

Supporting Information

A Polysulfide-Blocking Microporous Polymer Membrane Tailored for Hybrid Li-Sulfur Flow Batteries

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Experimental Details

Materials: Tetraglyme (G4), triglyme (G3), diglyme (G2), 3,3,3',3'-tetramethyl-1,1'-spiropyrindane-5,5',6,6'-tetraol and tetrafluoroterephthalonitrile were purchased from Sigma Aldrich. Lithium nitrate, sulfur (Puratronic, 99.9995 % (metals basis)), lithium sulfide (99.9 % (metals basis)), and lithium metal (99.9% (metals basis), 1.5 mm) were purchased from Alfa Aesar. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) was purchased from 3M. Celgard 2535 membrane was purchased from MTI Corporation. Ketjenblack EC-600JD was purchased from AkzoNobel.

General methods: Nuclear magnetic resonance (NMR) spectra were taken on a Bruker Avance II 500 MHz NMR spectrometer. Analysis of the polymer's molecular weight distribution was carried out using size exclusion chromatography on a Malvern Viscotek TDA 302 system. Residual water content for various solvents was determined by a Mettler Toledo C20 Coulometric Karl Fischer titrator. Electrochemical experiments and battery testing were conducted with a BioLogic VMP3 potentiostat. Scanning electron micrographs were obtained with a Zeiss Gemini Ultra-55 analytical scanning electron microscope equipped with in-lens and secondary electron detectors at a beam energy of 2 keV. Ellipsometric porosimetry (EP) was performed on a Semilab PS-1100 instrument with toluene or isopropanol.

Electrode details: Swagelok batteries were constructed using Swagelok unions purchased from Swagelok Northern California. Associated electrodes were made in-house from nickel 200 rods with outer diameters of 1.27 cm. Wells, which were 0.635 cm in diameter and 0.508 mm deep, were machined into the cathode current collectors. Gold was sputtered onto the cathode current collector surface. Anode current collectors were flat, bare nickel 200 surfaces.

Membrane preparation: PIM-1 was synthesized using a literature procedure.^{38,46} PIM-1 was dissolved in chloroform at a concentration of 12.5 mg mL⁻¹. Films of PIM-1 were cast by depositing 1 mL of solution into a 3.5 cm diameter Teflon well. The solvent was left to evaporate in a closed vacuum chamber under ambient pressure for 1 h or until

dryness. The films were further dried *in vacuo* overnight. The dried films were punched into 7/16-inch circles. Celgard® 2325 membranes were punched into 1/2-inch circles. All membranes were soaked in relevant electrolytes overnight before use.

Ionic conductivity measurements: Soaked membranes were sandwiched between two stainless steel blocking electrodes. Potentio electrochemical impedance spectroscopy (PEIS) was used with 50 mV AC bias scanning from 1 MHz to 100 mHz. The high frequency *x*-axis intercept is taken to be the resistance of the membrane. The membrane conductivity was then calculated taking into account the cell geometry.

Electrolyte and polysulfide preparation: The supporting electrolyte formulation for all battery cycling and conductivity measurements was 0.50 M LiTFSI. LiNO₃ was added to the electrolyte only for the crossover experiments detailed below. LiTFSI was dried for 16 h under vacuum at 150 °C. LiNO₃ was dried for 16 h under vacuum at 110 °C. Diglyme was tested for peroxides prior to use; if any were measured, it was stirred with alumina, filtered, and sparged with argon. Diglyme was dried with activated 3 Å molecular sieves until it measured < 20 ppm H₂O. Electrolyte was tested for water content and confirmed to contain < 30 ppm water before use. Solutions of Li₂S₈ (2.50 mol S L⁻¹ in electrolyte) were prepared by mixing Li₂S (0.287 g, 6.25 mmol), sulfur (1.40 g, 5.47 mmol), and 20 mL of electrolyte and heating at 60 °C until all solids were dissolved. Li₂S₈ solutions were kept at 60 °C in order to prevent precipitation of insoluble species and cooled to room temperature prior to use. Cathode slurry with 5% *w/w* conductive additive was made by adding 30.8 mg of Ketjenblack to 500 µL of Li₂S₈ solution and mixed for 15 min.

