

Supporting Information

Anions with a Dipole: Towards High Transport Number in Solid Polymer Electrolytes

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Table S1. Measured parameters and calculated crystallinity degree for the phase behavior for the as-prepared electrolytes.

Sample	T_g / °C ^[a]	T_m / °C	ΔH / J g ⁻¹	χ_c ^[b]
LiTFSI/PEO (20)	-36	55	61.9	42
LiTFEMSI/PEO (64)	-41	70	133.4	75
LiTFEMSI/PEO (20)	-29	63	79.6	53
LiTFEMSI/PEO (16)	-35	54	38.1	38
LiTFEMSI/PEO (8)	-32	-	-	-

^[a] The values are calculated as the onset of the glass transition.

^[b] The values were calculated by Equation 1.

Table S2. Measured parameters and calculated Li-ion transference number for LiTFSI/PEO and LiTFEMSI/PEO electrolytes.

Sample ^[a]	$\Delta V/\text{mV}$	$I_0 / \mu\text{A}$	$I_{\text{ss}} / \mu\text{A}$	R_0 / Ω	R_{ss} / Ω	$T_{\text{Li}^+}{}^{[a]}$
LiTFSI/PEO (20)	10	117.0	35.0	66.3	59.3	0.19
LiTFEMSI/PEO (20)	10	38.0	33.6	228.4	237.3	0.64

^[a] The values were calculated by Equation 2.

Table S3. The best-fitted results of the EIS spectra using the simplified equivalent circuit in Figure S5 for Li⁺ symmetric cells with LiTFSI/PEO and LiTFEMSI/PEO-based electrolytes.

Electrolyte	T / h	R _b / Ω cm ²	R _i / Ω cm ²
LiTFSI/PEO (20)			
	0	23	39
	40	24	47
	80	23	53
	120	22	55
	160	22	57
	200	21	59
	280	12	1
	360	-	-
	440	-	-
	520	-	-
	600	-	-
	680	-	-
	760	-	-
LiTFEMSI/PEO (20)			
	0	74	32
	40	73	35
	80	72	37
	120	71	39
	160	71	39
	200	70	42
	280	69	43
	360	68	47
	440	68	51
	520	68	53
	600	67	57
	680	67	58

