Electronic Supplementary Material (ESI) for Energy Advances.

A comparison of the impact of cation chemistry in ionic liquid-based lithium battery electrolytes

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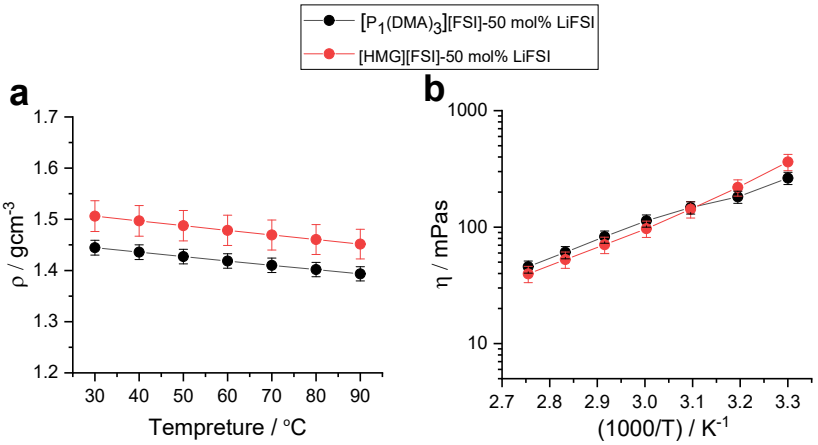

Figure S1. Densities and viscosities of $[P_1(DMA)_3][FSI]$-50 mol% LiFSI, [HMG][FSI]-50 mol% LiFSI solutions as a function of temperature

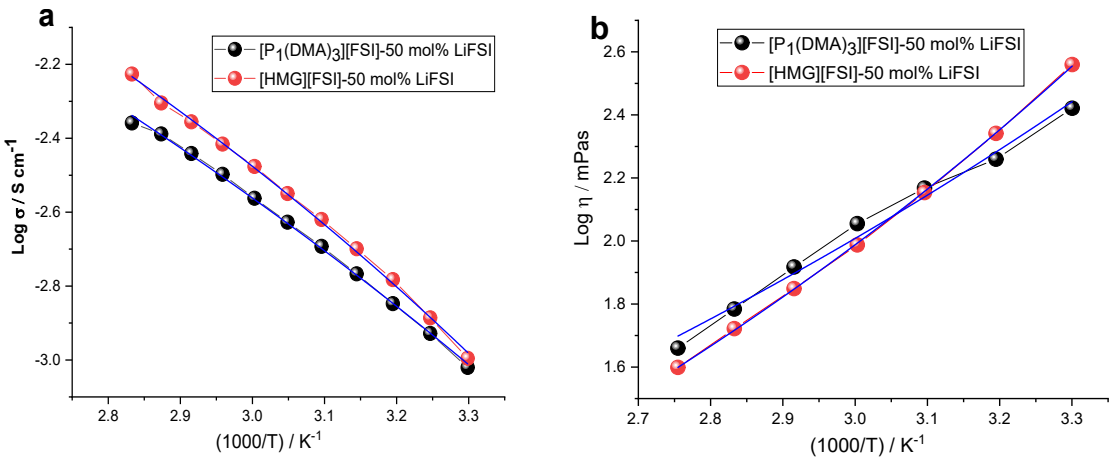

Figure S2. VFT plot of a) conductivities b) viscosity, for [HMG][FSI]-50 mol% LiFSI, and [P1(DMA)3)][FSI]-50 mol% LiFSI

