Electronic Supplementary Information (ESI)

A new supramolecular binder strongly enhancing electrochemistry performance for lithium-sulfur battery

Yuan Zuo, Ruliang Liu,* Xingcai Zhang, Reddeppa Nadimicherla, Junlong Huang, Yuheng Lu, Shaohong Liu, Dingcai Wu, Ruowen Fu*

Preparation of SEL. Supramolecular eutectic liquid (SEL) was prepared by simply mixing equimolar benzophenone (BP) and diphenylamine (DP) at ambient conditions within a day[1]. Preparation of SEL could be shortened by raising the mixing temperature.

Sample characterization. The nanomorphologies were visualized using a field emission scanning electron microscopy (FESEM, JSM-6330F). Thermogravimetric analysis (TGA, NetzschTG-209) was carried out to determine the sulfur content in the S/CNTs composite. Fourier transform infrared (FT-IR) spectra measurements were carried out on Bruker Tensor 27 a spectrometer in the frequency range of 4000-500 cm^{-1} with a resolution of 4 cm^{-1} with KBr as the reference diluent. The powder X-ray diffraction (PXRD) patterns were obtained by a D-MAX 2200 VPC diffractometer at 40 kV and 40 mA using Cu Ka radiation (l = 1.54 Å). Diffraction patterns were recorded over a 2θ angle range within 10^o to 70^o ($10^o < 2\theta < 70^o$) with a scan rate of 10^o min^{-1}. The contact angles were taken on a Kruss DSA100 using the sessile drop method at the room temperature.

The adhesion forces were measured by a peel-test experiment. A piece of carbon-coated Al foil was attached to another piece of carbon-coated Al foil using either the SEL binder or the PVDF binder in equal amounts. Next, a spring-loaded thrust meter was used to measure the forces that could make the Al foil completely peel off from the other Al foil. Finally, the reading from the spring-loaded thrust meter was taken.

Li-S cell. The sulfur cathode slurry was fabricated by mixing 70 wt% S/CNTs composite, 10 wt% Super P, and 20 wt% SEL binder in N-methyl-2-pyrrolidinone (NMP). It was then spread onto a piece of carbon-coated Al foil substrate, followed by drying 12 h at 55 °C under vacuum and cutting into small disks with a diameter of 12 mm. CNT/S composite was prepared in a sealed Teflon container by simply heating pre-mixed sulfur and CNT at a weight ratio of 5:5 or 7:3 for 12 h at 155 °C. The Li-S cells were assembled with CR2032 coin-type cells with S/CNTs cathode, commercial polypropylene separator (Celgard 2400), and lithium foil anode in an argon-filled glove box with moisture and oxygen content below 1.0 ppm. The sulfur loading mass is around 0.9 mg cm^{-2} in a piece of electrode. The used electrolyte was a freshly prepared solution of lithium bis(trifluoromethanesulfonyl)imide (1 M) in 1,2-dimethoxyethane and 1,3-dioxolane (1:1 by volume) with 1 wt% $LiNO_3$ additive. For comparison, sulfur electrodes with the polyvinylidene fluoride (PVDF) binder were also prepared with the same procedure.

Electrochemical test. Galvanostatic charging/discharging tests were operated in the potential range of 1.7-2.8 V at room temperature using a LAND CT2001A battery test system. Cyclic voltammetry (CV) profiles of the electrode were recorded on the electrochemical work station (CHI660E) between 1.7-2.8 V at a scan rate of 0.05 mV s^{-1}. EIS measurements were performed with the electrochemical work station (CHI660E) in the frequency range of 10 MHz-0.01 Hz.

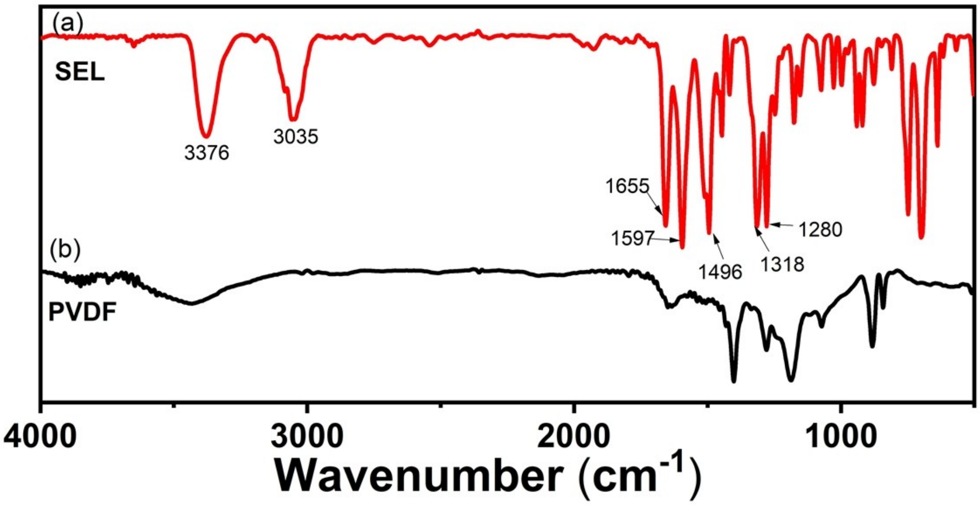

Fig. S1 FTIR for (a) SEL and (b) PVDF binders.