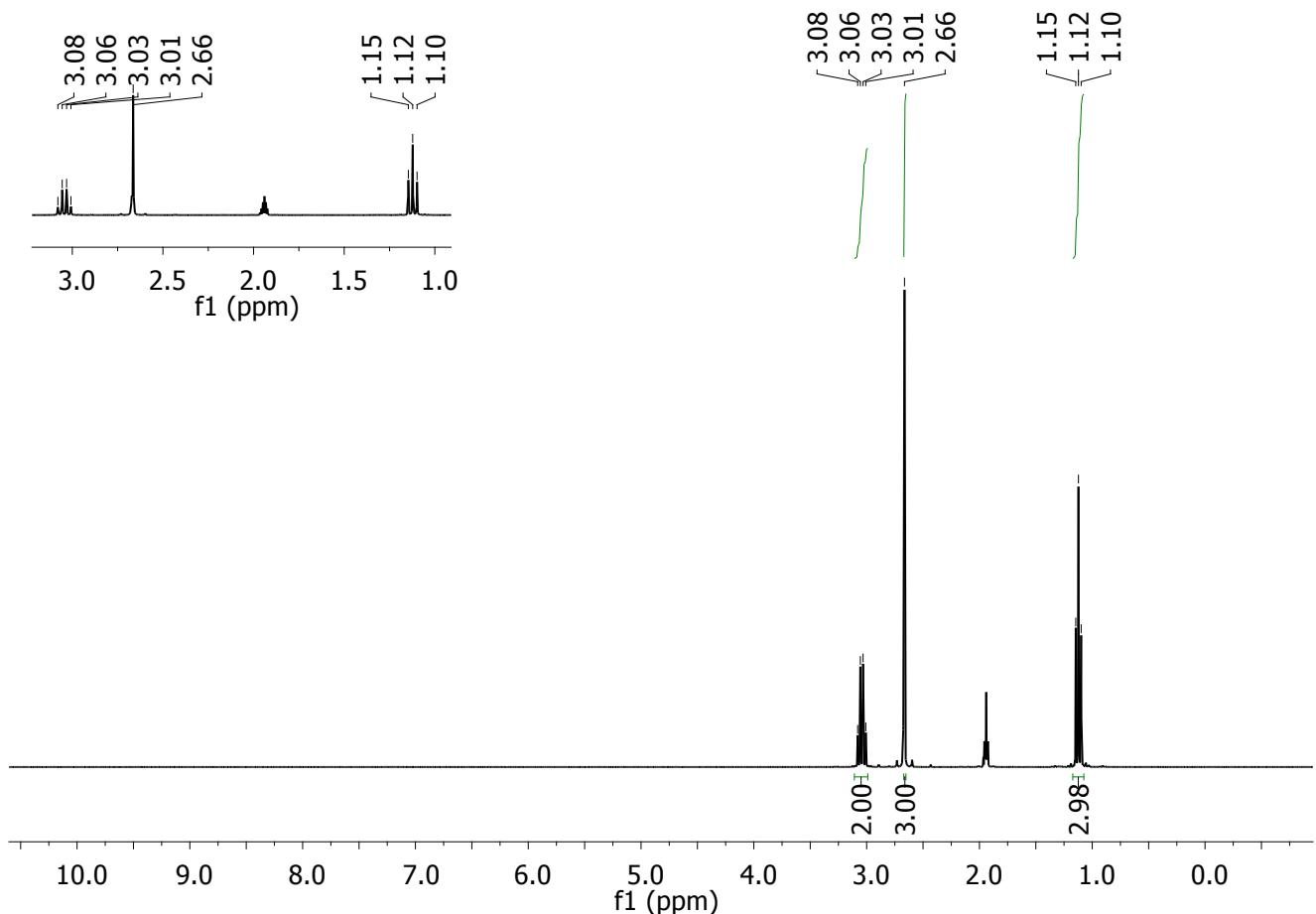


Figure S1a. ¹H NMR spectrum of LiTFEMSI.

