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## **Table of Contents**



Mesoporous  $Fe_3O_4@C$  submicrospheres with high conductivity and structural stability exhibit fascinating electrochemical performance.

## New Journal of Chemistry

Page 2 of 8

## ARTICLE

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# Mesoporous $Fe_3O_4@C$ submicrospheres evolved from a novel self-corrosion mechanism for high-performance lithium-ion Batteries

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In this work, mesoporous  $Fe_3O_4@C$  submicrospheres with a diameter of 500 nm were successfully synthesized *via* a template-free hydrothermal method. Time-dependent experiments revealed that this unique microstructure was evolved from a novel self-corrosion mechanism. As the anodic materials for lithium-ion batteries, these mesoporous  $Fe_3O_4@C$  submicrospheres exhibited the enhanced cycling performance (930 mA h g<sup>-1</sup> at a current density of 100 mA g<sup>-1</sup> after 50 cycles) and the high rate capabilities (910, 884, 770 and 710 mA h g<sup>-1</sup> at current densities of 100, 200, 500 and 1000 mA g<sup>-1</sup>, respectively). These outstanding electrochemical behaviors were ascribed to the enhanced structural stability and increased electrical conductivity arising from the porosity and carbon coating layers in the  $Fe_3O_4@C$  submicrospheres.

#### 1. Introduction

Compared with other rechargeable batteries, lithium-ion batteries (LIBs) have attached much attention due to their high energy density and power density, which could widely applied in energy storage devices and portable electronic devices.<sup>1-8</sup> Owing to the relative low theoretical capacity of 372 mA h g<sup>-1</sup>, however, graphite cannot meet the requirements of new emerging technologies. Thus exploring alternative anodic materials with high reversible capacity, rate capability as well as long cycle life has become an urgent task today. In this respect, magnetite (Fe<sub>3</sub>O<sub>4</sub>) is regarded as a promising candidate because of its high theoretical capacity (926 mA h g<sup>-1</sup>), low cost, natural abundance and environmental friendliness.9-13 Despite its fascinating features, Fe<sub>3</sub>O<sub>4</sub> often suffers from poor rate capability and low capacity retention arising from kinetic limitation, agglomeration and volume expansion during the Li<sup>+</sup> insertion/extraction process,<sup>14-18</sup> which strongly restrict its practical application.

To date, three general approaches have been proposed to overcome above intractable problems. The first One is to fabricate nanosized  $Fe_3O_4$  with various morphologies, such as nanowires, nanosheets, nanotubes and nanospheres.<sup>19-29</sup> It is considered as an efficient strategy to increase the specific surface area, leading to the sufficiently contact with electrolyte

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and active materials. Meanwhile, it can also shorten the diffusion length of Li<sup>+</sup> ions and achieve superior electrochemical dynamical behaviors. The second strategy is coating a thin carbon layer on the surface of Fe<sub>3</sub>O<sub>4</sub> materials, which can greatly enhance the electronic conductivity as well as keep the structure integrity against the volume expansion during the Li<sup>+</sup> insertion/extraction.<sup>30-34</sup> The third way is to design and tailor the microstructure of Fe<sub>3</sub>O<sub>4</sub> with high surface area and permeability, which has attracted intense attention.35, 36 Particularly, porous/hollow structures have abundant interspace voids, which can not only easily accommodate the mechanical stress induced by large volume change during the Li<sup>+</sup> insertion/extraction, but also guarantee the better penetration of electrolyte and the fast diffusion of Li<sup>+</sup> ions. In particular, Fe<sub>3</sub>O<sub>4</sub> with mesoporous structure is regarded as the ideal model for high performance electronic material. For example, Wang et al. have synthesized mesoporous Fe<sub>3</sub>O<sub>4</sub> nanorods by using FeOOH as precursor and followed by heating in Argon atmosphere.<sup>37</sup> Xu and his co-workers have reported the preparation of mesoporous Fe<sub>3</sub>O<sub>4</sub> microsphere by heating ferrous tartrate precursor in Nitrogen atmosphere.38 These traditional approaches to the synthesis of mesoporous Fe<sub>3</sub>O<sub>4</sub> is always a two-step process, which is complex and time comsuming. However, a facial and low cost approach to synthesize mesoporous Fe<sub>3</sub>O<sub>4</sub> remains a major challenge.