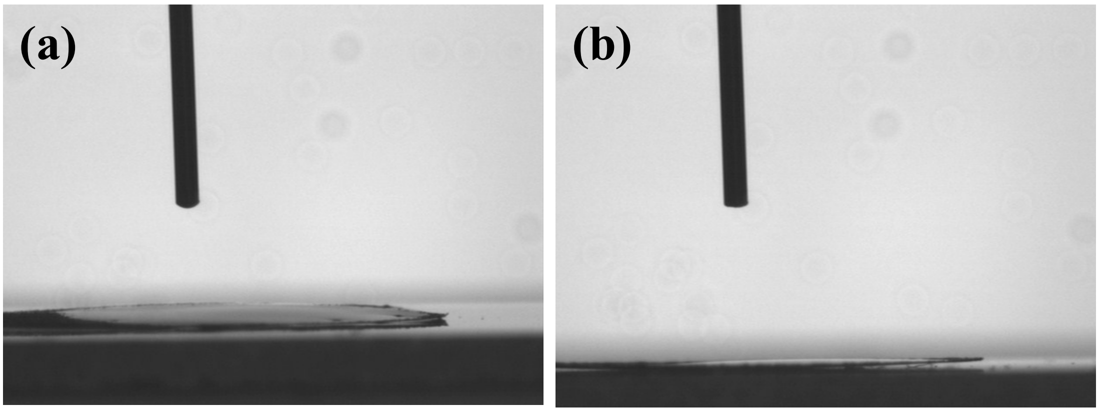

Fig. S2 Contact angle images of (a) S/CNTs-PVDF cathode and (b) S/CNTs-SEL cathode.

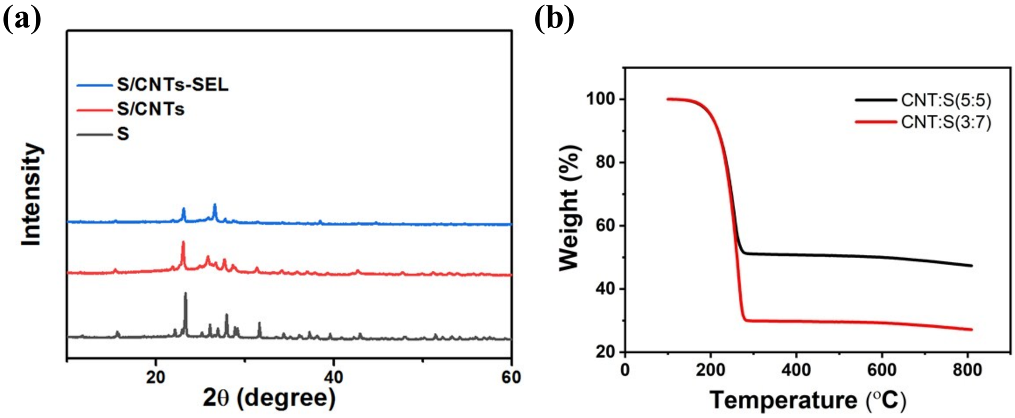

Fig. S3 a) The PXRD profiles for S, S/CNTs and S/CNTs-SEL nanocomposites spectra; b) the thermogravimetric analysis of S/CNTs composite with different sulfur loadings.

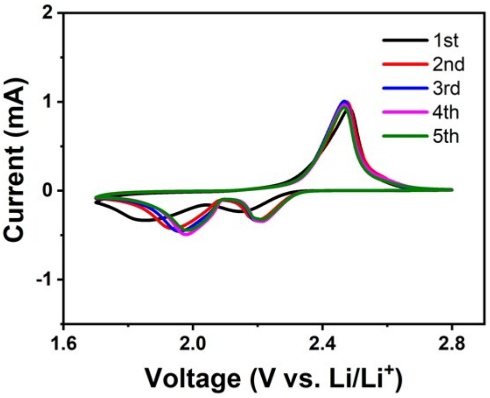

Fig. S4 Cyclic voltammetry (CV) of Li-S batteries with PVDF binder at a scan rate of 0.05 mV s^{-1}.

