Supplementary Information for

The influence of thermal degradation on the electrodeposition of aluminium from an air- and water-stable ionic liquid

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Materials and equipment description

The 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, or [C₄mpyr][NTf₂] (Ultra Pure, Merck), and AlCl₃ (99.99%, Fluka) were stored and used in an argon-filled glovebox with the H₂O and O₂ content maintained below 5 ppm. The water content of the IL determined by coulometric Karl-Fisher titration (Metrohm 756 KF Coulometer) was determined to be < 40 ppm H₂O, whilst ICP-MS analyses of the IL and AlCl₃ revealed no significant inorganic impurities.

Voltammetric measurements were performed in a jacketed electrochemical cell maintained at 80 °C using potential scan rates of 10 mVs⁻¹. A 1 mm diameter boron-doped diamond (BDD) disk working electrode and a 3 mm diameter glassy carbon rod counter electrode were used in a conventional 3-electrode setup along with a pseudo-reference electrode comprising a silver wire placed inside a glass luggin capillary. [C₄mpyr][NTf₂] containing high chloride concentrations from AlCl₃ provides a stable reference potential 0.76 V positive of the reversible potential for the ferrocene/ferricenium redox couple. BDD was chosen as the working electrode due to the favourable surface properties which are well suited for studying Al deposition¹. Further details on BDD electrode construction is described elsewhere². A Radiometer-Analytical Voltalab 40 PGZ301 potentiostat controlled by Voltamaster 4 software was used to perform electrochemical measurements.

Al deposits that were subsequently analysed using field-emission gun environmental scanning electron microscopy (FEG-ESEM) were obtained by electrodeposition onto 0.7 mm diameter gold wire electrodes with an exposed length of 5 mm. The deposits
were obtained using a fixed potential of -2.3 V, coinciding with the foot of the reduction peak, until 2.25C of charge was passed. Prior to FEG-SEM analysis, the deposits were thoroughly rinsed in isopropanol and warm deionised water to remove residual IL and AlCl₃. FEG-ESEM images were recorded at 10 kV (FEI-Quanta 400F).

The $^{27}$Al NMR spectra were recorded using a Bruker Av500 spectrometer operating at 130.3 MHz. The $^{27}$Al chemical shift values are reported relative to an aqueous solution of Al(NO₃)₃·9H₂O as an external reference. $^{13}$C NMR spectra were recorded using a Bruker Av400 spectrometer operating at 100.6 MHz.

References