Supporting information

Figure S1 summarises the Li cycling behaviour in the 3-electrode measurements for the various electrolyte systems, expressed in terms of the peak Li deposition current and the cycle efficiency (calculated as $q_{oxidation}/q_{reduction}$)

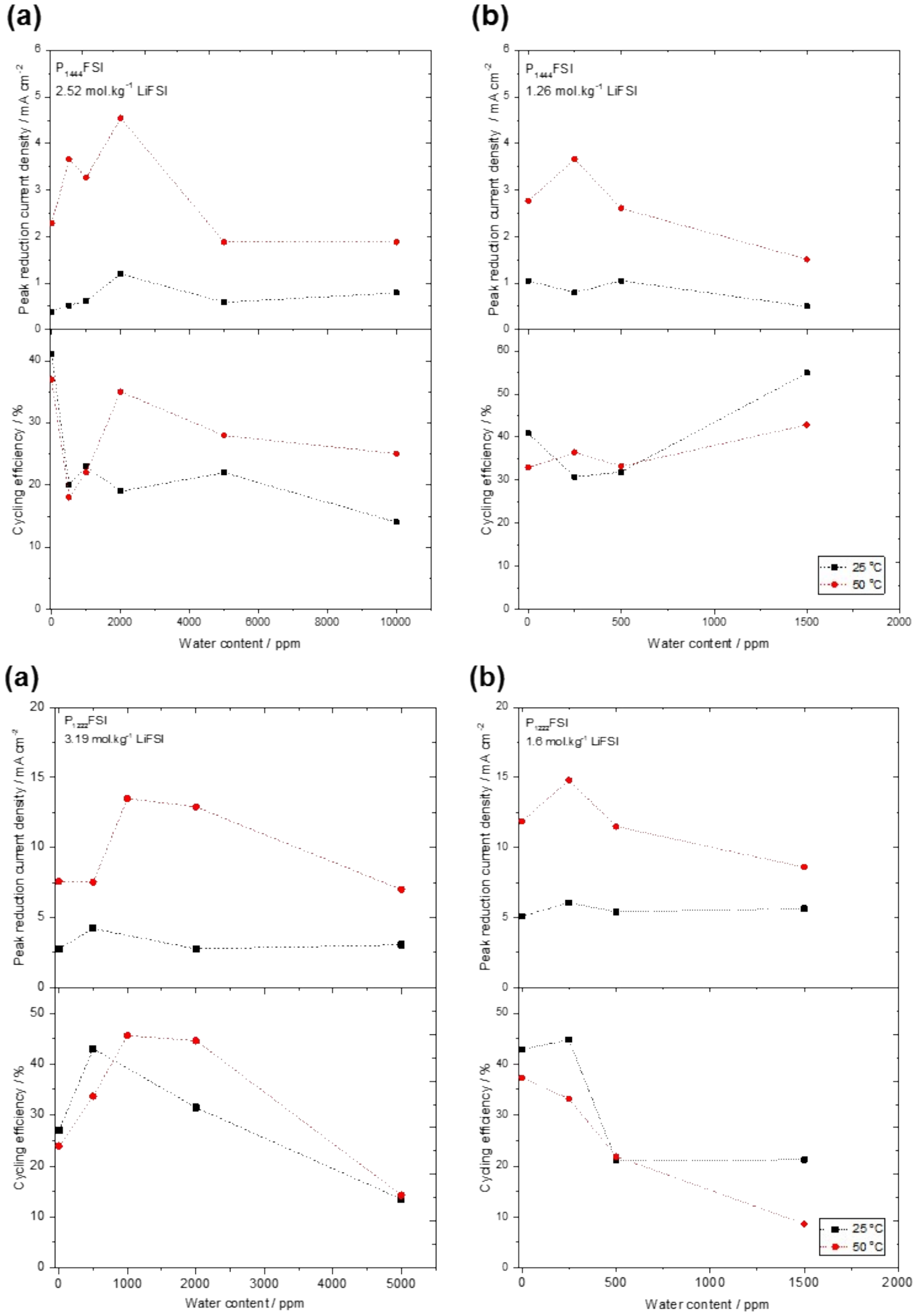


Figure S1. The peak reduction currents and cycling efficiencies. Values taken from the 10th cycle of the corresponding cyclic voltammogram.

