

Supplementary Information for:

Polysulfide dissolution control: The common ion effect

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Preparation of carbon/sulfur nano-composite – Commercially available sulfur powder (200 mg) and carbon black (Ketjen Black, 100 mg) were weighed separately, and were ball-milled together in N-methyl-2-pyrrolidone (5.0 mL) with a ball-mill (Pulverisette 23) at 40 Hz for 30 min. The ball-milled powder was dried in a 100 °C oven for a short time, and was subject to characterization.

Electrochemical Cycling – In a typical procedure, commercial sulfur powder (200 mg) and carbon black (100 mg) were ball-milled in N-methyl-2-pyrrolidone for 30 min together with polyvinylidene fluoride (PVdF) binder (25 mg), and cast on aluminum foil with a loading of sulfur of around 2 mg cm⁻². The composite electrodes were tested in 2032 coin cells using an electrolyte composed of 1.5 M or 5.0 M lithium trifluoromethanesulfonimide (LiTFSI) in the co-solvent of dimethoxyethane (DME) and 1, 3-dioxolane (DOL) 1: 1 (v/v) solution. The electrochemical cycling was carried out between 1.5 ~ 3.0 V, at a C/10 rate for the initial 3 cycles, and thereafter at C/2 (1C = 1,675 mA g⁻¹ of sulfur).

Characterization – The morphological feature of carbon black and carbon/sulfur nano-composite was observed with field-emission scanning electron microscopy (FE-SEM, Hitachi, S-4200) with EDX attachment, and transmission electron microscopy (Hitachi HD-2000 operating at 200 keV). The crystallographic structure was measured by powder X-ray diffraction using Cu K α_1 radiation ($\lambda = 1.5406 \text{ \AA}$, Rigaku D/MAX-2500/PC). The viscosities of electrolyte systems with varying concentrations of Li salt were measured by commercial viscometer (SV-10 from the A&D Company).

Preparation of Li₂S₆ and related analysis – A stoichiometric amount of commercially available sulfur powder and lithium was weighed in a glove box and was put in DME: DOL 1: 1 (v/v) solution. It was stirred for 24 h, to produce a saturated solution of Li₂S₆. 1 mL of this solution was mixed with 1 mL of 0 M, 3.0 M, and 5.0 M LiTFSI/DME/DOL solution, respectively, and stirred for 24 h, where significant amount of Li₂S₆ precipitation occurred in the solution containing lithium salt. Then, the liquid part was filtered from the precipitate by centrifuge. The 50 μ L taken from the clear solution containing dissolved Li₂S₆ and Li salt was

used as an electrolyte for a coin cell, where the cathode part was made of carbon black only, and the anode was made of lithium metal. The open circuit potential of these cells were observed to be around 2.25 V, and these cells were subject to potentiodynamic discharge down to 1.5 V, at a slow rate of 0.1 mV s^{-1} . The background line was measured at the same rate by the cell without any polysulfide addition into electrolyte with 5.0 M LiTFSI concentration. The amount of Li_2S_6 polysulfide present in each solution was calculated from the discharge capacity per mL of the added electrolyte assuming all Li_2S_6 in the electrolyte was converted to Li_2S when it was discharged to 1.5 V. Since theoretical capacity of Li_2S_6 is 1299.3 mAh/g, the amount of Li_2S_6 in gram and thus the concentration of Li_2S_6 in the electrolyte can be calculated. Discharge capacity per mL of the added electrolyte was obtained by integrating the area for the current vs. time curve of the potentiodynamic scan down to 1.5 V.

