## Supporting Information

# Self-Assembled Protein Nanofilter for Trapping Polysulfides and Promoting Li<sup>+</sup>-Transport in Lithium-Sulfur Batteries

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#### **1. Experimental Section**

Preparation of polymer-nanoparticle dispersion, separator and paper towel wet-coating. (1) Protein@CB dispersion. The gelatin protein (from porcine skin, Type A, Sigma Aldrich, Mw =  $50,000 \sim 100,000$  g/mol) was first dissolved in DI water or mixture of acetic acid (AA) and DI with weight ratio of AA/DI of 8:2 and pH of 2. The gelatin concentration was fixed as 3 wt%. Conductive nanoparticles, e.g. carbon black (MTI corp.), were then mixed with the gelatin solution with a loading of 50 wt% in the final protein/CB nanocomposite with the aid of ultrasonication to obtain homogeneous dispersion. In this case, gelatin works as a type of surfactant to disperse the nanoparticles. To improve the homogeneity, stability and flexibility of the resultant coating, a small amount of poly(ethylene oxide) (2 wt%) (Mw = 5,000,000 g/mol, Sigma) was added into the gelatin/CB dispersion, and then uniformly mixed by vigorous stirring for about 30 min. The suspension was casted onto the commercial separator (Celgard, PP/PE/PP, trilayer) by a film applicator (Dr. Blade) and then dried at room temperature to remove the solvents. (2) Chitosan/CB dispersion. Chitosan (medium Mw, Sigma Aldrich) was first dissolved in the same AA/DI mixed solvent as used for gelatin with a weight concentration of 1.6 wt%. Then, CB was mixed with chitosan with weight ratio of 1:1 by bowl mill (ca. 3 min.) and then bath sonication for ca. 10 min. The obtained dispersion was casted with the same condition as employed for gelatin@CB dispersion. (3) PVDF/CB dispersion. PVDF (Mw = 560,000 g/mol, Sigma Aldrich) was dissolved in NMP solvent with a concentration of 5 wt%. Then CB was mixed with PVDF solution by bowl mill for ca. 10 min. Two different CB loadings were used, e.g. 50 wt% and 80 wt%, designated as PVDF-CB50% and PVDF-CB80% respectively, to adjust the porous structures of the coating. (4) PVDF/PEO-CB dispersion. PVDF solution (5 wt%, NMP as solvent) was first heated up to 70 °C in oil bath. PEO powders (Mw = 5,000,000 g/mol) were then dissolved in PVDF solution with a concentration of PVDF/PEO of 2.5 wt% under vigorous stirring until homogeneity. After the PVDF-CB mixture solution was cooled down to room temperature,

CB was mixed with it by bowl mill for ca. 10 min. The coating layer was dried at 60 °C for ca. 12 hours to remove the solvent. The final thickness of all the nanocomposites coating was controlled to be in the range from 6 to 7  $\mu$ m. The loadings of carbon black in the separator coatings are: 0.23±0.01 mg/cm<sup>2</sup> for gelatin-CB, 0.13±0.02 mg/cm<sup>2</sup> for PVDF-CB80% and 0.11±0.02 mg/cm<sup>2</sup> for PVDF-CB50%.

Sulfur cathode preparation and Li-S cell assembly. The S-cathode was prepared by mixing 67.5 wt% sulfur powders (Sigma), 22.5 wt% carbon black and 10 wt% PVDF in NMP as solvent. The slurry was then casted onto aluminum foil and dried at 50  $\Box$ C overnight. The loading of active material was controlled around 1.6 mg/cm<sup>2</sup>. Another control S-cathode was prepared by mixing 47 wt% sulfur powders, 47 wt% carbon black and 6 wt% PVDF following the same procedures. For Li-S cell assembly, all the materials including bare separator and nanocomposites coated separators (PSNF@CS, PVDF-50%CB@CS and PVDF-80%CB@CS) and S-cathode were further dried in vacuum oven at 60  $\Box$ C for 12 hours to remove residual solvent and moisture, and then transferred into argon-filled glove box. The liquid electrolyte solution was composed of 1 M LiTFSI dissolved in mixed solvents of DOL and DME (1:1 by volume) with 2 wt% LiNO<sub>3</sub> as additive. One droplet of liquid electrolyte was applied onto the S-cathode and anode (lithium metal) surfaces respectively to ensure wetting. The electrolyte/sulfur ratio was kept constant around 3.8 mL/g. In the case of nanocomposites coated separators, the coated side was placed facing the S-cathode in order to trap the dissolved polysulfides. All these components were compressed under pressure of 500 psi in a coin cell (CR2032, MTI. Corp.).

