

## [Supporting Information]

# Factors Influencing Fast Ion Transport in Glyme-based Electrolytes for Lithium–Air Batteries

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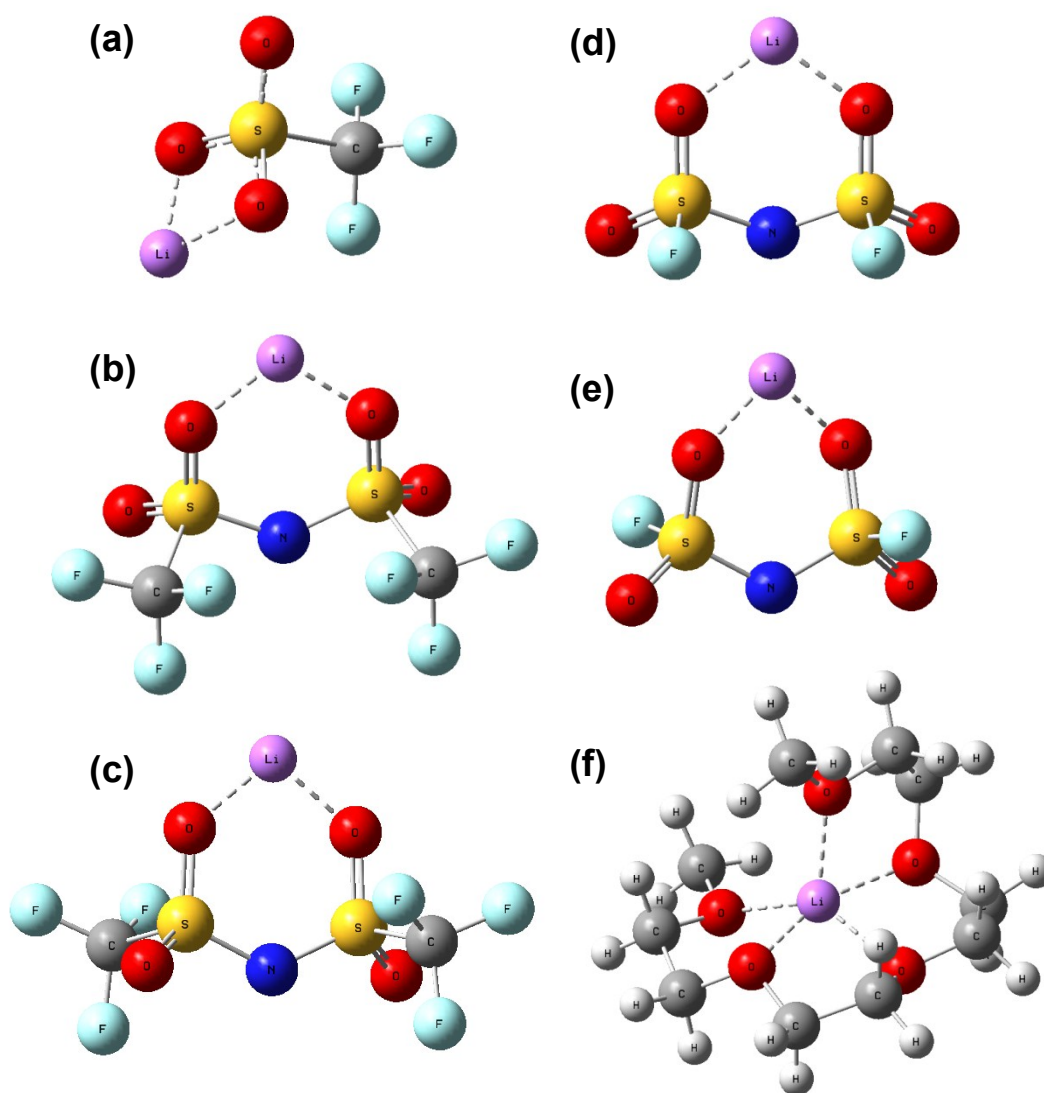
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**Table S1.** Self-diffusion coefficients  $D$  of ions and G4 solvent and transference number of cations  $t_{\text{Li}^+}$  at each measured temperature