In this work, we report a facile method to fabricate mesoporous  $Fe_3O_4@C$  submicrospheres *via* a template-free hydrothermal route based on a novel self-corrosion mechanism. These  $Fe_3O_4@C$  submicrospheres with the distinct porosity and uniform carbon layers could allow better penetration of electrolyte, achieve a higher reactive area, promote the mobility

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of ions/electrons and protect the structure integrity of  $Fe_3O_4@C$  submicrospheres. As a result,  $Fe_3O_4@C$  sample exhibits a high specific capacity, remarkable cycling stability and rate performance compared with bare  $Fe_3O_4$  submicrospheres.

#### 2. Experimental Section

#### 2.1 Synthesis of Fe<sub>3</sub>O<sub>4</sub> submicrospheres

In a typical procedure, FeCl<sub>3</sub>·6H<sub>2</sub>O (2.7 g) was dissolved in ethylene glycol (EG, 80 mL) to form a yellow solution under vigorous stirring. Then polyethylene glycol 6000 (PEG 6000, 2.0 g) and NaAc (7.2 g) were added to the above solution sequentially. After that, the mixed solution was transferred into a 100 mL Teflonlined stainless-steel autoclave and heated at 200 °C in an electric oven for 10 h. Finally, the autoclave was cooled to room temperature naturally. The products were harvested by a magnet and washed with distilled water and ethanol before drying at 80 °C for 12 h.

#### 2.2 Synthesis of Fe<sub>3</sub>O<sub>4</sub>@C submicrospheres

200 mg Fe<sub>3</sub>O<sub>4</sub> submicrospheres was dispersed in 80 mL distilled water by ultra-sonication to form a suspension, followed by adding 8.0 g glucose. Then the suspension was transferred to 100 mL Teflon-lined stainless-steel autoclave and heated at 180 °C for 4 h. The black precipitate product was collected by a magnet and washed with distilled water and ethanol before drying at 80 °C for 12 h. Finally, the black precipitate was carbonized at 500 °C for 4 h under a nitrogen atmosphere.

#### 2.3 Materials characterization

Powder X-ray diffraction (XRD) was carried out with an X'Pert pro diffractometer using Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm). The morphologies of samples was characterized by scanning electron microscopy (SEM, Hitachi S-4700) and transmission electron microscope (TEM, FEI, Tecnai G2 F30) equipped with an energy dispersive spectroscopy (EDS) detector. Nitrogen adsorptiondesorption was detected by Brunanuer-Emmett-Teller (BET) tests using an ASAP 2020 (Micromeritics Instruments) surface area and pore analyzers. The thermogravimetric analysis (TGA) was carried on SDTQ600 using oxygen atmosphere. The Fourier transform infrared (FT-IR) spectra were carried out on the Nicole 6700 FT-IR spectrometer.

#### 2.4 Electrochemical Measurements

The electrochemical performances of samples were tested using CR2025 coin-type cells. The working electrode was fabricated by mixing the active material (Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@C), acetylene black and polyvinylidene fluoride (PVDF) at a weight ratio of 70:15:15, and pasted on pure Cu foil. 1 M solution of LiPF<sub>6</sub> in ethylene carbonate (EC)-dimethyl carbonate (DME) (1:1 in volume) was used as the electrolyte with a Celgard membrane as the separator.

Cyclic voltammetry (CV) measurement was carried out at 0.1 mV s<sup>-1</sup> within the range of 0.05-3.0 V on the CHI650B electrochemical workstation. Electrochemical impedance spectroscopy (EIS) measurements were conducted on this electrochemical workstation at the charge state of 3.0 V after 50 cycles in frequency range of 0.1 to  $10^6$  Hz at room temperature.

The charge-discharge test was carried out on a Neware battery test system with the voltage window of 0.05-3.0 V at room temperature.

