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Speciation of Aluminium in Mixtures of the Ionic Liquids [C₃mpip][NTf₂] and [C₄mpyr][NTf₂] with AlCl₃: An Electrochemical and NMR Spectroscopy Study**

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Abstract: This paper reports on the electrodeposition of aluminium on several substrates from the air- and waterstable ionic liquids 1-propyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)amide ([C₃mpip][NTf₂]) and 1butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ([C4mpyr]- $[NTf_2]$, which contain anhydrous AlCl₃. At an AlCl₃ concentration of 0.75 molal, no evidence for aluminium electrodeposition was observed in either system at room temperature. However, aluminium electrodeposition becomes feasible upon heating the samples to 80°C. Aluminium electrodeposition from bis(trifluoromethylsulfonyl)amide-based ionic liquids that contain AlCl₃ has previously been shown to be very dependent upon the AlCl₃ concentration and has not been demonstrated at AlCl₃ concentrations below 1.13 molal. The dissolution of AlCl₃ in [C₃mpip][NTf₂] and [C₄mpyr]-[NTf₂] was studied by variable-temperature ²⁷Al NMR spectroscopy to gain insights on the electroactive species responsible for aluminium electrodeposition. A similar change in the alumini-

Keywords: aluminum • cyclic voltammetry • electrodeposition • ionic liquids • NMR spectroscopy um speciation with temperature was observed in both ionic liquids, thereby indicating that the chemistry was similar in both. The electrodeposition of aluminium was shown to coincide with the formation of an asymmetric fourcoordinate aluminium-containing species with an ²⁷Al chemical shift of δ = 94 and 92 ppm in the [C₃mpip][NTf₂]– AlCl₃ and [C₄mpyr][NTf₂]–AlCl₃ systems, respectively. It was concluded that the aluminium-containing species that give rise to these resonances corresponds to the electroactive species and was assigned to [AlCl₃(NTf₂]⁻.

Introduction

Aluminium is the most abundant metallic element in the earth's crust but due to its reactivity it does not occur in nature as the free metal. The Hall–Héroult electrolytic process, which was developed in 1886, is the main industrial method used worldwide for primary aluminium production.^[1] In this process, calcined alumina, derived from baux-

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[**] [C₃mpip][NTf₂]=1-propyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)amide; [C₄mpyr][NTf₂]=1-butyl-1-methylpyrrolidinium bis-(trifluoromethylsulfonyl)amide. ite by means of the Bayer Process, is dissolved in a molten cryolite (Na₃AlF₆) bath maintained at approximately 960 °C, in which it is electrolysed and reduced to aluminium metal. The classical Hall–Héroult process has several inherent disadvantages such as high capital and energy demands, and environmental issues associated with perfluorocarbon (PFC) emissions (e.g., CF₄ and C₂F₆) caused by anode effects. Similarly, the two commercial processes for electroplating of aluminium, namely, the SIGAL^[2] and REAl^[3] processes have the disadvantage of employing flammable and volatile materials. Considerable research effort has been spent on developing alternatives to these aluminium electrodeposition processes; however, no commercially feasible and cost-competitive alternative processes have evolved to date.

It has long been recognised that significant energy savings could be achieved if aluminium metal could be produced at lower temperatures and aluminium electroplating processes made greener by replacing the organic solvents with less volatile and non-flammable media. This requires a medium with specific properties or characteristics. Electrodeposition of aluminium in aqueous solutions is unfeasible due to the