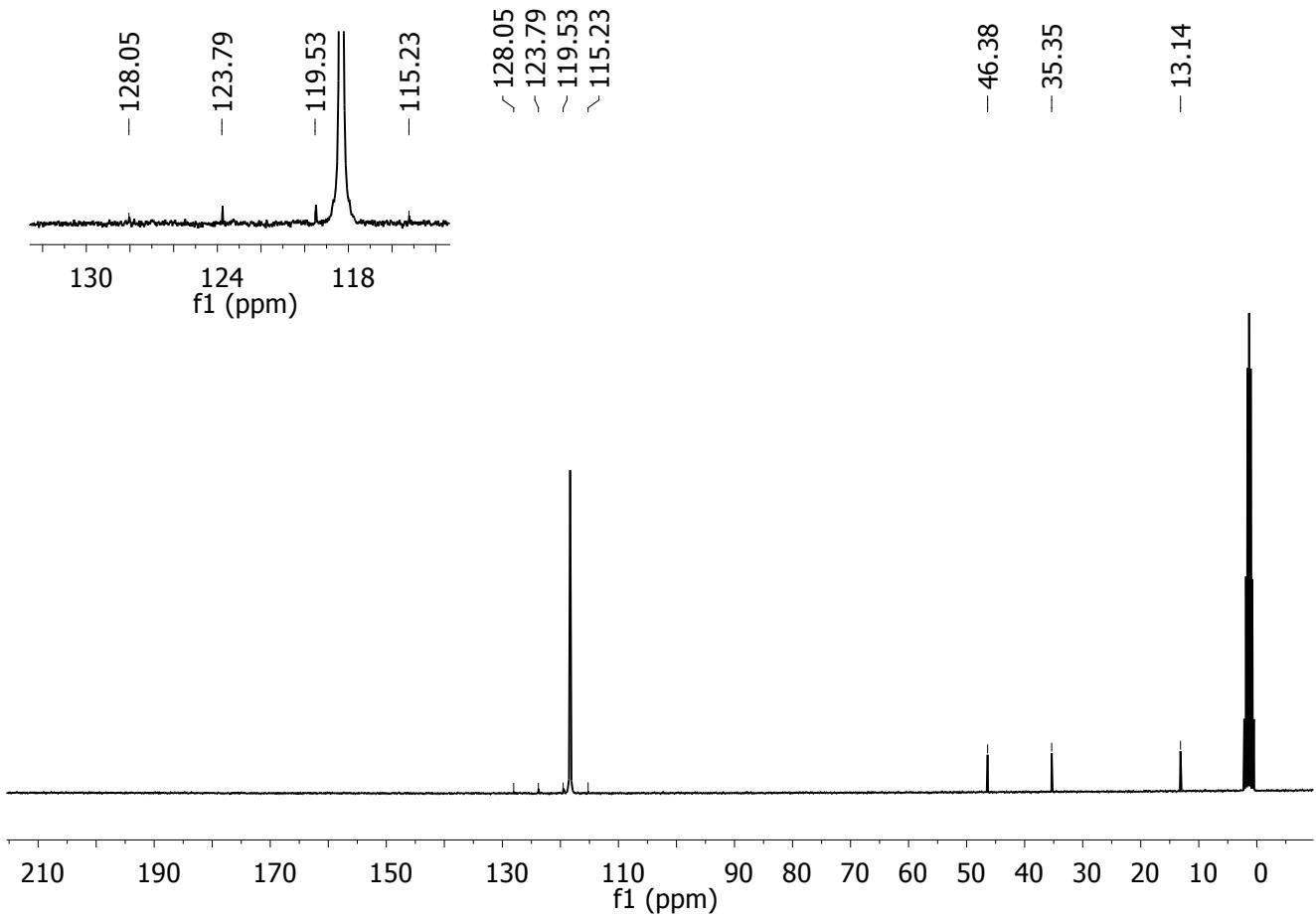


Figure S1b. ^{13}C NMR spectrum of LiTFEMSI.

