Supporting Information

Experimental Details

Preparation of lithium polysulfide electrolyte blends. In an argon-filled glove box, lithium sulfide (99.98%, Sigma Aldrich) and sulfur (dried, 100 mesh, sublimed, Sigma Aldrich) were added into a vial in ratios to give the desired average Li_2S_n composition (Equation 1), followed by adding electrolyte (1 M LiTFSI in DOL). The blends were then allowed to stir at 60°C for at least 72 h and then at room temperature for at least 48 h. The blends were filtered using PTFE syringe filters (0.2 µm, dried) to remove any excess precipitate before analysis. The concentration of the prepared blends is always noted in terms of the total atomic sulfur ($[S]_T^{blend.}$ / M) e.g. Li_2S_8 (1.25 M in DOL) gives an atomic sulfur concentration of 10 M, as Li_2S_8 contains 8 sulfur atoms (8 x 1.25 M = 10 M).

$$Li_2S + \frac{(n-1)}{8} S_8 \rightarrow Li_2S_n$$

Equation 1 – Preparation of Li_2S_n where the average chain length n can be varied

Gravimetric determination of total atomic sulfur content. In an argon-filled glove box, known quantities of the lithium polysulfide electrolyte solutions (filtered) were taken and placed into round bottom flasks (RBFs). These were sealed using rubber septa and taken outside of the glove box and into the fume cupboard. The rubber septa were used to ensure that the contents of the RBFs were kept under an inert argon atmosphere to prevent the loss of the polysulfides as hydrogen sulfide. Ammonium hydroxide (28-30%, Sigma Aldrich) was then added to each RBF slowly using a needle and syringe, followed by hydrogen peroxide (30%, Sigma Aldrich) whilst stirring. Once the reactions had ceased, the reaction mixtures were heated to 40 °C for 1 h. The solutions were then diluted using water (deionized) followed by hydrochloric acid (HCl, 37%, Sigma Aldrich) until the solution is slightly acidified (pH < 7). Excess barium nitrate (≥99%, Sigma Aldrich) was added and the solution stirred for 1 h. The mixtures were each poured into pre-weighed glass crucibles (porosity grade 4, 30 mL) and filtered under vacuum. Each barium sulfate retentate was then washed with water (deionized) and the glass crucibles were placed in the vacuum oven (80 °C) for ~60 h. Each of the glass crucibles was then removed, allowed to cool and weighed.

UV-Vis spectroscopic measurements. UV-Vis absorption measurements were made using an Ocean Optics DH-2000-BAL UV-Vis NIR light source, which was switched on for at least 30 minutes before use in order to allow the spectrometer to reach operating temperature and stabilize the light output. Quartz cuvettes were used (1 cm path length), which had been modified to accommodate a screw cap lid. This allowed the cuvettes to be filled in an argon-filled glove box, sealed, transferred out of the glove box and measured on the UV-Vis spectrometer, without contamination by moisture/oxygen. Ferrocenium tetrafluoroborate ($FcBF_4$, dried, 95%, Sigma Aldrich) was dissolved 1,3-dioxolane (DOL, anhydrous, Sigma Aldrich) for at least 1 hour to give a known concentration. The solution was then filtered to remove small particles that raise the UV-Vis baseline using a syringe filter (PTFE, 0.2 µm pore size). A UV-Vis spectrum was obtained of the $FcBF_4$ in DOL stock solution. Then, aliquots (different volumes) of the polysulfide electrolyte solution under analysis were added to a known volume of the $FcBF_4$ in DOL solution. The solutions were then shaken and a UV-Vis spectrum was obtained for each.

Analysis of Data

Polysulfide electrolyte blends and estimating precipitate composition.

Concentrations of solid sulfur, S, and lithium sulfide, Li2S, used to prepare the blends in this work (note that for simplicity, all concentrations are reported in terms of the atomic sulfur concentration):

Average composition in the blend	$[S]_T^{blend}$ / M	$[S]_{starting}$ / M	$[Li_2S]_{starting}$ / M
Li_2S_8	10	8.75	1.25
Li_2S_8	20	17.5	2.5
Li_2S_6	10	8.33	1.67
Li_2S_6	20	16.7	3.33

Calculation of the amount of solid sulfur and Li_2S that would be required to obtain the congruent solution, with $[S]_T^{sol}$ is 6 M and average composition corresponding to Li_2S_4, considering that all the solids will fully dissolve:

