Polyphenyl Polysulfide: A New Polymer Cathode Material for Li-S Battery

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Experimental:

Materials

4,4'-Thiobisbenzenethiol ($HSC_6H_4SC_6H_4SH$, 98%, TCI), sulfur (S_8, 99.5%, Aladdin), carbon disulfide (CS_2, 99%, J&K), toluene ($C_6H_5CH_3$, 99%, Kermel), diethylamine ($(CH_3CH_2)_2NH$, anhydrous, 99.5%, Sigma-Aldrich), 1,2-dimethoxyethane (DME, 99%, Damas-beta), Bucky paper (NTL), Li-S electrolyte (commercial Li-S electrolyte: 1.0 M LiTFSI in DOL:DME=1:1 vol.% with 1.0 wt.% $LiNO_3$, Canrd), and potassium bromide (KBr, FTIR Grade, 99.5%, Aladdin) were purchased and used as received.

Methods:

Polymer synthesis

The synthesis of the polymers was carried out in an argon-filled glove box. Appropriate amounts of 4,4'-thiobisbenzenethiol (TBBT) and sulfur were weighed according to the molar ratios of the reaction. The mass of TBBT is 0.15 g (0.599 mmol) and the corresponding sulfur masses are 0.0192 g (0.599 mmol, TBBT:S molar ratio = 1:1), 0.0384 g (1.198 mmol, TBBT:S molar ratio = 1:2), 0.0576 g (1.797 mmol, TBBT:S molar ratio = 1:3), and 0.0768 g (2.396 mmol, TBBT:S molar ratio = 1:4), respectively. The obtained polymers are designated as PPPS-11, PPPS-12, PPPS-13, and PPPS-14, respectively. The weighed TBBT and sulfur were dissolved in 4 mL of carbon disulfide and toluene mixture solution (1:1 v/v), which was stirred until the solids were completely dissolved. Then, 20 μL diethylamine was added as a catalyst and a large amount of H_2S bubbles was generated immediately. The reaction solution was stirred at room temperature for 12 hours. The solutions, after completion of the reaction, were used to prepare polymer films for material characterization and electrodes for electrochemical characterization.

Electrode fabrication

First, the purchased Bucky paper was cut into 0.95 cm^2 (D = 1.1 cm) discs, each of which weighs approximately 1.9 mg (2 mg cm^{-2}). Then they were dried in a vacuum oven at 100 ºC overnight. To prepare the electrodes, 40, 40, 35, or 30 μL of polymer solution was injected into a Bucky paper disc for PPPS-11, PPPS-12, PPPS-13, and PPPS-14, respectively. They were then removed from the glove box and placed in the air oven at 80 ºC for 12 hours to remove the solvent. Finally, the carbon paper loaded with polymer was obtained. The polymer mass loadings are 1.49, 1.68, 1.64, and 1.55 mg respectively. These cathodes were used for electrochemical characterizations.

Preparation of polymer film

The solvent of the polymer solution prepared above was volatilized in a fume hood at room temperature, and then it was placed in an air flow oven to be dried. The cast polymers were used for material characterizations.

Li half-cell preparation

Li half-cells were assembled in an Argon-filled glove box. CR-2032 coin cells were used. Commercial Celgard 2400 was cut into 2.8 cm^2 (D = 1.9 cm) disc as the separator. Commercial nickel mesh was cut into hemispheres with a diameter of 1.3 cm and a thickness of 3.2 mm, which was used as a spacer. The Li half-cells were crimped and they consist of: positive electrode shell | carbon paper loaded with polymer | 20 μL Li-S electrolyte | separator | 20 μL Li-S electrolyte | Li metal | nickel mesh | negative electrode shell.

Material characterizations

X-ray diffraction (XRD) was performed by Rigaku MiniFlex600 X-ray diffractometer with Cu Kα radiation source. The samples were protected in the sample holder from air with Kapton film. The scanning rate is 0.2° min^{-1} and the scanning range is 10° to 80°.

Fourier transform infrared spectroscopy (FTIR) was collected by NEXUS 470 infrared spectrometer. The scanning range is 400-4000 cm^{-1}. The test sample is a transparent disc made from the substance (TBBT or polymer) and KBr mixed together. UV-Vis spectra were collected with Cary 5000 UV-VIS-NIR spectrometer. The scanning range is 200-800 cm^{-1}.

Element analysis was tested by Flash EA 1112 Automatic Element Analyzer. Samples were pre-heated at 80 °C overnight before the measurements. Samples weighing 1.8-2.1 mg were placed in small tin cups. The furnace temperature is 950 ºC.

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) were tested by STA 409 PC Simultaneous Thermal Analyzer. The temperature test range is 30-800 ºC and the carrier gas is air. Samples were pre-heated at 80 °C overnight before the measurements. Raman spectroscopy was performed by Lab RAM HR Evolution Laser Raman spectrometer.

