

Electronic Supplementary Information (ESI)

***In situ* formation of ultrahigh molecular weight polymers in highly concentrated electrolytes and their physicochemical properties**

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Table S1. Polymerisation conditions and characterisation of the polymers synthesised in

this study.

solvent	salt	salt conc. (M)	[M]/[I] ratio ^a	M_n (kDa) ^b	M_w (kDa) ^b	PDI ^b	monomer conversion (%) ^c	
TEGDME	non.	0	200	41	56	1.36	99.7	
			1000	91	159	1.76	97.4	
			2500	220	490	2.22	95.0	
			5000	300	778	2.59	88.8	
			10000	454	1045	2.30	80.4	
	LiFSI	1.0	1.0	200	39	52	1.31	99.7
				1000	172	334	1.94	99.8
				2500	283	575	2.04	99.8
				5000	429	848	1.98	99.3
				10000	534	1356	2.54	99.0
		1.5	10000	639	1193	1.87	97.0	
		2.0	10000	1077	1806	1.68	96.0	
		2.5	10000	1188	1908	1.61	95.4	
		3.2	3.2	200	93	191	2.05	99.9
				1000	338	713	2.11	99.8
				2500	508	1003	1.97	99.6
				5000	919	1642	1.79	99.2
				10000	1225	2002	1.63	99.9
		LiTFSI	2.8	10000	1068	1734	1.62	99.4
		LiBF ₄	3.9	10000	1489	2314	1.55	99.9
LiNO ₃	4.0	10000	743	1518	2.04	98.6		
DMC	non.	0	200	33	43	1.31	97.9	
			1000	75	148	1.98	94.6	
			2500	156	403	2.58	82.9	
			5000	271	893	3.29	66.7	
			10000	369	1265	3.43	62.7	
	LiFSI	4.7	4.7	200	99	182	1.84	99.9
				1000	365	702	1.92	99.6
				2500	715	1213	1.70	99.5
				5000	1103	1672	1.52	99.7
				10000	1170	2154	1.84	99.8
		5.5	5.5	200	158	329	2.08	99.8
				1000	571	963	1.68	100.0
				2500	1216	1749	1.44	99.7
				5000	1624	2298	1.41	99.9
				10000	1944	2545	1.31	98.8
FEC	4.2	4.2	200	169	320	1.89	99.8	
			1000	651	1121	1.72	99.9	
			2500	1112	1606	1.44	99.8	

			5000	1423	1902	1.34	99.8
			10000	1753	2509	1.43	99.8

^amolar ratio of the MMA monomer to the V-65 initiator. ^bmeasured via GPC. ^cdetermined from ¹H-NMR.