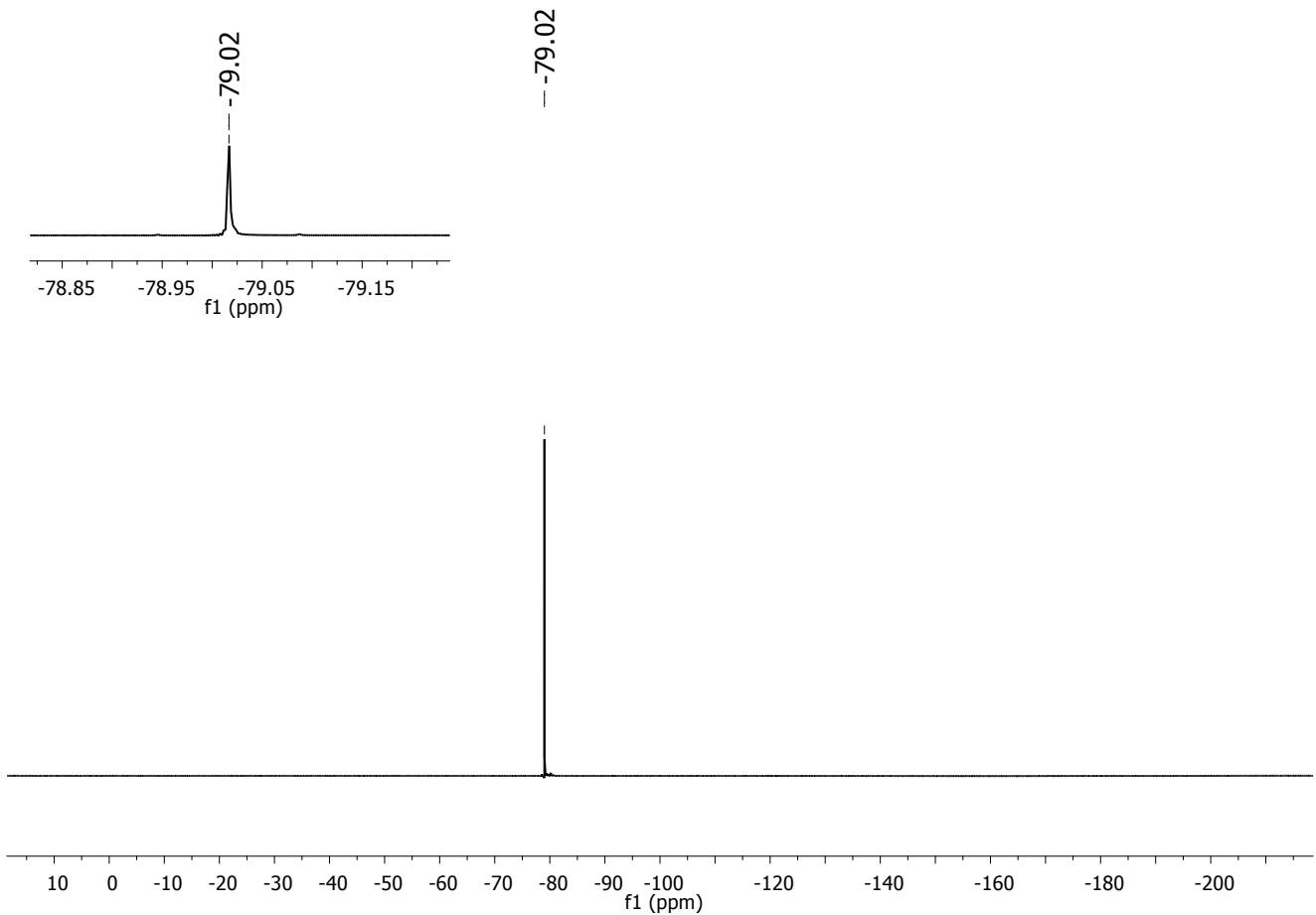


Figure S1c. ¹⁹F NMR spectrum of LiTFEMSI.

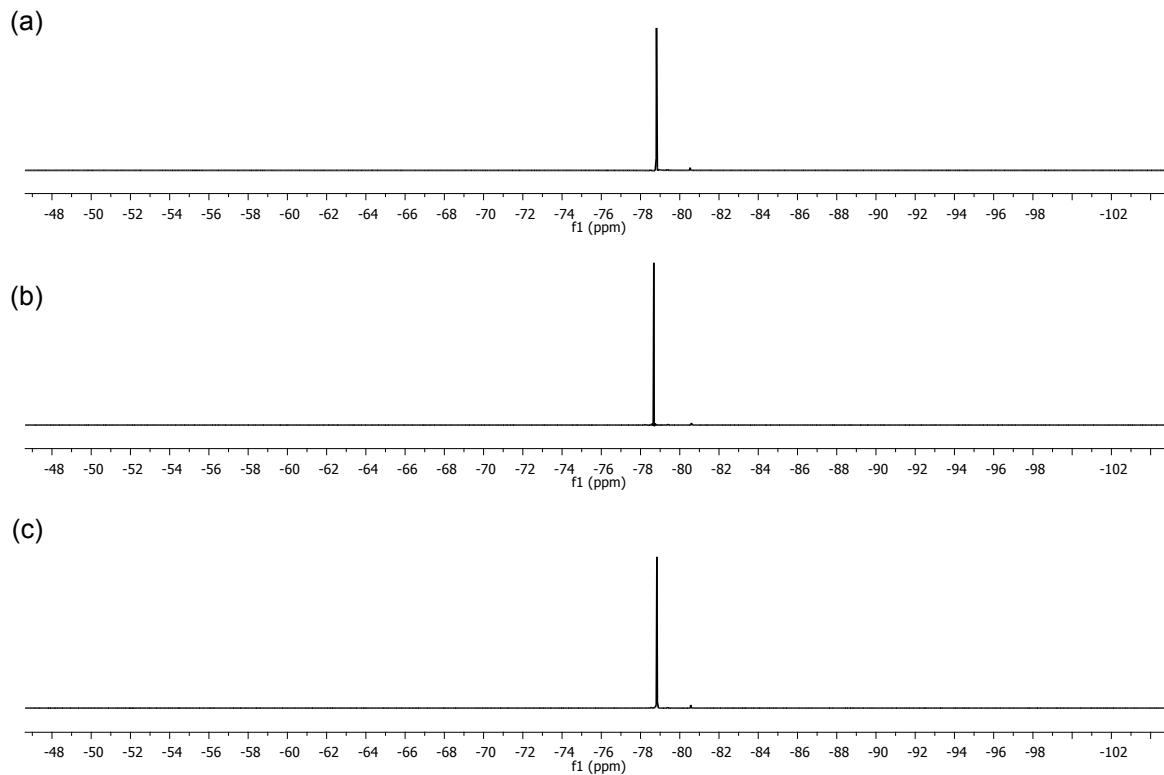


Figure S2. ^{19}F NMR spectra of the aqueous solution of LiTFEMSI under different conditions. (a) pristine solution, (b) solution being kept at 80 °C and pH = 2 for 7 days, (c) solution being kept at 80 °C and pH = 12 for 7 days.

