

## Supporting Information

### Application of Li<sub>2</sub>S to Compensate for Loss of Active Lithium in Si-C anode

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## Experimental

### Synthesis of the Si-C composite

For the preparation of Si-C composites, the raw materials used for Si-C composite were silicon powders (Aldrich) with a particle size below 100 nm, synthetic battery-grade graphite powders (Jiangxi Zichen Technology Co. Ltd.), and petroleum derived pitch. In a typical procedure, Silicon, graphite and pitch (mass ratio:15:15:70) were mixed thoroughly in ethanol under sonication for 2 h, followed by vigorous stirring for 12 h to form a homogeneous slurry. Then the resulting composite precursors were collected after drying under vacuum. Finally, the Si-C composites were obtained by pyrolyzing the composite precursors at 900 °C for 3 h at a heating rate of 5 °C/min under argon atmosphere.

### Synthesis of the Cathode and Si-C electrode

For the preparation of the cathode, e.g. LiFePO<sub>4</sub> in this work, deionized water was used as the solvent, and the LiFePO<sub>4</sub> powders, conductive additives (Super P), carboxymethyl cellulose (CMC) and styrene-butadiene rubber (SBR) (92:5:1:2) as binders were mixed together to form a uniform slurry. Then, the slurry was coated on aluminum foil. The prepared electrodes were put into the oven at 55 °C for 5 h and then cut into discs (14 mm in diameter) using a cutting machine. The loading level of active material in LiFePO<sub>4</sub> electrode was ~8.2 and ~10.5 mg/cm<sup>2</sup>. For the preparation of the Si-C electrode, deionized water was also used as the solvent, and the prepared Si-C powders, Super P, CMC and SBR (93:2:2:3) were mixed together to form a uniform slurry. Then, the slurry was coated on copper foil. The prepared electrodes were put into the oven at 55 °C for 5 h and then cut into discs (14 mm in diameter) using a cutting machine. The loading level of active material in Si-C electrode was ~2.5 mg/cm<sup>2</sup>. These discs were all put into an oven at 120 °C for 6 h.

### Synthesis of Li<sub>2</sub>S Slurry and electrode

For the synthesis of Li<sub>2</sub>S Slurry and electrode, commercial lithium sulfide powders (Li<sub>2</sub>S, 99.9% trace metals basis) were purchased from Alfa Aesar. Anhydrous ethanol (99.5%, <0.005% water) and poly(vinylpyrrolidone) powders (PVP, K90 average Mw 360,000) were purchased from Sigma-Aldrich. The powders and ethanol were used as the starting materials. In a typical procedure, 0.3 g Li<sub>2</sub>S was added to 20 mL anhydrous ethanol and stirred for 12 h at room temperature. The Li<sub>2</sub>S solution sat for a few hours, and the supernatant was removed and placed into another bottle by a pipette. Then, 0.15 g Ketjenblack carbon black (KB) as conductive additives and 0.05 g PVP as binder were added into the solution, and the solution was agitated by an ultrasonic needle for 1 h and further stirred for 12 h to form a uniform slurry. Finally, the slurry was uniformly coated on carbon paper by a brush. The prepared electrode was put into an oven at 120 °C under vacuum for 6 h and then cut into 14 discs (14 mm in diameter) by a cutting machine.

### Synthesis of Li<sub>2</sub>S coating on the surface of LiFePO<sub>4</sub> electrode

To balance the cathode and Si-C anode in a full cell, 40 μL Li<sub>2</sub>S/KB/PVP slurry, was coated on the LiFePO<sub>4</sub> electrode with loading level of ~8.2 mg/cm<sup>2</sup>. The prepared electrode was placed on a heating plate at 60 °C for 2 h and then heated to 120 °C for 10 h. The amount of Li<sub>2</sub>S/KB/PVP (~1 mg for 40 μL) was calculated by measuring the weight of the LiFePO<sub>4</sub> and LiFePO<sub>4</sub> (Li<sub>2</sub>S) electrodes with a high precision balance. The LiFePO<sub>4</sub> electrode with Li<sub>2</sub>S/KB/PVP coating is assigned as LiFePO<sub>4</sub> (Li<sub>2</sub>S) electrode.