Average composition in the congruent solution	$[S]_T^{blend}$ / M	$[S]_{starting}$ / M	$[Li_2S]_{starting}$ / M
Li_2S_4	6	4.5	1.5

Estimation of the amounts of sulfur and Li_2S that would remain as precipitate in the blend if the congruent solution composition was achieved upon reaction of sulfur and Li_2S. It is seen that all blends contain an excess of both Li_2S and sulfur, except for the case of the 10 M Li_2S_8 blend that does not contain enough Li_2S to form the congruent solution:

Average composition in the blend	$[S]_T^{blend}$ / M	$[S]_{ppte}$ / M	$[Li_2S]_{ppte}$ / M
Li_2S_8	10	8.75 - 4.50 = 4.25	1.25 - 1.50 = -0.25
Li_2S_8	20	17.5 - 4.5 = 13.0	2.5 - 1.5 = 1.0
Li_2S_6	10	8.33 - 4.50 = 3.83	1.67 - 1.50 = 0.17
Li_2S_6	20	16.7 - 4.5 = 12.2	3.33 - 1.50 = 1.83

Calculating total sulfur content $[S]_T^{sol.}$ in polysulfide electrolyte solutions. After the mass of barium sulfate ($BaSO_4$) was determined for a given volume of polysulfide electrolyte solution, the atomic sulfur concentration of that solution can be calculated. The moles of $BaSO_4$ is determined, which is equivalent to the moles of atomic sulfur (S) present and as the volume of polysulfide electrolyte solution analyzed is known, the atomic sulfur concentration $[S]_T^{sol.}$ can be calculated. See worked example:

Li_2S_8 (10 M $[S]_T^{blend.}$)
Relative molecular mass (RMM) of $BaSO_4$ = 233.43 g mol^{-1}
Polysulfide volume analyzed = 1.5 mL
$BaSO_4$ mass present = 1.9336 g

Moles of $BaSO_4$= 1.9336 g / 233.43 g mol^{-1} = 8.3 x 10^{-3} moles
Moles of $BaSO_4$ = Moles of S = 8.3 x 10^{-3} moles

$[S]_T^{sol.}$ = 8.3 x 10^{-3} moles / 0.002 dm^{-3} = 4.1 M

Calculating average sulfur oxidation state (S^{m-}) of polysulfide electrolyte solutions. The UV-Vis redox titration data for the 10 M $[S]_T^{blend.}$ Li_2S_8 polysulfide electrolyte solution is used as an example for the calculation (Figure 1).