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reduction of water to hydrogen at the cathode before a sufficiently high negative potential can be applied to reduce the aluminium ions. Electrolytes for aluminium electrodeposition must therefore be aprotic such as molten salts or nonaqueous organic solvents. The electrodeposition of aluminium metal at temperatures below 100 °C has been demonstrated in a number of organic solvents.^[4] However, the success of these systems has been limited by small electrochemical windows, low electrical conductivities, flammability and high volatility. A new class of molten salts, termed room temperature ionic liquids (ILs),^[5] which are salts that are molten at, or near, ambient temperature, provided a new avenue for low-temperature aluminium electrodeposition. Many ionic liquids have properties such as wide electrochemical windows, high conductivities and good solubility of metal salts, which makes them potentially useful as electrolytes in a number of applications such as batteries,^[6] fuel cells,^[7] electrodeposition,^[8] catalysis^[9] and organic synthesis.^[10]

Aluminium electrodeposition at ambient temperatures using chloroaluminate ionic liquids has been extensively studied and successfully demonstrated.^[4,11–27] Numerous studies have shown that aluminium electrodeposition from chloroaluminate ionic liquids can only occur from Lewis acidic melts, that is, ones in which the mole fraction of AlCl₃ is greater than $0.5.^{[28-32]}$ In these melts, the dinuclear Al₂Cl₇ species present in solution is the only reducible species within the electrochemical window of the ionic liquid that yields aluminium metal. Despite successful electrodeposition of aluminium from chloroaluminate ionic liquids, these materials are extremely air- and water-sensitive and therefore not considered to be commercially attractive.

The advent of air- and water-stable ionic liquids in $1992^{[33]}$ that were AlCl₃-free catalysed a renewed interest in ionic liquids for low-temperature aluminium production. Aluminium electrodeposition from three air- and water-stable ionic liquids, namely, 1-butyl-1-methylpyrrolidinium bis(trifluoro-methylsulfonyl)amide ([C₄mpyr][NTf₂]), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([C₄mpyr][NTf₂]) that contain anhydrous AlCl₃ was recently first reported by the research group of Endres.^[34,35] The cationic constituent of the NTf₂-based ionic liquid was found to influence the morphology of the aluminium deposits.

Addition of metal salts to air- and water-stable ionic liquids, as is necessary for electrodeposition, leads to complex chemistry due to the composition of these ionic liquids and the Lewis basicity of the anionic constituent. Metal speciation in solution will affect the thermodynamics and kinetics of metal ion reduction and will ultimately determine the viability of the electrodeposition application. In terms of aluminium, the mechanism by which it is electrodeposited from NTf₂-based ionic liquids is not yet fully understood. In our recent study,^[36] we concluded on the basis of ²⁷Al NMR spectroscopy and Raman data and also density functional theory (DFT) calculations that the electroactive species in the $[C_4mpyr][NTf_2]-AlCl_3$ system was either 4-coordinate $[AlCl_3(NTf_2)]^-$ or six-coordinate $[AlCl_2(NTf_2)_2]^-$. A similar study conducted simultaneously with ours made similar findings.^[37]

In this paper we report on the electrodeposition of aluminium onto several substrates from solutions of anhydrous AlCl₃ in the ionic liquid 1-propyl-1-methylpiperidinium bis-(trifluoromethylsulfonyl)amide ([C₃mpip][NTf₂]; Scheme 1a)



Scheme 1. Structures of a) [C₃mpip][NTf₂] and b) [C₄mpyr][NTf₂].

as a function of AlCl₃ concentration and temperature. By using variable-temperature ²⁷Al and ¹³C NMR spectroscopy correlated to electrodeposition results, we aim to shed further light on the electroactive species in NTf₂-based ionic liquids and resolve the inconclusive findings in our previous study. This particular NTf₂-based ionic liquid was chosen for this study because its mixtures with AlCl₃ displayed simpler phase behaviour than mixtures of [C4mpyr][NTf2] and [C₂mim][NTf₂] with AlCl₃. The electrodeposition and speciation of aluminium in mixtures of [C₄mpyr][NTf₂] (Scheme 1b) with AlCl₃ was re-examined due to the results obtained from the [C₃mpip][NTf₂]-AlCl₃ mixtures. An understanding of the deposition mechanism in NTf₂-based ionic liquids will assist in the identification of a better ionic liquid system for aluminium electrodeposition, and these insights will in turn facilitate the development of a commercial process.

