using a Land CT2001A battery tester. The specific capacity was calculated according to the total mass of Fe<sub>2</sub>O<sub>3</sub> and carbon in composites. Cyclic voltammetry (CV) measurements and electrochemical impedance spectra (EIS) were performed on CHI660D electrochemical workstation.

# 3. Results and discussion

Thermogravimetric (TG) analysis of the Fe<sub>2</sub>O<sub>3</sub>@C composites in air shows the weight loss between 300 and 600 °C, which corresponds to the combustion of carbon matrix (Figure 1a). Fe<sub>2</sub>O<sub>3</sub> loadings in the two samples are different based on the magnitude of corresponding mass loss, i.e. 47 wt% for C-Fe-N-47 and 61 wt% for C-Fe-N-61, which are prepared through varying the impregnation and conversion times. Figure 1b reveals the power X-ray diffraction (XRD) patterns of the samples, in which all peaks are in good agreement with  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (maghemite phase JCPDS card No. 39–1346). The phase constitution is in consistent with our previous report [27]. By comparing the two XRD patterns in Figure 1b, one can figure out that the Fe<sub>2</sub>O<sub>3</sub> particle size in C-Fe-N-47 (6.4 nm) is smaller than that of C-Fe-N-61 (7.1 nm). The two estimated particles sizes are slightly larger than the pore diameter (5.5 nm) of carbon matrix, implying that the Fe<sub>2</sub>O<sub>3</sub> NPs might grow along the pore channels under the high confinement effect of carbon walls.



Figure 1. TG curves under air flow (a) and wide-angle XRD patterns of two Fe<sub>2</sub>O<sub>3</sub>@C composites with different Fe<sub>2</sub>O<sub>3</sub> loadings (b)

To directly investigate the morphology and microstructure of the two as-prepared  $Fe_2O_3@C$  composites, transmission electron microscopy (TEM) was employed. From Figure 2(a) and 2(b), one can clearly observe that  $Fe_2O_3$ NPs are highly dispersed and homogeneously encapsulated in the mesopore channels with a uniform size of 5–7 nm in the C-Fe-N-47 composite, which is in agreement with the XRD result. By looking at the external surface of the C-Fe-N-47, no bulky aggregates are visible. Similar to the above results, the  $Fe_2O_3$  in C-Fe-N-61 is also fully located within the carbon tubes and the composite exhibits a perfect hexagonal mesostructure (Figure 2c, 2d). It reveals that ammonia hydrolysis in situ and subsequent thermal treatment is an effective way to encapsulate particles in the CMK-5 matrix. We thought this can be ascribed to the interaction between hydroxide products with higher melting point and carbon walls, which is effective to prevent  $Fe_2O_3$  migrating out of mesopore channels and achieve high encapsulation degree [28]. It is evident that, compared with exposed  $Fe_2O_3$  NPs, the direct contact interface between highly encapsulated  $Fe_2O_3$  and electrolyte is easily reduced to a great extent.



Figure 2. TEM images of two Fe<sub>2</sub>O<sub>3</sub>@C composites. (a, b) C-Fe-N-47, (c, d) C-Fe-N-61

 $N_2$  adsorption measurements were conducted to determine the pore features of two Fe<sub>2</sub>O<sub>3</sub>@C composites. As seen in Figure 3, both samples exhibit microporous feature, indicating the space of CMK-5 matrix was partially filled. The calculated textural parameters of two composites are summarized in Table 1. It is clear that the C-Fe-N-47 composite has a higher BET surface and larger total pore volume than the C-Fe-N-61 ( $688 \text{ m}^2 \cdot \text{g}^{-1}$  vs.  $341 \text{ m}^2 \cdot \text{g}^{-1}$  and