Electrolyte		Self-diffusion coefficient / $10^{-10} \text{ m}^2 \text{ s}^{-1}$			Transference
		$D_{\text{G4}}$	$D_{\text{Li}^+}$	$D_{\text{anion}}$	number of cation
					$t_{\text{Li}^+}$
1.0 M LiOTf/G4	333 K	3.4	2.1	2.2	0.49
	323 K	2.6	1.5	1.6	0.48
	313 K	1.9	1.1	1.2	0.48
	303 K	1.4	8.0	0.84	0.49
1.0 M LiTFSI/G4	333 K	2.5	1.9	2.0	0.49
	323 K	2.0	1.4	1.6	0.47
	313 K	1.5	1.0	1.2	0.46
	303 K	1.1	0.70	0.88	0.44
1.0 M LiFSI/G4	333 K	2.7	1.8	2.6	0.41
	323 K	2.2	1.4	1.8	0.44
	313 K	1.6	1.0	1.3	0.44
	303 K	1.2	0.73	0.97	0.43
0.50 M LiTFSI/G4	333 K	4.3	3.1	3.1	0.50
	323 K	3.4	2.2	2.6	0.46
	313 K	2.7	1.6	1.9	0.46
	303 K	1.9	1.1	1.3	0.46
2.0 M LiTFSI/G4	333 K	0.83	0.79	0.81	0.49
	323 K	0.59	0.53	0.59	0.47
	313 K	0.40	0.35	0.40	0.47
	303 K	0.26	0.22	0.25	0.47
2.7 M LiTFSI/G4	333 K	0.42	0.43	0.43	0.50
	323 K	0.30	0.30	0.30	0.50
	313 K	0.19	0.20	0.19	0.51
	303 K	0.12	0.12	0.12	0.50

**Table S2.** Viscosity  $\eta$  of G4-based electrolytes at each measured temperature

Electrolyte		Viscosity $\eta$ / mPas	Inverse of viscosity $\eta^{-1}$ / mPas <sup>-1</sup>
	333 K	3.6	0.28
1.0 M	323 K	4.5	0.22
LiOTf/G4	313 K	5.7	0.18
	303 K	7.4 <sub>5</sub>	0.13
	333 K	4.6	0.22
1.0 M	323 K	5.7	0.17
LiTFSI/G4	313 K	7.5	0.13
	303 K	10	0.10
	333 K	4.4	0.23
1.0 M	323 K	5.5 <sub>5</sub>	0.18
LiFSI/G4	313 K	7.2	0.14
	303 K	9.6	0.10
	333 K	2.7	0.37
0.50 M	323 K	3.3	0.30
LiTFSI/G4	313 K	4.1	0.24
	303 K	5.2	0.19
	333 K	13	0.075
2.0 M	323 K	18.5	0.054
LiTFSI/G4	313 K	26.5	0.038
	303 K	41	0.025
	333 K	25	0.039 <sub>5</sub>
2.7 M	323 K	35	0.028
LiTFSI/G4	313 K	53	0.019
	303 K	85	0.012



**Fig. S1.** Optimized geometries of the  $\text{Li}^+$ -anion and  $\text{G4-Li}^+$  complexes. (a)  $\text{Li}^+$ - $\text{OTf}^-$ , (b) cis-type  $\text{Li}^+$ - $\text{TFSI}^-$ , (c) trans-type  $\text{Li}^+$ - $\text{TFSI}^-$ , (d) cis-type  $\text{Li}^+$ - $\text{FSI}^-$ , (e) trans-type  $\text{Li}^+$ - $\text{FSI}^-$ , and (f)  $\text{G4-Li}^+$  (5 coordination). B3LYP/6-311+G\*\*.