Supporting Information for

Hollow-Sphere Iron Oxides Exhibiting Enhanced Cycling Performance as Lithium-Ion Battery Anodes

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Experimental Section

Synthesis of Fe_2O_3 hollow microspheres

Chemicals were purchased from Sinopharm chemical reagent Co., Ltd and with analytical grade. 60 ml of aqueous solution with 0.5 g of potassium ferricyanide and 0.075 g of ammonium dihydrogen phosphate was poured into an autoclave with 80 ml of volume, and maintained at 180 ^{o}C for 24 h to synthesize the precursor. Then, the brick-red precursor was washed, dried and heated in air at 500 ^{o}C for 2 h with a heating ramp of 5 ^{o}C min^{-1} to convert Fe_2O_3 hollow microspheres.

Material characterization

The samples were investigated by X-ray diffraction (a step width of 2^{o}, Cu Kα radiation, Bruker D8) and photoelectron spectroscopy (Al X-ray source, Physical Electronics PHI5700ESCA), scanning (HITACHI S-4800) and transmission (JEM-2100) electron microscopy, N_2 adsorption isotherms (Quantachrome NovaWin) and thermal gravimetric analysis in air (a heating rate of 5 ^{o}C min^{-1}, NETZSCH TG 209F3) to obtain the information about structure, element valence, surface area and pore size.

Electrochemical test

The working electrodes were fabricated with a slurry of 70% active materials, 20% acetylene black and 10% binder (SBR : CMC = 1 : 1, wt%) in deionized water coated on copper foil. After dried, the loading mass of active materials was ~1.5 mg cm^{-2}. The half-cell configuration (CR-2025) was assembled with electrolyte of 1 M $LiPF_6$ in EC and DMC (1 : 1 vol%) and lithium foil as the counter electrode. The potential range of 0.01 V- 3 V was for electrochemical tests. The frequency range of 100 KHz - 0.01 Hz was for electrochemical impedance spectroscopy (EIS) and the cell rested for 8 h before test. The operations were performed by using an Ar-filled glovebox (Mikrouna, German), an electrochemical workstation (CHI660E, China) and NEWARE battery testers at room temperature.

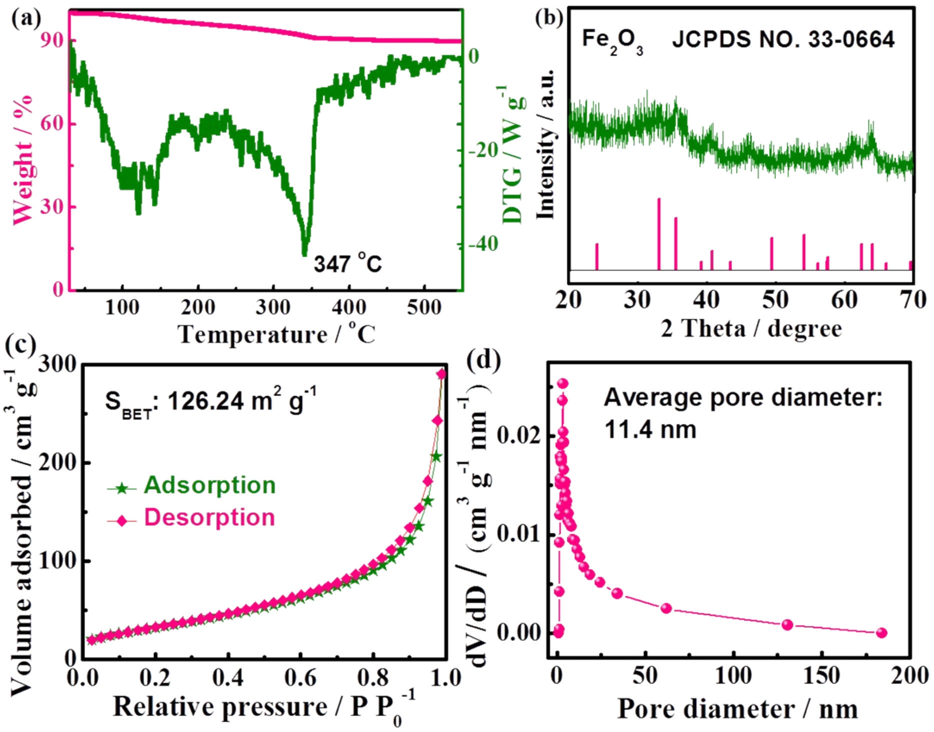


Fig. S1 a) TGA with a heating ramp of 5 °C min^{-1}, b) XRD patterns, c) N_2 adsorption/desorption isotherms, and d) pore size of Fe_2O_3 hollow microspheres.