Figure S2 shows the cyclic voltammograms for the plating and stripping of Li in the various electrolytes at 50 °C, as done in Figure 3 at 25 °C.

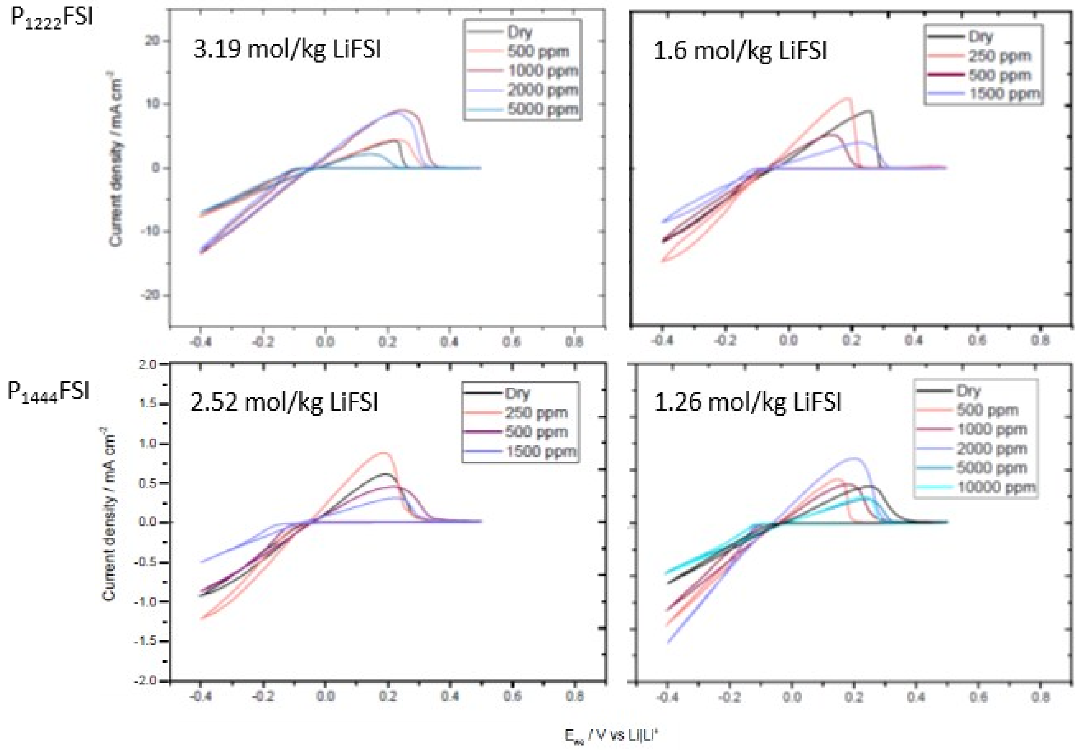


Figure S2. A comparison of CVs for the 10th cycle at various water concentrations for $P_{1222}FSI$ and $P_{1444}FSI$ at 50 °C.

The long-term cycling behaviour of a Li|Li symmetrical cell using $P_{1222}FSI$ and $P_{111i4}FSI$ electrolytes are shown in Figure S3. Cycling at a current of 1 mA/cm^2 and step time of 1 h was carried out until both cells were stopped when the cell with $P_{111i4}FSI$ failed.