 $0.36 \text{ cm}^3 \cdot \text{g}^{-1}$  vs.  $0.21 \text{ cm}^3 \cdot \text{g}^{-1}$ ). Based on the pore volume (2.16 cm<sup>3</sup> \cdot \text{g}^{-1}) of the parent carbon and the bulk density (5.24 g·cm<sup>-3</sup>) of Fe<sub>2</sub>O<sub>3</sub>, the filling degrees of the mesopores can be estimated, which is ca. 8 vol% for C-Fe-N-

47 and ca. 14 vol% for C-Fe-N-61 [4]. The low filling degree implies the high-efficient ion transport pathways. Meanwhile, the measured tap densities of these samples are listed in Table 1.

| Sample             | Fe <sub>2</sub> O <sub>3</sub><br>(%) | $S_{ m BET}$<br>(m <sup>2</sup> ·g <sup>-1</sup> ) | $V_{\text{total}}$<br>(cm <sup>3</sup> ·g <sup>-1</sup> ) | $ ho_{	ext{tap}}$<br>(g·cm <sup>-3</sup> ) | D <sub>size</sub><br>(nm) | Initial<br>efficiency (%) | Capacity after 100 cycles $(mAh \cdot g^{-1})$ |
|--------------------|---------------------------------------|--|---|--|---------------------------|---------------------------|--|
| CMK-5 <sup>b</sup> | 0                                     | 1770   | 2.16  | 0.12                                       | -                         | 39                        | 470  |
| C-Fe-N-47          | 47                                    | 688  | 0.36  | 0.73                                       | 6.4                       | 63                        | 683  |
| C-Fe-N-61          | 61                                    | 341  | 0.21  | 0.95                                       | 7.1                       | 62                        | 488  |

<sup>a</sup> BET specific surface area ( $S_{\text{BET}}$ ) was calculated over the  $P/P_0$  range from 0.03 to 0.25;  $V_{\text{total}}$ : total pore volume at  $P/P_0 \approx 0.99$ ;  $\rho_{\text{tap}}$ : tap density based on the ratio of the mass and the volume of powders;  $D_{\text{size}}$ : crystallite sizes were estimated by the Scherrer formula. <sup>b</sup> A part of data is adapted from our previous work [4]

Motivated by these structural features, the electrochemical lithium storage properties of as-prepared Fe<sub>2</sub>O<sub>3</sub>@C nanocomposites as anode materials were evaluated by cyclic voltammetry (CV). In the first cathodic scan for the C-Fe-N-47 sample as shown in Figure 4(a), two small peaks at 1.6 (P1) and 0.7 V (P2) as well as an obvious peak at 0.2 V (P3) are observed. The peak centered at 1.6 V can be attributed to a small amount of lithium inserted into the crystal structure of Fe<sub>2</sub>O<sub>3</sub> without structure change, and the peak at 0.7 V can be assigned to the transformation from hexagonal  $\alpha$ -Li<sub>r</sub>Fe<sub>2</sub>O<sub>3</sub> to cubic Li<sub>2</sub>Fe<sub>2</sub>O<sub>3</sub> as suggested in refs. [31,32]. The large peak at 0.2 V can be attributed to the reduction from  $Fe^{2+}$ to Fe<sup>0</sup>, accompanied with irreversible decomposition reaction of electrolyte. On the other hand, in the anodic polarization process, two broad overlapping peaks were recorded at about 1.7 and 1.85 V, corresponding to the oxidation of  $Fe^{0}$  to  $Fe^{2+}$ and further oxidization to  $Fe^{3+}$  [31]. Meanwhile, there is still an anodic peak at 2 V and the peak current decreases with subsequent cycles, indicating the occurrence of irreversible reactions. For the second cycles, the cathodic peaks of both electrodes shift to a more positive potential, resulting from the decrease in polarization. This phenomenon is likely due to the rearrangement of active particles during charge/discharge processes, leading to a better electrical contact with the conducting carbon matrix [33]. When comparing the two samples, the CV curves of C-Fe-N-47 exhibit less change than those of C-

Fe-N-61 highlighted by red dotted square (Figure 4b), indicating better cycle stability of C-Fe-N-47 samples. Meanwhile, the cathodic peak potential in Figure 4a is lower than that in Figure 4(b), and this could be ascribed to smaller size effect of Fe<sub>2</sub>O<sub>3</sub> NPs and easier ion transport in the composites, which is in good accordance with the above conclusion.