#### 3. Results and discussion

#### 3.1 Structure and Morphology Characterization

Fig.1a displays a typical XRD pattern of the Fe<sub>3</sub>O<sub>4</sub>, which is in good agreement with face-centered cubic Fe<sub>3</sub>O<sub>4</sub> (JCPDS card No. 65-3107). No second phase is found, indicating the high purity of Fe<sub>3</sub>O<sub>4</sub> product. Compared to the Fe<sub>3</sub>O<sub>4</sub> sample, no obvious peaks corresponding to graphite can be detected in Fe<sub>3</sub>O<sub>4</sub>@C submicrospheres (Fig. 2b), suggesting the carbon coating may exist in amorphous. The FT-IR spectrum is further applied to confirm the exact crystalline phase of product. As shown in Figure S1, only one peak can be observed at around 570 cm<sup>-1</sup>, which is the characteristic peak of Fe<sub>3</sub>O<sub>4</sub>.<sup>39</sup>



Figure 1 XRD patterns of a)  $Fe_3O_4$  submicrospheres and b)  $Fe_3O_4@C$  submicrospheres.

Fig. 2a presents the SEM image of Fe<sub>3</sub>O<sub>4</sub> submicrospheres obtained at 200 °C for 10 h via a solvothermal route. These Fe<sub>3</sub>O<sub>4</sub> submicrospheres have a uniform particle size with a diameter of 500 nm. Meanwhile, large numbers of pores can be observed on the surface Fe<sub>3</sub>O<sub>4</sub> submicrospheres, indicating a porous spherical structure. The detailed morphological and structure features were further studied by TEM tests. The scanning transmission electron microscope (STEM) image (Fig. 2b) confirms the porous structure of Fe<sub>3</sub>O<sub>4</sub> submicrospheres. Interestingly, these pores are tunnel-like, connecting the inner to the outside, which can facilitate a good contact between active materials and electrolyte. The high magnification TEM image of a single Fe<sub>3</sub>O<sub>4</sub> submicrosphere is displayed in Fig. 2c. The corresponding selected area electron diffraction (SAED) pattern reveals a good crystalline nature of Fe<sub>3</sub>O<sub>4</sub>. The detailed crystallographic information of Fe<sub>3</sub>O<sub>4</sub> submicrospheres is surveyed by the high resolution transmission electron microscopy (HRTEM) as shown in Fig. 2d (rectangle region in Fig. 2c). The spacing between adjacent lattice fringe calculated from HRTEM is 0.29 nm, consisting well with (220) plane of face-centered cubic Fe<sub>3</sub>O<sub>4</sub>.



Figure 2 a) SEM image of  $Fe_3O_4$  submicrospheres; b) STEM image of  $Fe_3O_4$  submicrospheres; c) high magnification TEM image of  $Fe_3O_4$  submicrospheres and SAED pattern of  $Fe_3O_4$  submicrospheres (inset); d) HRTEM image of  $Fe_3O_4$  submicrospheres.



Figure 3 a-d) SEM images of the samples obtained at different reaction time; e) XRD patterns of the samples obtained at different reaction time; f) Schematic illustration of the formation process of the meosoporous  $Fe_3O_4$  submicrospheres.

The detailed formation process of mesoporous  $Fe_3O_4$ submicrospheres were investigated by time-dependent XRD and SEM experiments. Only irregular nanoparticles are observed after a reaction time of 2 h (Fig. 3a). The corresponding XRD pattern (Fig. 3f) can be indexed to  $Fe_2O_3 \cdot H_2O$  (JCPDS card No. 13-0092), suggesting the  $Fe^{3+}$  has not been reduced by EG at the early time. When the reaction time is extended to more than 5 h, all diffraction peaks are in good agreement with face-centered cubic  $Fe_3O_4$  (JCPDS card No. 65-3107). The morphologies of samples from 5 to 24 h are depicted in Fig. 3b-d. After 5 h reaction, the obtained  $Fe_3O_4$  are solid submicrospheres with a uniform diameter of 500 nm (Fig. 3b). When the reaction time prolongs to 10 h (Fig. 3c), porous  $Fe_3O_4$  submicrospheres are emerged with no significant size changes. With the reaction time increases to 24 h, the particle size of these  $Fe_3O_4$  submicrospheres is obviously reduced. Even some particles collapse.