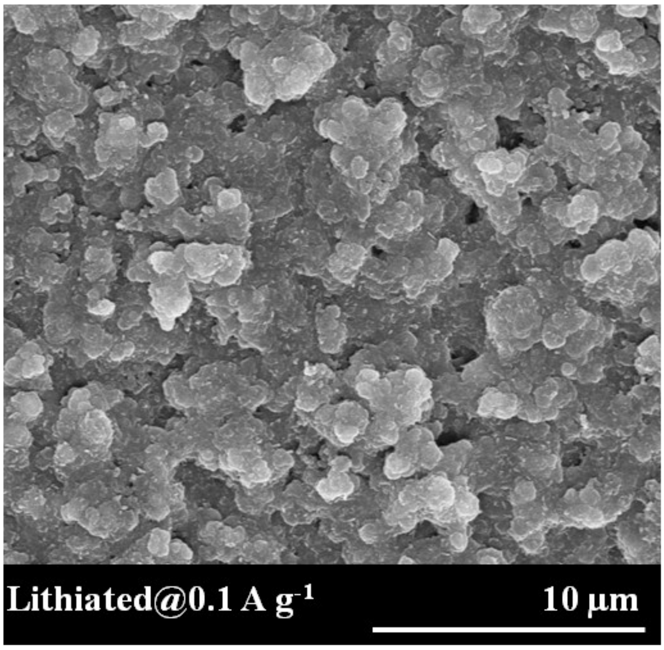


Fig. S2 SEM images of Fe_2O_3 anodes after the first lithiated at low current densities of 0.1 A g^{-1}.

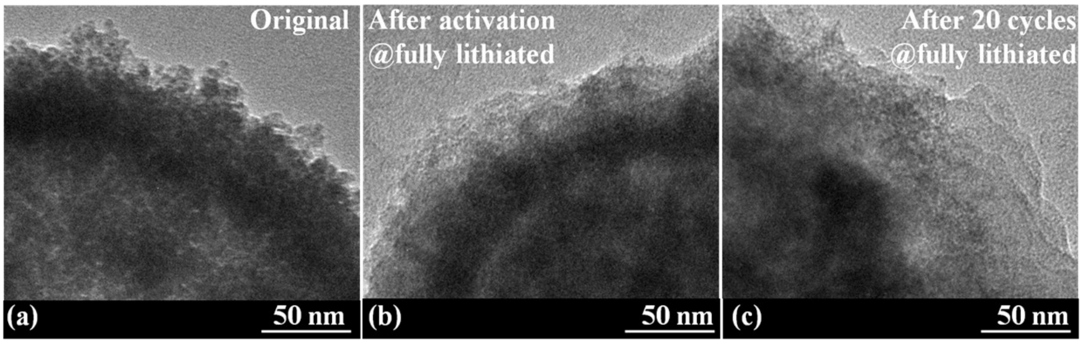


Fig. S3 TEM images of Fe_2O_3 hollow microspheres at various cycle number: a) original; b) activated; c) 20-cycled.

