Nano Electrochemical Reactors of Fe₂O₃ Nanoparticles Embedded in Shells of Nitrogen-doped Hollow Carbon Spheres as High-Performance Anodes for Lithium-Ion Batteries

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Experimental section

Material synthesis

All chemicals were of analytical grade, and were used without any further purification. In a typical synthesis, a methanolic solution (25 mL) of ferrous sulfate (FeSO₄·7H₂O, 278 mg) was added into a methanolic solution (25 mL) of 2-methylimidazole (328 mg) and PVP (K-30, 0.3 g) drop by drop slowly using a syringe (10 ml). The whole reaction process was kept at room temperature with agitated stirring. After being stirred for 5 min, the reaction was aged at room temperature without any interruption for 24 h. The resulting white precipitation was centrifuged and washed with several times with methanol and finally dried under oven at 60 °C. To obtain Fe₂O₃@N-C, the resulting Fe-based zeolitic imidazolate frameworks were direct annealed at 620 °C for 1 h with a heating rate of 10 °C/min in air. When the resulting Fe-based zeolitic imidazolate frameworks were direct annealed at 820 °C for 1 h with a temperate ramp of 10 °C/min in air, pure Fe₂O₃ without carbon residues was obtained.

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Material characterization

The powder X-ray diffraction (XRD) patterns of all samples were recorded with a X-ray diffractometer (Japan Rigaku D/MAX- γ A) equipped with Cu-K α radiation (λ = 1.54178 Å) over the 20 range of 10-70°. Field emission scanning electron microscopy (FE-SEM) images were collected on a JEOL JSM-6700 M scanning electron microscope. Transmission electron microscopy (TEM) images were taken on a Hitachi H-800 transmission electron microscope using an accelerating voltage of 200 kV, and high-resolution transmission electron microscope (HRTEM) (JEOL-2011) was operated at an acceleration voltage of 200 kV. The specific surface area was evaluated at 77 K (Micromeritics ASAP 2020) using the Brunauer-Emmett-Teller (BET) method, while the pore volume and pore size were calculated according to the Barrett-Joyner-Halenda (BJH) formula applied to the adsorption branch. Thermogravimetric analysis (TGA) was carried out using a Shimadzu-50 thermoanalyser under nitrogen flow. X-ray Photoelectron Spectrum (XPS) was performed on an ESCALAB 250 X-ray Photoelectron Spectrometer with Al Ka radiation. The FT-IR spectrum was determined using a Magna-IR 750 spectrometer in the range of 400-4000 cm⁻¹ with a resolution of 4 cm⁻¹.

Electrochemical measurements

The electrochemical performance of the Fe₂O₃@N-C was examined by using CR 2032 coin-type cells *versus* Li with 1 M LiPF₆ in the ethylene carbonate and diethyl carbonate (EC/DEC = 1:1, v/v) as the electrolyte. To prepare a working electrode, active material (Fe₂O₃@N-C, 60 wt%), conductive material (acetylene black, 20 wt%), and binder (polyvinylidene fluoride (PVDF), 20 wt%) were milled for 1 h, and then coated onto the surface of a copper foil current collector. The density of the active material is about 1 mg cm⁻² and the film thickness was about 100 µm. The cells were assembled in an argon-filled glove box with both the moisture and the oxygen content bellow 1 ppm (Mikrouna, Super(1220/750/900)). The electrode capacity was measured by a galvanostatic discharge-charge method in the voltage range between 0.01 and 3.0 V on a battery test system (Neware CT-3008W).



Figure S1. FESEM images (a,b) and TEM images (c,d) of as-prepared Fe-ZIF precursor.



Figure S2. Particle size distribution of as-prepared Fe-ZIF precursor.



Figure S3. IR spectra of (a) the 2-methylimidazolate linker and (b) the resulting Fe-ZIF precursor.

Figure S3 shows the IR spectra of the 2-methylimidazolate linker and the resulting Fe-ZIF precursor, respectively, in which the spectrum for Fe-ZIF precursor is different from that of the primitive 2-methylimidazolate linker. The broad peak at 590 cm⁻¹ for Fe-ZIF precursor can be attributed to Fe-N bond,¹ indicating the formation of Fe-ZIF.



Figure S4. XRD pattern of the resulting Fe-ZIF precursor.

Figure S4 shows XRD pattern of the resulting Fe-ZIF precursor with two broad peaks, indicating the successfully synthesis of Amorphous Fe-ZIF precursor, similar to

reported ZIF.²



Figure S5. TGA curves of the Fe-ZIF precursor with a temperate ramp rate of 10 °C/min.



