Supplementary information

Interphase control for high performance lithium metal batteries using ether aided ionic liquid electrolyte

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Fig. S1: (a) Flammability test conducted by soaking the separator with electrolytes and holding the fire source for 10 secs. (i) 100IL electrolyte after 1 sec of ignition, (ii) after 10 secs of ignition, (iii) 80IL20DME electrolyte after 1 sec of ignition, (iv) after 10 secs of ignition. In all the cases, the electrolytes did not catch fire which proves their non-flammability. (b) Wettability of separator (3501) before and after the soaking of the electrolyte (i)100IL and (ii) 80IL20DME electrolyte, Contact angle measurement of (iii)100IL and (iv) 80IL20DME where the contact angle is lesser for the hybrid 80IL20DME suggesting higher wettability of the electrolyte.



Fig. S2: Long-term NMC811|Li cell cycling using 80IL20DME electrolyte at 50 °C within the potential range 2.8 V- 4.4 V at a current density of 0.5 mA/cm² after two formation cycles at 0.1 mA/cm². NMC811 has an areal loading ~6.4 mg/cm² and a thin Li source (50 μm) was used to study the cell cycling.



Fig. S3: Comparison of NMC622|Li cell cycling using 80IL20DME electrolyte at room temperature and 50 °C within the potential range 2.8 V- 4.3 V at a current density of 0.5 mA/cm² after two formation cycles at 0.1 mA/cm². NMC622 has an areal loading ~6 mg/cm² and a thin Li source (50 μm) was used to study these cells cycling.



Fig. S4: (a) Voltage profile of NMC622 (mass loading ~ 22.4 mg/cm²) vs. Li (thickness 100μm) cell cycling using 80IL20DME electrolyte at room temperature, (b) Long term cell cycling until cell failure



Fig. S5: (a) Rate performance of NMC622 (cathode areal loading ~22.4 mg/cm²) vs. Li (thickness 100µm) cell cycling at room temperature at a constant charge rate 0.5 mA/cm² with different discharge rates, (b) Constant discharge rate of 0.5mA/cm² with different charge rates.



Fig. S6: (a) Voltage profile and (b) long term cycling of NMC622 (mass loading ~ 22.4 mg/cm²) vs. Cu cell using 80IL20DME electrolyte at room temperature, (c) Li metal plating/stripping profile on Cu working electrode, (d) Li plating/stripping coulombic efficiency.

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References	Electrolyte	Anode free system	LIRR
Fan et al., Nature	1 M LiPF_6 in	Cu NMC811	96.6%*
Nanotechnology, 2018 ¹	FEC/FEMC/HFE		(30 cycles)
	(2:6:2)		
Weber et al., Nature Energy,	1 M LiDFOB+	Cu NMC532	99.8%*
2019 ²	0.2 M LiBF ₄ in		(50 cycles)
	FEC/DEC (1:2)		
Alvarado <i>et al., Energy</i> &	2.3 m LiTFSI+	Cu NMC622	98.9%*
<i>Environmental Science</i> , 2019 ³	4.6 m LiFSI in		(54 cycles)
	DME		
Lin et al., Angewandte Chemie,	6 m LiFSI in	Cu Li _{1.31} NMC811	99.83%
2021 4	DME		(100 cycles)
This work	3.2 m LiFSI in	Cu NMC 622	99.2%#
	80IL20DME		(50 cycles)

 Table S1. Comparison of LIRR values using state-of-the art electrolytes for anode free systems

*The LIRR values of these systems reported in the respective articles have been adapted from the work summarised by Nanda *et al.* ⁵

[#]Our work has been carried out between the potential range 4.3V and 3V which suggests a 90% depth of discharge ⁶.

System with	Total	Total	Discharge	Average	Stack	Energy
80IL20DME	thickness	weight	capacity	voltage of	specific	density
electrolyte	of stack	of stack	mAh/cm ²	discharge	energy	(Wh/l)
	(µm)	(mg/cm ²)	(after	curve (after	(Wh/kg)	
			formation	formation		
			cycle)	cycle)		
				(V)		
NMC622 Li	355	59	3.86	3.67	480	798
Cu NMC622	263	61	3.98	3.74	488	1132

Table S2. Parameters for stack energy density (ED) calculation

The theoretical stack energy density (ED) has been calculated where the stack is considered as double side coated high loading NMC cathode and Al current collector (NMC622|Al|NMC622), two layers of separator, and the Li metal anode (thickness 100 μ m). The mass of electrolyte was not included in the calculation to allow the comparison with literature reports. In the anode free cell, Li metal was replaced by a Cu current collector (thickness 8 μ m). The above parameters are considered for discharged cell configuration. This stack design has been adopted from the work by Dahn and co-workers ⁷.