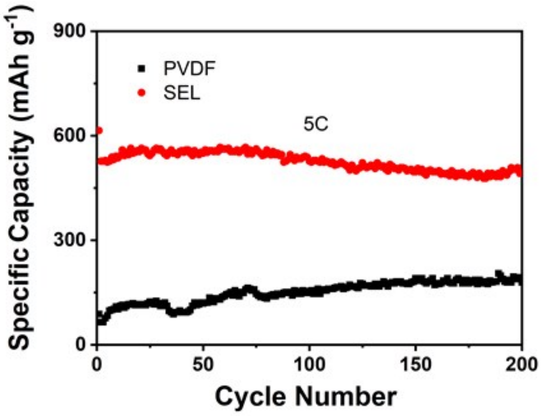

Fig. S5 Cycling performance of Li-S batteries with different binders at 5 C.

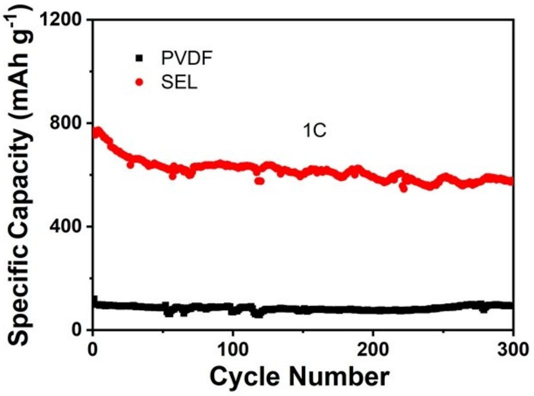

Fig. S6 Cycling performance of Li-S batteries with 70% sulfur loading at 1 C for different binders.

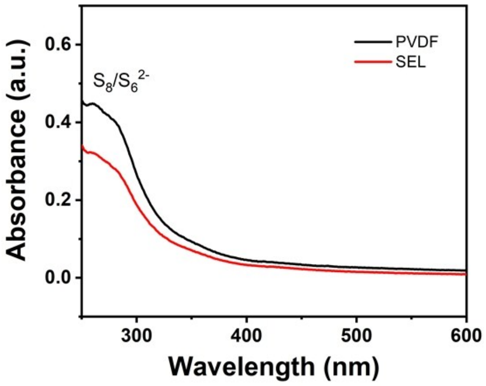

Fig. S7 UV/Vis absorption spectra of DME solution with S/CNTs-SEL and S/CNTs-PVDF electrodes for 100 cycles.

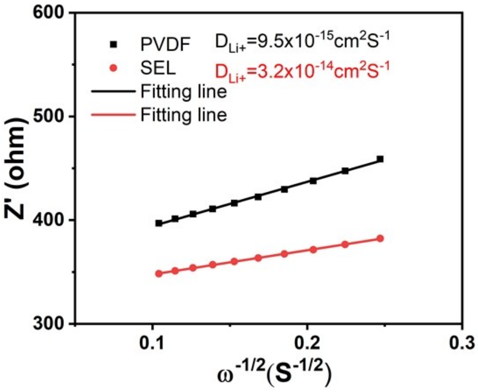

Fig. S8 Real part of the complex impedance versus $\omega^{-1/2}$ for S/CNTs-SEL and S/CNTs-PVDF electrodes before cycling.

The lithium diffusion coefficient was calculated by using the following equations[2].

$$D_{\mathrm{Li}} = \frac{R^2T^2}{2A^2n^4F^4C_{\mathrm{Li}}^2\sigma^2}$$

where D_{Li} is the diffusion coefficient, R is the gas constant, T means the temperature, A is area of the electrode, n is the number of electrons involved, F is the Faraday constant, C_{Li} is the concentration of lithium ion in the electrolyte, ω is the angular frequency and the σ is the Warburg factor, which can be obtained from the slopes of lines in Figure S7.

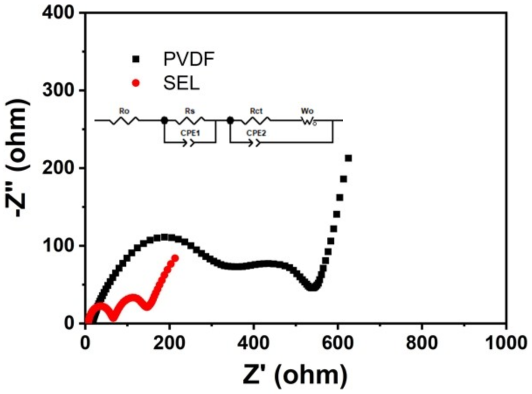

Fig. S9 Electrochemical impedance spectroscopy (EIS) of electrodes with PVDF and SEL binders after 500 cycles at 3C.

Reference

1. C. B. Kim, K. B. Jeong, B. J. Yang, J. W. Song, B. C. Ku, S. Lee, S. K. Lee and C. Park, *Angew. Chem., Int. Ed.*, 2017, **56**, 16180-16185.
2. J. Chen, L. Yang, S. Fang, S. Hirano, K. Tachibana, *J. Power Sources*, 2012, **200**, 59-66.