Figure 3. N2 adsorption isotherms of C-Fe-N-47 and C-Fe-N-61 composites



Figure 4. Cyclic voltammograms of two Fe<sub>2</sub>O<sub>3</sub>@C composites for the initial five cycles at a scan rate of 0.5 mV·s<sup>-1</sup>

Cycle performance can provide straightforward evidence about electrochemical properties in reversible capacity and cyclability. We tested the cycle performance of the  $Fe_2O_3@C$ composites at a current density of 200 mA $\cdot$ g<sup>-1</sup> based on the same total mass of composite. As shown in Figure 5(a), the capacity of C-Fe-N-61 fades sluggishly from 620 mAh·g<sup>-1</sup> at the second cycle to 488 mAh·g<sup>-1</sup> after 100 cycles, only 79% capacity retention against that of the second cycle. In sharp contrast, the C-Fe-N-47 composite exhibits improved cycle stability and a high reversible specific capacity under a relatively low Fe<sub>2</sub>O<sub>3</sub> loading. A high reversible capacity of  $683 \text{ mAh} \cdot \text{g}^{-1}$  was retained over 100 cycles, which is corresponding to 99% capacity retention against that of the second cycle. It is obvious that by increasing the Fe<sub>2</sub>O<sub>3</sub> loading from 47 wt% to 61 wt%, both the reversible capacity and cycle stability decrease, and this phenomenon has also been reported in other iron oxides and carbon composites [34]. According to the loadings and the bulk density of Fe<sub>2</sub>O<sub>3</sub>, it can be calculated that the residual pore volume in Fe<sub>2</sub>O<sub>3</sub>@C

composites can buffer to which extent the volume expansion. The estimated values are 400 vol% of volume expansion for Fe<sub>2</sub>O<sub>3</sub> in C-Fe-N-47 and less than 180 vol% for that of C-Fe-N-61, which is much lower than the inherent volume expansion (>200 vol%) of Fe<sub>2</sub>O<sub>3</sub> [35]. These results suggest that the buffer space in C-Fe-N-47 is enough for the volume expansion of Fe<sub>2</sub>O<sub>3</sub> NPs, therefore, the structure kept intact. Meanwhile, the higher special surface area in C-Fe-N-47 facilitates Li<sup>+</sup> transport, which is responsible for the higher reversible capacity. Therefore, it is extremely important to accurately and rationally control Fe<sub>2</sub>O<sub>3</sub> loading for improving the electrochemical properties of Fe<sub>2</sub>O<sub>3</sub>@C composites. To the best of our knowledge, both reversible capacity and cycle stability of C-Fe-N-47 are comparable to those of reported Fe<sub>2</sub>O<sub>3</sub>@C anodes for LIBs [24,26,36]. Furthermore, the coulombic efficiency of C-Fe-N-47 is as high as 63%, which is apparently higher than that of pure CMK-5 anodes (39%) reported in Ref. [4].



Figure 5. Cycle performance (a), rate capability with increasing current density (b) and Nyquist plots before (c) and after 30 cycles (d) of two  $Fe_2O_3@C$  composites

