

Electronic Supplementary Information:

Experimental Section

Chemicals: 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide [C₄mpyrr][NTf₂] and 1-butyl-1-methylpyrrolidinium bromide [C₄mpyrr]Br were prepared in house following standard procedures reported in the literature.¹ Appropriate amounts of the ionic liquid salt were dissolved in approximately 400 μl of the ionic liquid. For the saturated solution 200 μl of ionic liquid was used in order to minimise the amount of ionic liquid required. The solutions were stirred for approximately 24 hours to allow for full dissolution.

Instrumental:

XPS experiments were performed as follows: samples of the ionic liquids were supported in shallow dish stubs, which were introduced into the instrument *via* a turbo molecular pumped entry lock. The entry lock was pumped for about 30 minutes before the sample was introduced into the analysis chamber. XPS was performed in an ion pumped UHV chamber equipped with a VG nine channel CLAM4 electron energy analyser (base pressure 5×10^{-9} torr). 250 Watt unmonochromated Mg X-ray excitation was used. The CLAM 4 has variable slits for small area analysis. The largest slit (5mm) was used in this case with no apertures selected. The analyzer was operated at constant pass energy of 100 eV. Data was obtained using VGX900-W operating system. Peak areas were measured after background subtraction following methods of Shirley.²

Electrochemical experiments were performed using a computer controlled μ-Autolab potentiostat (Eco-Chemie, Netherlands). Solutions were prepared by diluting

10 μ l of the XPS samples (0.436 Br atom % and saturated solution) up to 420 μ l with [C₄mpyrr][NTf₂], giving 8.6 and 17.8mM solutions respectively. A conventional two-electrode arrangement was employed, with a platinum electrode (10 μ m diameter) as the working electrode. A 0.5mm diameter silver wire was used as a quasi-reference electrode. The electrodes were housed in a glass “T-cell”³ specifically designed for examining microsamples of RTILs under a controlled atmosphere. The microelectrode was modified with a section of disposable micropipette tip, creating a small cavity above the disk into which ~20 μ l of ionic liquid was placed.

The microelectrode was polished on soft lapping pads (Kemet Ltd., UK) using 1.0 μ m and 0.3 μ m aqueous-alumina slurries (Buehler, Illinois). The microdisk radius was calibrated electrochemically by analysing the steady-state voltammetry of a 2mM solution of ferrocene in acetonitrile, containing 0.1M TBAP as a supporting electrolyte, using a value for the diffusion coefficient of $2.3 \times 10^{-9} \text{ m}^2\text{s}^{-1}$ at 298K.⁴

Chronoamperometric experiments: Chronoamperometric transients were achieved using a sample time of 0.1s. The potential was held at 0V for 20 s for pre-treatment, then the potential was stepped to the required value and the current was measured for 10 s. Fitting of the experimental data was achieved using the nonlinear curve fitting function available in Origin 7.0 (MicroCal Software Inc.), following the Shoup and Szabo⁵ approximation, as employed by Evans *et al.*⁶ The equations used in this approximation are sufficient to describe the current response to within an accuracy of 0.6%, and are given below

$$I = -4nFDc_r f(\tau)$$

$$f(\tau) = 0.7854 + 0.8863\tau^{-1/2} + 0.2146e^{-0.7823\tau^{-1/2}}$$

$$\tau = \frac{4Dt}{r_d^2}$$

where n is the number of electrons transferred, F is the Faraday constant, D is the diffusion coefficient, c is the initial concentration of parent species, r_d is the radius of the microdisk, and t is the time.

The software was instructed to perform 100 iterations on the data, fixing the value for the electrode radius, which was previously calibrated. When the experimental data had been optimised, a value for the diffusion coefficient and the product of the number of electrons multiplied by the concentration was obtained.

References:

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4. M. Sharp, *Electrochim. Acta*, 1983, **28**, 301.
5. D. Shoup and A. Szabo, *J. Electroanal. Chem.*, 1982, **140**, 237.
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