Results and Discussion

[C₃mpip][NTf₂]-AlCl₃ system: AlCl₃ dissolves slowly in [C₃mpip][NTf₂] with stirring and gentle heating at 50 °C. Up to mole fraction of AlCl₃ (x_{AlCl_3}) of 0.39 the mixture is a clear solution, but at x_{AlCl_3} =0.43 the mixture forms a paste and starts to solidify (Table 1). By x_{AlCl_3} =0.50, the mixture is a homogeneous solid at room temperature that becomes a clear solution at 80 °C. No biphasic behaviour was observed in the range $0 < x_{AlCl_3} < 0.50$.

Brausch et al.^[38] reported that a large number of ionic liquids of the general type [cation][NTf₂], in which the cation was a pyridinium- or imidazolium-based heterocycle, exhibited biphasic behaviour in the presence of a certain concentration of AlCl₃. Similar biphasic behaviour was also witnessed by Zein El Abedin et al.^[34,35] in solutions of AlCl₃ in [C₄mpyr][NTf₂] and [C₂mim][NTf₂] but not in those of [P_{66,6,14}][NTf₂]. Furthermore, all of these biphasic NTf₂based ionic liquid-AlCl₃ systems exhibited true thermomorphic behaviour as they became monophasic upon heating to 80 °C.

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Table 1.	Phase	behaviour	of	[C ₃ mpip][NTf ₂]–AlCl ₃	mixtures	of	various
composit	tions.						

x_{AlCl_3}	Mole ratio IL/AlCl ₃	$AlCl_3$ concentration $[mol kg^{-1}]^{[a]}$	Phases ^[b]
0.20	4:1	0.60	clear solution
0.24	3.1:1	0.75	clear solution
0.34	2:1	1.2	clear solution
0.39	1.6:1	1.5	clear solution
0.43	1.3:1	1.8	paste
0.50	1:1	2.4	white solid

[a] The AICl₃ concentration is expressed in terms of molality rather than molarity. [b] At room temperature.

Aluminium electrodeposition was successfully demonstrated from several NTf₂-based ionic liquids that contain AlCl₃ in which the ionic liquid cation component was either $[C_4mpyr]^+$, $[C_2mim]^+$ or $[P_{6,6,6,14}]^+$.^[34,35,39] However, aluminium electrodeposition only occurred above a critical AlCl₃ concentration ($\geq 1.6 \text{ M}$). In these systems, the cation component of the ionic liquid appeared to influence the size of the electrodeposits. Hence, the cation appears to modify but does not exert a strong influence over the electrodeposition process. The presence of the NTf₂⁻ anion in each of these ionic liquids is noteworthy and suggests it strongly influences the electrodeposition process. Although weakly coordinating, it determines the aluminium speciation in solution and consequently determines the thermodynamic limits of the process, that is, the critical cell voltage.

The electrodeposition of aluminium from solutions of AlCl₃ in [C₃mpip][NTf₂] was examined on glassy carbon, gold, platinum and iron substrates at relatively high (x_{AlCl_3} = 0.50) and low (x_{AlCl_3} =0.24) AlCl₃ concentrations between 25 and 100 °C. These experiments were conducted in conjunction with variable-temperature ²⁷Al NMR spectroscopic experiments to try and gain some insight on the reducible aluminium-containing species in NTf₂-based ionic liquids.

Figure 1 shows a cyclic voltammogram of the mixture at $x_{AICl_3}=0.50$ on a glassy carbon electrode at 80 °C. The electrode potential was scanned negatively from the open circuit



Figure 1. Cyclic voltammogram recorded on a glassy carbon electrode in a $[C_3mpip][NTf_2]$ mixture at $x_{AICl_3}=0.50$ at 80°C. Scan rate was 10 mV s⁻¹.