*Morphology, wetting property and porosity characterizations.* The morphology of all the samples was characterized by Scanning Electron Microscopy (SEM) (Quanta 200F). The wetting property of the suspension on the commercial separator was characterized by contact angle by using OCA 15 plus contact angle analyzer. The suspensions were prepared with the

same solid concentration to generate droplets. The commercial Celgard separator (PP/PE/PP, trilayer) was used as substrate and five measurements at different locations were done to ensure consistency. The porosity of the nanocomposites was measured via n-butanol uptake. The nanocomposites were prepared by coating the various CB dispersions on aluminum foils by Dr. Blade. The thickness of all the dried nanocomposite coatings was controlled around 8  $\mu$ m. The weight of the nanocomposites was measured before and after immersion in n-butanol for 2 h. The porosity of the nanocomposites was calculated via equation (1):

Porosity = 
$$(m_b/\rho_b) / (m_b/\rho_b + m_p/\rho_p) \times 100\%$$
 (1)

where  $m_b$ ,  $m_p$  are the weight of n-butanol and nanocomposites, and  $\rho_b$ ,  $\rho_p$  are the density of n-butanol and nanocomposites, respectively.

*Mechanical properties measurement.* The gelatin/CB and PVDF/CB dispersions (loading of CB: 50 wt%) were casted on Al foil by Dr. Blade. The thickness of the dry nanocomposites was controlled around 10  $\mu$ m. The mechanical properties were measured by using a rheometer (HR-2, TA Instruments) via indentation. Briefly, the nanocomposite samples were placed on a sample holder. A steel tip with a diameter of 8 mm on the top was moving toward the sample at a constant speed of 1  $\mu$ m/s until reaching a maximum axial force of 35 N. The axial force was recorded with time.

*Electrochemical testing.* Sheet resistance of the PSNF coated on separator surface was measured by four-probe method using Keithley 2400. A homemade sample holder that can be tightly closed was used to measure the resistivity. The top cover of the sample holder was attached with four needles parallelly aligned with 1 cm spacing. The inner and outer two needles connected with one resistivity tester to test the voltage and current, respectively. The coating samples were placed in the sample holder with intimate contact with the needles. Five measurements were conducted to ensure consistency. The thickness of the PSNF was controlled around 10  $\mu$ m. The electrochemical performance of the Li-S cells was examined by S-4

cycling the cells between 2.8 and 1.5 V by using a battery analyzer (BST8-MA, MTI) at room temperature. Electrochemical impedance spectroscopy (EIS) was used to measure the impedance of the cells via an electrochemical workstation (CHI660E) over a frequency range of  $0.01-10^6$  Hz.

*Pressure drop testing.* The pressure drop of the separator samples was measured by a manometer (UEi, EM201-B) under different flow rates controlled by the home-made set-up as illustrated in **Figure 6 (a)**<sup>[1]</sup>. The air flow rate was controlled by a syringe and a pump employed for electrospinning. A circular separator sample with a diameter of ca. 37 mm was placed in a homemade sample holder to perform pressure-drop testing.

#### 2. Simulation section

#### 2.1. Molecular structure of Li<sub>2</sub>S<sub>4</sub>

To simplify the simulation, only  $Li_2S_4$  which is an intermediate product of the discharge process in Lithium-Sulfur batteries was studied in this work. An accurate coordinate file of  $Li_2S_4$  is required for a molecular simulation. Due to the insufficient data from experiments, all structure information is obtained from the first principle calculation. In order to fully understand the discharge mechanism in Lithium-Sulfur batteries, plenty of quantum-chemical studies and first principle simulations have been studied and stable molecular structures of polysulfides have been discussed<sup>[2-5]</sup>. In this study, a stable molecular structure of  $Li_2S_4$  was taken from density functional theory (DFT) calculations in Jand's work<sup>[5]</sup>, which provides detailed bond lengths for Li-Li and Li-S, and those calculated bond lengths are in good agreement with the results obtained by Wang et al<sup>[4]</sup>. The dihedral angle of S-S-S-S in  $Li_2S_4$ was chosen from a similar structure of  $Na_2S_4$  in Daly's work<sup>[6]</sup>. With all the information listed above, a molecular structure of  $Li_2S_4$  can be described as **Figure S1**.



Figure S1. Molecular structure of Li<sub>2</sub>S<sub>4</sub> at stable state.

#### 2.2. Force parameters of Li<sub>2</sub>S<sub>4</sub>

We performed MD simulations using the following general form of interaction potential between the different components.

$$U = \sum_{bonds} K_b (b - b_0)^2 + \sum_{angles} K_\theta (\theta - \theta_0)^2 + \sum_{dihedrals} K_\varphi (1 + \cos(n\varphi + \varphi_0)) + \sum_{nonbonded} \left\{ 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{\epsilon_0 r_{ij}} \right\}$$

Where,  $K_b$ ,  $K_{\theta}$ ,  $K_{\phi}$  are force constants;  $b_0$ ,  $\theta_0$  are equilibrium bond lengths and angles,  $\phi$ , n are dihedral phases and periodicities. Intermolecular parameters  $\epsilon_{ij}$ ,  $\theta_{ij}$ ,  $q_i$ ,  $q_j$  are the Lennard-Jones well depth and radius between atoms i and j, the partial atomic charge of atom i and j, respectively. Force constant  $K_b$  was estimated based on a simulated Raman Spectra data from Partovi-Azar's work<sup>[7]</sup>.  $K_{\theta}$  and  $K_{\phi}$  were chosen from similar angles and dihedrals to make sure those force constants can maintain the correct molecular structure of  $Li_2S_4$  throughout the entire MD simulation. Partial charges on each atom considered in our simulation were determined from Jand's simulation results<sup>[4]</sup>. The van der Waal parameters of Li and S in  $Li_2S_4$  were copied of Li from amber force field and S in  $S_8$  from CHARMM force field, respectively.