On the basis of the time-dependent experiments above, a schematic diagram is displayed to illustrate the formation process of mesoporous Fe<sub>3</sub>O<sub>4</sub> submicrospheres, as shown in Fig. 3e. First of all, FeCl<sub>3</sub>·6H<sub>2</sub>O transforms into Fe<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O instead of Fe<sub>3</sub>O<sub>4</sub> nanoparticles after 2 h.<sup>21</sup> When the reaction time is extended, initial nanoparticles are reduced by EG and grow into solid Fe<sub>3</sub>O<sub>4</sub> submicrospheres.<sup>40</sup> With the reaction time prolongs to 10 h, the surface of solid Fe<sub>3</sub>O<sub>4</sub> submicrospheres will be etched to form a porous structure. With the reaction time extends to 24 h, Fe<sub>3</sub>O<sub>4</sub> submicrospheres are further etched from the surface to interior, leading to the collapse of the spherical structure. According to the previous literatures, Yin et al. has reported the similar phenomena.<sup>41, 42</sup> During the crystal growth process, EG plays a crucial role in the formation of Fe<sub>3</sub>O<sub>4</sub> submicrospheres. NaAc is added to prevent particles agglomeration. As for PEG, it is not only a surfactant but also another reagent against particles agglomeration.<sup>43</sup> Simultaneously, these Fe<sub>3</sub>O<sub>4</sub> submicrospheres will be etched by H<sup>+</sup> ions generated from the hydrolysis of FeCl<sub>3</sub> with elongating the reaction time. Consequently, mesoporous Fe<sub>3</sub>O<sub>4</sub> submicrospheres are formed. However, as the reaction time reaches to 48 h, H<sup>+</sup> will further etch Fe<sub>3</sub>O<sub>4</sub> submicrospheres and break into small fragments. Therefore the formation process of mesoporous Fe<sub>3</sub>O<sub>4</sub> submicrospheres can be explained to a selfcorrosion mechanism.



Figure 4 a) SEM image of  $Fe_3O_4@C$  submicrospheres; b) low magnification and c) high magnification image of  $Fe_3O_4@C$  submicrospheres; d) HRTEM image of  $Fe_3O_4@C$  submicrospheres.

ARTICLE

In order to improve the high structural stability of porous Fe<sub>3</sub>O<sub>4</sub> submicrospheres, the as-prepared Fe<sub>3</sub>O<sub>4</sub> sample was coated with a thin carbon layer via a facile hydrothermal route using glucose as carbon source. After carbonizing at 500 °C for 4 h under a nitrogen atmosphere, Fe<sub>3</sub>O<sub>4</sub>@C submicrospheres were obtained. Compared with Fe<sub>3</sub>O<sub>4</sub> submicrospheres, the as-prepared Fe<sub>3</sub>O<sub>4</sub>@C submicrospheres (Fig. 4a) have no obvious changes in morphology and size. However, there is a carbon layer coated on the surface of Fe<sub>3</sub>O<sub>4</sub> sample as shown in Fig. 4b and 4c. Fig. 4d is the HRTEM image of Fe<sub>3</sub>O<sub>4</sub>@C sample taken from the rectangle region of Fig. 4c. Both the inner Fe<sub>3</sub>O<sub>4</sub> submicrosphere and the outer carbon layer can be seen clearly. The carbon layer with a thickness of about 2 nm is uniform and continuous. According to many previous literatures,<sup>21, 44</sup> well coated carbon layers can enhance the electronic conductivity as well as accommodate the mechanical stress induced by the large volume change during the Li<sup>+</sup> insertion/extraction. The thermal decomposition characteristic of Fe<sub>3</sub>O<sub>4</sub>@C submicrospheres was investigated hν thermogravimetric analysis (TGA) under oxygen atmosphere shown in Figure S2. A weight loss below 200 °C is due to the dissipation of absorbed water. There is a weight loss of 1.58% occurred around 350 °C, which can be attribute to the combustion of carbon. It is noted that  $Fe_3O_4$  will convert to  $Fe_2O_3$  when heated in oxygen atmosphere, resulting in a theoretical weight increase of 3.45%. Thus, the actual carbon content in Fe<sub>3</sub>O<sub>4</sub>@C submicrospheres is about 5%.



