Supporting Information

Molecular interactions in concentrated lithium sulfate solutions and their effect on electrochemical dissolution of iron

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S1. Characterisation and properties of the Li_2SO_4 solutions

Table S1: Properties of Li_2SO_4 solutions made up through dissolution of appropriate mass of salt into 30 g of water. Concentration in mol dm^{-3} calculated using mols per volume of the solution after addition of 30 g water.

Concentration / mol kg^{-1}	Volume after addition of 30 g water	concentration / mol dm^{-3}	pH
0.10	30	0.10	7.03
0.40	30	0.40	6.50
1.00	31	0.97	5.80
1.81	32	1.70	5.26
1.98	32.5	1.83	5.10
2.49	32.5	2.30	4.79

Table S2: Literature values for Li_2SO_4 solutions at approximately the same concentration as used in this study (from reference 22 in main text)

Concentration /mol kg^{-1}	Conductivity / mS cm^{-1}	Viscosity / mPa s
0.4057	36.7	1.26
0.7952	56	1.55
1.1924	66.8	1.89
1.5788	72.5	2.31
1.9562	74.7	2.82
2.603	71.6	4.02

S2. Description of in situ ATR IR spectroelectrochemical cell

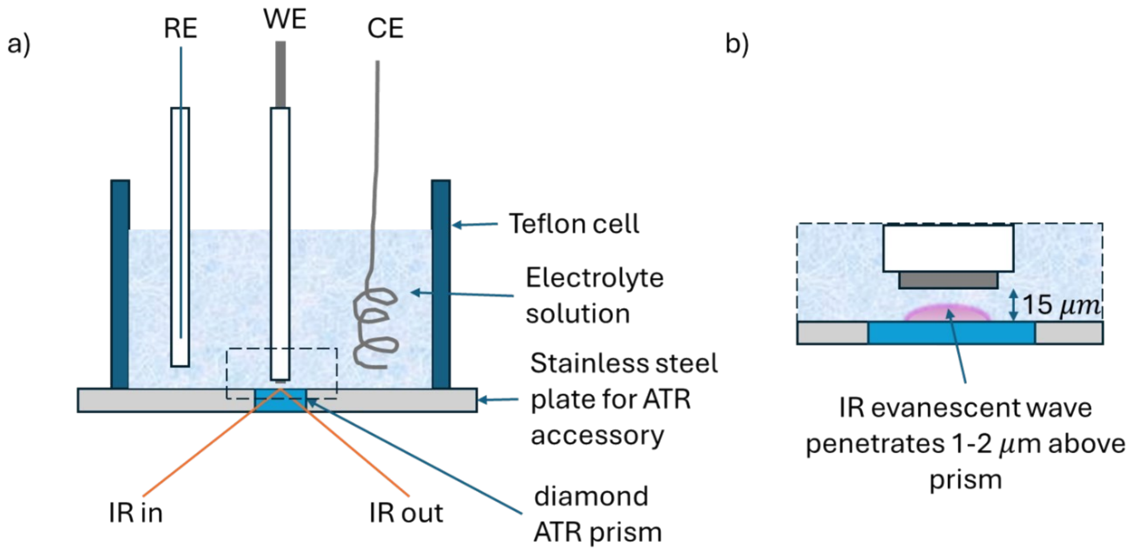

Fig S1: a) Cross section schematic (not to scale) of ATR IR spectroelectrochemical cell used in this work: RE = reference electrode (Ag / AgCl); WE = working electrode (1mm diameter Fe wire insulated with Teflon tape); CE = counter electrode (Pt coil). b) Zoomed in view (not to scale) of dotted area shown in a) showing approximate distances between WE and diamond prism and penetration of IR evanescent wave above the prism.

S3. Calculation of Diffusion coefficients of $Fe(CN)_6^{4-}$ in different Li_2SO_4 concentration electrolytes.

