

Supporting Information

Table S1: R_1 and R_2 of symmetrical Li||Li coin cells with 1-PF₆-C, 1-TFSI-C, 1-TFSI-E and 3-TFSI-E after various days under OCV conditions.

R_1	Day	1-PF ₆ -C / Ω	1-TFSI-C / Ω	1-TFSI-E / Ω	3-TFSI-E / Ω
	0	6 \pm 1	4 \pm 1	9 \pm 7	10 \pm 2
	1	5 \pm 1	3 \pm 1	9 \pm 8	12 \pm 1
	5	5 \pm 1	3 \pm 1	9 \pm 6	12 \pm 1
	8	14 \pm 1	3 \pm 1	3 \pm 1	8 \pm 4

R_2	Day	1-PF ₆ -C / Ω	1-TFSI-C / Ω	1-TFSI-E / Ω	3-TFSI-E / Ω
	0	391 \pm 63	105 \pm 12	140 \pm 5	138 \pm 13
	1	540 \pm 133	96 \pm 1	235 \pm 9	174 \pm 20
	5	706 \pm 71	84 \pm 11	333 \pm 61	164 \pm 1
	8	838 \pm 188	79 \pm 5	366 \pm 95	158 \pm 11

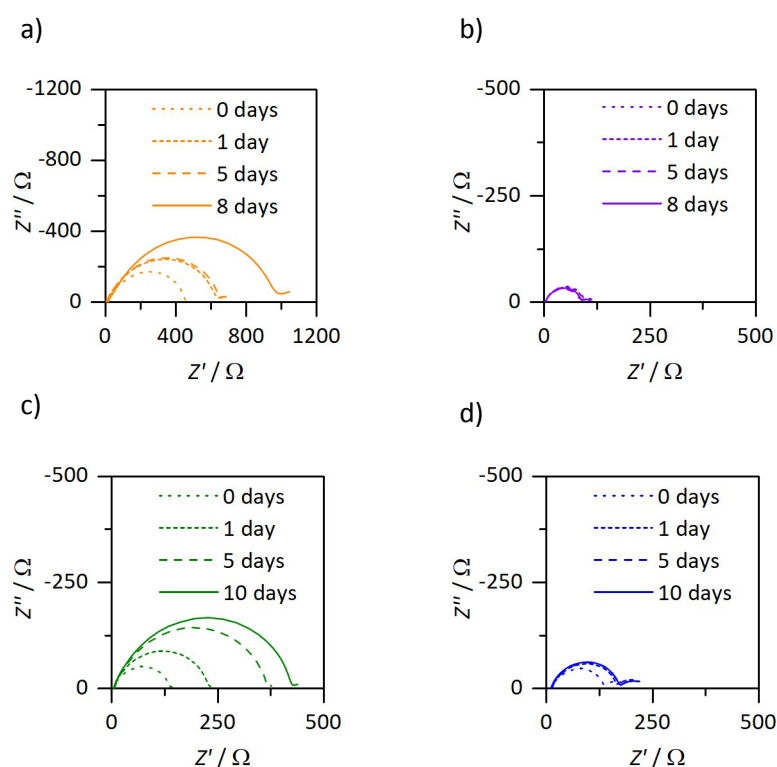


Figure S1: Impedance development of symmetrical Li||Li coin cells under open circuit voltage conditions containing electrolyte a) 1-PF₆-C (1 M LiPF₆ in EC:DEC (3:7)), b) 1-TFSI-C (1 M LiTFSI in EC:DEC (3:7)), c) 1-TFSI-E (1 M LiTFSI in DME:DOL (1:1)), and d) 3-TFSI-E (3 M LiTFSI in DME:DOL (1:1)).

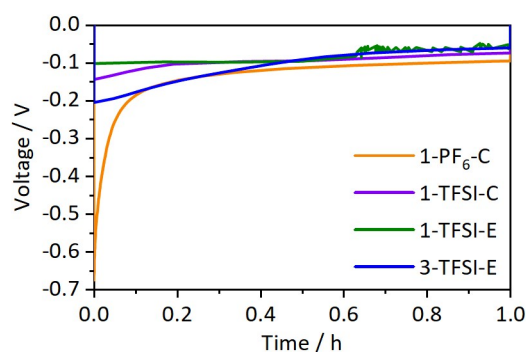


Figure S2: Development of the overvoltage of the first discharge step at a current density of 0.5 mA cm^{-2} in symmetrical Li||Li thin film pouch cells containing 1-PF₆-C (1 M LiPF₆ in EC:DEC, 3:7, orange), 1-TFSI-C (1 M LiTFSI in EC:DEC, 3:7, purple), 1-TFSI-E (1 M LiTFSI in DME:DOL, 1:1, green), and 3-TFSI-E (3 M LiTFSI in DME:DOL, 1:1, blue), respectively.

