Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Application of super-concentrated phosphonium based ionic liquid electrolyte for anode-free lithium metal batteries

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– Supplementary information

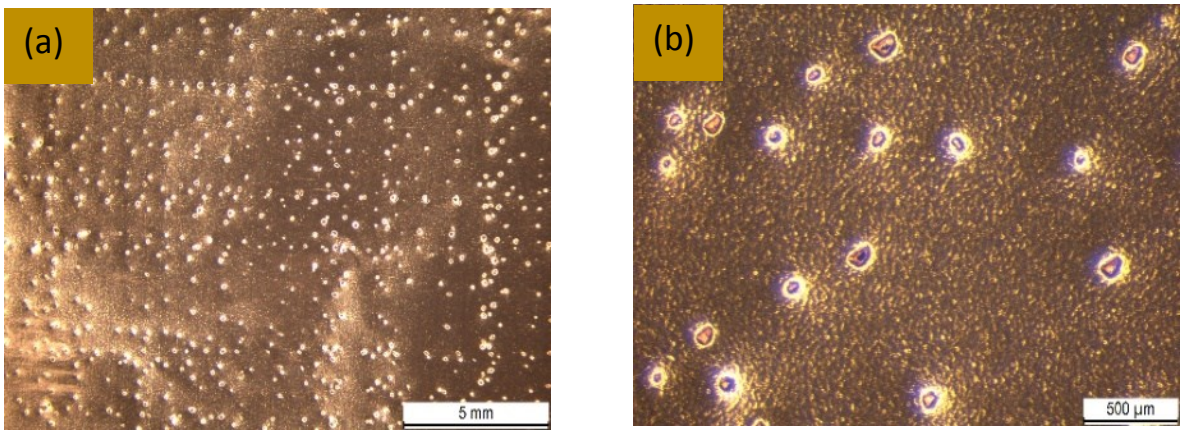

Figure S1: digital images of (a) and (b) micro-patterned copper foil

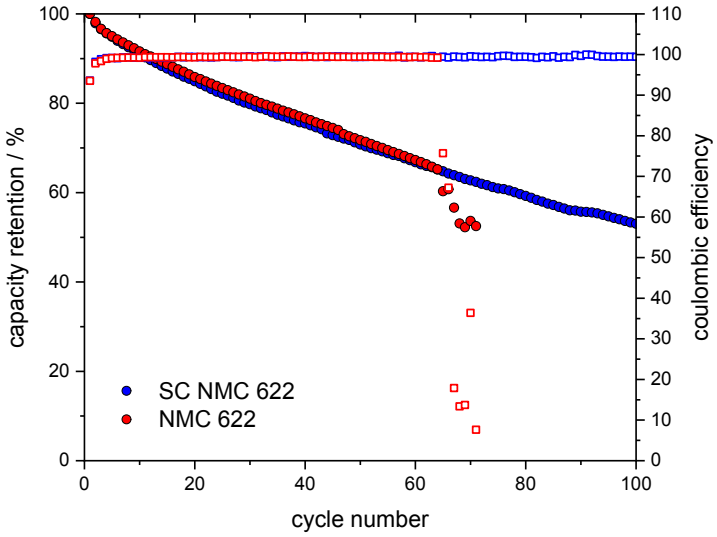

Figure S2: Capacity retention and coulombic efficiency for polycrystalline NMC 622 || p-Cu (red) and single crystal NMC 622 || p-Cu (blue) at C/2 (1.75 mA/cm^2) and 100 cycles at 50 °C. Polycrystalline cells started to fail after 65 cycles.

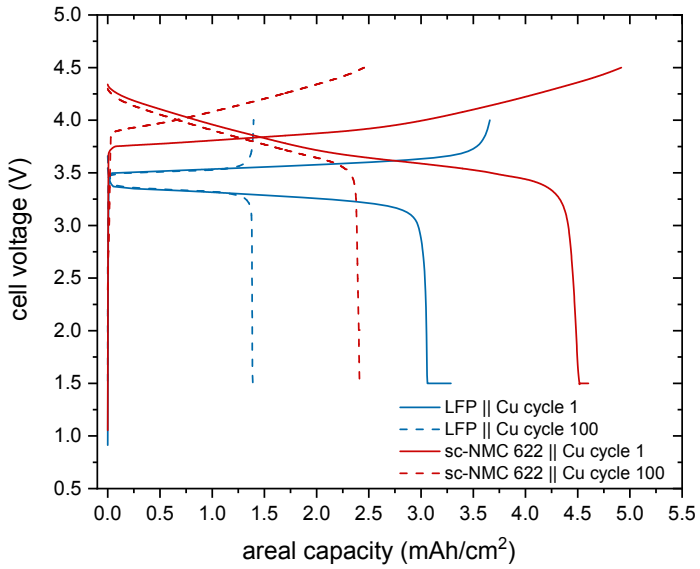

Figure S3: voltage profiles for LFP || Cu cell (blue) and sc-NMC622 || Cu cell (red) for 1st cycle (solid line) and 100th cycle (dash line)

Physicochemical properties of the P_{1222}FSI ionic liquid electrolyte

Table S1. Ionic conductivity of the phosphonium based electrolyte at 25 °C and 50 °C

Ionic liquid electrolyte	Ionic conductivity at 25 °C (mS/cm)	Ionic conductivity at 50 °C (mS/cm)
3.2 m LiFSI in P_{1222}FSI	0.94	2.40

The electrochemical window of neat P_{1222}FSI ionic liquid is from -0.25 V to +4.75 V vs. Li/Li$^+$ [1]