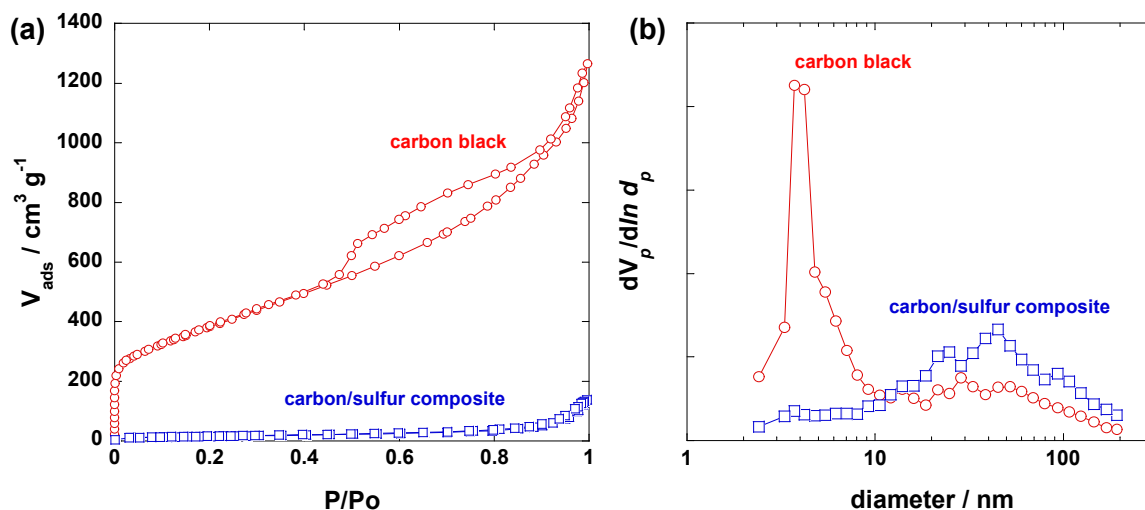


Fig. S1. (a) Nitrogen isotherms at 77 K and (b) the corresponding Barrett-Joyner-Halenda (BJH) pore size distributions for a carbon black, and a carbon/sulfur nano-composite after ball milling. The surface area and the pore volume were reduced dramatically after the ball-milling, which implies that the small micropores/ mesopores of the carbon black were filled with the sulfur after the ball-milling. The surface area and the pore volume of carbon black and nano-composite were $1368 \text{ m}^2/\text{g}$, $1.79 \text{ cm}^3/\text{g}$ and $54 \text{ m}^2/\text{g}$, $0.20 \text{ cm}^3/\text{g}$, respectively.

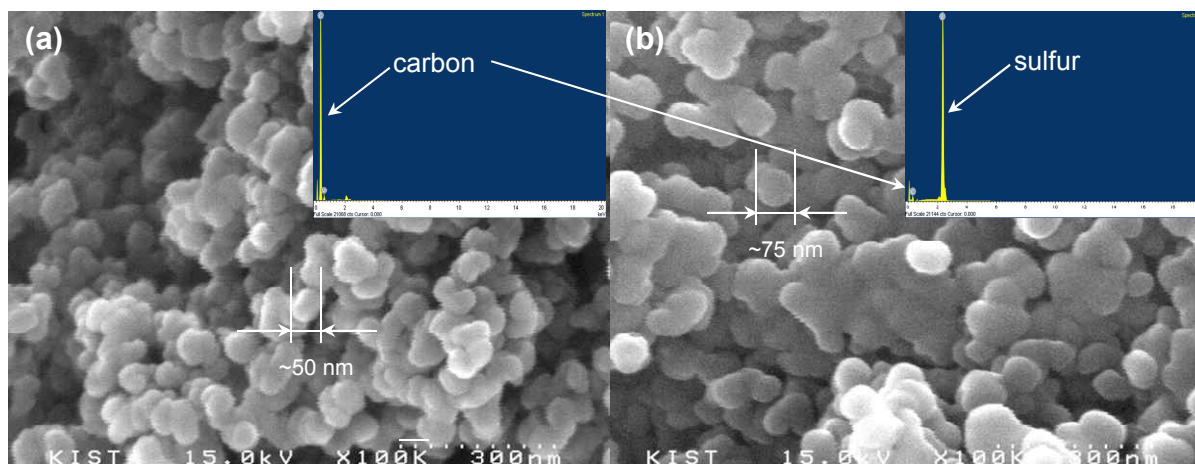


Fig. S2. SEM images for (a) carbon black, and (b) carbon/sulfur nano-composite after ball milling, with EDX analysis results (inset), which shows the existence of sulfur on the surface. EDX was taken for the entire SEM image area.