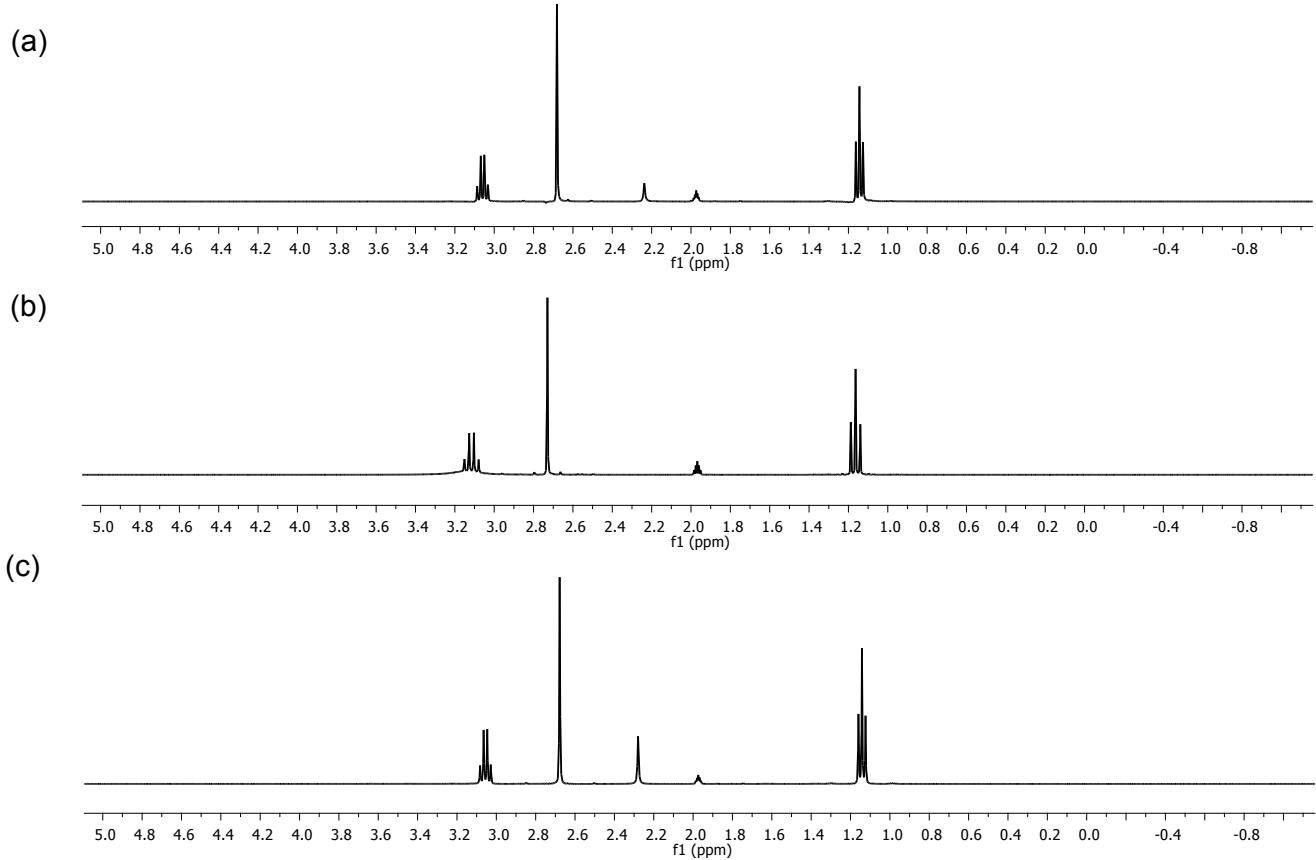


Figure S3. ^1H NMR spectra of the aqueous solution of LiTFEMSI under different conditions. (a) pristine solution, (b) solution being kept at 80 °C and pH = 2 for 7 days, (c) solution being kept at 80 °C and pH = 12 for 7 days.