Figure 5 a) Nitrogen adsorption-desorption isotherm loop and b) pore-size distribution curve of Fe<sub>3</sub>O<sub>4</sub>@C.

The BET special surface area and porosity of  $Fe_3O_4@C$  submicrospheres were examined by nitrogen adsorption-desorption analysis. The BET special surface area of  $Fe_3O_4@C$  submicrospheres is calculated to 20.31 m<sup>2</sup> g<sup>-1</sup>. As shown in Fig. 5a, it is a typical mesoporous material, which belongs to the type IV in the IUPIC classification with a distinct hysteresis. This hysteresis is mainly ascribed to the slit-like pores, corresponding to the SEM and TEM images (Fig. 4). Based on the Barrett-Joyner-Halenda (BJH) model (Fig. 5b), the main pore distribution of  $Fe_3O_4@C$  submicrospheres is in range of 10-50 nm, consisting well with the mesoporous feature.

#### 3.2 Electrochemical Performance

To evaluate the electrochemical performances of mesoporous  $Fe_3O_4@C$  and  $Fe_3O_4$  submicrospheres, two samples were assembled as the coin-typed cells for the LIB application, respectively. Fig. 6a shows the CV curves of  $Fe_3O_4@C$  in the voltage window of 0.05-3 V at a scanning rate

of 0.1 mV s<sup>-1</sup>. A sharp cathodic peak is located at about 0.5 V in the first cathodic sweep, indicating the converting of Fe<sub>3</sub>O<sub>4</sub> to Fe and the formation of amorphous of Li<sub>2</sub>O (Fe<sub>3</sub>O<sub>4</sub> + 2Li<sup>+</sup> + 2e<sup>-</sup>  $\rightarrow$  Li<sub>2</sub>(Fe<sub>3</sub>O<sub>4</sub>); Li<sub>2</sub>(Fe<sub>3</sub>O<sub>4</sub>) + 6Li<sup>+</sup> + 6e<sup>-</sup>  $\rightarrow$  3Fe<sup>0</sup> + 4Li<sub>2</sub>O). Meanwhile, in the anodic sweep, a wide peak is detected at about 1.75 V, which is due to the reversible oxidation of Fe to Fe<sup>3+</sup>.<sup>22, 45, 46</sup> Obviously, the intensity of cathodic peak drops significantly in the second cycle, suggesting the occurrence of irreversible reaction and the formation of solid electrolyte interphase (SEI) films. During the following cycles, all the CV curves are almost overlapped. These results demonstrate the high electrochemical reversibility of Fe<sub>3</sub>O<sub>4</sub>@C sample. In addition, the reduction and oxidation peaks are both positively shifted in the following two cycles, implying the polarization of electrode at the first cycle.<sup>47, 48</sup>



**Figure 6** a) CV cures of Fe<sub>3</sub>O<sub>4</sub>@C at a scan rate of 0.1mV s<sup>-1</sup>; b) chargedischarge profiles of Fe<sub>3</sub>O<sub>4</sub>@C at a current of 100 mA g<sup>-1</sup>; c) cycling performance of Fe<sub>3</sub>O<sub>4</sub>@C and Fe<sub>3</sub>O<sub>4</sub> at a current of 100 mA g<sup>-1</sup>; d) rate performance of Fe<sub>3</sub>O<sub>4</sub>@C and Fe<sub>3</sub>O<sub>4</sub> at different current densities; chargedischarge profiles of e) Fe<sub>3</sub>O<sub>4</sub>@C and f) Fe<sub>3</sub>O<sub>4</sub> at different current densities.

