Supplementary Information

Activated Li₂S as a High-Performance Cathode for Rechargeable Lithium-Sulfur Batteries

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Experimental

Preparation of Li₂S catholyte

Appropriate amount of P₂S₅ (99+ %, Acros Organics) were dissolved in tetraethylene glycol dimethyl ether (TEGDME, 99+ %, Acros Organics). In order to prepare the Li₂S catholyte, commercially available Li₂S particles (99+ %, Acros Organics) were suspended in the P₂S₅-containing electrolyte and heated overnight at 50 °C. Following a similar procedure, Li₂S bulk particles were pre-treated in TEGDME without P₂S₅ as a reference.

Preparation of carbon nanofiber current collector

Carbon nanofibers (CNF, 120 mg, Pyrograf Products Inc.) were dispersed in a miscible solution of de-ionized water (700 mL) and isopropyl alcohol (50 mL), ultrasonicated for 15 min, and collected by vacuum filtration to obtain a free-standing CNF paper. The product CNF paper was dried in an air-oven for 24 h before being punched out into circular disks with 1.2 cm diameter for use as the current collector.

Electrochemical test

Lithium trifluoromethanesulfonate (LiCF₃SO₃, 98 %, Acros Organics, 1 M) and LiNO₃ (99+ %, Acros Organics, 1 M) in TEGDME is used as the anolyte. The corresponding catholyte was loaded onto the CNF current collector before placing the Celgard separator, anolyte, lithium-metal anode, and assembled into CR2032 coin cells inside an argon-filled glovebox. The Li₂S loading was ~ 1 mg cm⁻². The corresponding P₂S₅ concentrations in the cell are 0.12 g/mL (molar ratio of Li₂S : P₂S₅ = 10 : 1), 0.17 g/mL (molar ratio of Li₂S : P₂S₅ = 7 : 1), 0.24 g/mL (molar ratio of Li₂S : P₂S₅ = 5 : 1), and 0.4 g/mL (molar ratio of Li₂S : P₂S₅ = 3 : 1). Electrochemical impedance spectroscopy (EIS) measurements were performed directly after the cell assembly and with an impedance analyzer (Solartron 1260 A) in the frequency range of 1 MHz to 0.1 Hz with an AC voltage amplitude of 5 mV at OCV. The cyclic voltammetry (CV) profiles were obtained with a VoltaLab PGZ 402 potentiostat with a

scan rate of 0.05 mV s^{-1} from 1.5 to 4.0 V after the initial charge from OCV to 4.0 V.

Galvanostatic cycling was conducted with an Arbin battery cyclers at room temperature. The cells were charged from OCV to 4.0 V (vs. Li^+/Li) in the investigation of the initial charge of the P_2S_5 -activated Li_2S cathodes. The cells were cycled between 1.8 and 3.0 V in the investigation of cycling performance.

Characterization

Morphology of the Li_2S cathode materials was examined by scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDS, FEI Quanta 650) and scanning transmission electron microscopy (STEM, Hitachi S-5500). Crystal-structural characterization was performed with a Rigaku X-ray diffraction instrument with $\text{CuK}\alpha$ radiation from 10 to 80° at a scan rate of $0.02^\circ \text{ s}^{-1}$. Kapton film was used to protect the Li_2S cathode materials and cycled electrodes during the characterization. The surface chemistry of P_2S_5 -activated Li_2S cathodes was examined by X-ray photoelectron spectroscopy (XPS, Kratos Analytical Company) analysis. All spectra were fitted in CasaXPS software with Voigt functions after subtraction of a Shirley-type background. Constraints on the sulfur and phosphorous component peaks were applied as below: (i) an energy difference of 1.18 eV (sulfur) and 0.86 eV (phosphorous) between $2p_{3/2}$ and $2p_{1/2}$ peaks, (ii) a peak area ratio of 2:1 between $2p_{3/2}$ and $2p_{1/2}$ peaks, and (iii) equal full-widths at half-maximum. Raman spectra were recorded from 200 to 2000 cm^{-1} with WITTEC Alpha300 S micro-Raman System at room temperature with a 488-nm laser.

Figure S1. Electrochemical performance of the commercially available (a) Li₂S and (b) P₂S₅ cathode materials in the first cycle between 1.8 and 4.0 V (C/10, the cells were charged to 4.0 V first).

Figure S2. The high-frequency region of the electrochemical impedance spectra (EIS) of the cells with the pristine Li_2S and the P_2S_5 -activated Li_2S cathodes when the molar ratio between Li_2S and P_2S_5 is 10:1, 7:1, 5:1, and 3:1.

Figure S3. A SEM image showing a pristine Li₂S particle.

Figure S4. EDS (a) sulfur (in red) and (b) phosphorus (in green) elemental mappings of the P_2S_5 -activated Li_2S particles when the molar ratio between Li_2S and P_2S_5 is 5 : 1; (c) EDS line scan showing sulfur and phosphorus distributions along the diameter of one P_2S_5 -activated Li_2S particle. The scales in (c) represent the positions along the diameter of one P_2S_5 -activated Li_2S particle.

Figure S5. Low-magnification SEM images of (a) the pristine Li_2S particle and P_2S_5 -activated Li_2S particles when the molar ratio between Li_2S and P_2S_5 is (b) 10:1, (c) 7:1, and (d) 5:1. The particle distribution was analyzed by the image processing software (ImageJ). The tables in each figure give the mean particle projection area and maximum particle projection area in μm^2 .

Figure S6. SEM image of the P_2S_5 -activated Li_2S particles when the molar ratio between Li_2S and P_2S_5 is 3:1.

Figure S7. XRD pattern of the P_2S_5 -activated Li_2S after the first discharge. The molar ratio between Li_2S and P_2S_5 is 7:1.

Figure S8. Raman spectra of the pristine Li₂S and P₂S₅-activated Li₂S when the molar ratio of Li₂S:P₂S₅ is 7:1.

Figure S9. (a) SEM image, (b) magnified SEM image, and (c) EDS sulfur (red) and phosphorous (green) elemental mappings of the lithium-metal anode after the 100th charge in the cell containing P₂S₅-activated Li₂S cathode (the molar ratio between Li₂S and P₂S₅ is 7 : 1).

Figure S10. SEM image of the P₂S₅-activated Li₂S cathode surface after the 100th charge (the molar ratio between Li₂S and P₂S₅ is 7:1).

Table S1. Surface chemical composition of P₂S₅–activated Li₂S particles determined by XPS

Li ₂ S : P ₂ S ₅ (molar ratio)	Peak	Binding energy (eV)	Percentage (at.%)
10:1	S 2p	162.6	3.43
	S 2p	161.0	29.53
	S 2p	159.8	2.41
	Li 1s	55.0	47.73
	Li 1s	54.1	3.67
	P 2p	131.9	13.22
7:1	S 2p	162.4	3.38
	S 2p	160.9	28.26
	S 2p	159.6	1.49
	Li 1s	54.8	54.43
	P 2p	131.7	12.44
5:1	S 2p	162.3	4.61
	S 2p	160.9	22.09
	Li 1s	54.7	62.59
	P 2p	131.9	10.71
3:1	S 2p	163.0	19.78
	S 2p	161.4	22.55
	Li 1s	55.0	38.41
	P 2p	134.1	6.07
	P 2p	132.4	6.35
	P 2p	131.4	6.84
P ₂ S ₅	S 2p	163.5	18.69
	S 2p	162.1	35.84
	P 2p	133.9	45.46