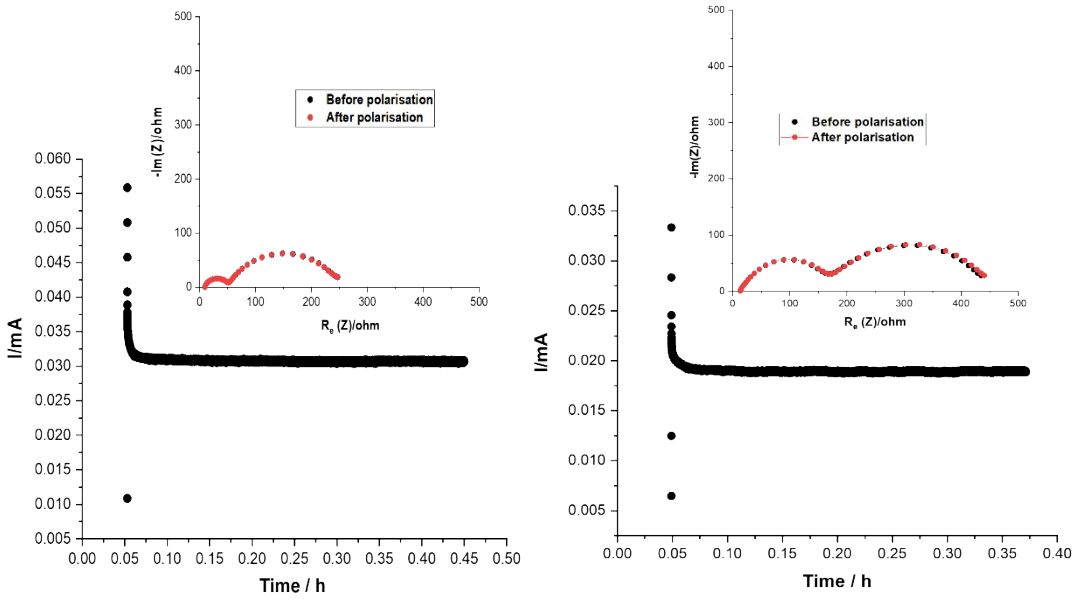

Figure S3. Chronopotentiometry (V= 0.1 V) of Li symmetrical cells a) $[P_1(DMA)_3][FSI]$-50 mol% LiFSI, b) [HMG][FSI]-50 mol% LiFSI, $[P_{111i4}][FSI]$-50 mol% LiFSI, at 50 °C. Inset shows EIS plots before and after polarisation.

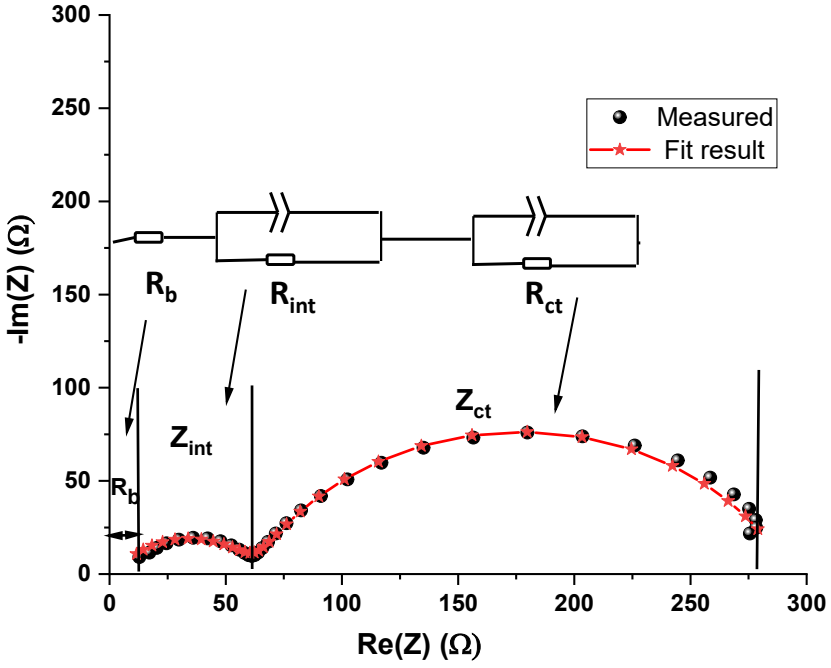

Figure S4. Example of a fitted impedance spectrum gained from symmetrical lithium cell containing 50 mol% LiFSI in [HMG][FSI] after 10th cycle, The spectrum is fitted to a two-element layer model equivalent circuit.

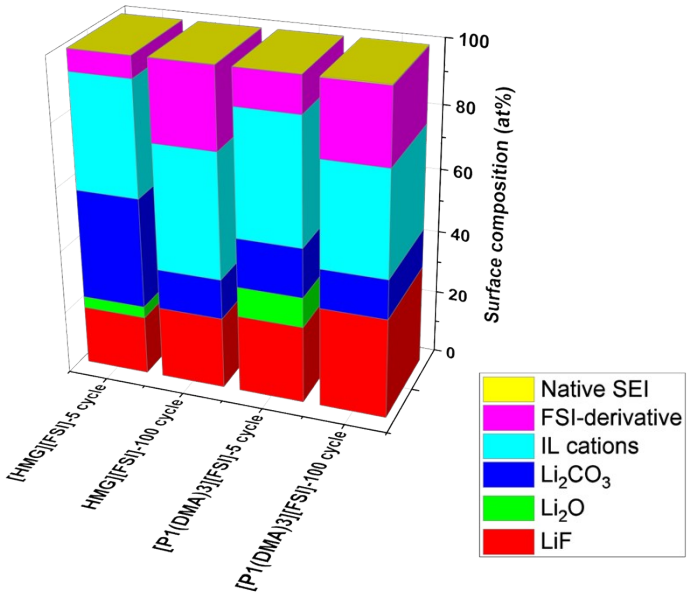

Figure S5. Surface composition (atomic %) spectra of the Li surface after 5 and 100 cycles using 50 mol% LiFSI in $[P_1(DMA)_3][FSI]$ and [HMG][FSI].