### Electrochemical characterization

Coin cells of CR2032 type were assembled in an argon-filled glove box (Lab Star, Braun, Germany) to evaluate the electrochemical properties and mechanisms of the electrodes. The LiFePO<sub>4</sub>, LiFePO<sub>4</sub> (Li<sub>2</sub>S) and Li<sub>2</sub>S electrode were used as the cathode, and Si-C (full cell) and lithium plates (half cell) were used as the anode. The full cell was balanced according to the capacities of the cathode

and Si-C with a ratio of 1: 1.1. Lithium hexafluorophosphate (1 M) dissolved in ethylene (EC): dimethyl carbonate (DMC) (1:1 by volume with 1% VC, BASF, Suzhou, China) was used as the electrolyte. A PP/PE/PP was used as the separator. All the cells,  $\text{Li}_2\text{S}/\text{KB}/\text{PVP}$  half cell for 1.8-3.8 V,  $\text{LiFePO}_4$  and  $\text{LiFePO}_4(\text{Li}_2\text{S})$  half cells for 2.5-3.8 V and  $\text{LiFePO}_4/\text{Si-C}$  and  $\text{LiFePO}_4(\text{Li}_2\text{S})/\text{Si-C}$  full cells for 2.1-3.8 V, were galvanostatically charged and discharged on a Land auto battery tester (Wuhan Land). All the cells were cycled at 0.05C in the 1st cycle and 0.2C for the following cycles. The specific capacities and current rates were calculated according to the mass of  $\text{Li}_2\text{S}$  for the  $\text{Li}_2\text{S}$  cathode and the mass of  $\text{LiFePO}_4$  for the  $\text{LiFePO}_4$  and  $\text{LiFePO}_4(\text{Li}_2\text{S})$  cathode. All C rates are based on the theoretical capacity of  $\text{Li}_2\text{S}$  (1 C = 1166 mA/g) and  $\text{LiFePO}_4$  (1 C = 160 mA/g).

### Materials characterization

The CR2032 coin cells of  $\text{LiFePO}_4$  and  $\text{LiFePO}_4(\text{Li}_2\text{S})$  full cells were disassembled in an argon-filled glove box (Lab Star, Braun, Germany) in the 1st and 10th discharge state. The cathode electrodes were thoroughly washed with anhydrous DMC to remove the residual electrolytes and were dried in the antechamber of the glove box under vacuum overnight prior to characterization and analyses.

X-ray diffraction (XRD) characterization. The XRD diffraction patterns were recorded on a Bruker D8 ADVANCE X-ray diffractometer (Germany) using  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15406 \text{ nm}$ ) from  $10^\circ$  to  $80^\circ$  with the Sample-Saver storage container under purified, protecting argon at a scan rate of 0.1 s per  $0.02^\circ$ .

Scanning electron microscopy (SEM) characterization. The morphology and microstructure were characterized by SEM on a HITACHI SU-4800 instrument with the Sample-Saver storage container under purified, protecting argon. The elemental composition and mapping were conducted and performed by energy dispersive X-ray (EDX) analyses on an SEM HITACHI SU-4800 instrument operated at 15 kV.

The TEM characterization was performed on a TEM JEOL 2010F instrument with a field emission gun and operated at an acceleration voltage of 200 kV.

X-ray photoelectron spectroscopy (XPS) characterizations were carried out on a photoelectron spectrometer using  $\text{Mg K}\alpha$  radiation (ESCALAB 250, Sigma Probe, Thermo VG Scientific Co. Ltd.). The binding energy calibrations were corrected using the signal of the C 1s peak (284.8 eV) to eliminate charging of the samples during the analysis.

### Results

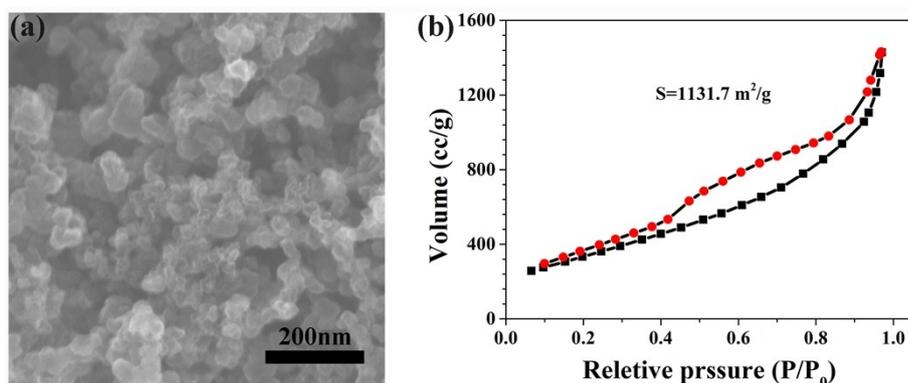


Fig. S1. (a) Typical SEM image of KB. (b) BET results of KB.