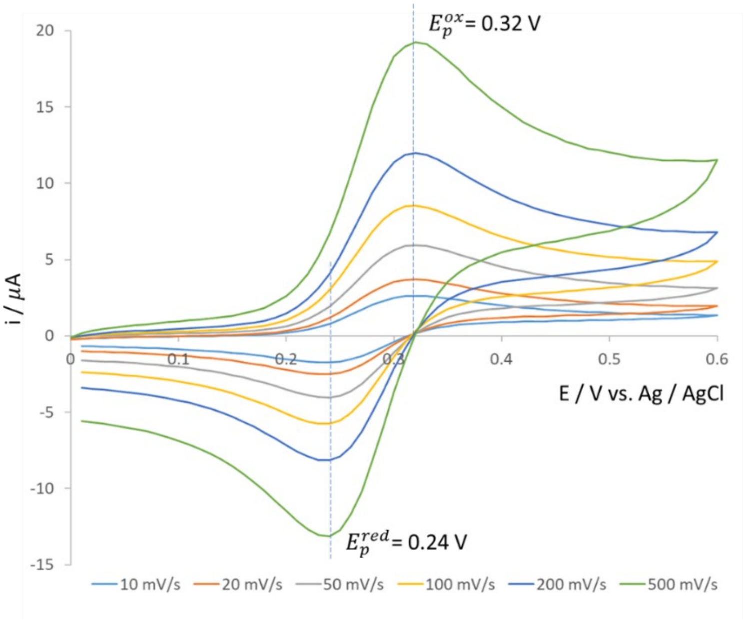

Fig S2: Cyclic voltammograms (CV) of 1 mM $Fe(CN)_6^{4-}$ in 1 m Li_2SO_4 at different scan rates (carbon working electrode area = 0.0707 cm^2). Dashed lines indicate position of peak maximum for oxidation and reduction which is independent of scan rate. Peak separation is 80 mV.

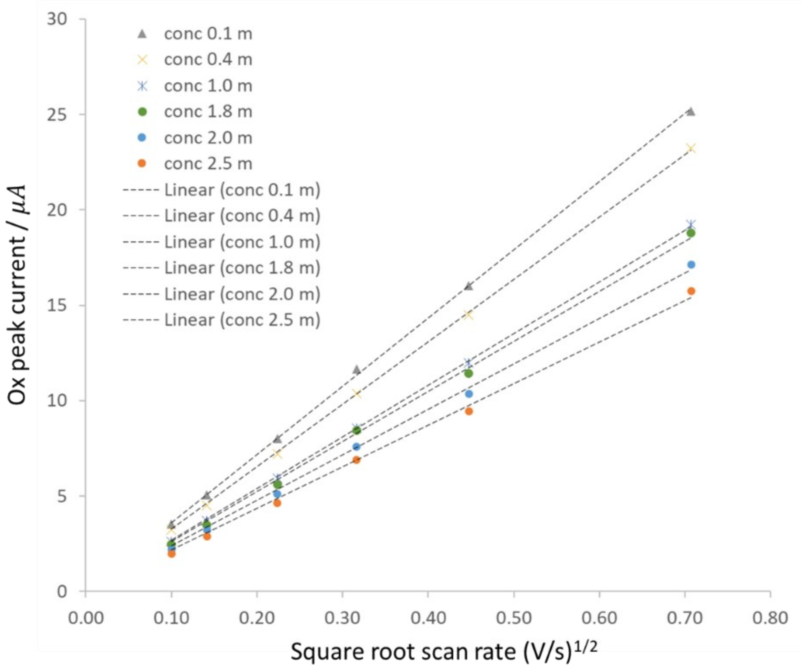

Figure S3: Plot of peak oxidation current from Cyclic Voltammogram (CV) of 1 mM $Fe(CN)_6^{4-}$ dissolved in Li_2SO_4 aqueous electrolyte against square root of scan rate. Legend shows concentration of Li_2SO_4 used. Linear fits pass through the origin. Electrode was a carbon disk of area 0.0707 cm^2.