The charge-discharge profiles of mesoporous  $Fe_3O_4@C$  submicrospheres with a voltage window from 0.05-3 V at a current density of 100 mA g<sup>-1</sup> are presented in Fig. 6b. The first charge and discharge capacity of mesoporous  $Fe_3O_4@C$  submicrospheres are 1097.5 and 1568.9 mA h g<sup>-1</sup>, respectively, leading to a low Columbic efficiency of 70%. The large irreversible capacity (471.4 mA h g<sup>-1</sup>) is arisen from the irreversible reaction including the decomposition of electrolyte and the formation of SEI film in the first discharge process.<sup>30, 49</sup> These results also match well with the intensity changes of cathodic peaks in the CV curves (Fig. 6a). Moreover, the discharge plateau (~0.8 V) in the first discharge profile makes a

Table 1 Kinetic parameters of Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>@C electrodes

Sample	$R_{s}\left(\Omega ight)$	$R_{\rm f}(\Omega)$	CPE 1		R (O)	CPE 2		$D(cm^2 s^{-1})$
			Y	n	$\mathbf{R}_{ct}$ (S2)	Y	n	
Fe <sub>3</sub> O <sub>4</sub>	28.42	104.7	1.3 x 10 <sup>-5</sup>	0.9	152.78	2.4 x 10 <sup>-5</sup>	0.62	4.6 x 10 <sup>-15</sup>
Fe <sub>3</sub> O <sub>4</sub> @C	13.83	25.0	5.4 x 10 <sup>-5</sup>	1	92.28	8.0 x 10 <sup>-5</sup>	0.8	4.8 x 10 <sup>-14</sup>

clear distinction with the plateau ( $\sim 1$  V) in following cycles, further indicating the occurrence of irreversible reaction in the first cycle. From the second cycle onward, the charge-discharge profiles are almost overlapped and the Columbic efficiency reaches to 95%, which could be attributed to the reversible reduction-oxidation reaction between Fe<sub>3</sub>O<sub>4</sub> and Fe and the formation of stable SEI films.

cycle The performance of mesoporous Fe<sub>3</sub>O<sub>4</sub>@C submicrospheres and Fe<sub>3</sub>O<sub>4</sub> submicrospheres with a voltage window from 0.05-3 V at a current density of 100 mA g<sup>-1</sup> are depicted in For Fig. 6c, respectively. mesoporous Fe<sub>3</sub>O<sub>4</sub>@C submicrospheres, a slight decrease of reversible capacity can be detected in the initial 10 cycles. In the following 40 cycles, mesoporous Fe<sub>3</sub>O<sub>4</sub>@C submicrospheres exhibit a favorable cycling stability with a high reversible capacity of 930 mA h g<sup>-1</sup> after 50 cycles. Meanwhile, the Columbic efficiency increases from 70% (first cycle) to 95% (from the second cycle onward). Compared to mesoporous Fe<sub>3</sub>O<sub>4</sub>@C submicrospheres, the electrochemical performance of Fe<sub>3</sub>O<sub>4</sub> submicrospheres is unsatisfactory. The capacity of Fe<sub>3</sub>O<sub>4</sub> submicrospheres continues to decline, and retains only 316 mA h g<sup>-1</sup> after 50 cycles. Apparently, the mesoporous Fe<sub>3</sub>O<sub>4</sub>@C submicrospheres exhibit much better long-term cycling performance than Fe<sub>3</sub>O<sub>4</sub> submicrospheres. Furthermore, the electrochemical performance of various Fe<sub>3</sub>O<sub>4</sub>@C anode materials reported previously also has been listed in Table S1. The electrochemical performance of mesoporous Fe<sub>3</sub>O<sub>4</sub>@C submicrospheres is comparable to previous reports as shown in Table S1, which present fascinating long-term cycling performance and excellent structural stability.

It is noted that the discharge capacities of mesoporous  $Fe_3O_4@C$  submicrospheres are higher than 1000 mA h g<sup>-1</sup> from the second cycle to fifth cycle shown in Fig. 6c. This similar phenomenon has been reported before.<sup>33, 46, 51</sup> The possible reasons have been proposed as follows. On the one hand, it is very difficult to form a stable SEI film during the initial several cycles for all the oxides nanomaterials. The repeated formation and decomposition of SEI film will continuously consume Li<sup>+</sup> ions, resulting in a high capacity. On the other hand,  $Fe_3O_4@C$  submicrospheres have a high porosity, which could increase the contact area between the active materials and electrolyte. However, the penetration process of electrolyte could not be finished by a cycle since the activation process of electrolyte feasonal electrolyte is higher than the theoretical value in the initial several cycles.