#### 2.3. Computational Setup

The interaction between polysulfide and protein filter in organic electrolyte was performed by Molecular dynamic simulation using GROMACS package  $(5.0.5 \text{ version})^{[8]}$  with CHARMM36 force field<sup>[9]</sup> for 200 ns. Gelatin, a mixture of peptides and proteins produced by partial hydrolysis of collagen extracted from the skin, bones and animals was randomly placed at the bottom of a simulation box of ~77 x 77 x 77 Å<sup>3</sup>, and the backbone was constrained throughout the simulation to mimic a fixed protein coating on the carbon black as a filter according to the experiment. The electrolyte [1,3-dioxolane (DOL) and Dimethoxyethane (DME)] were mixed with the ratio of 1:1 (V/V) as solvent, and 30 Li<sub>2</sub>S<sub>4</sub> molecules were added to the bulk system. The CGENFF (CHARMM generalized force field) was used for DOL and DME electrolyte<sup>[10]</sup>. The long-range Coulomb interactions were treated with the PME method, while the van der Waals (vdW) interactions were handled with a 1.2 nm cutoff distance. Periodic boundary conditions were applied in all three directions. The simulation system was prepared and visualized using PACKMOL<sup>[11]</sup>and VMD<sup>[12]</sup>, respectively.

### 3. Supplementary table and figures

Coating	PVDF/CB	Gelatin/CB (prep. solvent: <mark>DI</mark> )	Gelatin/CB (prep. solvent: <mark>AA/DI)</mark>
Porosity (%)	33.7	12.0	45.7
Thickness (µm)	6.8	6.2	6.4

Table 1. Physical properties of various CB-based nanocomposite coating



Figure S2. Wetthing behavior of PVDF/CB dispersion on separator and microstructure of PVDF/CB coating. (a) Digital photo of casted PVDF/CB dispersion on separator. The inset is contact angle of PVDF/CB dispersion on separator. (b) - (c) SEM images of PVDF/CB nanocomposite.



**Figure S3.** Physical properties of gelatin/CB coating and gelatin solution in DI water. (a) Digital photo showing gelatin/CB dispersion on separator. The inset is contact angle of gelatin/CB dispersion on separator. (b) Digital photo showing wrapping behavior of Celgard separator with gelatin/CB coating. (c) Digital photo showing gelatin dissolved in DI water started to gel in 2 h.



**Figure S4. Microstructures of gelatin/CB coating prepared in DI water.** (a) – (d) SEM images of gelatin/CB coating at different magnifications.



**Figure S5.** Physical properties of gelatin/CB coating and gelatin solution in AA/DI mixture solvent. (a) (a) Digital photo showing gelatin/CB dispersion on separator. The inset is contact angle of gelatin/CB dispersion on separator. (b) Digital photo of Celgard separator with gelatin/CB coating. (c) Digital photo showing gelatin dissolved in AA/DI without gelation in 2 h.



Figure S6. Microstructures of gelatin/CB coating prepared in AA/DI mixture solvent. (a)

- (d) SEM images of gelatin/CB coating at different magnifications.



**Figure S7.** Compression stress versus indentation time for PSNF as compared with PVDF-CB50%.



**Figure S8. Unit structure of gelatin.** The functional groups interactive with polysulfides are indicated in the red boxes.



**Figure S9.** Charge/discharge profiles of Li-S cells fabricated with LiNO<sub>3</sub>-free electrolyte, which contain PSNF and bare separator.



**Figure S10. Microstructures of PVDF-CB50% coating.** (a) – (d) SEM images of PVDF-CB50% coating at different magnifications.



Figure S11. Cycle stability of Li-S cell with 47 wt%-sulfur cathode.



Figure S12. Morphology study of PVDF-CB80% with additional 2 wt% of PEO, desingnated as PVDF/PEO-CB, and electrochemical performance of Li-S cells with the above PVDF/PEO-CB coating on separator. (a) – (b) SEM imgages of PVDF/PEO-CB coating at different magnifications; (c) Charge/discharge profiles of Li-S cells with PSNF at varying current rates; (d) – (e) Charge/discharge profiles at varing current rates, and cycle stability of Li-S cells with PVDF/PEO-CB coating on separator, respectivley.



**Figure S13.** Morphology of PSNF before and after 200 cycles of charging/discharging. (a) – (b) SEM images of the PSNF before and after 200 cycles of charging/discharging, respectively.

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