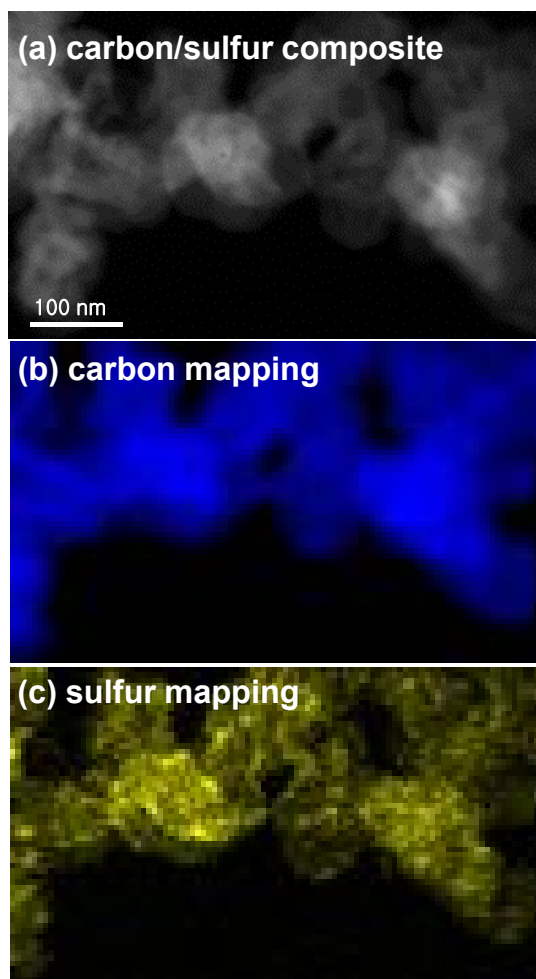


Fig. S3. (a) TEM image for a carbon/sulfur nano-composite and EDX elemental mapping for (b) carbon and (c) sulfur, which shows the homogeneous distribution of coated sulfur on the carbon surface.

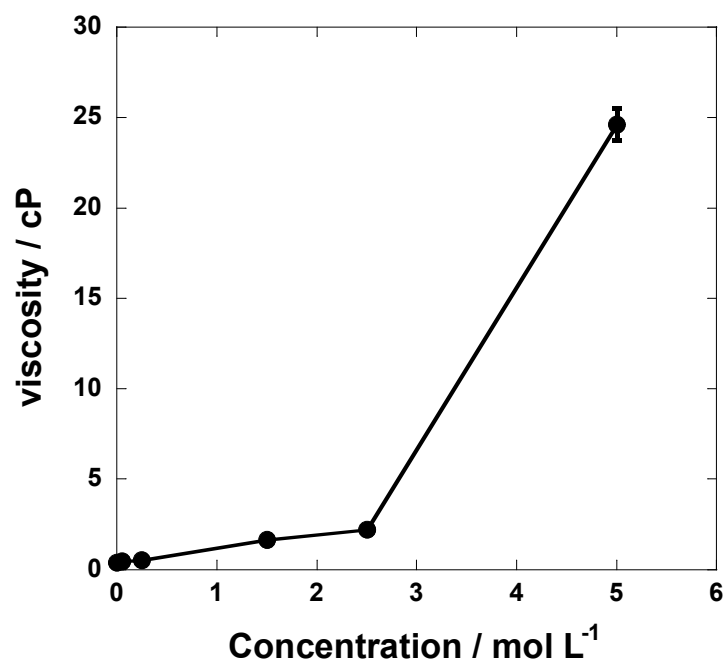


Fig. S4. The viscosity of electrolyte solution containing varying amounts of Li salt. The solvent is DME/DOL, and the Li salt is LiTFSI. The viscosity increases sharply at a higher than 1.5 M concentration.