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potential at 10 mVs⁻¹. Aluminium was electrodeposited from this solution onto glassy carbon when the applied potential was negative of -0.9 V (vs. Fc/Fc⁺). The shape of the voltammogram, in particular the current loop at potentials negative of -1.0 V, suggests aluminium was deposited by a nucleation and growth mechanism,^[40,41] the same mechanism by which metals are electrodeposited from aqueous solutions. A broad cathodic peak was observed at -0.4 V, which remains unassigned. It appeared only after the addition of AlCl₃; however, it is not due to the electrodeposition of aluminium metal. On the reverse scan, a small anodic peak was observed at 0.3 V, which is attributed to incomplete reoxidation of the electrodeposited aluminium. Complete reoxidation of aluminium may be kinetically hindered or the aluminium surface may become passivated. Similar incomplete reoxidation of electrodeposited aluminium was observed in [C₄mpyr][NTf₂]-AlCl₃ mixtures.^[34] This is in contrast to [C₂mim][NTf₂]-AlCl₃ and [P_{6,6,6,14}][NTf₂]-AlCl₃ mixtures in which complete reoxidation of electrodeposited aluminium was observed.[35] This different oxidative electrochemical behaviour is difficult to explain, as each of the systems has similar Cl⁻ and NTf₂⁻ anions available for the solvation of the Al³⁺ ions. Variation of the ionic liquid cation is not expected to impact on the reoxidation process unless it interacts with the aluminium surface and brings about its passivation.

The aluminium electrodeposits obtained at 80 °C were identified by elemental analysis using energy-dispersive Xray spectroscopy (EDS) in a scanning electron microscope (SEM), and corroborative evidence was provided by X-ray diffraction. Example SEM micrographs of aluminium films obtained on gold, platinum, iron and glassy carbon substrates are shown in Figure 2. The films shown were obtained using different experimental conditions. Four different electrode materials were chosen so we could qualitatively assess the substrate effect on aluminium electrodeposi-



Figure 2. SEM micrographs of metallic aluminium films electrodeposited at 80°C onto a a) gold (-0.9 V, 200 mC passed), b) platinum (-1.2 V, 150 mC passed), c) iron (-0.9 V, 205 mC passed) and d) glassy carbon (-0.9 V, 210 mC passed) electrode from a [C₃mpip][NTf₂] mixture at x_{AlCl_3} =0.50.

Chem. Eur. J. 2010, 16, 3815-3826

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tion. Electrodeposition onto an electrode surface involves several interdependent and reversible transformations of the solvated metal ions including desolvation, reduction, adsorption, surface migration and coalescence with other adsorbed metal atoms. The electrode material can affect all of these steps, sometimes strongly, and the morphology of the deposits may differ as a result. Taking into account the electrodeposition conditions were not identical, deposits on gold, platinum and glassy carbon were broadly similar. By contrast, the deposit on iron appears finer-grained. As is usual for electrodeposition, we observed a strong dependence of the deposit morphology on the deposition potential. At low overpotentials (just negative of the potential where electrodeposition begins) the deposits were generally coarsegrained and rough. By contrast, high overpotentials produced micro- and nano-structured deposits. On polished metal electrodes, high overpotentials and short deposition times sometimes produced mirror-like films. In Figure 3, an



Figure 3. a) SEM micrograph and b) EDS profile of a fractured film of metallic aluminium electrodeposited at 100 °C onto a gold electrode from a $[C_3mpip][NTf_2]$ mixture at $x_{AICI_3}=0.50$ using a deposition potential of -0.9 V for 90 min (200 mC passed).