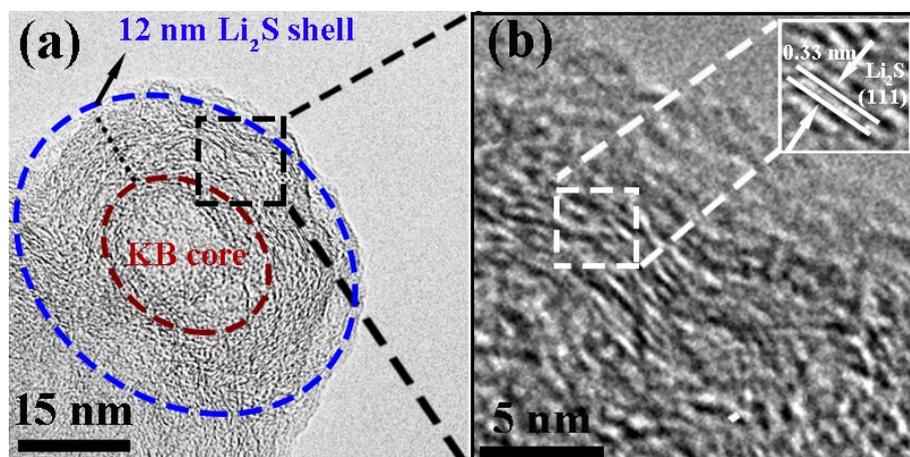


Fig. S2. (a) HRTEM images of the  $\text{Li}_2\text{S}/\text{KB}$  nano-composite. (b) Enlarged region corresponding to the black square in (a).

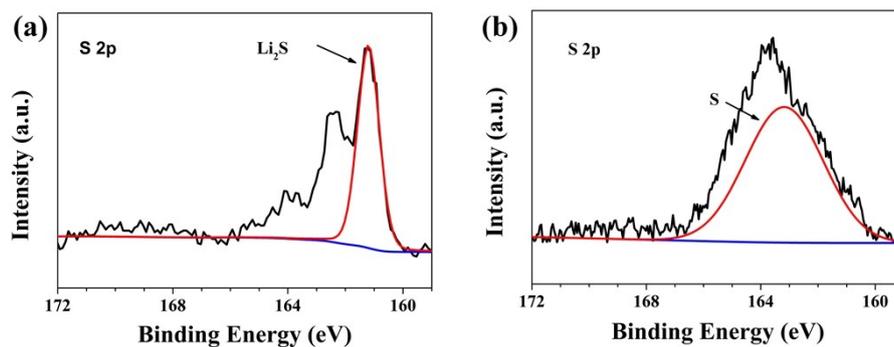


Fig. S3. XPS spectra of S 2p of  $\text{Li}_2\text{S}$  electrode (a) before cycle and (b) after 1<sup>st</sup> cycle, respectively.

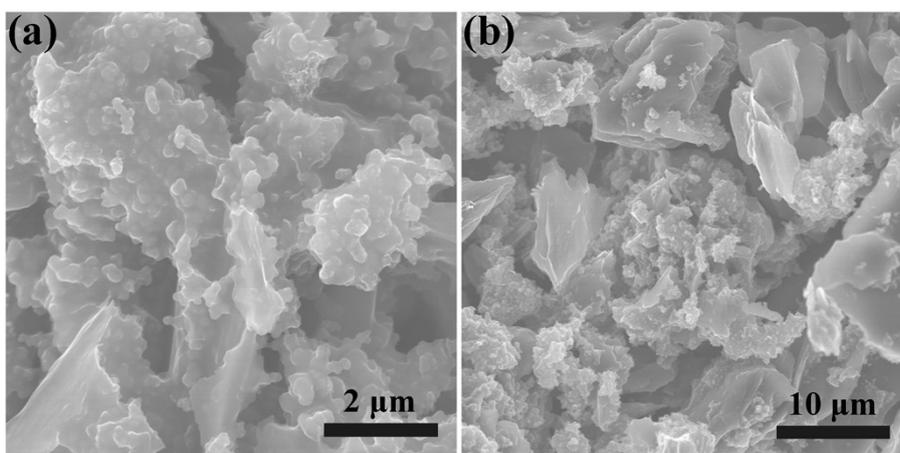


Fig. S4. SEM images of Si-C.

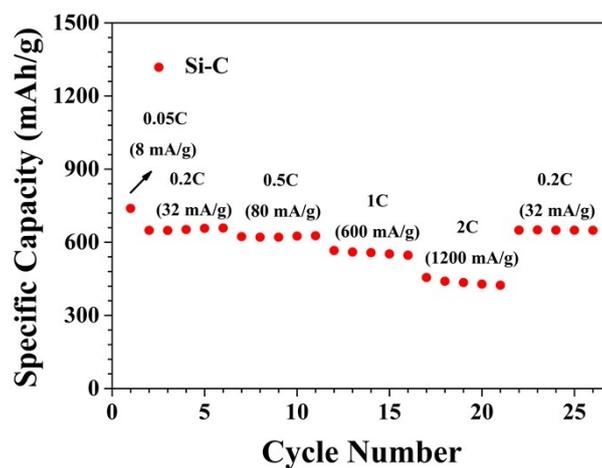


Fig. S5. Rate performance of a typical Si-C half cell.