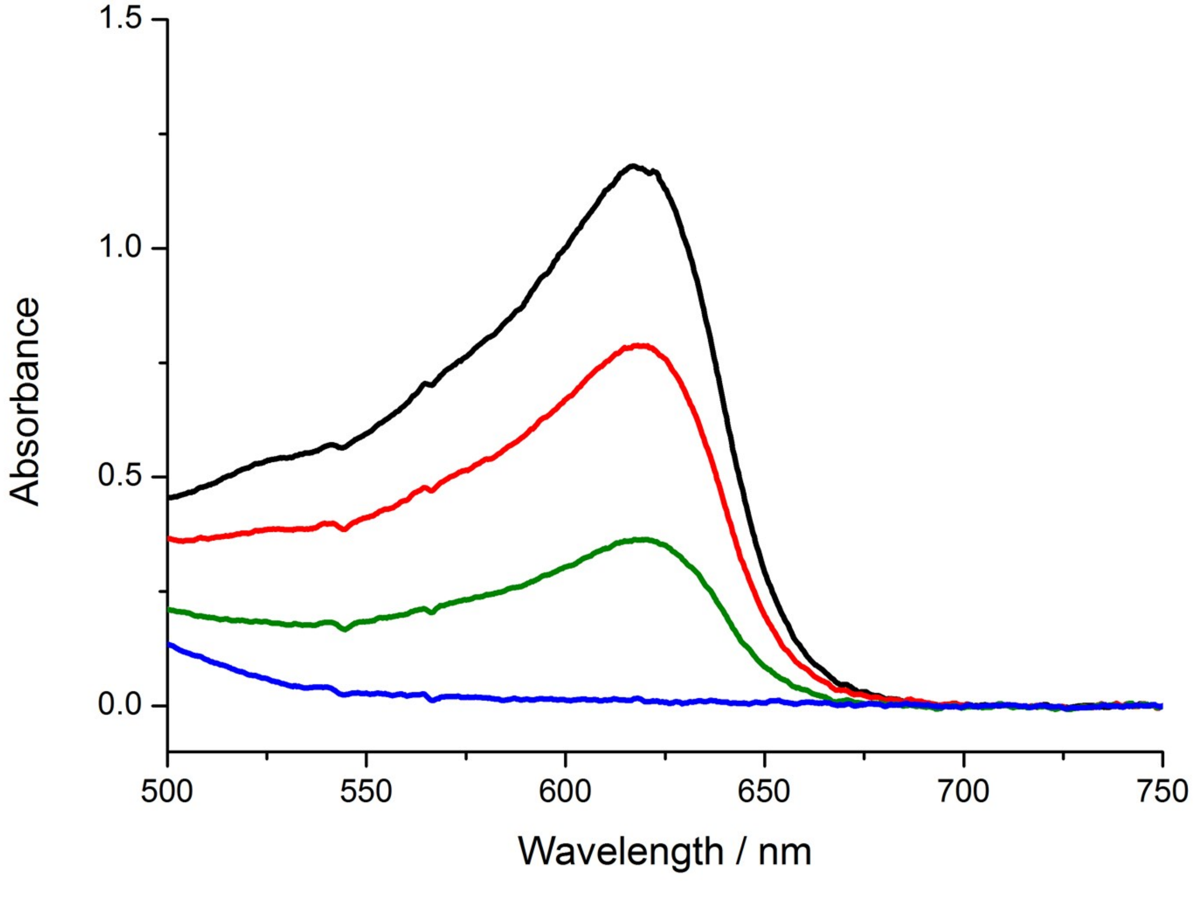

Figure 1 – UV-Vis spectra with baseline correction obtained for $FcBF_4$ solutions in DOL (3 mM, 2 mL) after addition of known aliquots of polysulfide solutions obtained from the 10 M $[S]_T^{blend}$ Li_2S_8 blend (— 0 uL, — 1.2 uL, — 2.4 uL, — 3.6 uL).

The peak at 620 nm was analyzed by plotting the absorbance at 620 nm against the volume of polysulfide solution added (Figure 2).