SEM micrograph of a film deliberately fractured to reveal its interior structure can be seen along with its EDS analysis, which indicates pure aluminium metal. An XRD pattern of an aluminium film electrodeposited at -1.0 V for 90 min at 80 °C on an iron electrode is shown in Figure 4. Peaks char-



Figure 4. X-ray diffractogram of an aluminium deposit obtained on an iron electrode at 80°C from a [C₃mpip][NTf₂] mixture at $x_{AICl_3}=0.50$ using a deposition potential of -1.0 V for 90 min (206 mC passed). PTFE = polytetrafluoroethylene.

acteristic of crystalline aluminium were evident in the XRD pattern along with those characteristic of the iron substrate and its insulating Teflon (PTFE) sheath. Crystal size calculations from the XRD data show the average crystallite size in this deposit was (78 ± 10) nm.

At $x_{AlCl_3} = 0.24$, at which the [C₃mpip][NTf₂]-AlCl₃ mixture is a clear liquid at room temperature, aluminium could only be electrodeposited at temperatures ≥ 80 °C. This suggests that a favourable change in the aluminium chemistry occurred upon increasing the temperature. The electroactive aluminium-containing species from which metallic aluminium is derived during constant voltage electrodeposition only appears to be present in solution above this threshold temperature. The chemical speciation of aluminium in a $[C_3 mpip][NTf_2]$ -AlCl₃ mixture at $x_{AlCl_3} = 0.24$ was therefore investigated by variable-temperature ²⁷Al NMR spectroscopy to firstly gain insight on the effect of temperature on the aluminium chemistry in [C₃mpip][NTf₂], and secondly, to obtain evidence for the electroactive aluminium-containing species. The mixture was also examined by variable-temperature ¹³C NMR spectroscopy; however, no significant changes to the ¹³C spectrum were noted.

²⁷Al NMR spectroscopy has been widely used to study the chemical speciation of aluminium in chloroaluminate melts,[42-47] as it directly probes the aluminium, which changes speciation upon varying the melt composition. The AlCl₄⁻ and Al₂Cl₇⁻ species present in Lewis basic and Lewis acidic chloroaluminate melts, respectively, have been differentiated and assigned on the basis of their ²⁷Al resonance line widths. Since ²⁷Al is a quadrupolar nucleus (I=5/2), the line width of the ²⁷Al resonance can provide information about the symmetry around the aluminium atom in the aluminium species. Tetrahedral AlCl₄⁻ exhibits a sharp signal, as the high symmetry around the Al centre reduces quadrupolar relaxation. In contrast, the Al₂Cl₇⁻ species of lower symmetry exhibits a broad signal due to efficient nuclear quadrupolar relaxation. However, ²⁷Al NMR spectroscopy has been used sparingly to study chemical speciation of aluminium in water-stable ionic liquids. We recently reported the ²⁷Al NMR spectra for [C₄mpyr][NTf₂]-AlCl₃ at various compositions,^[34] and Eiden et al.^[37] reported similar spectra for [C₂mim][NTf₂]-AlCl₃ mixtures. Both 4-coordinate and 6coordinate aluminium-containing species were detected in both systems. The dominant 4-coordinate species was assigned to AlCl₄⁻, whereas the minor 6-coordinate species was assigned to the Al(NTf₂)₃ complex formed in situ. For these systems, ²⁷Al NMR spectroscopic studies could not provide definitive evidence on the nature of the electroactive species.

The ²⁷Al NMR spectra of a [C₃mpip][NTf₂]–AlCl₃ mixture at x_{AlCl_3} =0.24 were recorded between 25 and 130 °C at 15 °C intervals. The spectra acquired at 25 and 130 °C are displayed in Figure 5. The impact of temperature on the δ = 100–85 and –30–10 ppm regions of the ²⁷Al NMR spectrum is highlighted in Figure 6a and b, respectively. At 25 °C, the spectrum is dominated by a strong resonance at δ = 104 ppm, which is indicative of a 4-coordinate aluminium



Figure 5. The ²⁷Al NMR spectra acquired at 25 and 130 °C for a [C₃mpip]-[NTf₂]-AlCl₃ mixture at x_{AlCl_3} =0.24. Trace at 130 °C is offset by δ = 5 ppm for clarity.