Table S3: Average gradients from 3 repeats of CV experiments used to calculate D using Equation 2 in main text with A = 0.0707 cm^2 and $c_{ferrocyanide}$ as given in table (approx. 1 x 10^{-6} mol cm^{-3})

Conc Li_2SO_4 / m	$c_{ferrocyanide}$/ mol cm^{-3}	Av. Gradient / $\mu A\ V^{-1/2} s^{1/2}$	Average D x 10^{-6} / cm^2s^{-1}

0.1	1.03 x 10^{-6}	12.22	(3.3 ± 0.2)
0.4	1.06 x 10^{-6}	12.57	(2.61 ± 0.02)
1.0	1.09 x 10^{-6}	11.98	(1.74 ± 0.03)
1.8	1.09 x 10^{-6}	11.37	(1.57 ± 0.04)
2.0	1.04 x 10^{-6}	10.41	(1.45 ± 0.01)
2.5	1.04 x 10^{-6}	10.58	(1.20 ± 0.01)

Errors on D from repeated measurements too small to be plotted on Figure 1 in main manuscript. Error bars calculated from uncertainty in mass of ferrocyanide from 4 d.p. balance of ± 0.0002 g, propagating to error in D of 0.1 x 10^{-6} cm^2s^{-1}.

S4. Cyclic Voltammetry (CV) of Fe electrode in different Li_2SO_4 solutions

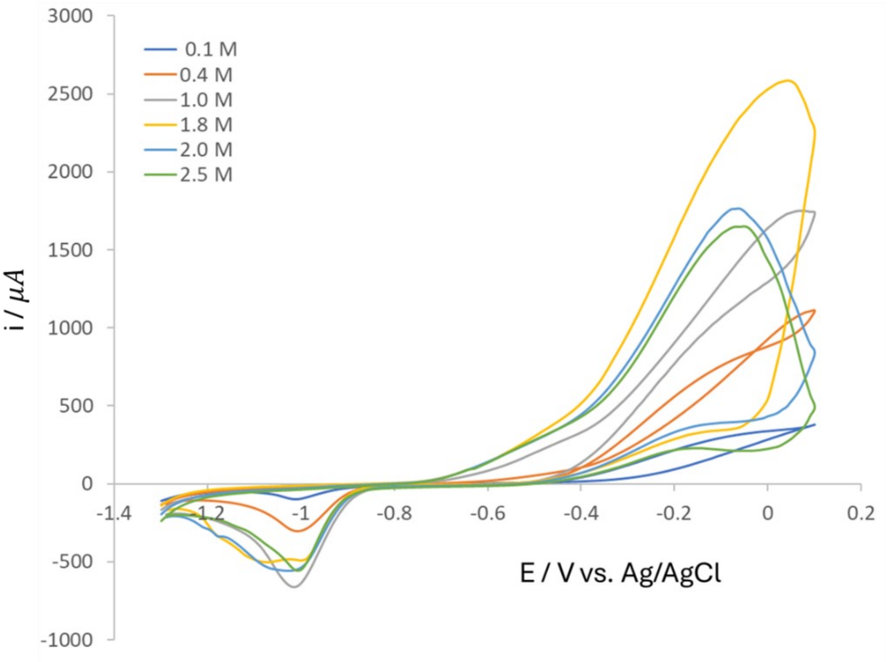

Figure S4: Complete CVs for Fe electrode (1mm diameter) in different Li_2SO_4 electrolyte solutions, scan rate 0.1 V s^{-1}. Fifth consecutive scan at fresh electrode surface shown in each case. Forward scans for these CVs are shown in Figure 3 in the main text.

