Supplementary Information

Pyrite FeS₂ as an efficient adsorbent of lithium polysulfide for improved lithium-sulfur batteries

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1. Experimental

Materials: All chemicals, unless specified otherwise, were purchased from Sigma-Aldrich. Elemental sulfur (S₈, \geq 99.5%) and iron disulfide (FeS₂, -325 mesh, 99.8%) were used as received; Lithium sulfide (Li₂S, 99%), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), and lithium nitrate (LiNO₃, 99.99%) were dried at 110 °C under vacuum for 10 h; Triglyme, dimethyl ether (DME), and 1,3-dioxolane (DOL) were dried over 4 A molecular sieves for a week.

Structural characterizations: Morphology of FeS_2 powder was observed and energy dispersive X-ray (EDX) analysis was conducted on a Quanta 200F scanning electron microscope; X-ray diffraction (XRD) was performed on a Rigaku Ultima III diffractometer (Cu K α radiation); Raman spectra were collected using a Renishaw inVia Raman microscope.

 Li_2S_9 solution: A 0.5 mol kg⁻¹ Li₂S₉-triglyme solution was prepared following Rauh et al's procedure.¹ Briefly, stoichiometric amounts of S₈ and Li₂S were weighed into a calculated amount of triglyme solvent followed by heating at 80 °C for 6 h, which led to a red-dark solution with a moderate viscosity. In a glove-box free of moisture and oxygen, the resultant solution was diluted using trigylme to 0.005 mol kg⁻¹, which led to a change of the solution's color from reddark to slight green. In order to examine the adsorption of lithium polysulfide to FeS₂ host, small amount of FeS₂ powder was added into a 0.005 mol kg⁻¹ Li₂S₉ solution and hand-shaken for ~1 minute, followed by centrifuging and observing the color of the upper solution.

*Treatment of FeS*₂ *by Li*₂*S*₉: Small amount of FeS₂ particles was added to a 0.5 mol kg⁻¹ Li₂S₉-triglyme solution, followed by heating at 80 °C for overnight. Resultant solid was collected simply by pouring the upper solution out, and washed using a 1:1 (wt.) DME/DOL mixed solvent for five times. In each washing, the solid was collected by carefully pouring the upper solution out. The final product was dried at 80 °C under vacuum for 8 h.

Cell components and assembly: Sulfur cathodes having a general composition by weight of (77-x)% S, x% FeS₂, 10% Super-P carbon, 10% Ketjenblack EC-300JD carbon black, and 5% binder were coated onto a carbon-coated aluminum foil by using poly(acrylonitrile-methyl methacrylate) (ANMMA, AN/MMA= 94:6, MW=100,000, Polysciences, Inc.) as the binder and N-methyl pyrrolidinone as the solvent. Resultant cathode was punched into 1.27 cm² circular discs and dried at 60 °C under vacuum for 16 h. Typically, the sulfur cathode had a sulfur

loading of 2.0 ± 0.1 mg cm⁻². A solution consisting of 0.25 mol kg⁻¹ LiTFSI-0.25 mol kg⁻¹ LiNO₃ dissolved in a 1:1 (wt.) DME/DOL mixed solvent was used as the electrolyte. Using a Celgard 3410 membrane as the separator, the 2030-size coin cell was assembled and filled with 15 µL electrolyte. The cell was cycled galvanostatically at 0.5 mA cm⁻² between 1.7 V and 2.8 V for Li-S cell and between 1.0 V and 2.6 V for Li-FeS₂ cell on a Maccor Series 4000 cycler. Additionally, a 3.5 mAh capacity limit was applied to the charging process.

Electrochemical test: Using a Solartron SI 1287 Electrochemical Interface and a SI 1260 Impedance/Gain-Phase Analyzer, ac-impedance of the cell was measured at open-circuit potential over a frequency range from 100 kHz to 0.01 Hz with a 10 mV oscillation. The collected impedance spectrum was analyzed using a Zview software (Scribner and Associates, Inc.).

2. Note to Fig. S2

It is shown by comparing Fig. S2a and Fig. S2c that the Li_2S_9 -treatment resulted in a significant narrow in the particle size distribution of FeS₂ with disappearance of numerous small FeS₂ particles. This is because the small FeS₂ particles that were stably suspended in the solution could not be collected in the separating and washing steps, which has been verified by the fact that small FeS₂ particles were observed to precipitate out of the poured-out solution after standing for several days. The C and O in EDX spectra were attributed to the conductive adhesive that was used to fix powder sample in SEM observation. It is also possible that small amounts of oxygen are present on the FeS₂ surface because of the oxidation in air.² It is needed to note that the calculated S/Fe weight ratio in FeS₂ is 1.1484, which is much higher than the measured value by the EDX analysis (S/Fe=0.9649 for the commercial FeS₂ product, as shown in Fig. S2b). This means that the EDX is not a good tool for the accurate elemental analysis. However, the EDX may give a credible comparison when the analyses are conducted under the same conditions. Comparing of Fig. S2b and Fig. S2d reveals an increase in the S/Fe weight ratio, suggesting the chemical adsorption of Li₂S₉ to FeS₂ host.

3. Figure



Fig. S1 Color of Li_2S_9 -trigylme solutions. (a) 0.5 mol kg⁻¹, and (b) 0.005 mol kg⁻¹.



Fig. S2 SEM image of FeS₂ particles. (a) before, and (b) after the treatment by a 0.5 mol kg⁻¹ Li_2S_9 -trigylme solution at 80 °C for overnight.



Fig. S3 SEM image and EDX spectrum of FeS_2 before (a & b) and after Li_2S_9 -treatment (c & d).



Fig. S4 Fe-S binary phase diagram, modified from Ref. 3.

References

- 1. R. D. Rauh, F. S. Shuker, J. M. Marston and S. B. Brummer, *J. Inorg. Nucl. Chem.*, 1977, **39**, 1761.
- 2. T. Kendelewicz, C. S. Doyle, B. C. Bostick and G. E. Brown Jr, *Surface Science*, 2004, **558**, 80.
- 3. http://www.factsage.cn/fact/documentation/FTmisc/Fe-S.jpg