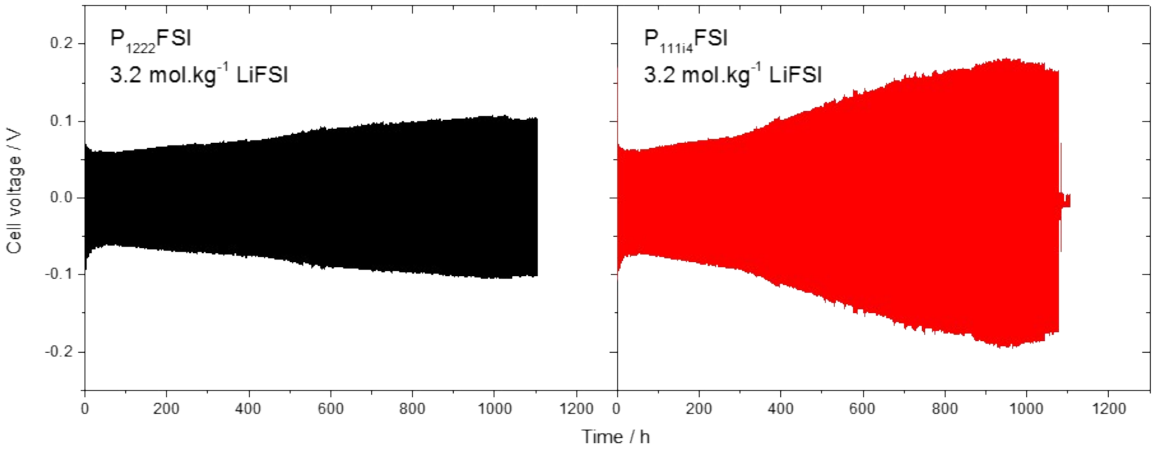


Figure S3. Long-term symmetric Li|Li cell cycling using a step time of 1 h at 1 mA.cm^{-2} at ambient temperature. Cells were prepared using dry P_{1222}FSI and P_{111i4}FSI.

Figure S4 shows a comparison of the Li cycled surfaces from Li|Li symmetrical cells using P_{1222}FSI with 3.2 mol/kg LiFSI after 10 cycles at 1 mA/cm^2 for a 1 h step time. The electrodes cycled with the addition of 5000 ppm water show a rougher, patchier surface deposit.

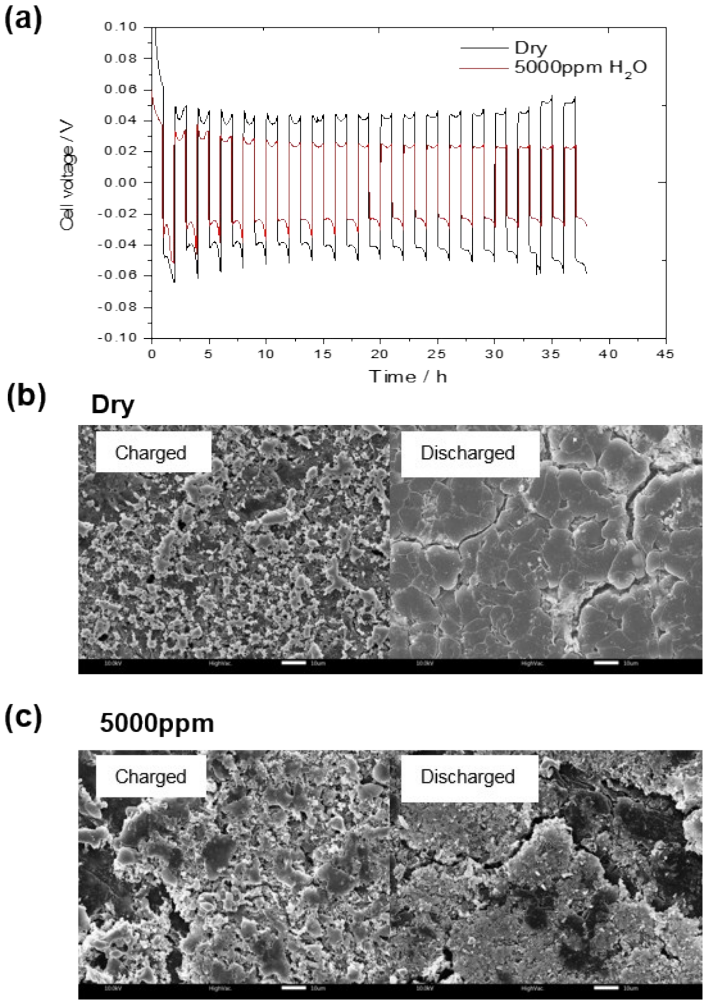
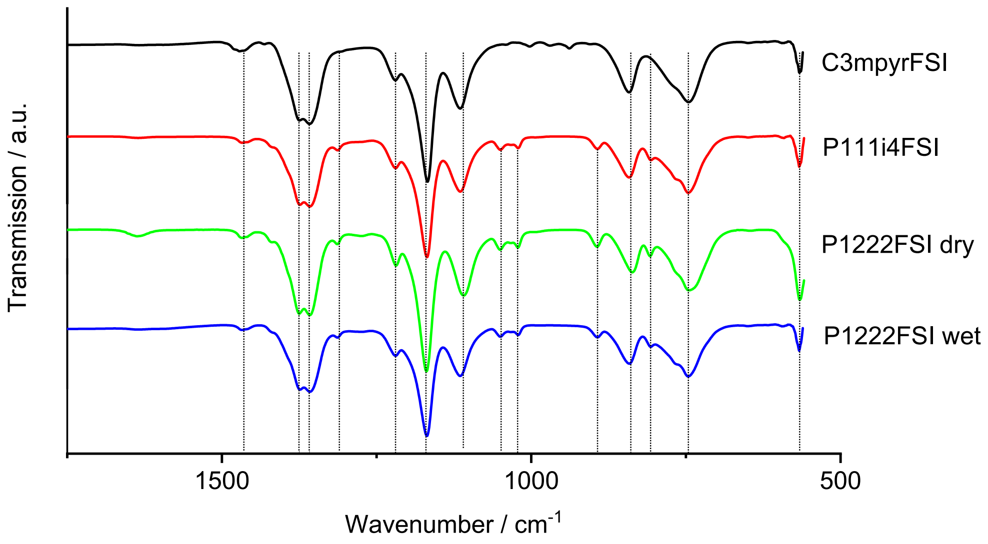