Fig. S7: NMC622 (mass loading ~ 22.4 mg/cm²) vs Li cell cycling using 100IL and 80IL20DME electrolytes at a high current density of 1.75 mA/cm² at elevated temperature 50 °C. The cycling were carried out after two formation cycles at 0.35 mAh/cm² current density. Elevated temperature was chosen to facilitate the neat IL (100IL) electrolytes' cycling since it

is very viscous at room temperature (see the table below for other physical properties).

Chemical Composition	Electrolyte Name	Bulk ionic conductivity (mS/cm)	Ionic conductivity with separator (mS/cm)	Viscosity (mPa.S)	Density (g/cc)	⁷ Li Diffusivity (m ² /s)
3.2m LiFSI in C3mpyrFSI IL	100IL	0.66	0.07	450	1.55	2.7E-12
3.2m LiFSI in C3mpyrFSI IL/DME 80/20 (wt%)	80IL20DME	2.37	0.76	92	1.43	1.22E-11

Table S3. Physical properties of ionic liquid electrolytes at 20 $^\circ\mathrm{C}$ 8



Fig. S8: a) EIS plot after 10 cycles in Li|Li symmetrical cell, b) R_{electrolyte} vs. cycle number, c) R_{SEI} vs. cycle number using 100IL (black) and 80II20DME (red) electrolytes



Fig. S9: Comparison of XPS spectra of S 2p, N 1s and F 1s of post cycling Li|Li symmetrical cell after 100 cycles by using 100IL and 80IL20DME electrolytes.



Fig. S10: Comparison of XPS spectra of C 1s, O 1s, Li 1s, S 2p, N 1s and F 1s on Li metal anode after 50 cycles of NMC622 vs. Li cell by using 100IL and 80IL20DME electrolytes at a current density of 1.75 mA/cm².



Fig. S11: XPS spectra of (a) Ni 2p and (b) Mn 2p after 50 cycles at 1.75 mA/cm² current density using 80IL20DME electrolyte; (c) Ni 2p and (d) Mn 2p after 50 cycles at 1.75 mA/cm² current density using 100IL electrolyte. Both the electrolytes show no Ni and Mn dissolution after cycling.



Fig. S12: Radial distribution function (RDF) and coordination number calculated between selected Li⁺ and FSI (N_{FSI}) or Li⁺ and DME (O_{DME}) in different Z intervals of [0.0 : 0.6] nm from the Li electrode surface. (a) Li-N_{FSI} RDFs for 100 IL, (b) Li-N_{FSI} RDFs for 80IL20DME, (c) Li-O_{DME} RDFs for 80IL20DME.



Fig. S13. Optimized geometries, energies of molecular orbitals, and calculated biding energy at MP2/6-311++G(d,p) level for (a-b) trans and (d-f) cis conformation [Li(FSI)₃]⁻² complexes with 2:1, 1:2, and 0:3 coordination A₂/A₃ ratio found in the innermost layer of 100IL and 80IL20DME systems. The color codes of atoms are as follows: lithium (violet), nitrogen (dark blue), sulfur (yellow), oxygen (red), fluorine (light blue). Optimized geometries, energies of molecular orbitals, and calculated biding energy at MP2/6-311++G(d,p) level for (g, h) trans and (i, j) cis conformation [Li(DME)(FSI)₂]⁻¹ complexes 1:1, and 0:2 coordination A₂/A₃ ratio for FSI⁻ anions. The color codes of atoms are as follows: lithium (violet), nitrogen (dark blue), sulfur (yellow), oxygen (red), fluorine (light blue), carbon (brown), white (hydrogen). Quantum calculation were carried out with the Gaussian (G09) package using density functional theory (DFT)⁹. The geometrical structures and vibrational modes of all single ions and molecules were calculated at Møller-Plesset second order perturbation theory level (MP2) with a 6-31+G(d,p) basis set in a gas phase, whereas less computationally expensive M05-2X/6-31+G(d,p) method was applied for large clusters ¹⁰. Total energies of clusters and their frontier orbitals were obtained via single point calculations with polarizable basis set MP2/6-311++G(d,p) ^{11,12}. The cluster binding energy of [Li(FSI)₃]⁻² and [Li(DME)(FSI)₂]⁻¹ was $E_{binding} = E_{total} \left(\left[Li(FSI)_3 \right] \right]^{-2} \right) - E_{total} \left(Li^+ \right) - 3 * E_{total} (FSI)$ calculated as and $E_{binding} = E_{total} \left(\left[Li(DME)(FSI)_2 \right] \right]^{-1} \right) - E_{total} \left(Li^+ \right) - E_{total} (DME) - 2 * E_{total} (FSI)_2 \right)$ respectively.

