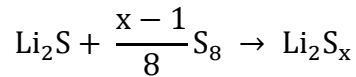


SI Appendix:

Supporting Text

Materials: Reagent-grade Li_2S (99.9%) and P_2S_5 (99%) were purchased from Aldrich and Sulfur (S_8) from Alfa Aesar. Hydroxy-terminated perfluoropolyether (PFPE-diol, $M_n = 1000$ g/mol) was purchased from Santa Cruz Biotechnology and lithium bis(trifluoromethanesulfone)imide (LiTFSI), was purchased from Novolyte. All chemicals were used as received.

Preparation of samples for X-ray absorption spectroscopy (XAS) measurements: Glass and hybrid pellets were prepared as described above. An polystyrene-*b*-poly(ethylene oxide) (SEO) diblock copolymer was synthesized on a high vacuum line via sequential anionic polymerization (1), having polystyrene and poly(ethylene oxide) block molecular weights of 247 kg/mol and 116 kg/mol, respectively. Lithium sulfide (Li_2S) and elemental sulfur (S_8) are known to react in solution to form lithium polysulfide species according to the following reaction (2):



Here, ‘x’ denotes the length of the polysulfide dianion chain that would be formed if only one type of polysulfide were formed. Here, ‘x’ was set to be 8, and stoichiometric amounts of Li_2S and S_8 were added accordingly (3). The final concentration of the Li_2S_8 in SEO is denoted by an ‘r’ value, where ‘r’ is the ratio of lithium ions to ethylene oxide moieties. For the SEO/ Li_2S_8 membrane used here, $r = 0.085$. SEO/ Li_2S_8 mixtures were made by dissolving Li_2S , S_8 , and SEO in dimethylformamide (DMF) and mix at 90 °C on a heating plate for 24 hours in a sealed vial. The SEO/ Li_2S_8 samples were obtained by drying the mixed solutions in a Teflon petri-dish at 75 °C under argon for 3 days, followed by drying at 50 °C under vacuum for 15 hours. To prepare the pellet/SEO/ Li_2S_8 assembly, discs of the SEO/ Li_2S_8 membrane were punched and pressed to the pellet. This assembly was placed between FEP bags and then pressed together using a hand-press. The temperature of the assembly and hand press were then set to 75 °C for three days under argon. Applying significant force to the underside of the pellet, the pellet broke into several smaller pieces, while the polymer membrane remained intact. These pieces of pellet were then pulled off the membrane, and the side that was in contact with the SEO/ Li_2S_8 was then probed using XAS.

Preparation of samples for transference number measurements: Lithium symmetric cells were prepared by hand-pressing of hybrid membrane electrolytes between two lithium metal chips (250 μm). Nickel current collector tabs are placed on each lithium metal electrode and the cells were vacuum sealed in a pouch bag. Steady state technique was used to estimate the lithium transference number, t^+ , at a temperature of 30 °C (4). This method combines dc polarization and ac impedance spectroscopy. An initial ac impedance measurement is performed to determine the initial interfacial resistance, R_{int}^0 , which is followed by a chronoamperometry using a dc potential, ΔV , of 80 mV to record the current evolution from its initial value, I^0 , until a steady current, I^∞ is obtained. At this point, ac impedance spectroscopy is used to get the interfacial resistance, R_{int}^∞ . t^+ is calculated by: $t^+ = I^\infty(\Delta V - I^0 R_{int}^0) / I^0(\Delta V - I^\infty R_{int}^\infty)$

Preparation of samples for electrochemical window measurements: Cyclic voltammetry was conducted to investigate the electrochemical stability of hybrid electrolytes. A stainless steel disk was the working electrode and a lithium metal chip served as the counter electrode. The electrodes were pressed against each face of the membrane and potential sweeps were performed using a VMP3 (Bio-Logic) potentiostat with a scanning rate of 1 mV/s.