Figure 6. The impact of temperature on the a) $\delta = 100-85$ ppm and the b) $\delta = -30-10$ ppm regions of the ²⁷Al NMR spectrum for a [C₃mpip]-[NTf₂]-AlCl₃ mixture at $x_{AlCl_3}=0.24$. Spectra acquired at 15 °C intervals from 25 to 130 °C.

species. A weaker resonance at $\delta = -19$ ppm with a shoulder at $\delta = -21$ ppm was also observed, which is indicative of 6coordinate aluminium species. These observations are similar to those made in the [C₄mpyr][NTf₂]-AlCl₃^[36] and [C₂mim][NTf₂]-AlCl₃^[37] mixtures. According to the ²⁷Al chemical shifts, the resonances at $\delta = 104$ ppm were assigned to the AlCl₄⁻ species, whereas the resonances at $\delta = -19$ and -21 ppm were assigned to the Al(NTf₂)₃ complex, which has several isomers. The broad resonance located around $\delta = 66$ ppm is due to aluminium in the solid material used in the probe construction and not due to the sample.

Upon increasing the temperature from 25 to 130 °C, the overlapping broad resonances at $\delta = -19$ and -21 ppm due to isomers of the Al(NTf₂)₃ complex coalesced into a single narrow resonance at $\delta = -18$ ppm as fast chemical exchange takes place between the 6-coordinate aluminium-containing species (see Figure 6b). No variation in the chemical shift of

the major resonance at $\delta = 104$ ppm due to AlCl₄⁻ was observed upon increasing the temperature, as indicated by the data in Table 2.

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Table 2. ²⁷Al NMR chemical shifts (δ) and line widths ($\Delta v_{1/2}$) of resonances in the spectra of a [C₃mpip][NTf₂]–AlCl₃ and [C₄mpyr][NTf₂]–AlCl₃ mixture at x_{AlCl_3} =0.24 recorded between 25 and 130 °C.

T [°C]	$\delta ~[\mathrm{ppm}]~(\Delta u_{\prime_{/2}}~[\mathrm{Hz}])^{\mathrm{[a,b]}}$					
L - J	[C ₃ mpip][NTf ₂]-AlCl ₃	[C4mpyr][NTf2]-AlCl3				
25	104 s (89), -19 w, -21 sh	103 s (63), 97 vw, -19 w, -22 sh				
40	104 s (49), 98 vw, -18 w, -21 sh	103 s (34), 97 vw, -19w, -23 sh				
55	104 s (29), 98 vw, -18 w, -21 sh	103 s (23), 97 vw, -19 w, -23 sh				
70	104 s (22), 98 vw, -18 w, -21 sh	103 s (19), 97 vw, 93 vw, -19 w, -23 sh				
85	104 s (23), 98 vw, 94 w, -18 w, -21 sh	103 s (22), 97 vw, 94 sh, 92w, -5 vw, -19 w				
100	104 s (27), 98 vw, 94 m, -3 vw, -18 m	103 s (34), 97 vw, 94 sh, 92 w, -5 vw, -19 w				
115	104 s (40), 98 vw sh, 94 m, -3 vw, -18 m	103 s (61), 94 sh, 92 m, -5 vw, -19 m				
130	104 s (47), 98 vw sh, 93 m, -4 vw, -18 m	103 s (106), 94 sh, 92 m, -5 vw, -19 m				

[a] Full peak width at half-height, $\Delta \nu_{i_2}$ [Hz], in parentheses. [b] s = strong, m=moderate, w=weak, vw=very weak and sh=shoulder.