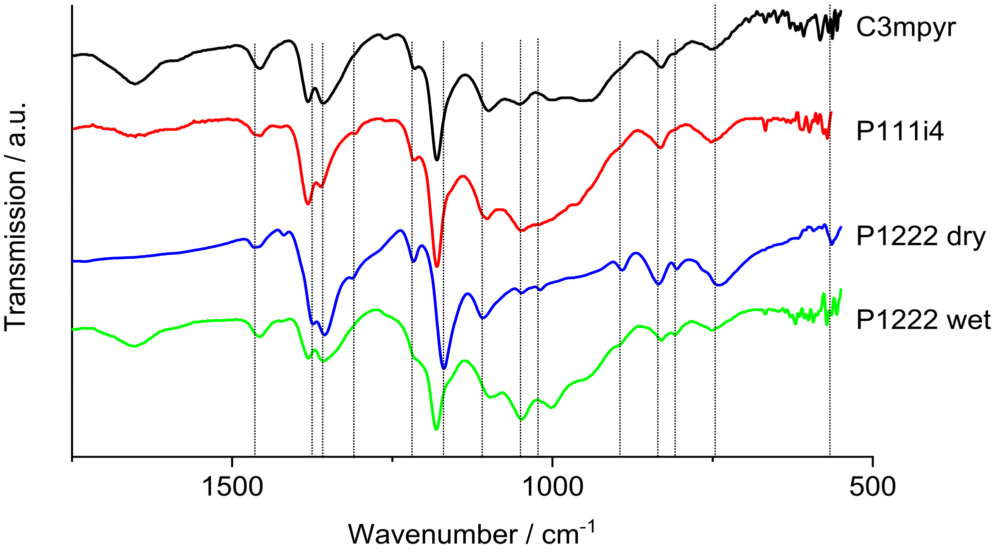
Figure S4. (a) Voltage profile and (b,c) SEM image of Li surfaces taken from Li|Li symmetric cell after 20 cycles in P_{1222}FSI with 0.64 mol.kg^{-1} LiFSI at 1 mA.cm^{-2}, 1 h step time. V_{acc} = 10 kV; scale bar = 10 μm.

Peak assignments for Li electrodes cycled in P111i4FSI with 3.8 mol/kg LiFSI are shown tabulated Figure S5. These peak positions are shown as dashed lines in Figure 6g for illustrative purposes when comparing to P_{1222}FSI and C_3mpyrFSI.