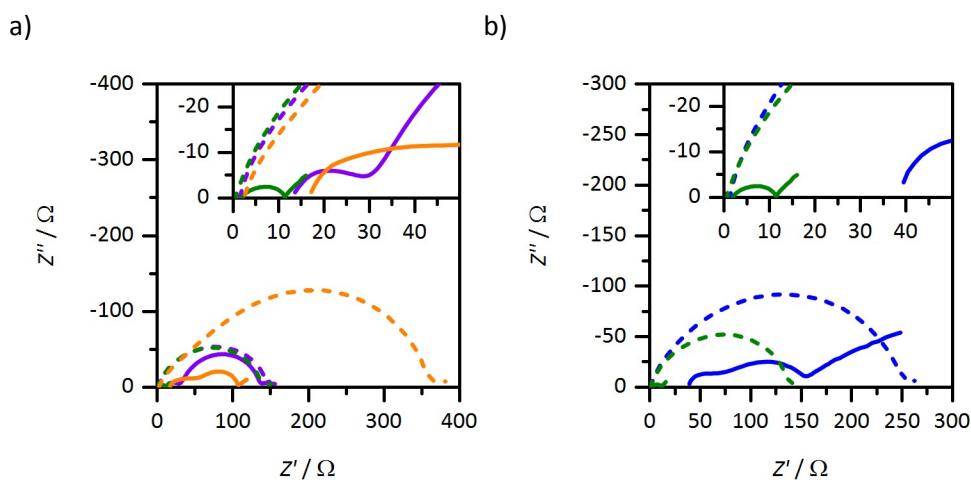


Figure S3: Impedance development of symmetrical Li||Li thin film pouch cells containing 1-PF₆-C (1 M LiPF₆ in EC:DEC, 3:7, orange), 1-TFSI-C (1 M LiTFSI in EC:DEC, 3:7, purple), 1-TFSI-E (1 M LiTFSI in DME:DOL, 1:1, green), and 3-TFSI-E (3 M LiTFSI in DME:DOL, 1:1, blue) before (dashed) and after (solid) 300 cycles at 0.5 mA cm^{-1} .