Figure S6. XRD pattern of the resulting sample obtained at 425 °C.

Figure S5 shows the thermogravimetric analysis (TGA) curves of Fe-ZIF precursor. It is found that Fe-ZIF precursor underwent significant weight loss of 12.6 % from room temperature to 160 °C, indicating the loss of H₂O molecules from the porous structure. When the degradation temperature was further increased to 430 °C, a second weight

loss of 17.6 % was observed between 160 and 430 °C due to the decomposition of metal-organic frameworks. Interestingly, the weight increases at about 360 °C, indicating the oxidization of the centered Fe atoms into Fe₂O₃. XRD pattern (Figure S6) demonstrates that the sample obtained at 430 °C contains the composites of Fe₂O₃ and Fe-ZIF precursor. The third section of weight loss from 470 to 620 °C can be attributed to carbonization of the linkers and further degradation of Fe-ZIF precursor. Therefore, in order to ensure calcination of as-prepared precursor completely, a temperature of 620 °C was chose for the conversion of Fe-ZIF precursor to Fe₂O₃@N-C composites.



Figure S7. Large-area FESEM image of 620T-10R.



Figure S8. Particle size distribution of 620T-10R.



Figure S9. XPS spectra of the as-prepared 620T-10R: (a) survey spectrum, (b) Fe 2p binding energy spectrum, (c) C 1s binding energy spectrum, (d) N 1s binding energy spectrum.

As shown in Figure S7a, the survey spectrum indicates the presence of Fe, O, N, and C in the resulting 620T-10R sample. Figure 4b is the Fe 2p XPS spectrum which shows two major peaks with binding energy at 712.0 and 725.2 eV, corresponding to Fe 2p_{3/2} and Fe 2p_{1/2}, respectively, accompanied by a shake-up satellite peaks (718.7 eV).^{3, 4} The results further confirm the formation of Fe₂O₃. The main peak centered at 284.6 eV can be assigned to the sp² hybridized C atoms, as shown in Figure S7c, while the another two peaks located at 285.4 and 287.3 eV can be assigned to the sp² and sp³ hybridized C atoms, respectively.⁵ The N 1s peak can be resolved into three peaks centered at 399.4, 401.5, and 402.7 eV, which correspondingly represent pyridinic, pyrrolic, and graphitic type of N atoms doped in the carbon network (Figure S7d).⁶



Fgure S10. FESEM and TEM images of 620T-5R (a, b,), 620T-2R (c, d) and 820T-10R (e, f), respectively.



Figure S11. XRD patterns of 620T-5R and 620T-2R, respectively.



Figure S12. XRD pattern of 820T-10R.



Figure S13. Raman spectra of 620T-5R (a), 620T-2R (b) and 820T-10R (c), respectively.



Figure 14. Cycle-life performance of 620T-10R at a current density of 1 C.



Figure S15. Subsequent rate capability test after three weeks interval and cycling performance after twice rate capability tests ($1C = 1000 \text{ mA g}^{-1}$).



Figure S16. TEM images of 620T-10R before cycling (a) and after 50 cycles (b) at a current density of 100 mA g^{-1} .



Figure S17. HRTEM images of 620T-10R after 50 cycles at a current density of 100 mA g⁻¹.



Figure S18. EDS mapping images of 620T-10R after 50 cycles at a current density of 100 mA g⁻¹.

Samples	Current density (mA g ⁻¹)	Cycle number	Capacity (mAh g ⁻¹)	Ref.
620T-10R	100	50	1573	this work
	1000	100	1142	
Fe ₂ O ₃ microboxes	200	30	945	7
α-Fe ₂ O ₃	200	50	911	8
α-Fe ₂ O ₃ multi-shell hollow microspheres	50	50	1702	9
α-Fe ₂ O ₃ multi-shelled hollow microspheres	400	50	1000	10
G-CNT-Fe	100	40	1024	11
Fe ₂ O ₃ @multi-walled carbon nanotubes	100	50	1147	12
Fe ₂ O ₃ /graphene	200	100	800	13
α -Fe ₂ O ₃ @C nanotubes	200	100	1174	14
Carbon-coatedα-Fe ₂ O ₃ nanorods	200	70	1126	15
HP-Fe-G	200	50	1100	4

Table S1. A comparison of the capacity of present work with reported Fe_2O_3 -based anode materials for LIBs.

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