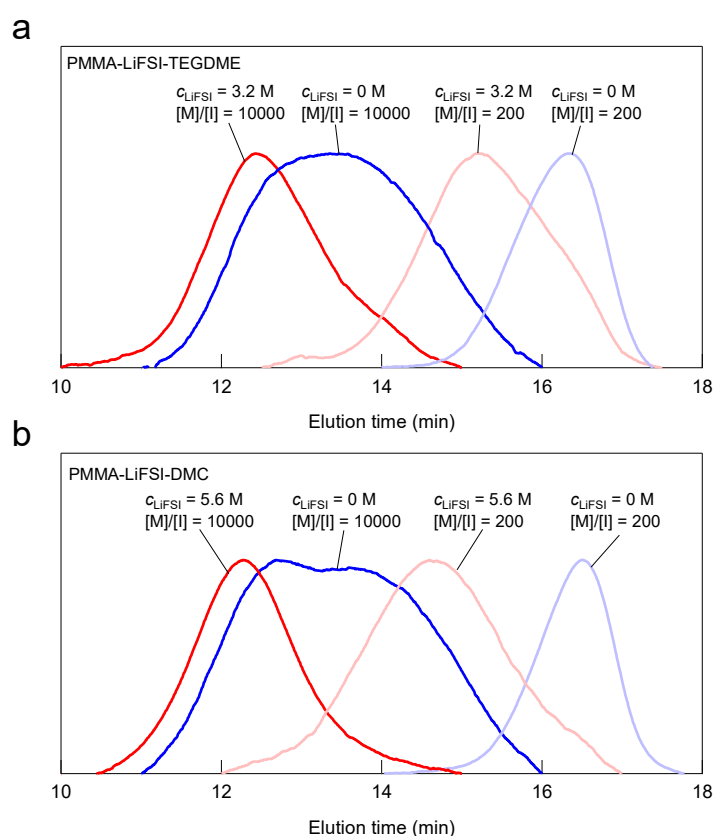


Fig. S1. GPC traces for (a) PMMA-LiFSI-TEGDME and (b) PMMA-LiFSI-DMC systems with different $[\text{M}]/[\text{I}]$ ratios and lithium salt concentrations. At high $[\text{M}]/[\text{I}]$ ratios and without the lithium salt, broad polydispersity was observed in both solvent systems (shown in blue); however, in the highly concentrated condition, a narrower unimodal peak was obtained (shown in red).

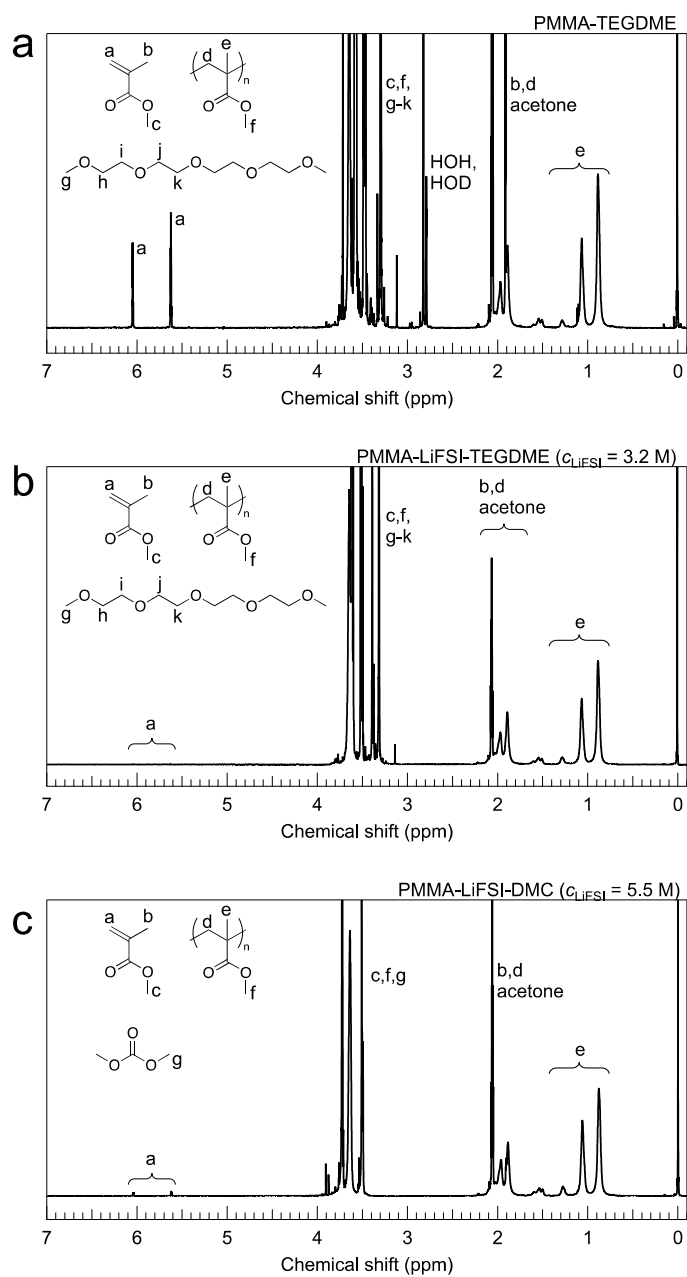


Fig. S2. ^1H NMR spectra of the polymerisation products of MMA in (a) pure TEGDME, (b) a 3.2 M LiFSI-TEGDME solution, and (c) a 5.5 M LiFSI-DMC solution.