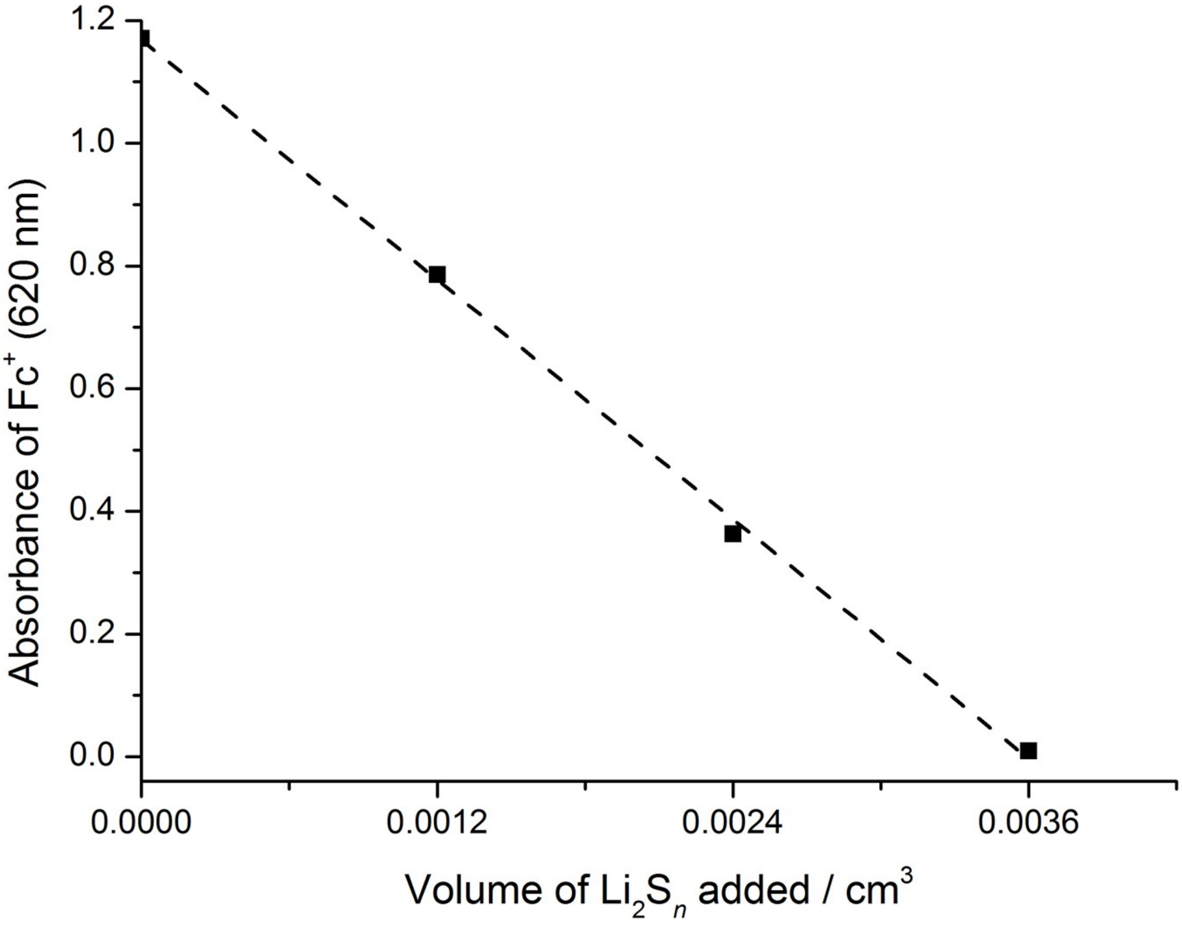

Figure 2 – Absorbance of FcBF$_4$ solution in DOL (3 mM, 2 mL) at 620 nm plotted against the volume of polysulfide solution obtained from the 10 M $[S]_T^{blend.}$ Li$_2$S$_8$ blend.

The slope of this plot was then calculated and used to evaluate the polysulfide concentration $[S_n^{2-}]$, the average atomic sulfur oxidation state (m in S^{m-}) and the average chain length of polysulfides (n in Li$_2$S$_n$):

$$\left[S_n^{2-}\right] = \frac{-\,slope\; V_{Fc^+}}{2\, l\, \varepsilon_{Fc^+}^{620\,nm}}$$

Equation 2 – Calculating the polysulfide concentration $[S_n^{2-}]$, where V_{Fc^+} is the volume of FcBF$_4$ solution used to react with each volume of Li$_2$S$_n$ solution in cm^3, l is the UV-Vis cell path length in cm and $\varepsilon_{Fc^+}^{620\,nm}$ is the molar extinction coefficient of FcBF$_4$ at 620 nm in M^{-1} cm^{-1}.

$$(a)\quad n\left(Li_2S_n\right) = \frac{[S]_T^{sol.}}{\left[S_n^{2-}\right]} \qquad\qquad (b)\quad m\left(S^{m-}\right) = \frac{2}{n\left(Li_2S_n\right)}$$

Equation 3 – (a) calculating the average polysulfide chain length i.e. n in Li$_2$S$_n$ and (b) Calculating the average atomic sulfur oxidation state in polysulfide solutions i.e. m in S^{m-}

Li_2S_8 (10 M $[S]_T^{blend.}$)
Slope = -326 cm^{-3}

$$\left[S^{2-}_{n}\right] = \frac{-326\ cm^{-3}\ .\ 2\ cm^{3}}{2\ .\ 1\ cm\ .\ 390\ M^{-1}cm^{-1}} = 0.83\ M$$

$$n\left(Li_2S_n\right) = \frac{4.1\ M}{0.83\ M} = 5.0\quad or\quad Li_2S_5\ (calculated\ without\ rounding\ errors)$$

$$m\left(S^{m-}\right) = \frac{2}{5.0} = 0.40$$

Calculating Li_2S, S and electrolyte mole fraction for ternary phase diagram. The number of moles of Li_2S, S and electrolyte were calculated for 1 mL of lithium polysulfide electrolyte solution (0.001 dm^3). It can be assumed that all the charge associated with the polysulfides is provided by Li_2S exclusively and hence the number of moles of Li_2S present should be equal the number of moles of double-charged polysulfides present (Equation 4).