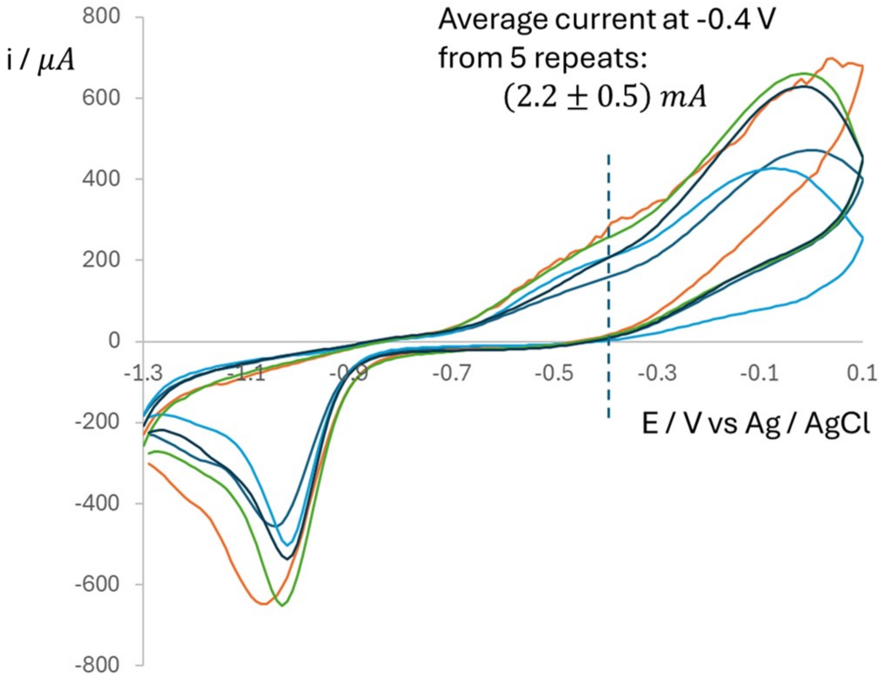

Figure S5: CVs for five separate freshly exposed Fe electrodes (1mm diameter) in 1.0 m Li_2SO_4 electrolyte solutions, scan rate 0.1 V s^{-1}. Fifth consecutive scan at fresh electrode surface shown in each case. Current at -0.4 V determined for each and average with error plotted in inset to Fig 3 in main text.

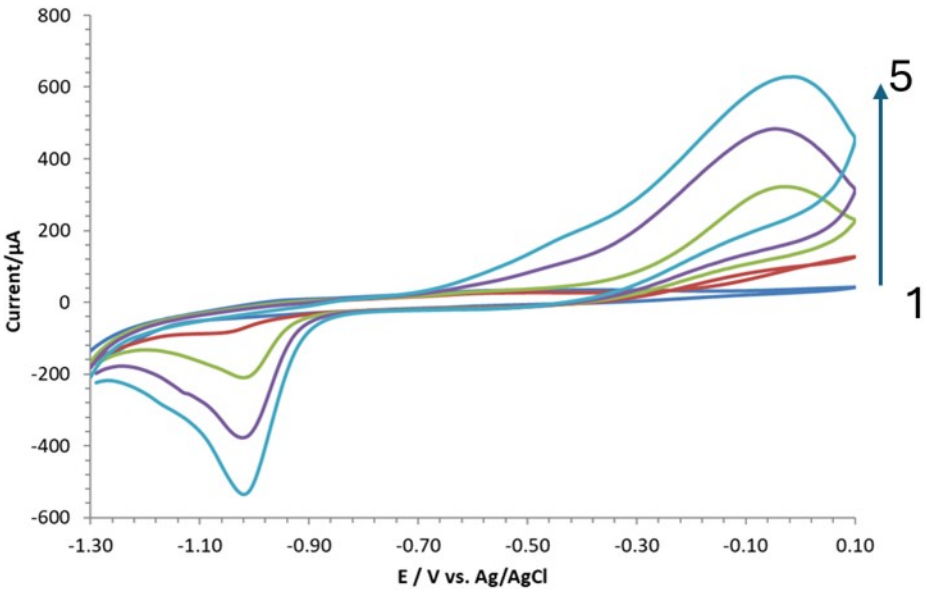

Figure S6: Consecutive CVs 1-5 for Fe electrode (1mm diameter) in 1.0 m Li_2SO_4 *electrolyte solutions, scan rate 0.1 V* s^{-1}.