In addition to the increased capacity and improved cyclability, composite C-Fe-N-47 also shows significantly excellent rate capability compared with C-Fe-N-61, as displayed in Figure 5(b). The cells were first tested at 400 mA·g<sup>-1</sup> for 20 cycles, followed by cycling at current densities increasing stepwise to 1500 mA·g<sup>-1</sup>. The C-Fe-N-47 ex-

hibits a high and stable capability of  $\sim 650 \text{ mAh}\cdot\text{g}^{-1}$  at 400 mA·g<sup>-1</sup>. Meanwhile, a stable discharge capacity is retained at  $\sim 430 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ , even at the current density of 1500 mA·g<sup>-1</sup>. Remarkably, when the current was restored to 400 mA·g<sup>-1</sup> after 80 cycles, the reversible capacity still delivered more than 650 mAh·g<sup>-1</sup>. In contrast, the capacity of C-Fe-N-61 drops rapidly even at a relatively low current density of 400 mA·g<sup>-1</sup>, and reaches only around 180 mAh·g<sup>-1</sup> at a current density of 1500 mA·g<sup>-1</sup>, indicating a poor rate capability. This also proves the above-mentioned conclusions.

To further verify why the unique structure of C-Fe-N-47 is responsible for good performance of the cells, the electrochemical impedance spectra (EIS) measurements of the two Fe<sub>2</sub>O<sub>3</sub>@C samples were conducted before and after 30 cycles by applying a sine wave with amplitude of 5.0 mV over a frequency range of 100 kHz-0.01 Hz (Figure 5c, 5d). It can be seen that the Nyquist plots are composed of one depressed semicircle and an inclined line. Generally, the diameter of semicircle at medium frequency is attributed to the Li<sup>+</sup> migration resistance  $(R_{sf})$  through the SEI films and the chargetransfer resistance  $(R_{ct})$  [5]. As it can be seen, the semicircle diameters of the two samples decrease substantially after 30 cycles. This change is likely due to the electrochemical milling effect with size decrease and rearrangement of active particles, which is in good agreement with the result of CV reported in Ref. [37]. Meanwhile, it is clear that the value of  $R_{\rm sf}$ +  $R_{ct}$  of C-Fe-N-47 is much smaller than that of C-Fe-N-61, indicating the faster Li<sup>+</sup> transfer and more benign SEI films.

In comparison of these two  $Fe_2O_3@C$  anode materials, C-Fe-N-47 composite shows higher reversible capacity and superior cycle stability as well as rate capability than C-Fe-N-61. This is ascribed to: the tubular mesoporous carbon not only provides confined nanospace for homogenously encapsulating nano-sized  $Fe_2O_3$ , but also effectively decreases the formation degree of SEI films on the surface of  $Fe_2O_3$ . Meanwhile, the excellent confinement effect of thin carbon walls prevents the aggregation and inactivation of  $Fe_2O_3$  NPs during charge-discharge processes. More importantly, adequate residual space in the composite can act as a "cushion" to accommodate the volume expansion and warrant the structure integrity of active  $Fe_2O_3$  as well as facilitate the ion transfer.

## 4. Conclusions

Fe<sub>2</sub>O<sub>3</sub> NPs have been introduced into a tubular mesoporous carbon matrix to integrate their advantages on the electrochemical performance for LIBs. Ultrafine Fe<sub>2</sub>O<sub>3</sub> NPs with 5-7 nm sizes were highly and homogenously encapsulated into CMK-5 matrix without obvious large particles on the outer surface through ammonia hydrolysis and subsequent thermal treatment. Electrochemical performance demonstrated that the  $Fe_2O_3@C$  composite with suitable  $Fe_2O_3$ loading of 47 wt% exhibits more outstanding electrochemical properties compared with the relatively higher Fe<sub>2</sub>O<sub>3</sub> loading of 61 wt%. The C-Fe-N-47 composite anode combines several advantages in one material, such as high reversible capacities (685 mAh $\cdot$ g<sup>-1</sup> of initial reversible capacity), excellent cycle performance (99% capacity retention against that of the second cycle after 100 cycles), and superior rate performance (ca. 430 mAh·g<sup>-1</sup> at 1500 mA·g<sup>-1</sup>) for LIBs. Optimistically, this type of tubular mesoporous carbon can load various metals or metal oxides with suitable filling rations to achieve high performance LIBs.

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