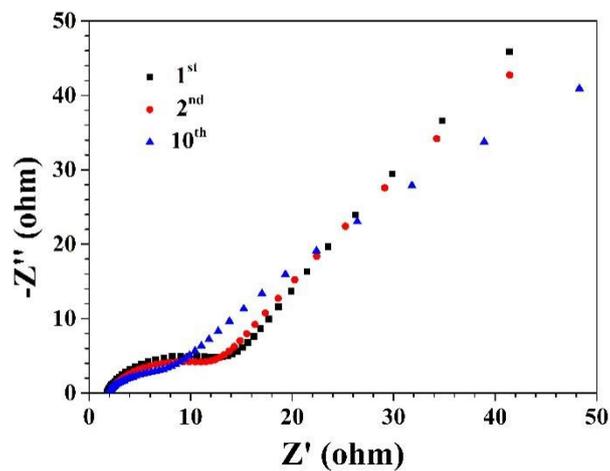


Fig. S6. Impedance spectra of the Si-C half cells after the 1<sup>st</sup>, 2<sup>nd</sup> and 10<sup>th</sup> cycles.

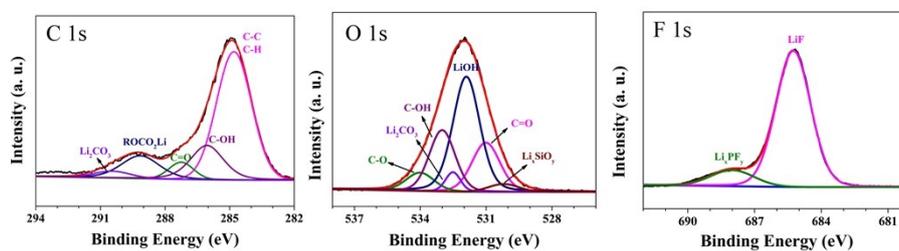


Fig. S7. C 1s, O 1s and F 1s XPS spectra of the Si-C anode after the 1<sup>st</sup> cycle.

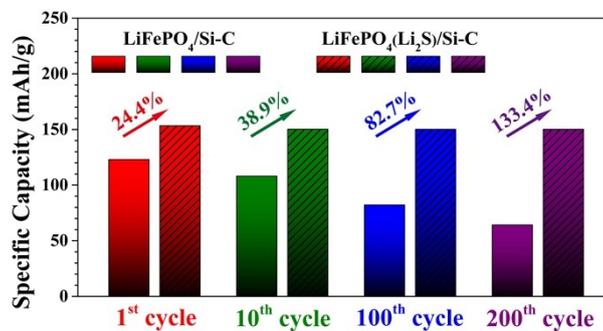


Fig. S8. Comparison of the discharge specific capacity for the LiFePO<sub>4</sub>/Si-C with LiFePO<sub>4</sub>(Li<sub>2</sub>S)/Si-C full cells in the 1<sup>st</sup>, 10<sup>th</sup>, 100<sup>th</sup> and 200<sup>th</sup> cycles.

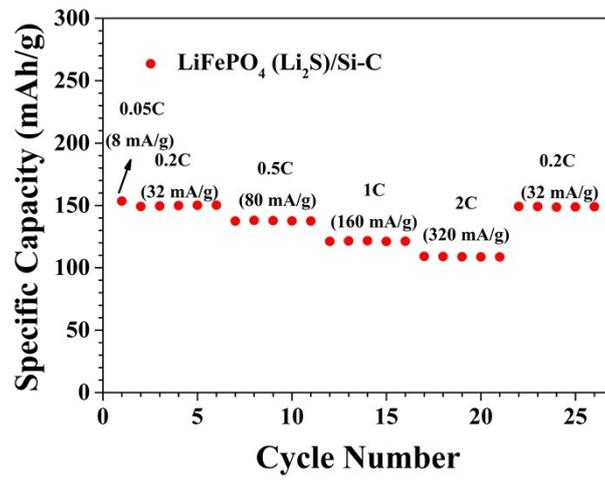


Fig. S9. Rate performance of a typical LiFePO<sub>4</sub>(Li<sub>2</sub>S)/Si-C full cell.