A symmetrical ionic liquid/Li salt system for rapid ion transport and stable lithium electrochemistry. <u>Supporting information</u>.

Synthesis procedure.

Acetonitrile (\geq 99.9%, Merck Milipore Australia), lithium bis(fluorosulfonyl)imide (Li[FSI]) (>99.9%, Coors tek US), 1-ethylpyrrolidine (97%, Sigma Aldrich Australia), bromoethane (98%, Sigma Aldrich Australia) and potassium bis(fluorosulfonyl)imide (\geq 99.9%, Suzhuo Fluolyte China) were all purchased commercially and used as received. Milli-Q water was used in all the synthesis. Most of the synthesis was performed under an argon atmosphere. The purity of the synthesized [C₂epyr][FSI] was confirmed by NMR, mass spectroscopy, elemental analysis, ion selective electrodes (ISE) and DSC. ¹H, ¹³C and ¹⁹F NMR spectra were collected on a Bruker instrument operating at 400 MHz, 100 MHz and 375 MHz respectively, in CD₃OD by referencing the solvent peak. Mass spectroscopy was performed on an Agilent 1200 series HPLC system. Elemental analysis was performed by the Campbell Microanalytical Laboratory, New Zealand. Bromide and potassium contents were determined by an Ionode Br selective electrode, or Hanna potassium selective electrode, respectively, after calibration with 10 and 100 ppm solutions of the respective ion.

N,N-Diethylpyrrolidinium bis(fluorosulfonyl)imide, [C2epyr][FSI]

[C₂epyr]Br was synthesised following a previously reported procedure.¹ *N*-Ethylpyrrolidine (8.03g, 81 mmol) was added to 100 mL of dry isopropanol and then ethylbromide (21 mL, 283 mmol) was added dropwise to the above stirred solution. The solution was heated at 45 °C for 24 hours under an inert atmosphere, during which time the reaction mixture turned yellow. The reaction was then cooled to room temperature and diethyl ether (100 mL) added dropwise until a solid white product started to separate out. The solution was then left in a freezer for 2 hours and the supernatant decanted. The solid product was filtered, washed with n-hexane twice, followed by drying *in vacuo* to get a white solid of [C₂epyr]Br (14.64 g, 89%). ¹H NMR (400 MHz, CD₃OD): δ 1.36 (tt, *J*_{HH} = 7.2 Hz, *J*_{HH} = 2 Hz, NCH₂CH₃, 6H), 2.2 (m, *CH*₂CH₂, 4H), 3.40 (q, *J*_{HH} = 7.2 Hz, NCH₂CH₃, 4H), 3.50 (m, *CH*₂NCH₂, 4H) ppm. ¹³C NMR (100 MHz, CD₃OD): 7.5 (*C*H₃), 21.5 (*C*H₂), 54 (NCH₂CH₃), 61.7 (*C*H₂NCH₂) ppm. ES⁺ *m*/*z* 128.1 (NC₈H₁₈)⁺, ES⁻ *m*/*z* 80.9 (Br)⁻. Anal. Calculated for C₈H_{18.5}N₁Br₁O_{0.25}; C, 45.18; H, 8.77: N, 6.58. Found: C, 45.27; H, 8.78: N, 6.46.

[C₂epyr]Br (14.64g, 70 mmol) was dissolved in 50 mL of water, and potassium bis(fluorosulfonyl)imide (15.88g, 72 mmol) was separately dissolved in 50 mL of water. Upon mixing the above solutions, a white precipitate formed instantly. After the addition of CH₂Cl₂ (100 mL) the solution was left stirring for an hour at room temperature. The organic layer was then washed with water (7 x 50 mL). The organic layer was dried *in vacuo* to get an off-white soft solid. This solid was dissolved in water (100 mL) followed by addition of 1 mL of CH₂Cl₂. The coloured impurities moved into the organic solvent layer. The layers were separated, and the water removed from the product *in vacuo*. The sample was further dried in vacuo for 48 hours at 50 °C to get a soft white solid of [C₂epyr][FSI] (11.8 g, 54 % yield). ¹H NMR (400 MHz, CD₃OD): δ 1.36 (tt, *J*_{HH} = 7.2 Hz, *J*_{HH} = 2 Hz, NCH₂CH₃, 6H), 2.2 (m, *CH*₂CH₂, 4H), 3.40 (q, *J*_{HH} = 7.2 Hz, NCH₂CH₃, 4H), 3.50 (m, *CH*₂NCH₂, 4H) ppm. ¹³C NMR (100 MHz, CD₃OD): 7.50 (CH3), 21.42 (CH2), 54.17 (NCH₂CH₃), 61.62 (CH₂NCH₂). ¹⁹F NMR (375 MHz, CD₃OD): 50.42 (F) ppm. ES⁺ *m/z* 128.1 (NC₈H₁₈)⁺, ES⁻ *m/z* 179.9 (FSI)⁻. Anal. Calculated for C₈H₁₈N₂ F₂O₄S₂; C, 31.16: H, 5.89: N, 9.08: S, 20.80. Found: C, 31.41; H, 5.92: N, 8.92: S, 20.80. Bromide content (Ion selective electrode) 15 ppm. Potassium content (Ion selective electrode) 23 ppm.

