

*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 [C<sub>4</sub>mpyr][NTf<sub>2</sub>] (Ultra Pure, Merck), and AlCl<sub>3</sub> (99.99%, Fluka) were stored and used in an argon-filled glovebox with the H<sub>2</sub>O and O<sub>2</sub> 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 H<sub>2</sub>O, whilst ICP-MS analyses of the IL and AlCl<sub>3</sub> 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<sup>-1</sup>. 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. [C<sub>4</sub>mpyr][NTf<sub>2</sub>] containing high chloride concentrations from AlCl<sub>3</sub> 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 deposition<sup>1</sup>. Further details on BDD electrode construction is described elsewhere<sup>2</sup>. A Radiometer-Analytical Voltalab 40 PGZ301 potentiostat controlled by Voltmaster 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  $\text{AlCl}_3$ . FEG-ESEM images were recorded at 10 kV (FEI-Quanta 400F).

The  $^{27}\text{Al}$  NMR spectra were recorded using a Bruker Av500 spectrometer operating at 130.3 MHz. The  $^{27}\text{Al}$  chemical shift values are reported relative to an aqueous solution of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  as an external reference.  $^{13}\text{C}$  NMR spectra were recorded using a Bruker Av400 spectrometer operating at 100.6 MHz.

### References

1. J.-P. Veder, M. D. Horne, T. Ruether, A. M. Bond and T. Rodopoulos, *Electrochem. Commun.*, 2012, **18**, 85-87.
2. L. Hutton, M. E. Newton, P. R. Unwin and J. V. Macpherson, *Anal. Chem.*, 2009, **83**, 1023-1032.