Fig. 6d shows the rate capacity of mesoporous  $Fe_3O_4@C$  submicrospheres and  $Fe_3O_4$  submicrospheres with a voltage window from 0.05-3 V at different current densities. The discharge capacities

of mesoporous Fe<sub>3</sub>O<sub>4</sub>@C submicrospheres are 910, 884, 770 and 710 mA h g<sup>-1</sup> at the rates of 100, 200, 500 and 1000 mA g<sup>-1</sup>, respectively. When the current density is back to 100 mA g<sup>-1</sup>, the discharge capacity still maintains 890 mA h g<sup>-1</sup>. However, the discharge capacities of Fe<sub>3</sub>O<sub>4</sub> submicrospheres are 585, 512, 356 and 277 mA h g<sup>-1</sup> at the rates of 100, 200, 500 and 1000 mA g<sup>-1</sup>, respectively. The representative discharge-charge profiles of Fe<sub>3</sub>O<sub>4</sub>@C and Fe<sub>3</sub>O<sub>4</sub> at different current densities are presented in Fig. 6e and f, respectively. With increasing current rates, the distance between the discharge plateaus and charge plateaus becomes larger. These phenomena are resulting from the kinetic effects of the material, rendering a higher overpotential, which is similar to previous literatures.<sup>52, 53</sup> In this work, however, the polarization of Fe<sub>3</sub>O<sub>4</sub>@C submicrospheres is slighter compared to the Fe<sub>3</sub>O<sub>4</sub> sample, demonstrating Fe<sub>3</sub>O<sub>4</sub>@C submicrospheres have a better kinetic behavior at a relative high current density.

Electrochemical impendence spectroscopy (EIS) is conducted to identify electrochemical dynamical behaviors of Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>@C, respectively. All samples are charged to 3.0 V after 50 cycles. As shown in Fig 7, the EIS spectra of two samples have the similar profile, which is composed of a quasi-semicircle in the high frequency and a straight slope line in the low frequency. The inset is an equivalent circuit model used to the simulation. The intercept of high frequency semicircle on Z axis can be ascribed to the resistance of electrolyte (R<sub>s</sub>). The high frequency semicircle is related to the SEI layer resistance (Rf) and capacitance (CPE1). The medium frequency one can be attributed to the charge-transfer resistance (R<sub>ct</sub>) and its double-layer capacitance (CPE2). The slope line in low frequency represents the Warburg impedance (Zw) of lithium ion diffusion. The detailed values of R<sub>f</sub> and R<sub>ct</sub> for Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>@C after 50 cycles are listed on the Table 1. As shown in Table 1, the R<sub>f</sub> of Fe<sub>3</sub>O<sub>4</sub>@C (25.0  $\Omega$ ) is much smaller than that of Fe<sub>3</sub>O<sub>4</sub> (104.7  $\Omega$ ), implying the SEI film of Fe<sub>3</sub>O<sub>4</sub>@C is thinner than Fe<sub>3</sub>O<sub>4</sub>. Generally, the thicker SEI film, the more consumption of Li<sup>+</sup> ions supplied by the cathodes, leading to a large irreversible capacity, the low Columbic efficiency and poor electronic conductive. Thus, the small Rf of Fe3O4@C will guarantee the better electrochemical performance. Moreover, the Rct of Fe3O4@C is 92.28  $\Omega$ , which is also smaller than Fe<sub>3</sub>O<sub>4</sub> (152.78  $\Omega$ ). The smaller R<sub>ct</sub> of Fe<sub>3</sub>O<sub>4</sub>@C allows better contact between the active materials and electrolyte, resulting in the enhanced electrode reaction kinetics and better cycling performance. The lithium ion diffusion coefficient is calculated according to the following two equations:

$$Z_{\rm re} = R_{\rm e} + R_{\rm ct} + \sigma_{\rm w} \, \omega^{-0.5} \tag{1}$$