(a) Ionic liquid electrolytes



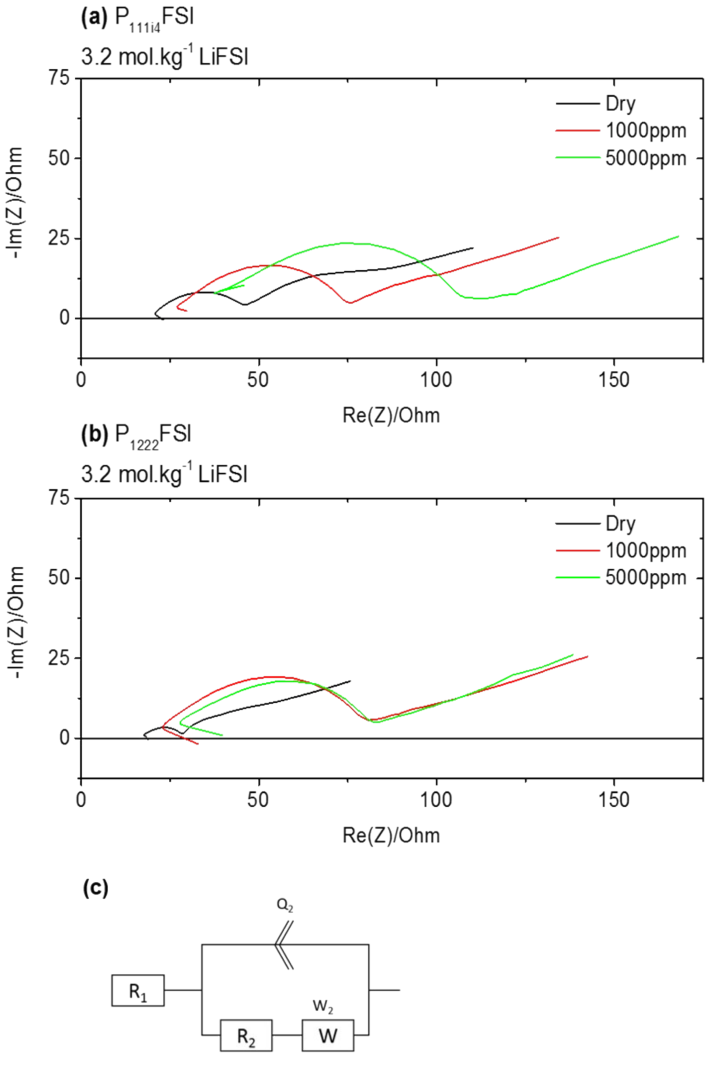
(b) Cycled Li metal electrodes



Peak assignment	**Peak position (cm^{-1})**
$\delta_a(SO_2)$	566
$v_s(SNS)$	746
$v_a(SNS)$ and $v(SF)$	843
$v(SO_2\text{-}N\text{-}SO_2)$	1114, 1168, 1220
$\tau(CH_2)$	1307
$v_a(SO_2)$	1358
$v_a(SO_2)$	1374
$\delta(CH_2)$ from P-CH_2	1421
$v(CH_2)v(CH_3)$	1471

Figure S5. FTIR spectra for the (a) ILEs and (b) lithium metal electrode surface after cycling at 1 mA/cm^2|1 mAh/cm^2 for 10 cycles. The table shows peak assignments for P_{111i4}FSI with 3.8 mol/kg LiFSI (the dashed lines in Figure 6e), as previously reported.[27]

An example of the EIS spectra obtained on the symmetrical Li|Li cells is shown in Figure S6. The electrochemical model used to obtain the resistance values tabulated in Table 2 is shown in Figure S6c.



$$Z(f) = R_1 + \frac{Q_2}{R_2 + W_2} = R_1 + \frac{R_2}{[\![R_2 Q_2 (i2\pi f)^{a_2}]\!] + \frac{\sqrt{2\sigma_2}}{\sqrt{i2\pi f}}}$$

Figure S6. EIS spectra for Li|Li symmetrical cells taken after 10 cycles at 1 mA/cm^2, 1 h step time using **(a)** P_{111i4}FSI and **(b)** P_{1222}FSI with 3.2 mol/kg LiFSI electrolytes with various concentrations of water. (c) shows the electrochemical model used to fit the first semi-circle and calculate the R1 and R2 values.