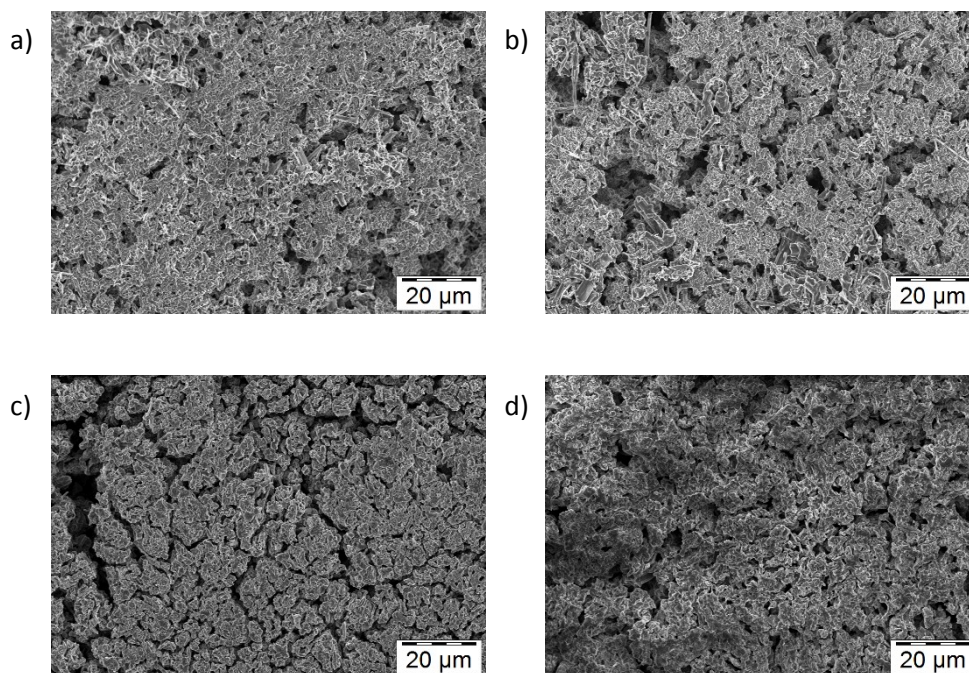


Figure S4: SEM images of lithium electrodes (WE) after 300 cycles at a current density of 0.5 mA cm^{-2} in symmetrical Li||Li thin film pouch cells with a) 1-PF₆-C, b) 1-TFSI-C, c) 1-TFSI-E and d) 3-TFSI-E.

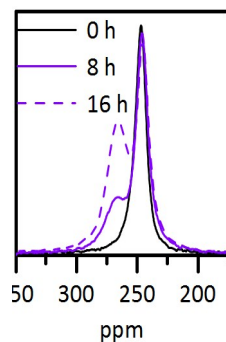


Figure S5: ⁷Li-NMR spectrum of a Li||Li thin film pouch cell containing 1-TFSI-C after 0 hour (one peak at 246 ppm), 8 hours (one peak at 246 ppm, one peak at 268 ppm) and 16 hours (one peak at 246 ppm, one peak at 266 ppm).

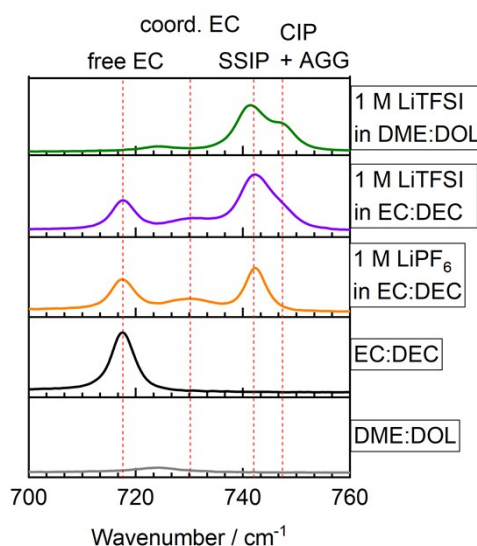


Figure S6: Raman spectra between 700 cm^{-1} and 800 cm^{-1} of DME:DOL (1:1, grey), EC:DEC (3:7, black), 1-PF₆-C (1 M LiPF₆ in EC:DEC, 3:7, orange), 1-TFSI-C (1 M LiTFSI in EC:DEC, 3:7, purple), and 1-TFSI-E (1 M LiTFSI in DME:DOL, 1:1, green). Both, uncoordinated TFSI⁻ and uncoordinated PF₆⁻ are visible at 740 to 742 cm^{-1} while the coordinated anion is shifted to higher wavenumbers.

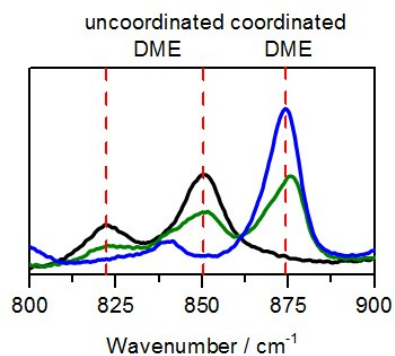


Figure S7: Raman spectra between 800 cm^{-1} and 900 cm^{-1} of DME:DOL (1:1, black), 1-TFSI-E (1 M LiTFSI in DME:DOL, 1:1, green) and 3-TFSI-E (3 M LiTFSI in DME:DOL, 1:1, blue).

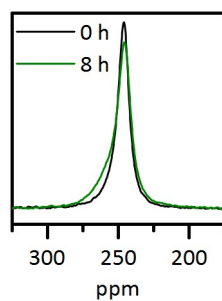


Figure S8: ^7Li -NMR spectrum of a $\text{Li} \parallel \text{Li}$ thin film pouch cell containing 1-TFSI-E after 0 and 8 hours, cycled with the application of an external pressure.