Supporting Figures

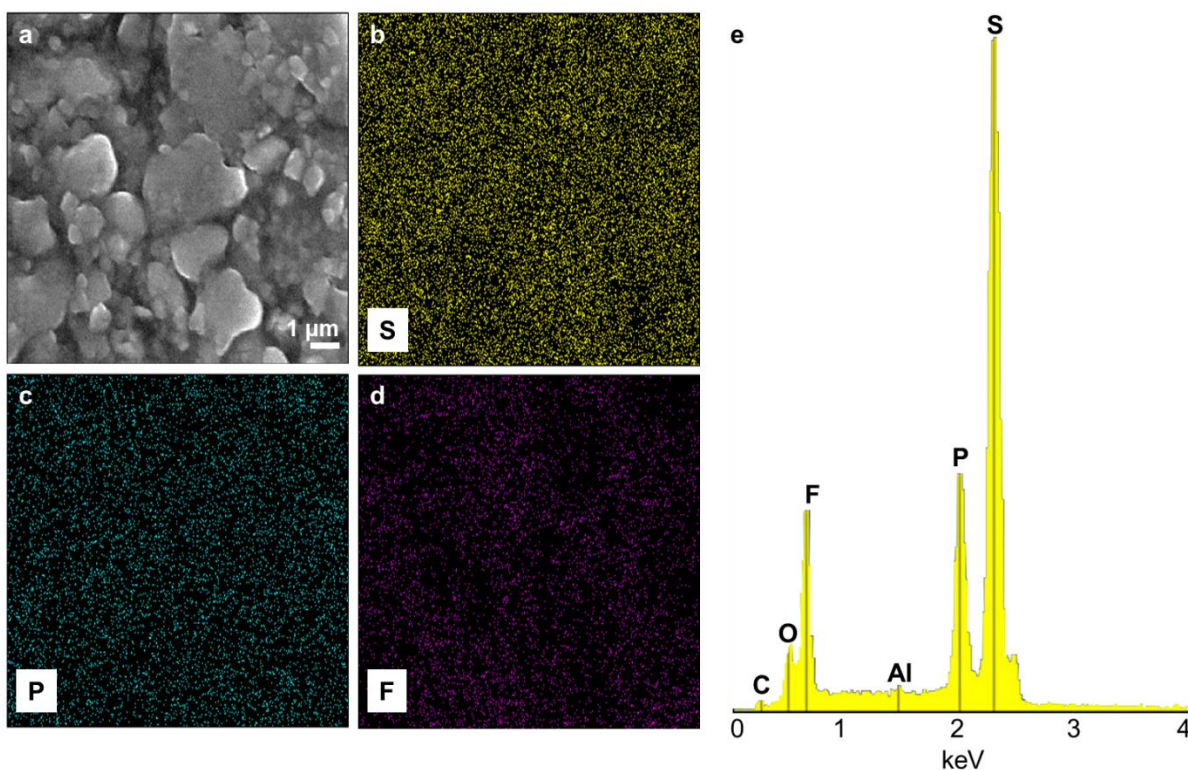


Fig. S1. SEM/EDS images of the hybrid membrane electrolyte. (a) SEM image of the hybrid membrane. (b) Elemental maps of Sulfur (S), (c) Phosphorus (P) and (d) Fluorine (F). (e) Electron spectrum of the hybrid membrane.

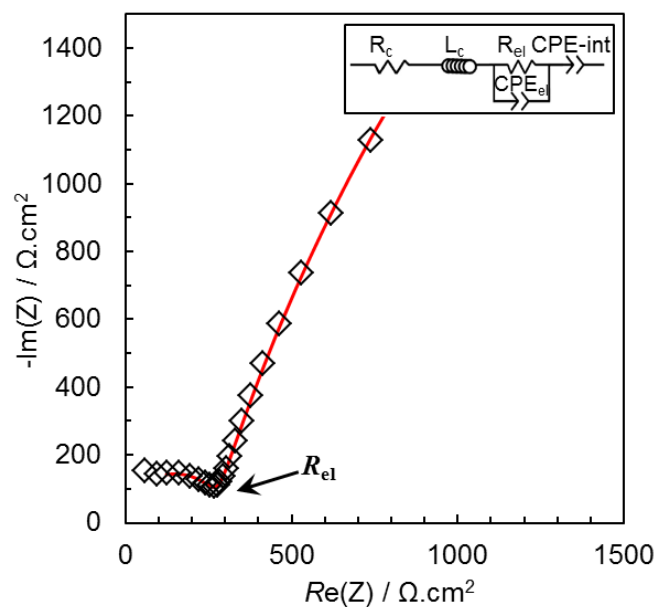


Fig. S2. Typical impedance spectrum at 30 °C of the hybrid electrolyte. (◇) Experimental data and (—) the line corresponds to fit using the electrical equivalent circuit shown in the inset.

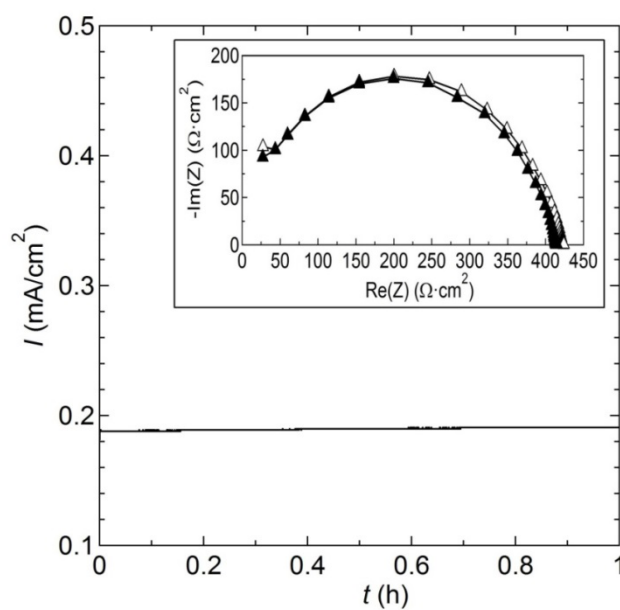


Fig. S3. Current density, I , as a function of time, t , for the hybrid membrane electrolyte during an 80 mV polarization at 30 °C. The inset shows the ac impedance of the cell (\triangle) before and (\blacktriangle) after polarization.

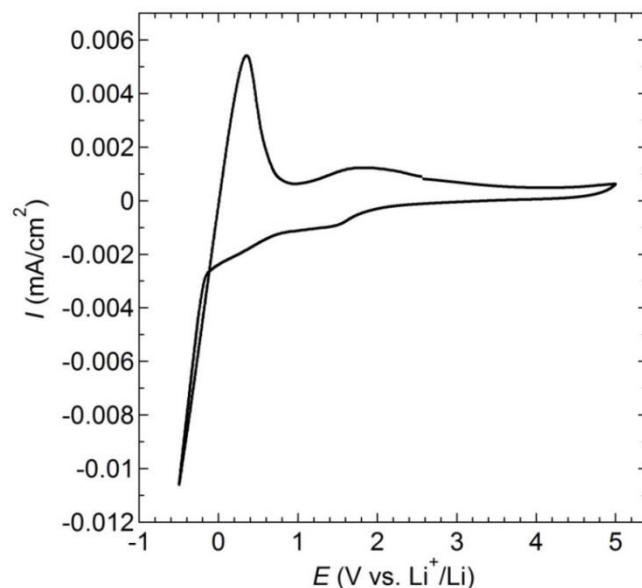


Fig. S4. Cyclic voltammogram of the hybrid membrane electrolyte obtained at 1 mV/s at 30 °C.

References

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