$$moles_{Li_2S_n} = moles_{Li_2S} = 0.001\ dm^3\left[S^{2-}_{n}\right]$$

Equation 4 – Calculating the moles of 'Li_2S' in 1 mL of polysulfide electrolyte solution

It can be assumed that all remaining moles of atomic sulfur in the polysulfide electrolyte solution not attributed to Li_2S are moles of S (Equation 5).

$$moles_S = \left(0.001\ dm^3\ [S]^{sol.}_{T}\right) - moles_{Li_2S}$$

Equation 5 – Calculating the moles of 'S' in 1 mL of polysulfide electrolyte solution

An estimate of the volume of electrolyte present in 1 mL of lithium polysulfides electrolyte solution can be made by substituting the volume taken by the moles of Li_2S and S present (Equation 6).

$$volume_{electrolyte} = 0.001\ cm^3 - \left(\frac{moles_{Li_2S}\ RMM_{Li_2S}}{density_{Li_2S}}\right) - \left(\frac{moles_S\ RMM_S}{density_S}\right)$$

Equation 6 – Calculating the moles of volume of electrolyte in 1 mL of polysulfide electrolyte solution, where RMM is the relative molecular mass in g mol^{-1}.

The total moles of electrolyte present can then be calculated taking into consideration the volume of electrolyte that will be LiTFSI and volume of electrolyte that will be DOL (Equation 7).

$$moles_{electrolyte}$$

$$= moles_{LiTFSI} + moles_{DOL} = \left(\frac{volume_{electrolyte} \left(\frac{volume_{LiTFS}}{volume_{LiTFSI} + vol} \right.}{RMM_{LiTFSI}} \right.$$

$$+ \left(\frac{volume_{electrolyte} \left(\frac{volume_{DOL}}{volume_{LiTFSI} + volume_{DOL}} \right) density_{DOL}}{RMM_{DOL}} \right)$$

Equation 7 – Calculating the moles of electrolyte (LiTFSI and DOL) in 1 mL of polysulfide electrolyte solution

The calculated $moles_{electrolyte}$ was then divided by 5 in order to stretch the data points towards the bottom of the ternary phase diagram (Figure 3). This effectively scales the vertical concentration axis so that the data points can be seen clearer.

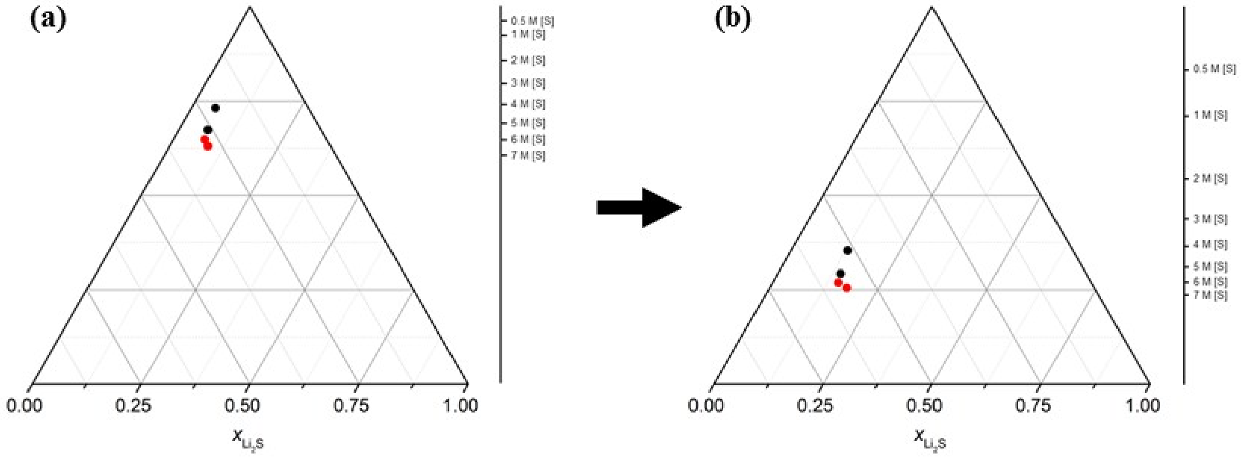

Figure 3 – (a) Ternary phase diagram without manipulating $moles_{electrolyte}$ and (b) ternary phase diagram with the $moles_{electrolyte}$ divided by 5 to stretch data towards bottom