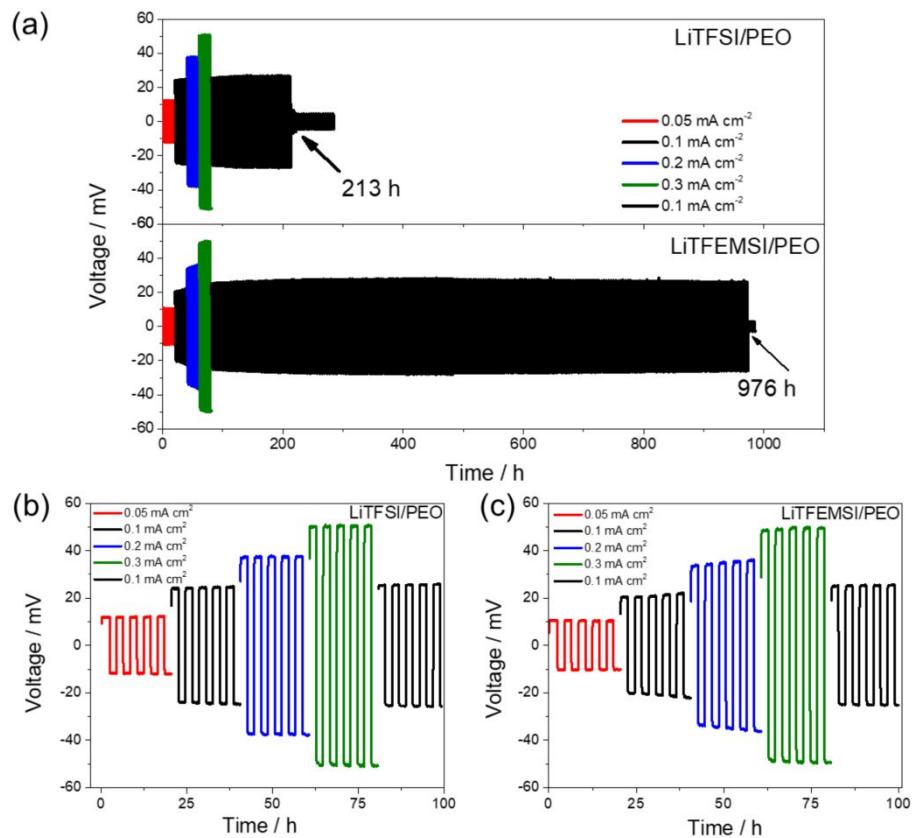


Figure S4. **a)** Galvanostatic cycling performance for the Li° symmetric cells at 70 °C at various current densities for the reference LiTFSI/PEO (20) and LiTFEMSI/PEO (20) electrolytes. Zoomed-in plots of the cycles at different current densities for **b)** LiTFSI/PEO and **c)** LiTFEMSI/PEO electrolytes.

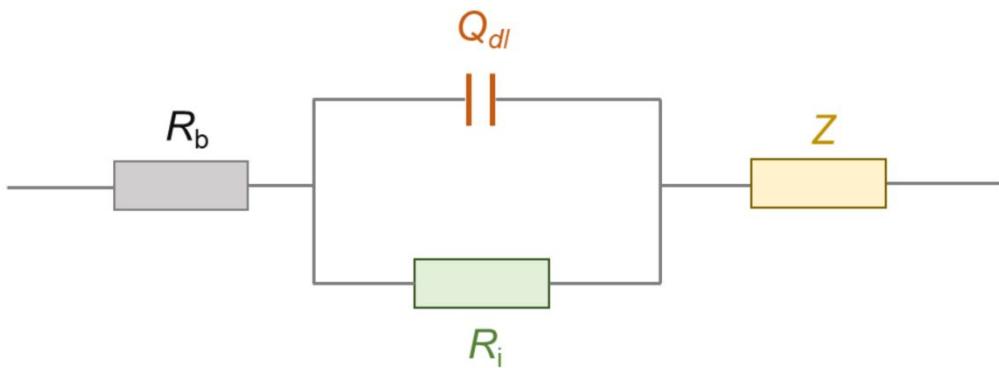


Figure S5. Equivalent circuit used for fitting the EIS spectra of Li symmetric cells. R_b is the bulk resistance, R_i is the interfacial resistance, Q_{dl} is the double layer capacity, and Z is the diffusive impedance, as detailed in previous work [1,2].

References

- Appetecchi, G.B.; Passerini, S., Poly(ethylene oxide)-LiN[SO₂CF₂CF₃]₂ polymer electrolytes: II. characterization of the interface with lithium, *J. Electrochem. Soc.* 2002, 149, A891-A897.
- Zhang, H.; Liu, C.; Zheng, L.; Xu, F.; Feng, W.; Li, H.; Huang, X.; Armand, M.; Nie, J.; Zhou, Z., Lithium bis(fluorosulfonyl)imide/poly(ethylene oxide) polymer electrolyte. *Electrochim. Acta* 2014, 133 (0), 529-538.