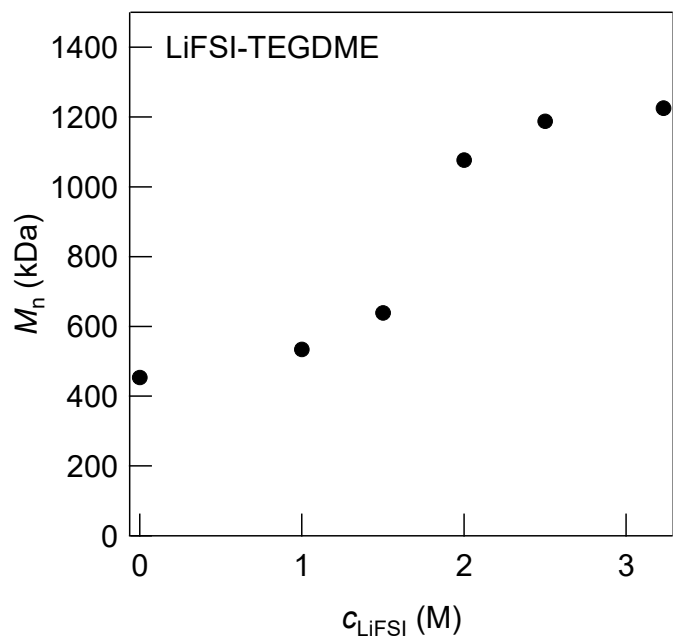


Fig. S3. Relationship between the M_n of PMMA and the concentration of lithium salt

(c_{LiFSI}) in the electrolyte. The $[\text{M}]/[\text{I}]$ ratio was 10,000.

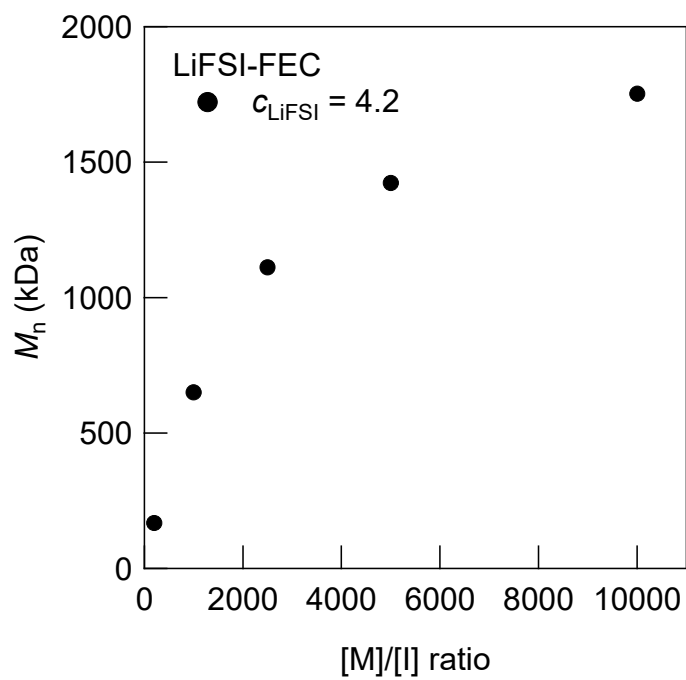


Fig. S4. Dependence of M_n on the $[\text{M}]/[\text{I}]$ ratio for a 4.2 M LiFSI-FEC system.

