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Engineering iron sulfide/carbon co-coated silicon nanoparticles as

lithium-ion battery anode displaying stable capacity and rate-performance

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Experimental

Materials

Si particles (diameter: 30 nm), Metallo-organic compound ferrocene, hydrogen peroxide, acetone, and sulfur powders were obtained from Aladdin. All chemicals were used directly without further purification.

Preparation of Si-Fe metal-organic frameworks (MOFs) precursor

In a typical process, 0.1 g of Si nanospheres and 0.2 g of metallo-organic compound ferrocene were added into 25 ml of acetone with stirring for 10 min. 2.0 mL of hydrogen peroxide was added into the mixture. After continual stirring for 30 min, the mixture was transferred into an autoclave and heated at 200°C for 48 h. After cooling down to room temperature, the sample was washed several times with deionized water, and dried at 60 °C for 12 h.

Preparation of Si@FeS/C

0.1 g of the Si-Fe MOFs and sulfur powders were putted in a quartz boat with mass ratio of 1:10, and calcined at 700 °C for 2 h with a heating rate of 2 °C min⁻¹ under Ar/H₂ (95%/5%) gas flow. After calcination, the Si@FeS/C was obtained. For comparison, FeS/C was also prepared through similar process without adding Si NPs.

Characterization

The sample was characterized by using an X-ray diffractometer (XRD, SMART APEX

II Brook, copper target). The morphology was observed by field emission scanning electron microscope (SEM, Hitachi S-8100), and transmission electron microscope (TEM, HT-7700, TecnaiG220S-Twin). A high-resolution TEM (HRTEM) was used to observe the lattice fringes. Energy dispersive X-ray spectroscopy (EDS) was employed for elemental mapping and studying the elemental distribution. X-ray photoelectron spectroscopy (XPS, EscalAB 250) and Raman spectroscopy (Renishaw in Via) were used for characterization. In order to characterize the carbon matrix, Raman spectroscopy (Renishaw in Via) was used. Prior to the Brunauer-Emmett-Teller (BET) test, the sample was degassed at 120 °C for 12 h in vacuum to remove water adsorbed on the surface, and then physical adsorption isotherms (adsorption-desorption branch) were recorded using a specific surface area tester (ASAP Micromeritics Tristar 2460).

Electrochemical tests

The active materials (70 wt%), acetylene black (20 wt%) and polyvinylidene fluoride (PVDF, 10 wt%) were mixed in a ratio of 7:2:1. The n-methyl-pyrrolidone (NMP) was used as diluent to disperse the mixture. Evenly-mixed slurry was coated on a Cu foil, dried in a vacuum oven at 80 °C for 24 h, and cut into 1.2 mm-diameter discs. The mass loading of the anode was about 1.2 mg cm⁻². The electrolyte consisted of 1 mol L⁻¹ LiPF₆ in ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl methyl-carbonate (EMC) with volume ratio of 2:6:2. The assembly was conducted in an argon-filled glove box. The galvanostatic charge-discharge (GCD) was tested on Neware Battery system. Cyclic voltammetry (CV, 0.1 mV s⁻¹ of sweep rate over the range of 0.01-3.0 V) and electrochemical impedance spectroscopy (EIS) test were performed an electrochemical workstation (CHI 660E). The time-voltage relationship was obtained by using galvanostatic intermittent titration technique (GITT) on a battery tester (Neware CT4008). At a current density of 0.2 A g⁻¹, the cell was charged/discharged to the preset potential in 10 min and stood by 2 h before going to next potential. For the assembly of full cells, the LiFePO₄ (LFP) cathode was prepared by mixing homemade LFP, acetylene black and PVDF with a weight ratio of 7:2:1 in NMP to form a slurry, which was casted onto Al foil. The electrolyte consisted of 1 mol L⁻¹ LiPF₆ in EC, DMC and EMC with volumetric ratio of 2:6:2.