S5. Time dependent in situ IR spectroelectrochemistry of Fe electrode interface in different Li_2SO_4 solutions

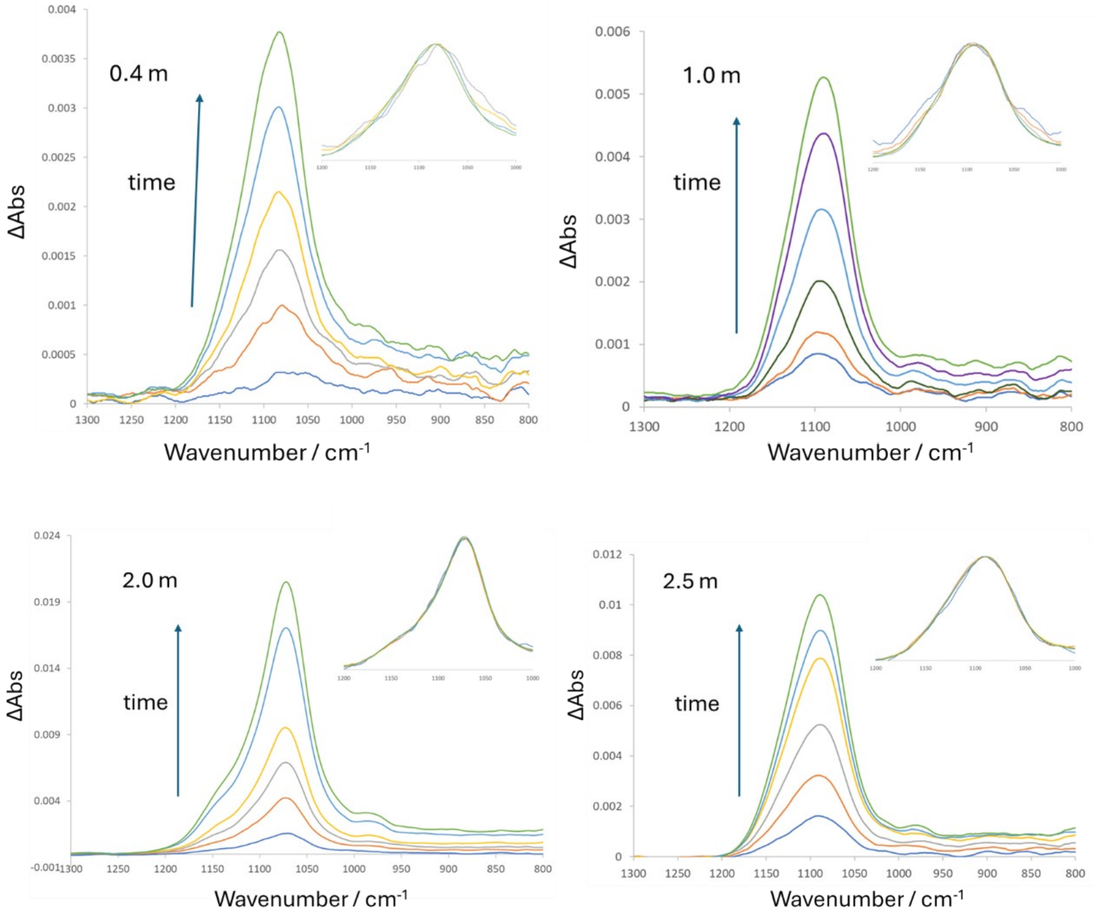

Figure S7: In situ IR difference spectra analogous to Fig 5 c) in main text. Changes to IR sulphate band as a function of time after application of -0.4 V to the Fe electrode in a solutions of 0.4, 1.0, 2.0 and 2.5 m Li_2SO_4: each spectrum recorded at 5 min increments for 30 min. Inset shows the spectra normalised to an absorbance of 1 at the peak maximum and overlaid.