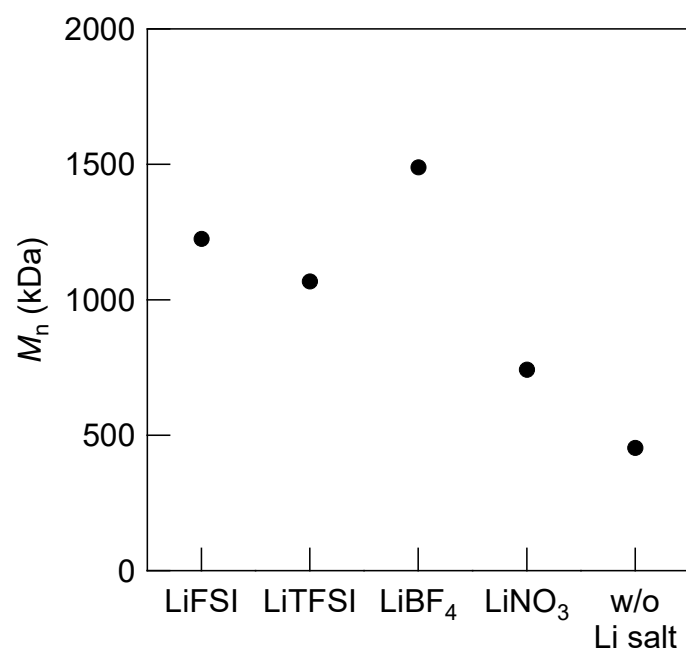


Fig. S5. M_n of PMMA obtained via polymerisation in pure TEGDME and equimolar mixtures of TEGDME and lithium salts with different counteranions.

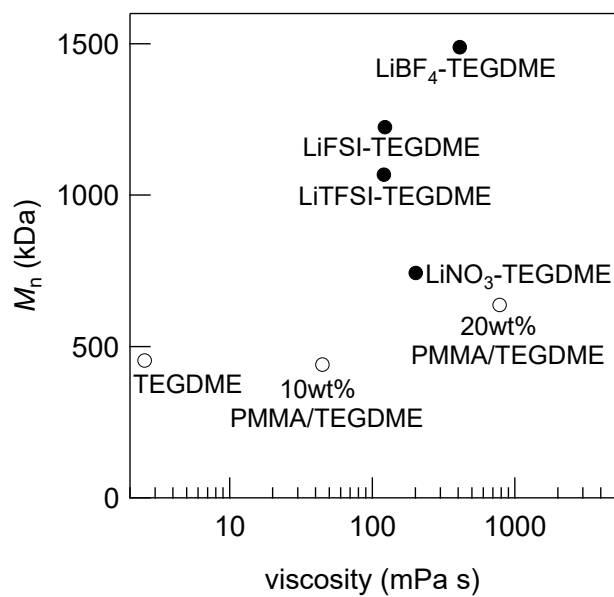


Fig. S6. The relationship between solvent viscosity and M_n for equimolar mixture systems composed of TEGDME and Li salts (closed circles), as well as viscosity-tuned non-ionic TEGDME systems (open circles). The viscosity of the non-ionic TEGDME systems was adjusted by dissolving commercial PMMA (120 kDa) at varying concentrations.