Electrochemical characterizations

The cyclic voltammetry (CV) test was performed by Bio-Logic SAS VMP-3. The potential was swept from open circuit voltage (OCV) to 1.8 V and then back to 3 V with a scanning rate of 0.05 mV s^{-1}. Battery cycling performance was tested by LANHE at 0.1C rate and 1C rate. 1C = 215.8, 382.2, 514.5, and 622.1 mA g^{-1} for PPPS-11, PPPS-12, PPPS-13, and PPPS-14, respectively. The batteries were galvanostatically discharged to 1.8 V and charged to 3 V.

Supporting figures:

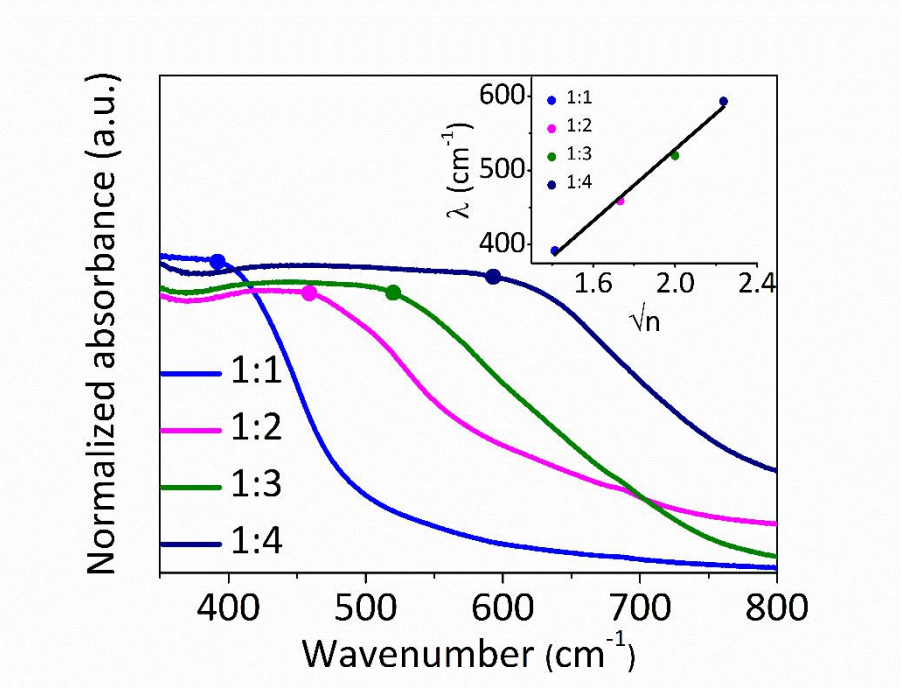

Figure S1. UV-Vis spectra of the polymers.

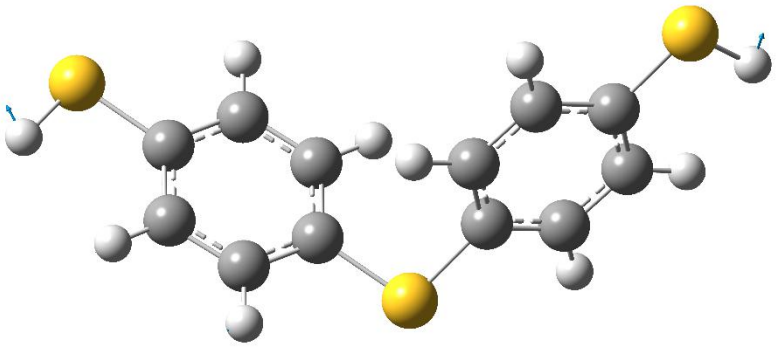

Figure S2. The optimized molecular structure and harmonic vibrational frequencies of 4,4'-thiobisbenzenethiol were calculated using density function theory (DFT) at M06-2X/6-31+G (d, p) level by Gaussian 09 software.[1] The nuclear displacements of the bending vibration of -SH group are shown in blue arrows. Carbon atoms are gray, hydrogens gray-white and sulfur yellow.

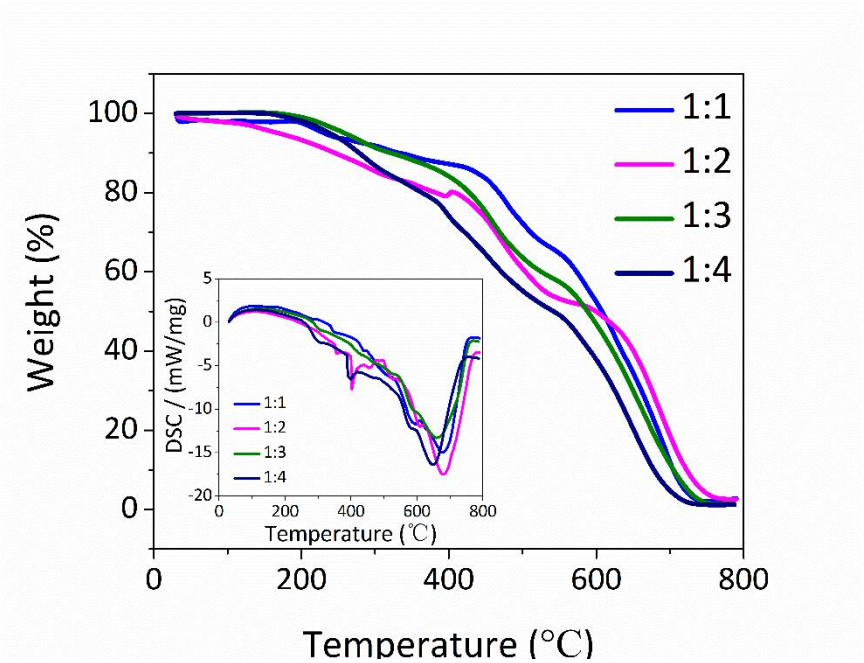

Figure S3. TGA and DSC plots of the cast polymers.