A new broad resonance became apparent at a chemical shift of $\delta = 94$ ppm in the spectrum recorded at 85 °C, which increased in intensity as the temperature was increased to 130°C (see Figure 6a). This resonance, which is indicative of a 4-coordinate aluminium-containing species, coincided with the ability to electrodeposit aluminium from this mixture at temperatures around 80 °C. It is therefore reasonable to conclude that this resonance is due to the electroactive species. In our earlier aluminium speciation study on the [C₄mpyr]-[NTf₂]-AlCl₃ system, we concluded on the basis of Raman data and DFT calculations that the electroactive species was either 4-coordinate [AlCl₃(NTf₂)]⁻ or 6-coordinate [AlCl₂- $(NTf_2)_2$ ^{-.[36]} Now, according to the variable-temperature ²⁷Al NMR spectroscopy and electrochemical data for the [C₃mpip][NTf₂]-AlCl₃ system, we conclude that the electroactive species is more than likely the 4-coordinate [AlCl₃- (NTf_2)]⁻ species. This is most likely the case in the [C₄mpyr][NTf₂]-AlCl₃ and [C₂mim][NTf₂]-AlCl₃ systems as well. The NTf_2^- ligand in the $[AlCl_3(NTf_2)]^-$ species behaves as a monodentate ligand that coordinates to the Al^{3+} ion either through a single O or N atom. The two potential 4-coordinate configurations for [AlCl₃(NTf₂)]⁻ were energetically indistinguishable according to DFT calculations.^[36]

A small resonance was also apparent at $\delta = 98$ ppm in the spectra collected between 40 and 130 °C. Takahashi et al.^[44] observed a similarly small resonance in the [C₂mim][Cl]–AlCl₃ chloroaluminate melt, which they identified to be a product of the reaction with residual water. [C₃mpip][NTf₂] is classified as a hydrophobic ionic liquid; however, it is still somewhat hygroscopic and has the capacity to dissolve sig-

nificant amounts of water $(x_{\rm H_2O} = 0.212 \text{ at } 25 \,^{\circ}\text{C})^{[48]}$ before phase separation occurs. Although [C3mpip][NTf2] was rigorously dried for several days, sometimes weeks, prior to use, such that analysis indicated it contained < 10 ppm of residual water, we cannot rule out some moisture absorption during the sample-handling process. This may be sufficient for a hydrolysis species of this nature to be present in low concentrations. In any case, it was concluded that the species that gives rise to this resonance cannot be the electroactive species, as it is still present in the spectra collected below 80°C, at which point aluminium electrodeposition is not possible. Furthermore, this resonance was also present in the spectrum of a [C₃mpip][NTf₂]-AlCl₃ mixture that had become electrochemically inactive over time. By electrochemically inactive we mean that the sample no longer vielded electrodeposits of aluminium. This will be discussed later.

On close inspection, a very weak broad resonance at $\delta = -3$ ppm was also noticeable in the spectra recorded between 100 and 130 °C (see Figure 6b). This signal may be due to the 6-coordinate [AlCl₂(NTf₂)₂]⁻ species postulated by us previously. However, due to its low concentration and the high temperature at which it appears to form, it is less likely to be the electroactive species in this mixture.

The ²⁷Al NMR spectra of a [C₃mpip][NTf₂]–AlCl₃ mixture at x_{AlCl_3} =0.50 was also recorded between 80 and 120 °C and were shown to be very similar to those collected for the x_{AlCl_3} =0.24 mixture, both in terms of the species detected and the relative resonance intensities. Thus, even at x_{AlCl_3} = 0.50, at which the AlCl₃ concentration is relatively high, the concentration of the species with an ²⁷Al chemical shift of δ =94 ppm, assigned to [AlCl₃(NTf₂)]⁻, is quite low based on the intensity of its resonance.