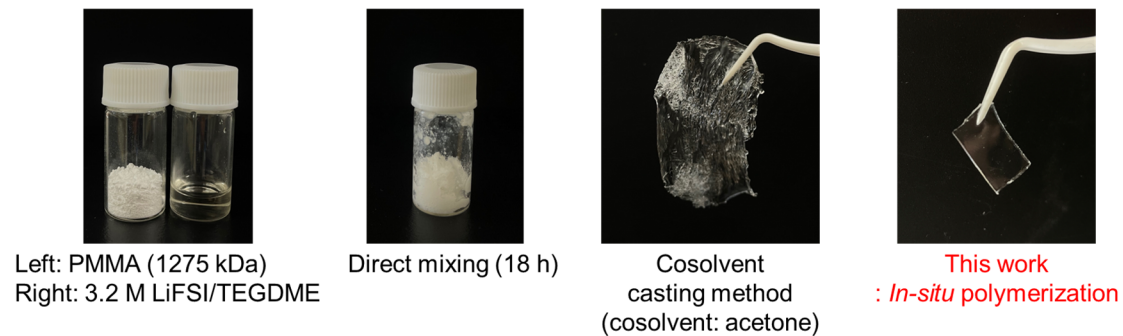


Fig. S7. Photographs of composites of ultrahigh molecular weight (UHMW) PMMA and a highly concentrated electrolyte (HCE) composed of an equimolar mixture of LiFSI and TEGDME ($c_{\text{LiFSI}} = 3.2\text{M}$) prepared by different methods. UHMW polymers are difficult to mix directly with the HCE due to their extremely slow relaxation kinetics. In the cosolvent casting method, the slow diffusion of the UHMW polymer relative to the cosolvent evaporation rate results in heterogeneous polymer precipitation. Evaporation of primary solvent also poses a challenge, as many HCEs are not completely nonvolatile. Compared to these methods, *in-situ* polymerisation of UHMW PMMA in HCEs resulted in homogeneous and transparent physical gels.

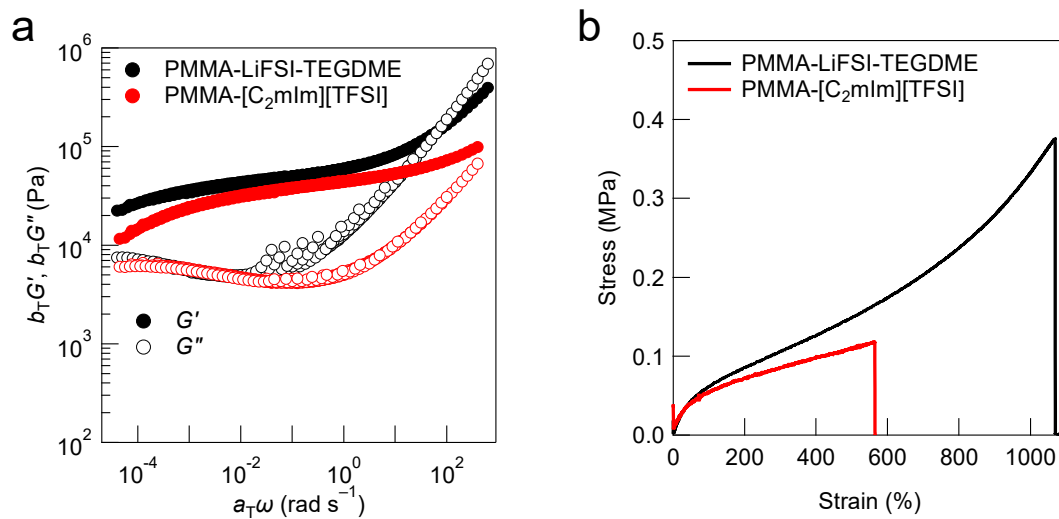


Fig. S8. Comparison of PMMA-LiFSI-TEGDME and PMMA-[C₂mIm][TFSI] UHMW

gels in (a) viscoelastic master curves and (b) stress-strain behaviour.