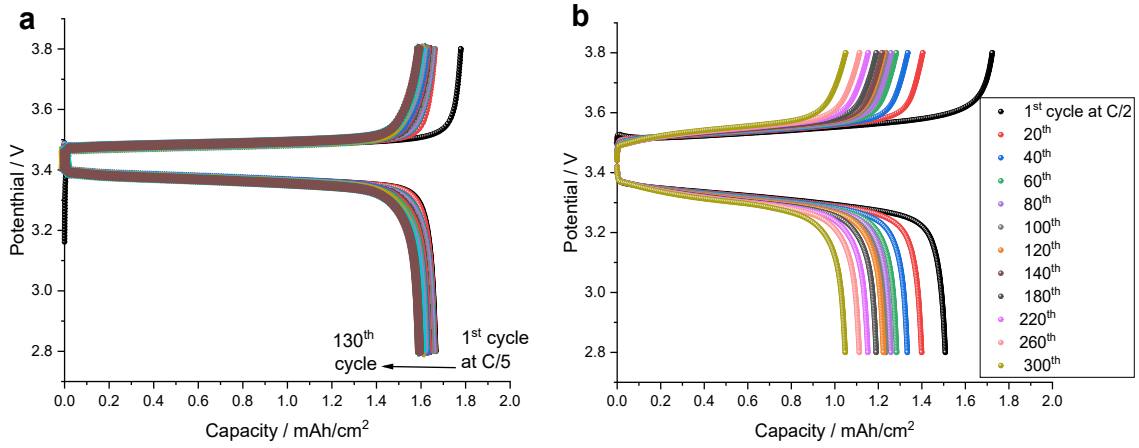

Figure S6. The charge/discharge curves of the $[P_1(DMA)_3][FSI]$-50 mol% LiFSI at a) C/5, b) C/2

Table S1. VFT fitting parameters extracted from the temperature dependent ionic conductivities.

	$\sigma_\circ$/ S cm^{-1}	B_σ/K	$T_{0,\sigma}$	D_σ	Tg-T_0	R^2
$[P_1(DMA)_3)][FSI]$-50 mol% LiFSI	0.14	560	192	2.9	0.4	0.999976
[HMG][FSI]-50 mol% LiFSI	0.23	575	197	2.9	14.4	0.999909

Table S2. VFT fitting parameters extracted from the temperature dependent viscosity.

	$\eta_\circ$/ mPa S	B_η/K	$T_{0,\eta}$	D_η	Tg-T_0	R^2
$[P_1(DMA)_3)][FSI]$-50 mol% LiFSI	0.2	850	170	5	20	0.979976
[HMG][FSI]-50 mol% LiFSI	0.35	892	174	5.1	41	0.999909

Table S3. Surface composition (atomic %) of the Li metal constituents after 5 and 100 cycles. estimated error for atomic compositions from region spectra is ±5%

	Li		F		O			C			N		
	LiF	**Li_2CO_3, Li_2O**	**LiF**	**$-SO_2F$, SF**	**Li_2O**	**Li_2CO_3**	**$N(SO_xF_y)$**	**C-H**	**C-N**	**C=N**	**-NS=O**	**IL cation**	**Native SEI**
[HMG][FSI]-**5 cycled**	43%	57%	21%	79%	7%	65%	28%	80%	13%	7%	79.15%	14.55%	6.30%
[HMG][FSI]-**100 cycled**	68%	32%	79%	21%	-	12%	88%	75%	18%	7%	52.48%	41.64%	5.87%
$[P_1(DMA)_3]$[FSI]-**5 cycled**	68 %	32%	75%	25%	20%	21%	59%	75%	17%	9%	44.2%	52.5%	3.28%
$[P_1(DMA)_3]$[FSI]-**100 cycled**	86 %	14%	75%	25%	-	27%	73%	77%	15%	8%	54.39%	37.13	8.48%

Table S4. A summary of the use of high-salt content IL-based electrolyte in LMBs reported in the literature

[1] Araño K, Mazouzi D, Kerr R, Lestriez B, Le Bideau J, Howlett P C, Dupre N, Forsyth M and Guyomard D 2020 Editors' choice—understanding the superior cycling performance of Si anode in highly concentrated phosphonium-based ionic liquid electrolyte *Journal of The Electrochemical Society* **167** 120520

[2] Forsyth M, Girard G M, Basile A, Hilder M, MacFarlane D, Chen F and Howlett P 2016 Inorganic-organic ionic liquid electrolytes enabling high energy-density metal electrodes for energy storage *Electrochimica Acta* **220** 609-17