First-principle calculations

Density functional theory (DFT) calculations were performed using the CASTEP program with the generalized gradient approximation (GGA) and Perdew-Burke-Ernzerhof (PBE) exchange-correlation functionals. A vacuum layer thickness of 15 Å was applied along the z-axis for the geometric models. The top surface atoms of each slab were relaxed, while the remaining atoms were kept fixed. The energy cutoff was set to 500 eV, and the Brillouin zone was sampled with a $2 \times 2 \times 1$ *k*-point grid.



Fig. S1 (a,b) SEM images of pristine Si NPs.



Fig. S2 (a-c) SEM and (d-f) TEM images of Si@FeS/C.



Fig. S3 TEM images of Si@FeS/C obtained by using different solvothermal reaction times: (a,b) 60 h and (c,d) 24 h.



Fig. S4 XRD patterns of (a) FeS/C and (b) Si.



Fig. S5 (a) SEM image, (b) line-scanning curves, (c) EDS spectrum of Si@FeS/C. The Cu signal comes from the Cu substrate during measurement.



Fig. S6 Raman spectra of Si@FeS/C, FeS/C, and Si.



Fig. S7 (a) The N_2 adsorption-desorption isotherms and (b) pore-size distribution of Si@FeS/C, FeS/C and Si.



Fig. S8 (a,b) SEM images of Si@FeS/C.



Fig. S9 (a) XPS survey spectrum of Si@FeS/C. XPS spectra of (b) Si 2p, (c) Fe 2p, (d) S 2p,

(e) C 1s.



Fig. S10 (a) CV profiles of FeS/C scanning at 0.1 mV s⁻¹. (b) CV curves of FeS/C scanning at 0.1 to 1.0 mV s⁻¹.



Fig. S11 CV profiles of Si anode scanning at 0.1 mV s⁻¹.



Fig. S12 (a) Cycling performance of Si@FeS/C, FeS/C, Si anodes at 0.4 A g^{-1} . (b) Cycling performance of Si@FeS/C anode at 1 A g^{-1} . The anodes were pre-cycled 10 times at 0.1 A g^{-1} for activation.



Fig. S13 (a,b) SEM images of Si@FeS/C after cycling 200 times at 0.2 A g^{-1} .



Fig. S14 (a) SEM and (b-e) mapping images of Si@FeS/C after 200 cycles at 0.2 A g^{-1} .



Fig. S15 (a,b) TEM images of Si@FeS/C anode after fully discharging to 0 V.



Fig. S16 (a,b) SEM images of FeS/C anode after cycling 200 times at 0.2 A g^{-1} .



Fig. S17 (a,b) SEM images of Si anode after cycling 200 times at 0.2 A g^{-1} .



Fig. S18 Galvanostatic discharge-charge curves of Si@FeS/C at different current densities

from 0.1-0.5 A g^{-1} .



Fig. S19 Cycling performance of Si@FeS/C anode under 50 °C at (a) 0.1 and (b) 0.2 A g^{-1} .



Fig. S20 (a) GITT time-potential distributions of Si@FeS/C at 50 °C. *In-situ* reaction resistances of Si@FeS/C during (b) discharge and (c) charge at 50 °C.



Fig. S21 (a,b) Bandgap structure of FeS. (c) Partial density of states (DOS).



Fig. S22 (a) before and (b) after cycling 200 times under 0.2 A g⁻¹. The insert presents equivalent circuit.



Fig. S23 (a) Capacity and (b) cycling curves of the full cell composing of Si@FeS/C anode and LiFePO₄ cathode cycling at 0.1 A g^{-1} .

Anode materials	Current density (A g ⁻¹)	Capacity (mAh g ⁻¹)	Cycle number	Ref.
Si@FeS/C	0.1	809	50	This work
	0.2	659	100	
Si/PA-C nanosheets	0.1	318	100	[1]
Si@mesocarbon microbeads	0.2	421	200	[2]
Si@C nanospheres	0.1	1038	50	[3]
Mesoporous Si@C	0.1	460	100	[4]
Hollow Si-Ni-C nanofabrics	0.2	524	100	[5]
Core-shell Si@C	0.1	713	50	[6]
Core-shell Si@C	0.2	683	50	[7]
P-Si/C nanoblocks	0.05	100	520	[8]

Table S1. Comparison on electrochemical performance of some Li-ion battery anodes.

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