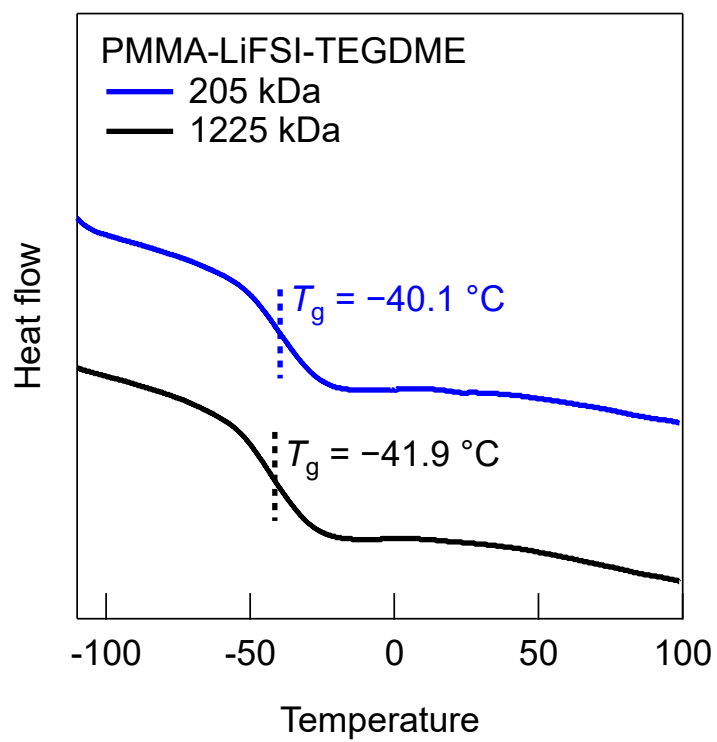


Fig. S9. DSC curves of PMMA-LiFSI-TEGDME systems with different molecular weights of PMMA.

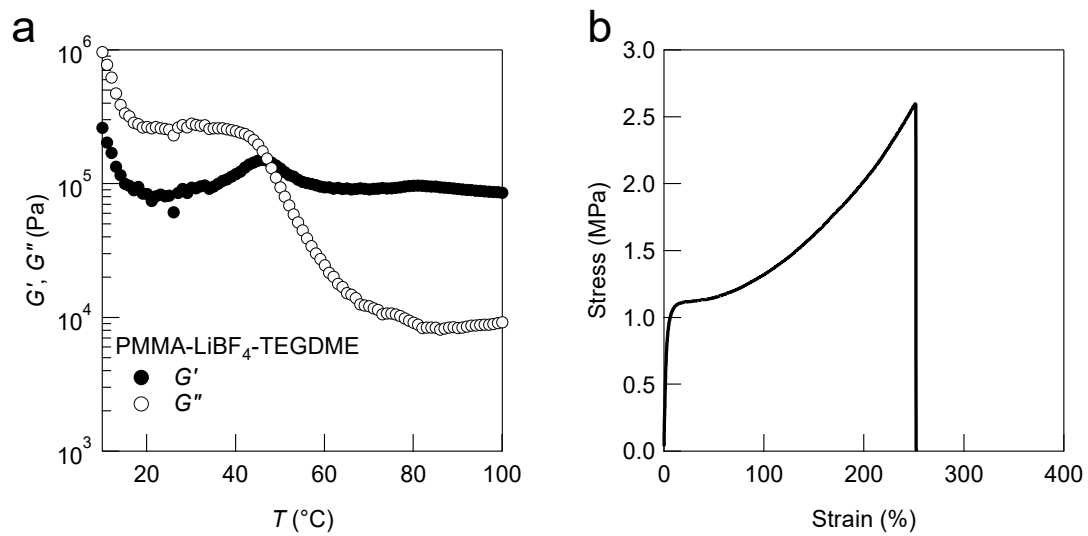


Fig. S10. (a) Temperature sweep measurement of the storage (G') and loss (G'') moduli, and (b) stress-strain curve from the tensile test for the PMMA-LiBF₄-TEGDME UHMW gel.