Electrolyte preparation. The [C₂epyr][FSI] and Li[FSI] were accurately weighed in an argon glove box and dissolved in dry acetonitrile. The acetonitrile was then removed under vacuum. The samples were further dried under high vacuum (0.2 mBar) for 48 hours: 24 hours at room temperature and then 24 hours at 50 °C.

Analysis procedure

Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC 822e or a NETZSCH DSC 214 Polyma. Samples (5-10 mg) were sealed in aluminium pans in an argon filled glove box. A scan rate of 10 °C/min was used, with three heating cycles. Samples were cooled for 30 minutes at the lowest temperature before the heating scans were conducted. The results reported are from the second heating run. The **viscosity** and **density** were measured on a dual Lovis 2000 M/ME from 20 to 50 °C. A 2.5 mm tube was used for the viscosity measurement.

The ionic conductivity was measured by electrochemical impedance spectroscopy (EIS) using a Biologic MTZ-35 impedance analyser. The neat [C₂epyr][FSI] sample was pressed into a pellet between two stainless steel disks. The pellet was then placed in a sealed barrel cell, composed of two stainless steel electrodes with a teflon spacer. The conductivity of the Li[FSI]-doped samples was measured using a sealed dip-cell, composed of two parallel platinum wires that are immersed in the sample, contained in a sample vial. Samples for conductivity were prepared and sealed using an argon filled glove box.

Lithium transference number (t_{Li}^+) was measured according to literature procedures, ² using Li | Li symmetrical cells made with CR 2032-type coin cells in an argon-filled glove box. Two 9 mm diameter lithium disks (Sigma-Aldrich, purity 99.9%) were used to enclose a 12mm diameter glass fiber separator (1.6 µm pore size and 260 µm thickness) soaked in the electrolyte. The symmetrical cells were stored for 24 hours in a 50 °C oven. The Transference number measurement was also performed at 50 °C. Chronoamperometry was used, where the symmetrical cells were polarized with a 10 mV potential for 30 minutes and the resulting current was recorded. Galvano electrical impedance spectroscopy (GEIS) was performed before and after the polarization, from 1 MHz to 50 mHz, and a 100µA current perturbation was applied.

Transference number can also be measured accurately using nuclear magnetic resonance (NMR).³⁻⁵ However, the method described by Bruce *et al.*² was chosen for this study to allow us to compare the transference number to our previous studies on analogous materials, and to other studies that employed the same technique.

Cyclic voltammetry and **average cycling efficiency** (ACE) were measured by a Biologic SP-200 potentiostat in a three-electrode cell, which was placed in an argon-filled glove box at room temperature. A Platinum working electrode was used, with 2.0mm² surface area. A lithium strip and a coiled lithium metal strip were used as quasi-reference and counter electrodes respectively. The counter electrode was coiled to ensure that the surface area was at least ten times the surface area of the working electrode. A 20 mV.s⁻¹ scan rate was used for cyclic voltammetry. The Coulombic efficiency for each cycle was calculated from the ratio of stripping charge to plating charge.

The electrochemical window of neat $[C_2epyr][FSI]$ was measured by cyclic voltammetry in the threeelectrode cell described above. The positive potential window was estimated from the point where the measured current was two times higher than the background current.



Figure S1 (a) The cyclic voltammogram of $[C_2epyr][FSI]$ used to estimate the electrochemical window. (b) The cyclic voltammogram of $[C_2epyr][FSI]$ (Red) compared to the $[C_2epyr][Li][FSI]_2$ (Blue).

The average cycling efficiency was measured according to literature procedures.^{6, 7} An initial excess of lithium deposit was plated by applying a 0.5 mA.cm⁻² current for 4 hours (a total charge of Q_{ex} = 2mA.h.cm⁻²). A quarter of the initial lithium deposit (Q_{ps} = Q_{ex} /4 =0.5mA.h.cm⁻²) was then cycled repeatedly at the same current density (0.5 mA.cm⁻²) for cycles of 1 hour of lithium deposition and 1 hour lithium stripping. The current density of 0.5 mA.cm⁻² was used as it gave the optimum cycling behaviour for this system, as identified in a series of preliminary experiments employing different current densities. The work presented in ref 6 was used as a reference point for these experiments. The best cycling efficiency data is shown in Figure 3b. An average cycling efficiency of > 90% over at least 40 cycles was reproduced with two additional samples of [C₂epyr][Li][FSI]₂.

References

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