Crossover experimental methods: Crossover measurements were made by placing respective membranes between the cell halves of a PermeGear Side-Bi-Side diffusion cell. To the permeate side of the cell was added 2.5 mL of supporting electrolyte (0.15 M LiNO₃, 0.5 M LiTFSI in diglyme) while to the retentate side was added 2.5 mL of 2.5 M S as Li₂S₈ in electrolyte. In this case, due to the presence of lithium as a reference electrode, LiNO₃ was necessary to prevent the reaction of polysulfides with the lithium.

Crossover was determined by cyclic voltammetry and square wave voltammetry measurements of the permeate side of the cell. Cyclic voltammetry allowed concentrations between 5.0–60 mM to be measured while square wave voltammetry allowed for measurements of concentrations ranging from 0.20–1.0 mM. Given the different rates of crossover between the two materials, both techniques were necessary as the Celgard crossover was too fast to be measured accurately with the SWV, and the PIM crossover was too slow to be measured in a convenient time frame with CV. A glassy carbon disc electrode (1 mm) was obtained from BAS Inc. (West Lafayette, IN), polished before use and used as the working electrode. Lithium metal was used as the reference and counter electrodes. A calibration curve for each electrochemical technique was obtained by measuring the current as a function of voltage for a set of known concentration polysulfide solutions (Figure S1 and S2). The concentration of polysulfide vs. time for the crossover measurements was then calculated using the linear equation determined from the calibration curves.

Battery cycling: Cathode slurry was spread evenly into the cathode well. Lithium chip was punched using a 7/16-inch bore and pressed onto the anode. Due to the safety concern of dendrite formation, membranes were sandwiched between two Celgard layers to isolate them from the lithium polysulfide slurry and the lithium anode surface. The tri-layer membrane was then pressed in between the two electrodes to assemble a Swagelok battery.

Computational Methods

First-Principles molecular dynamics simulations: The $S_8/Li-TFSI/Li_2S_x$ -TEGDME systems were simulated using a modified version of the mixed Gaussian and plane wave code¹ CP2K/Quickstep². We employed a triple- ζ basis set with two additional sets of polarization functions (TZV2P)³ and a 320 Ry plane-wave cutoff. The unknown exchange-correlation potential is substituted by the revised PBE generalized gradient approximation^{4,5}, and the Brillouin zone is sampled at the Γ -point only. Interactions between the valence electrons and the ionic cores are described by norm-conserving pseudopotentials^{6,7}. The Poisson problem is tackled using an efficient Wavelet-based

solver⁸. We overcome the poor description of the short-range dispersive forces within the PBE-GGA exchange-correlation functional by employing the DFTD3 empirical corrections of Grimme et al.⁹. In order to equilibrate the systems, we performed 10 ps of NPT dynamics, using a Nose-Hoover thermostat (temperature damping constant of 100 fs) and an Anderson barostat (pressure damping constant of 2 ps). Snapshots of the system were saved every step. The snapshot with a volume closest to the average of the last 5 ps of MD was then selected as input for an additional 20 ps simulation in the constant volume, constant temperature (canonical or NVT) ensemble.

Structural analysis: We estimated the “size” of the solvated lithium polysulfide species as the sum of two terms: 1) the radius of gyration of the solute (R_{gyr}) and 2) the size of the glyme solvation shell. All structural analyses were performed for every 10 snapshots from the last 20 ps of the NVT AIMD simulations (4,000 for each system). The R_{gyr} was computed as

$$R_{gyr} = \sqrt{\frac{1}{M} \sum_i m_i (r_i - r_{cm})^2}$$

where M is the total mass of the solute, R_{cm} is the center of mass and the sum is over all r_i atoms in the solute.

The solvation environment around each dissolved polysulfide was obtained calculating the Li – glyme (oxygen atom) and S – glyme pair distribution functions (PDF) from the last 20 ps NVT MD simulation. The 1st solvation shell was obtained from the minimum in the PDF after the first peak, and the number of solvent molecules obtained by simple integration.