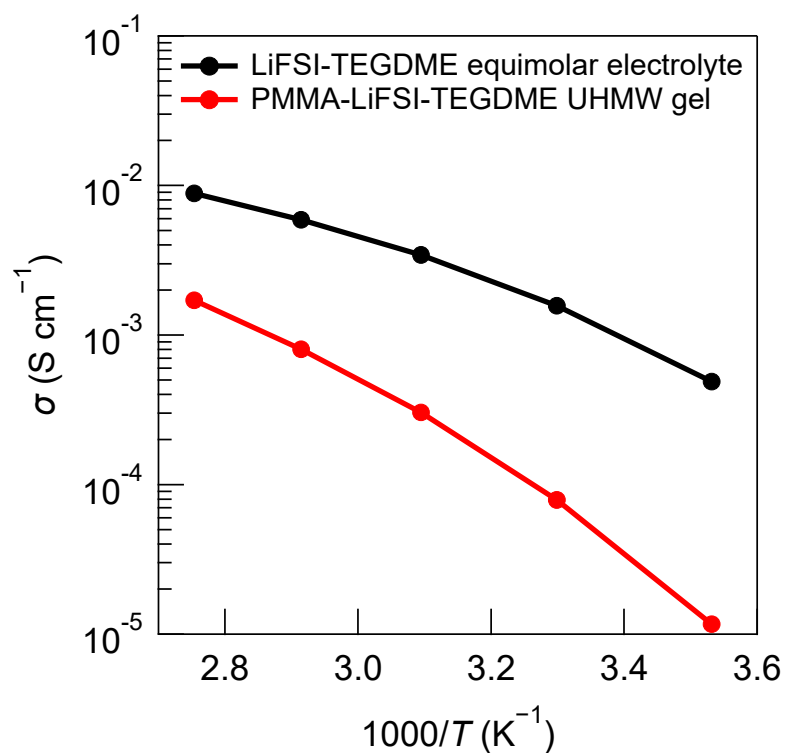


Fig. S11. Temperature dependence of ionic conductivity for the LiFSI-TEGDME equimolar mixture electrolyte and the corresponding PMMA-LiFSI-TEGDME UHMW gel.

Table S2. Ionic conductivity at 30 °C and lithium-ion transference number (t_{Li^+}) at 25 °C for the LiFSI-TEGDME equimolar mixture electrolyte and the PMMA-LiFSI-TEGDME UHMW gel.

electrolyte	Ionic conductivity (mS cm ⁻¹)	t_{Li^+}
LiFSI-TEGDME equimolar mixture	1.57	0.015 ^a
PMMA-LiFSI-TEGDME UHMW gel	0.08	0.2

^aThe value obtained from ref. S1

The t_{Li^+} was calculated by constructing a symmetrical cell using Li electrodes and combining DC polarisation and AC impedance measurements using a VMP3 potentiostat/galvanostat (Bio-Logic Science Instruments, France).^{S2} Electrochemical impedance spectroscopy measurements were performed with an amplitude of 10 mV and a frequency range of 100 mHz to 1 MHz, both before and after DC polarisation at 10 mV for 1 h. From the results obtained, the t_{Li^+} was calculated using the following equation:

$$t_{\text{Li}^+} = \frac{I_{\text{SS}}(\Delta v - I_0 R_0)}{I_0(\Delta v - I_{\text{SS}} R_{\text{SS}})}$$

where Δv stands for the polarisation voltage, I_0 is the initial current, I_{SS} is the steady-state current during the DC polarisation process, and R_0 and R_{SS} are the charge transfer resistances before and after polarisation, respectively.

It should be noted that the t_{Li^+} of the PMMA-LiFSI-TEGDME UHMW gel is higher than that of the neat LiFSI-TEGDME equimolar mixture. This could be attributed to the interaction of the imide anion with PMMA,^{S3} which may restrict the transport of anions, resulting in a higher t_{Li^+} .

Supporting references

- S1. S. Pfeifer, F. Ackermann, F. Sälzer, M. Schönhoff and B. Røling, *Phys. Chem. Chem. Phys.*, 2021, **23**, 628-640.
- S2. J. Evans, C. A. Vincent, P. G. Bruce, *Polymer* 1987, **28**, 2324-2328.
- S3. M. A. Susan, T. Kaneko, A. Noda and M. Watanabe, *J. Am. Chem. Soc.*, 2005, **127**, 4976-4983.