### Page 7 of 8

ARTICLE

D =0.5 (RT / A F<sup>2</sup>  $\sigma_w C$ )<sup>2</sup> (2) Where R<sub>et</sub> is charge transfer resistance, R<sub>e</sub> is electrolyte resistance,  $\omega$  is angular frequency ( $\omega = 2 \pi f$ ), R is the gas constant, T is the absolute temperature, F is Faraday's constant, A is the area of electrode surface and C is molar concentration of Li<sup>+</sup> ion. As demonstrated in Table 1, the lithium ion diffusion coefficient of Fe<sub>3</sub>O<sub>4</sub>@C and Fe<sub>3</sub>O<sub>4</sub> is 4.8 x 10<sup>-14</sup> cm<sup>2</sup> s<sup>-1</sup> and 4.6 x 10<sup>-15</sup> cm<sup>2</sup> s<sup>-1</sup>, respectively. Obviously, the Fe<sub>3</sub>O<sub>4</sub>@C sample has a better lithium ion diffusion coefficient.



Figure 7 EIS spectra of  $Fe_3O_4$  and  $Fe_3O_4@C$  after 50cycles. The inset is an equivalent circuit.



Figure 8 TEM images of a) Fe<sub>3</sub>O<sub>4</sub>@C submicrospheres and b) Fe<sub>3</sub>O<sub>4</sub> submicrospheres both after 50 cycles; c) HRTEM image of Fe<sub>3</sub>O<sub>4</sub>@C submicrospheres; d) FFT pattern of Fe<sub>3</sub>O<sub>4</sub>@C submicrospheres.

To further investigate the structure stability of materials, the cells after cycling were disassembled and analyzed by TEM again. The low magnification TEM image of mesoporous Fe<sub>3</sub>O<sub>4</sub>@C submicrospheres after cycling is presented in Fig. 8a. After 50 cycles at a current density of 100 mA g<sup>-1</sup>, the structure of mesoporous Fe<sub>3</sub>O<sub>4</sub>@C submicrospheres is maintained well.

However, the structure of  $Fe_3O_4$  submicrospheres has collapsed (Fig. 8b), which is arising from the large volume change during the Li<sup>+</sup> insertion/extraction. Therefore, it is easily concluded that the carbon coating layer can act as a barrier to protect the pulverization and keep the structural integrity. Additionally, Fig. 8c shows the HRTEM image of  $Fe_3O_4$ @C submicrospheres (marked as the rectangle region in Fig. 8a). Both the inner  $Fe_3O_4$  and outer (carbon layer and SEI film) are still clearly detected after 50 cycles. From the fast Fourier transform (FFT) pattern (Fig. 8d), the inner (Fe<sub>3</sub>O<sub>4</sub>) has transformed to polycrystalline, which is resulting from oxidation/reduction reaction during the charge-discharge process.

#### 4. Conclusions

In summary, we demonstrate a facile route to fabricate mesoporous Fe<sub>3</sub>O<sub>4</sub>@C submicrospheres via a novel selfcorrosion mechanism. The detailed formation process is surveyed by a time-dependent experiment. The reactive time is the key factor for achieving mesoporous Fe<sub>3</sub>O<sub>4</sub>@C submicrospheres. As the anodic materials for lithium-ion batteries, mesoporous Fe<sub>3</sub>O<sub>4</sub>@C submicrospheres exhibit enhanced electrochemical performance (930 mA h g<sup>-1</sup> after 50 cycles), which is attributed to the uniform carbon coating and the mesoporous structure. The porosity of Fe<sub>3</sub>O<sub>4</sub>@C could not only allow the better penetration of electrolyte, but also shorten diffusion pathways of Li<sup>+</sup> ions. Meanwhile, the uniform and continuous carbon coating layers greatly enhance the electronic conductivity and keep the structure integrity against the volume expansion during the Li<sup>+</sup> insertion/extraction. Therefore, these mesoporous Fe<sub>3</sub>O<sub>4</sub>@C submicrospheres are promising anode materials for high performance LIBs, and also can be used in other applications such as gas sensors, catalysts and supercapacitors.

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