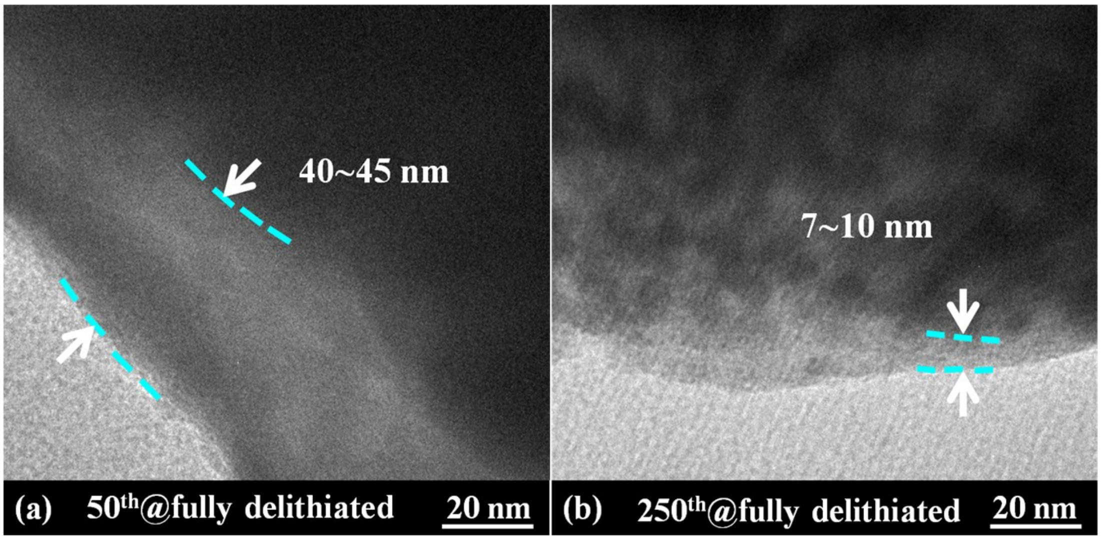
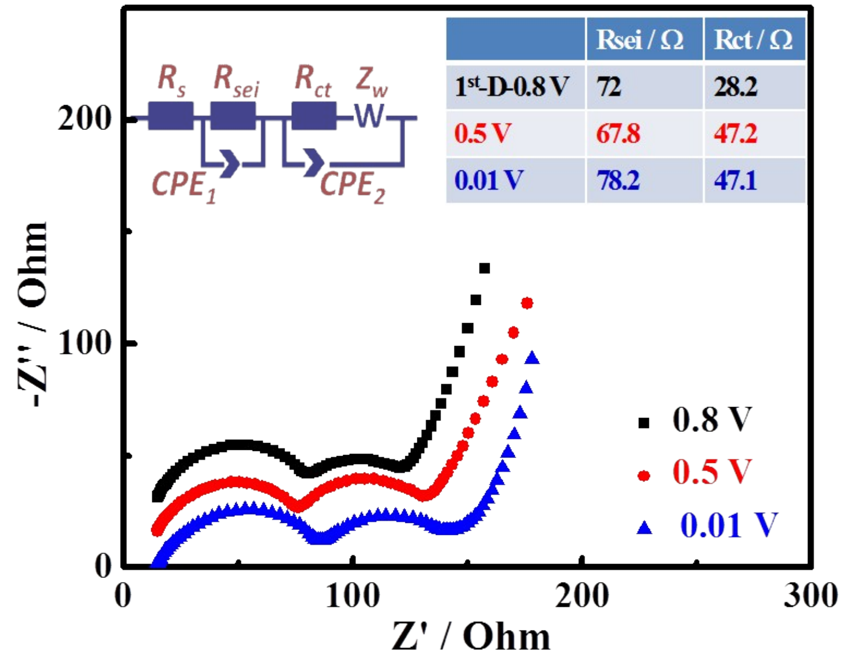


Fig. S4 TEM images of a) 50- and b) 250-cycled Fe_2O_3 materials at the delithiated state.



	Rsei / Ω	Rct / Ω
1st-D-0.8 V	72	28.2
0.5 V	67.8	47.2
0.01 V	78.2	47.1

Fig. S5 Nyquist plots at various voltages (0.8 V, 0.5 V and 0.01 V) during the first lithiation, and the insets of equivalent circuit and fitted impedance data.

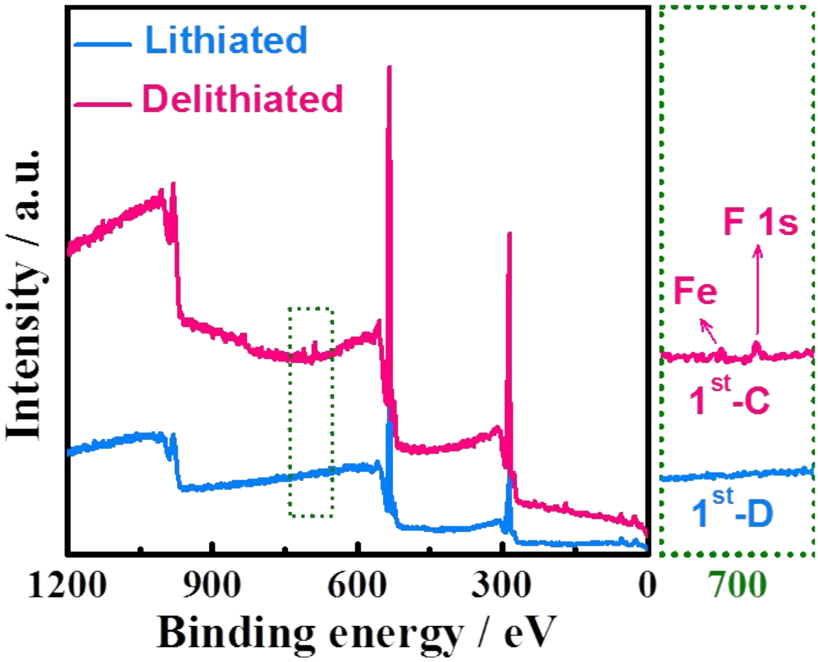


Fig. S6 XPS spectra of the first lithiated (blue) and delithiated (pink) Fe_2O_3, and the enlarged view of the green dashed line associated with F (LiF), which reveals a multilayer structure of SEI layer on surface of Fe_2O_3 materials.