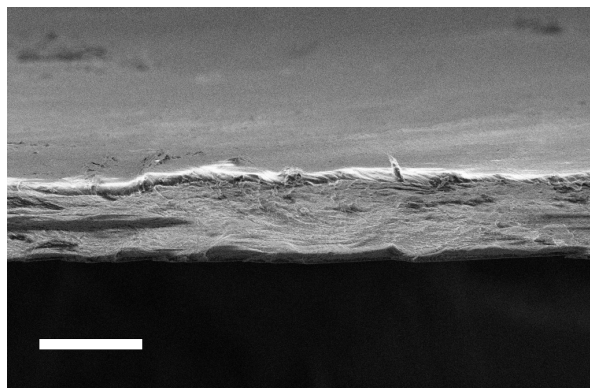


Figure S1. Cross-sectional scanning electron micrograph of a freestanding PIM-1 membrane. The scale bar is 10 μm .

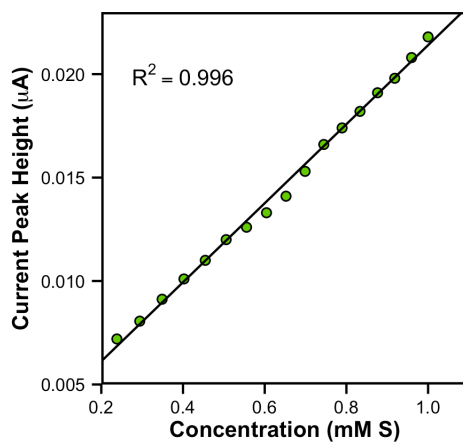


Figure S2. Calibration curve of current vs. concentration obtained via square wave voltammetry for the lower concentration regime.

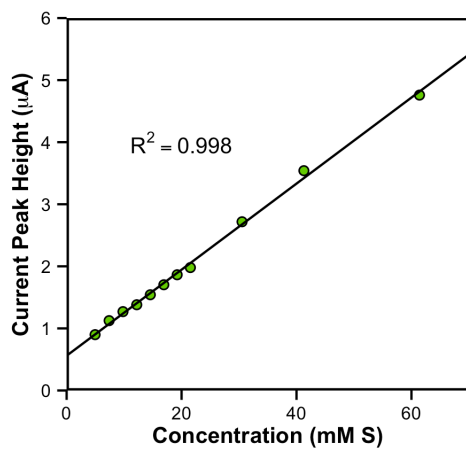


Figure S3. Calibration curve of current vs. concentration obtained via cyclic voltammetry for the higher concentration regime.

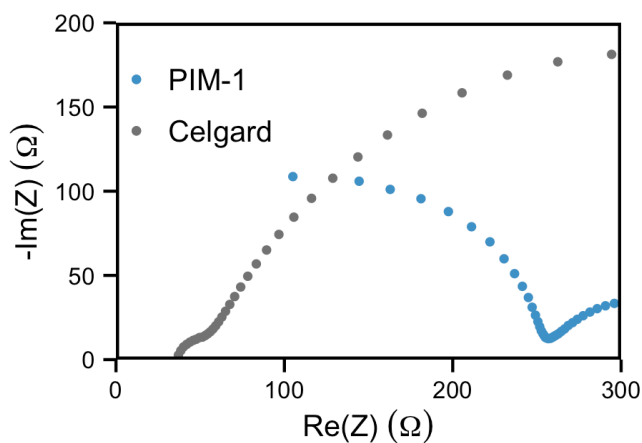


Figure S4. Electrochemical impedance spectroscopy (EIS) of Li-S cells configured with PIM-1 and Celgard as membranes, respectively. The membrane ionic conduction kinetics are represented by the sizes of high-frequency semicircles, which are 20.1 Ohms and 215.1 Ohms for Celgard and PIM-1, respectively.