Table S4. The composition of the innermost layer of 100IL and 80IL20DME within 0.60 nm from the Li(100) top surface. The number of each species was averaged from the whole 40 ns of MD trajectory.

Electrolyte type	Composition	Interface	Interface	Interface
	(Ions/Molecules)	composition at	composition at	composition at -
		$0 \ \mu C/cm^2$	-6.0 μC/cm ²	14.4 μC/cm ²
100IL	C3mpyr ⁺	17.65	24.0	6.73
	FSI [_]	34.59	23.61	46.72
	Li+	19.53	12.06	57.85
80IL20DME	C3mpyr ⁺	18.20	17.05	14.0
	FSI [_]	29.33	29.33 20.04	
	Li ⁺	15.50	19.0	43.0
	DME	5.19	14.01	5.65

Table S5. Simulated and experimental mass density (g/cm³) for 100IL and 80IL20DME at 298, 323,and 393 K. The error of density is calculated based on $(D_{MD}-D_{exp})/D_{exp} \times 100\%$.

Temperature, K	100IL			80IL20DME		
	MD,	Exp,	Error, %	MD,	Exp,	Error,
	g cm ⁻³	g cm ⁻³		g cm ⁻³	g cm ⁻³	%
298	1.552	1.54	0.77	1.448	1.418	2.11
323	1.53	1.52	0.65	1.442	1.399	3.07
393	1.462	_	_	1.353	—	_

Molecular Dynamics Simulation Details

Initially, the bulk phase of 100IL and 80IL20DME was analysed based on 216 ion pairs randomly packed in cubic simulation box using Packmol code ¹³. All electrolytes were equilibrated firstly at 293, 323 and 393 K for more than 10 ns using the NPT ensemble and the Nose-Hoover and Parrinello-Rahman methods for temperature and pressure coupling. The densities were calculated through additional 7 ns MD trajectory. The pressure is 1 bar. The electrostatic interactions were computed using PME methods. A FTT grid spacing of 0.1 nm and cubic interpolation for charge distribution were used to compute electrostatic interaction in reciprocal space. The cut-off distance of 1.2 nm was adopted for electrostatics and Van der Waals interactions. The LINCS algorithm was used to constrain the C-H bond. The Velocity Verlet integrator was adopted with a time step of 1 fs.

For the interface simulation, 600 ion pairs were used in the simulation box. The x and y dimensions of simulation box were fixed at 4.21 nm, while z dimension of the electrolytes were decided based on bulk phase densities calculated at 393 K. The extra vacuum space of two electrodes separation distance was adopted to compensate for image charge effect resulting from simulation in slab geometry ¹⁴ (Figure 8, supplementary). The electrodes charging was assigned by uniform distribution of elementary charges within the top layer of Li (100) surface (where, $\pm 16.0 \,\mu\text{C/cm}^2 = \pm 1.0 \,\text{e/nm}^2$). The initial annealing procedure of 12 ns was applied by gradually changing the temperature from 393 K to 700 K and back to 393 K in order to provide sufficient dynamic and reasonable interfacial structure ¹⁵. Then, the 40 ns NVT production run was conducted at 393 K. The short-range ion-surface interactions were calculated by PPE summation method with FFT grid spacing of 1.2 nm ¹⁶. Trajectory was written every 2 ps and analysed with MDAnalysis code whenever particular tool was unavailable in GROMACS package ¹⁷.



Fig. S14. Simulation box representation for Li (100) | 80IL20DME |Li (100) at 393 K.

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