[3] Eftekharnia M, Hasanpoor M, Forsyth M, Kerr R and Howlett P C 2019 Toward practical Li metal batteries: importance of separator compatibility using ionic liquid electrolytes *ACS Applied Energy Materials* **2** 6655-63

[4] Pathirana T, Rakov D A, Chen F, Forsyth M, Kerr R and Howlett P C 2021 Improving Cycle Life through Fast Formation Using a Superconcentrated Phosphonium Based Ionic Liquid Electrolyte for Anode-Free and Lithium Metal Batteries *ACS Applied Energy Materials* **4** 6399-407

[5] Zhang H, Qu W, Chen N, Huang Y, Li L, Wu F and Chen R 2018 Ionic liquid electrolyte with highly concentrated LiTFSI for lithium metal batteries *Electrochimica Acta* **285** 78-85

[6] Lewandowski A, Hollenkamp A, Donne S and Best A 2010 Cycling and rate performance of Li–LiFePO4 cells in mixed FSI–TFSI room temperature ionic liquids *J. Power Sources* **195** 2029-35

[7] Hasanpoor M, Saurel D, Barreno R C, Fraysse K, Echeverría M, Jáuregui M, Bonilla F, Greene G W, Kerr R and Forsyth M 2022 Morphological Evolution and Solid–Electrolyte Interphase Formation on LiNi0. 6Mn0. 2Co0. 2O2 Cathodes Using Highly Concentrated Ionic Liquid Electrolytes *ACS Applied Materials & Interfaces* **14** 13196-205

[8] Evans T, Olson J, Bhat V and Lee S-H 2014 Effect of organic solvent addition to PYR13FSI+ LiFSI electrolytes on aluminum oxidation and rate performance of Li (Ni1/3Mn1/3Co1/3) O2 cathodes *J. Power Sources* **265** 132-9

[9] Chaudoy V, Ghamouss F, Jacquemin J, Houdbert J-C and Tran-Van F 2015 On the performances of ionic liquid-based electrolytes for Li-NMC batteries *J. Solution Chem.* **44** 769-89

[10] Heist A and Lee S-H 2019 Improved stability and rate capability of ionic liquid electrolyte with high concentration of LiFSI *Journal of The Electrochemical Society* **166** A1860

ILs	Salt	Concentration	Anode	Cathode	C-rate	Discharge capacity	T / °C	Cycle life	Cathode mass loading/capacity	Ref
$[P_{1222}][FSI]$	LiFSI	3.2 mol/kg	Si	NCA	C/5	3 mAh cm^{-2}	50			[1]
$[P_{1i444}][FSI]$	LiFSI	3.8 mol/kg	Li metal	NMC111	1C (0.25 mA/cm^2	130 mAh g^{-1}	RT	200	0.3 mAh/cm2	[2]
$[P_{1222}][FSI]$	LiFSI	3.2 mol/kg	Li metal	LFP	C/2	3.3 mAh/cm^2	50	120	3.5 mAh cm^{-2}	[3]
$[P_{1222}][FSI]$	LiFSI	3.2 mol/kg	Li metal	NMC622	C/2	1.7 mAh/cm^2		50	3.5 mAh cm^{-2}	[4]
$[C_{3m}pyr][FSI]$	LiTFSI	50 mol%	Li metal	LiCoO2	C/10	150 mAh g^{-1}	60	60	1.60 mg/ cm2= 0.25 mAh/cm2	[5]
$[C_{3m}pyr][FSI]$	LiTFSI	50 mol%		LiFePO4	C/10	125 mAh g^{-1}	RT	100	1.40 mg/ cm2= 0.20 mAh/cm2	[5]
$[C_{3m}pyr][FSI]$	LiFSI	3.2 mol/kg	Li metal	LFP	C/2	3.3 mAh/cm^2	50	280	3.5 mAh cm^{-2}	[3]
$[C_{3m}pyr][FSI]$	LiTFSI	0.5 mol/kg	Li metal	LFP	C/10	153 mAh g^{-1}	50	400	1.8 mg/cm2	[6]
$[C_{3m}pyr][FSI]$	LiFSI	3.2 mol/kg	Li metal	NMC622	C/2	0.98 mAh/cm^2	50	100	1 mAh/cm2	[7]
$[C_{3m}pyr][FSI]$	LiFSI	1.2 mol/L	Li metal	NMC111	C/10	150 mAh/g	25	20	3 mg cm^2	[8]
$[C_{4m}pyr][FSI]$	LiTFSI	1.0 mol/L	Li metal	NMC111	C/10	146 mAh/g	25	-	-	[9]
$[C_{3m}pyr][FSI]$	LiFSI	4.2 mol/kg	Li metal	NMC811	1C	125 mAh/g	22	1000	6.0–6.5 mg cm^{-2}	[10]