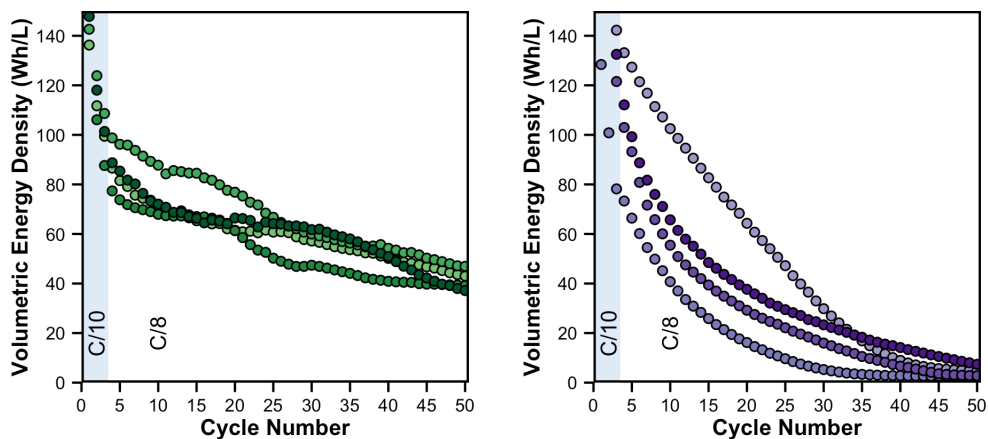


Figure S5. Volumetric energy densities of all batteries tested (*catholyte formulation: 2.5 M S as Li_2S_8 in diglyme containing 0.50 M LiTFSI*) with either PIM-1 membrane (*green circles, left panel*) or Celgard membrane (*purple circles, right panel*).

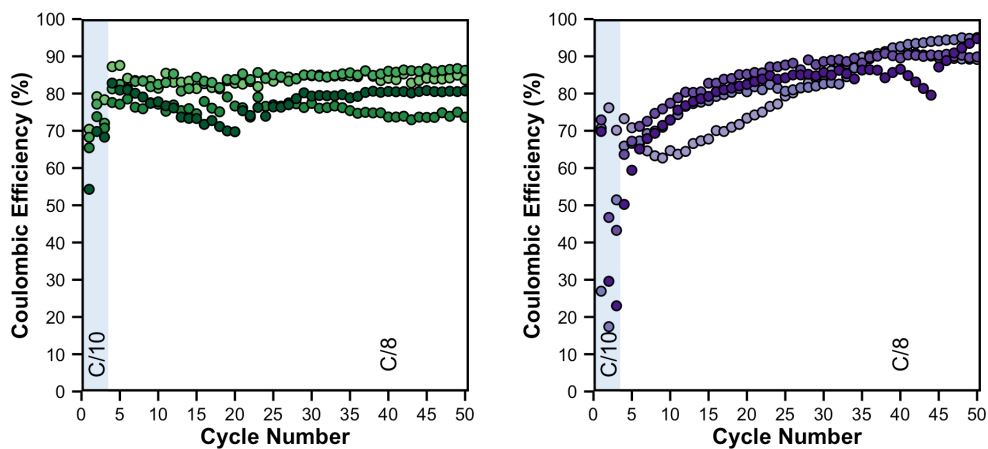


Figure S6. Coulombic efficiencies of all batteries tested (*catholyte formulation: 2.5 M S as Li_2S_8 in diglyme containing 0.50 M LiTFSI*) with either PIM-1 membrane (*green circles, left panel*) or Celgard membrane (*purple circles, right panel*).