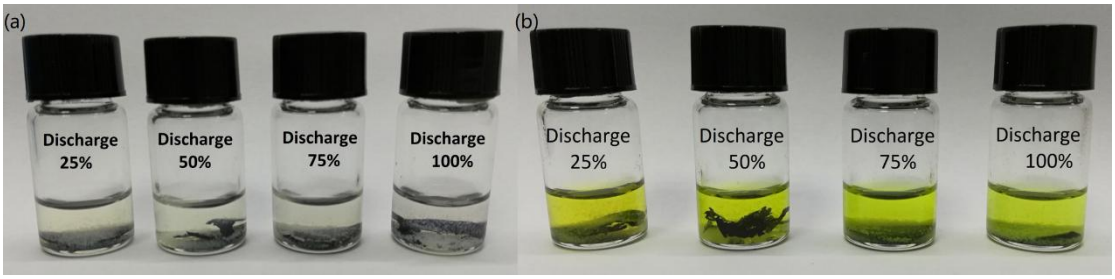

Figure S4. (a) PPPS-11 and (a) PPPS-13 electrodes in DME in the discharge state of 25%, 50%, 75%, and 100%.

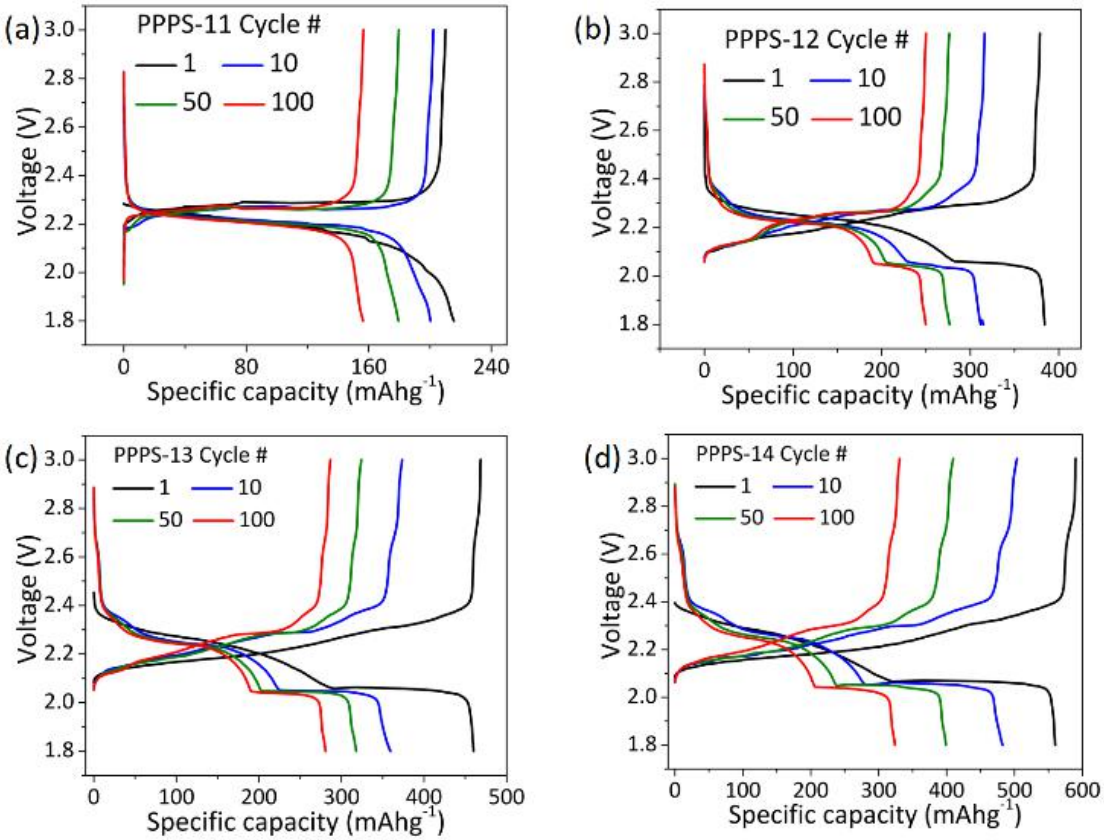

Figure S5. Discharge and recharge voltage profiles of cells with (a) PPPS-11, (b) PPPS-12, (c) PPPS-13, and (d) PPPS-14 cathodes at different cycles.

(1) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, B. M. V.; Petersson, G. A.; Nakatsuji, H. e. a. Gaussian 09, Revision D.01, Gaussian, Inc.: Wallingford, CT. **2010**.