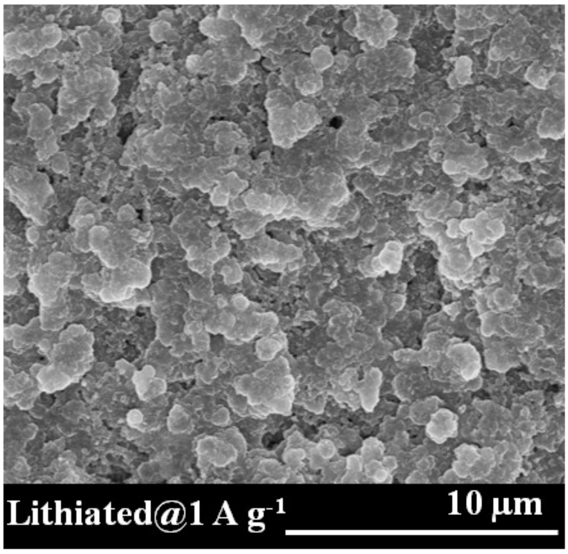


Fig. S7 SEM images of Fe_2O_3 anodes after the first lithiated at high current densities of 1 A g^{-1}.

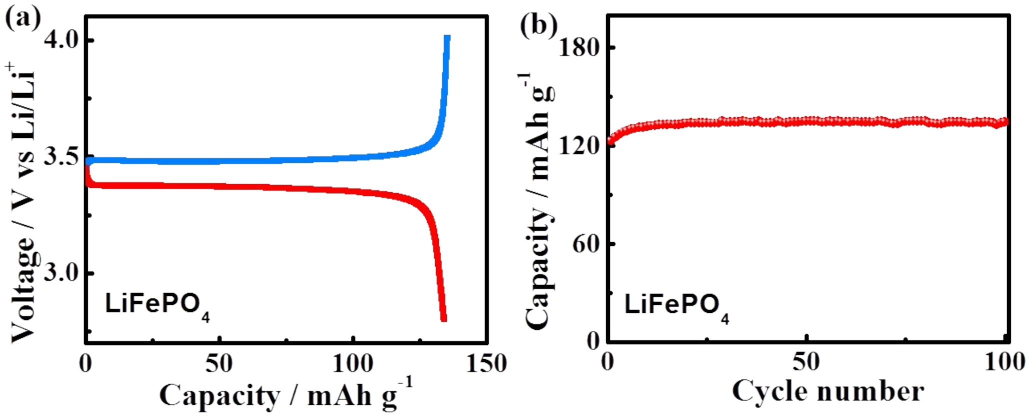


Fig. S8 a) Discharge-charge profiles, and b) cycling performance at 1 C of $LiFePO_4$ cathodes.

Table S1 Comparison of Fe_2O_3 hollow spheres and other Fe_2O_3-based materials with Li^+ storage performance.

LIB anodes	**Cycling performance**	**References**
Fe_2O_3 hollow spheres	**829 mAh g^{-1} after 1000 cycles at 1 A g^{-1}**	**This work**
Carbon-coated Fe_2O_3 nanofibers	1252 mAh g^{-1} after 200 cycles at 1 A g^{-1}	[S1]
Hierarchical Fe_2O_3@C@MnO_2@C multishell nanocomposities	850 mAh g^{-1} after 100 cycles at 0.5A g^{-1}	[S2]
Spindle-like Sn-doped Fe_2O_3	805 mAh g^{-1} after 500 cycles at 1 A g^{-1}	[S3]
Fe_2O_3/SnSSe hexagonal nanoplates	755 mAh g^{-1} after 1000 cycles at 0.2 A g^{-1}	[S4]
Fe_2O_3-carbon fiber composites	634 mAh g^{-1} after 150 cycles at 0.05 A g^{-1}	[S5]
Fe_2O_3-MnO_2 hollow spheres	494 mAh g^{-1} after 500 cycles at 0.5 A g^{-1}	[S6]
Flower-like FeS/Fe_2O_3 composite	460 mAh g^{-1} after 500 cycles at 0.2 A g^{-1}	[S7]
SnO_2-Fe_2O_3-C hollow spheres	415 mAh g^{-1} after 1000 cycles at 2 A g^{-1}	[S8]
Fe_2O_3@N-doped carbon foam	372 mAh g^{-1} after 500 cycles at 1 A g^{-1}	[S9]
Fe_2O_3 nanocones	276 mAh g^{-1}after 1000 cycles at 5 A g^{-1}	[S10]

References

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