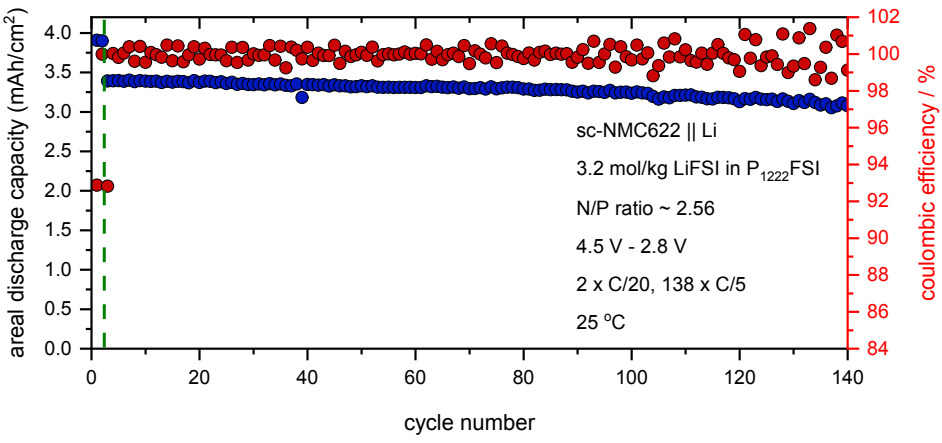

Figure S4: areal discharge capacity and coulombic efficiency for sc-NMC 622 || Li at 25 °C. Li foil thickness 50 µm. The cells were cycled with 2 formation cycles at C/20 and C/5 for 138 cycles. Capacity retention 90.7% and average coulombic efficiency 99.92% (excluding formation cycles)

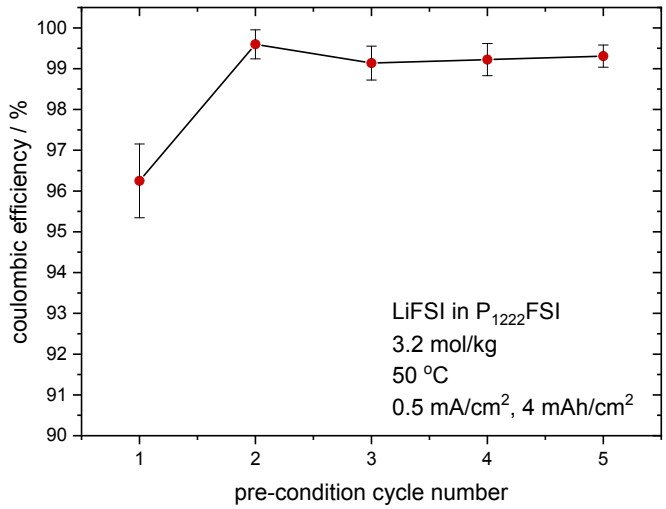

Figure S5: Coulombic efficiency vs cycle number for Li || Cu cells during pre-conditioning stage. At least 5 cycles were needed for consistent stabilisation of the copper substrate prior to measuring the average coulombic efficiency of Li metal.

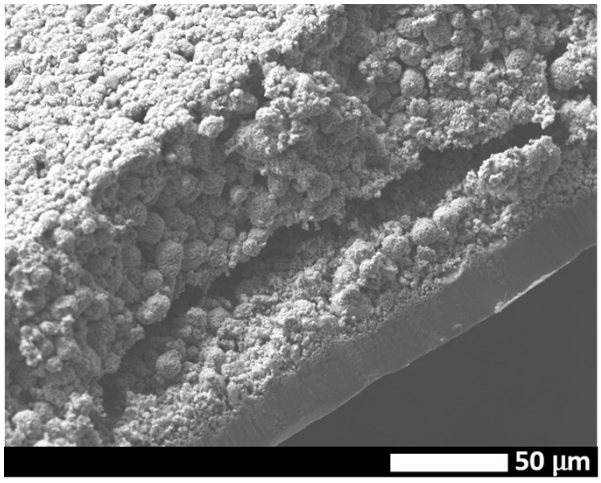

Figure S6: Cross section of the partially delaminated polycrystalline NMC622 electrode after cell failure (after 73 cycles).

Table S2: Stack energy cell parameters for Li-ion (Graphite || LFP, Graphite || SC NMC 622) and Li metal (Li || LFP, Li || SC NMC 622) used in this study. A cell stack is comprised of double sided LFP or SC NMC 622 on an Al current collector | separator | double sided graphite electrode | separator. For the lithium metal cell, the coated graphite electrode was substituted by a pure lithium metal. The mass of electrolyte was not included for stack energy density calculation to allow comparison with literature reports. The extra lithium from the cathode

plated on the lithium electrode was taken into calculation. Upon cycling the lithium metal electrode will undergo expansion and this was also not taken into the stack thickness calculation.

	Li-ion (LFP)	Li metal (LFP)	Li-ion (SC NMC 622)	Li metal (SC NMC 622)
Stack mass (mg/cm^2)	**80**	**58**	**79**	**58**
Stack thickness (µm)	**580**	**463**	**362**	**258**
Average voltage (V)	**3.2**	**3.28**	**3.7**	**3.67**
Stack specific energy (Wh/kg)	**274**	**375**	**319**	**585**
Stack energy density (Wh/L)	**375**	**465**	**695**	**1308**

References

[1] K. Periyapperuma, J.M. Pringle, L. Sanchez-Cupido, M. Forsyth, C. Pozo-Gonzalo, Fluorine-free ionic liquid electrolytes for sustainable neodymium recovery using an electrochemical approach, Green Chem. 23 (2021) 3410–3419. doi:10.1039/d1gc00361e.