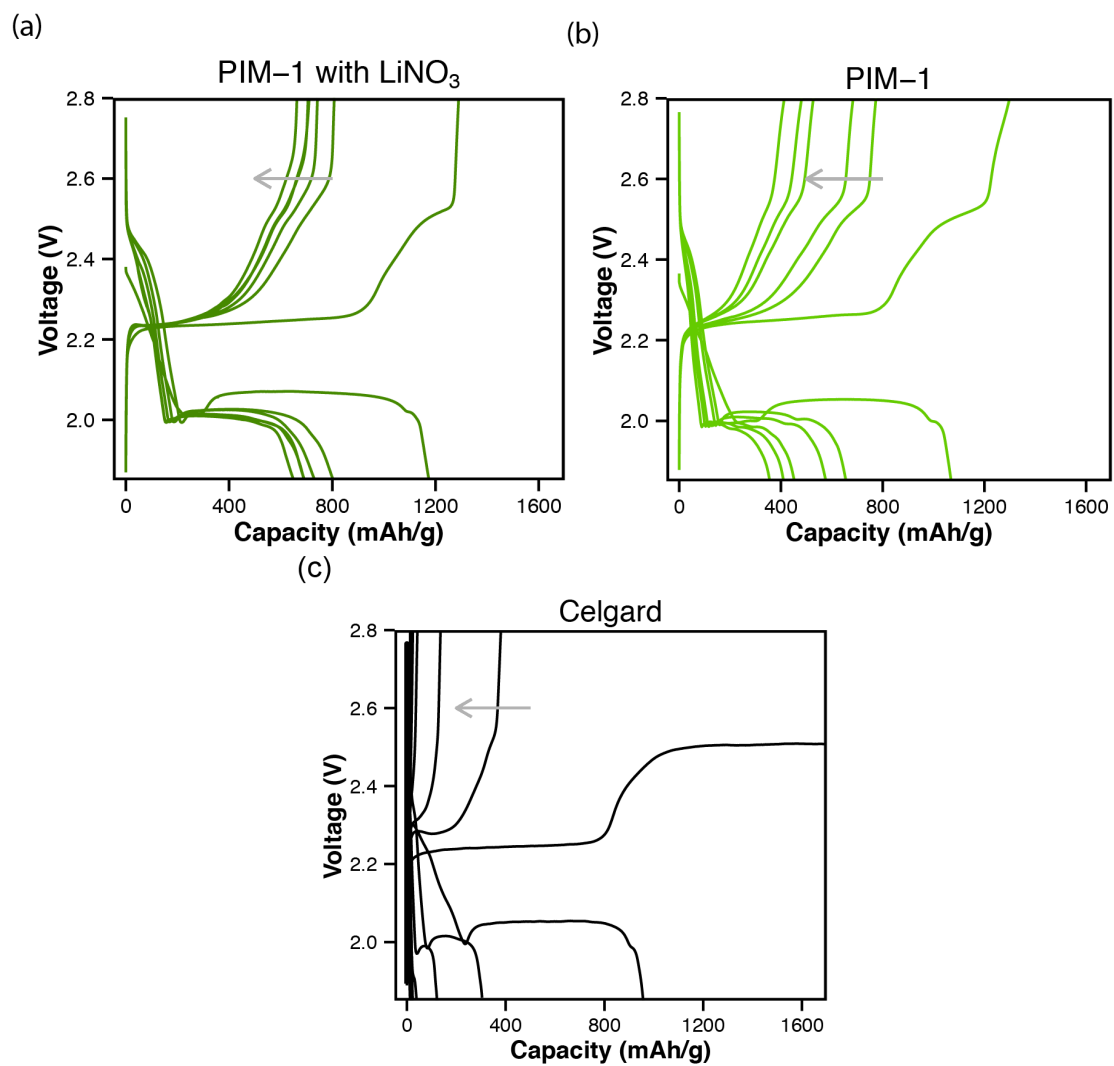


Figure S7. Discharge and charge profiles for LI-S batteries configured with: (a) PIM-1 membrane separators and LiNO_3 electrolyte additive; (b) PIM-1 membrane separators without LiNO_3 electrolyte additive; and (c) Celgard separators without LiNO_3 additive at the 1st, 10th, 20th, 30th, 40th, and 50th cycles. The arrows indicate the direction of higher cycle number.

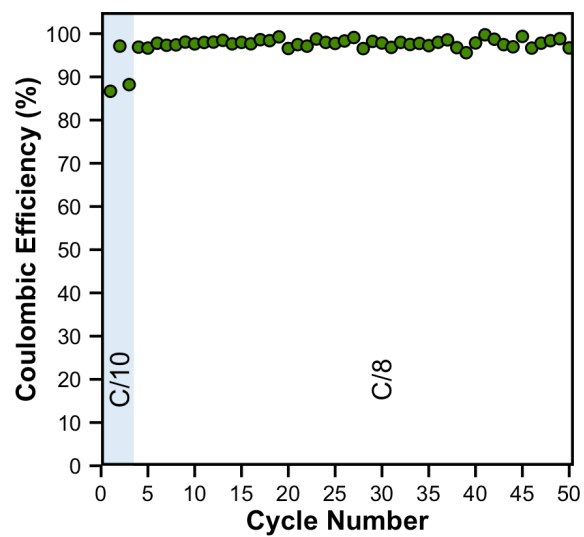


Figure S8. Representative Coulombic efficiency of a Li-S battery configured with a PIM-1 membrane separator and LiNO_3 as an electrolyte additive.

References

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