As alluded to earlier, a discernible change in the properties and appearance of a [C₃mpip][NTf₂]-AlCl₃ mixture at $x_{AlCl_3} = 0.50$ was observed during exhaustive electrochemical examination over numerous consecutive days, which included repeated thermal cycling between room temperature and 130°C. The mixture gradually became a pale brown liquid that froze below room temperature and electrodeposits of aluminium became harder to obtain. An aged or electrochemically inactive solution was examined by ¹³C and ²⁷Al NMR spectroscopy between 80 and 130 °C to determine whether the changes were detectable by NMR spectroscopy. The ²⁷Al NMR spectrum only exhibited a major resonance at $\delta = 104$ ppm and a minor resonance at $\delta = 98$ ppm (Figure 7a). Observation of the latter in this electrochemically inactive solution is evidence that the species responsible for this resonance is not the electroactive species. This resonance was also more prominent than in the spectrum of the freshly prepared solution, which could suggest that inactivation of the solution is due to moisture adsorption. The resonance observed at $\delta = -18$ ppm in the spectrum of a freshly prepared solution due to six-coordinate Al(NTf₂)₃ was absent in the spectrum of the inactive solution. We suspect this is because after several days the $Al(NTf_2)_3$ complex completely precipitated out of solution. The ¹³C NMR spec-



Figure 7. a) ²⁷Al NMR spectra and b) the proton-decoupled ¹³C NMR spectra that highlight the resonances due to the CF₃ moiety of a freshly prepared electrochemically active and an aged electrochemically inactive sample of [C₃mpip][NTf₂]–AlCl₃ at x_{AlCl_3} =0.50 acquired at 100°C.

trum of the inactive solution contained a quartet centred on $\delta = 120$ ppm due to the chemically equivalent CF₃ moieties of the NTf₂⁻ anion (Figure 7b). Two CF₃ quartets were, however, observed in the ¹³C NMR spectrum of a freshly prepared solution, which indicated chemical interaction between NTf₂⁻ and the added AlCl₃. The two quartets are attributed to "coordinated" and "uncoordinated" NTf₂⁻ with the former due to NTf₂⁻ in either Al(NTf₂)₃ or [AlCl₃-(NTf₂)]⁻, or both. Disappearance of the second CF₃ quartet in the aged solution suggests that NTf₂⁻ exists in only one chemical environment, which is the "uncoordinated" state, unless fast chemical exchange is taking place. This also confirms that the species observed in the aged solution with an ²⁷Al chemical shift of $\delta = 98$ ppm does not contain NTf₂⁻.

It is unclear what caused the gradual colouration of the $[C_3mpip][NTf_2]$ -AlCl₃ mixture at x_{AlCl_3} =0.50 and whether it is associated with the inactivation of the mixture. A similar colour change in $[C_2mim][NTf_2]$ -AlCl₃ and $[C_2mim][Cl]$ -AlCl₃ mixtures was recently reported and it was suggested that it was due to the electrochemical decomposition of the $[C_2mim]^+$ cation at electrode potentials below the stability limit of the cation.^[39] No evidence of any $[C_3mpip]^+$ decomposition products was noted in the ¹³C NMR spectra of the inactive solution. From the synthesis of ionic liquids it is well known that a ppm level of impurities generates significant colouration of typically colourless ionic liquids. Impurities at this concentration would go undetected by NMR spectroscopy.

[C₄mpyr][NTf₂]-AlCl₃ system: It has been reported in the literature that aluminium cannot be electrodeposited from [C₄mpyr][NTf₂]-AlCl₃ mixtures at AlCl₃ concentrations below 1.6 M.^[34] Solutions with $x_{\text{AlCl}_3} < 0.32$ are therefore

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deemed electrochemically inactive in terms of aluminium recovery. This is in contrast to our observations from a $[C_3mpip][NTf_2]$ -AlCl₃ mixture at x_{AlCl_3} =0.24. To ascertain why the aluminium electrochemistry in these two NTf₂based ionic liquids appears to be different, we investigated the chemical speciation of aluminium in a $[C_4mpyr][NTf_2]$ -AlCl₃ mixture at x_{AlCl_3} =0.24 by variable-temperature ²⁷Al NMR spectroscopy and compared it to that of $[C_3mpip][NTf_2]$ -AlCl₃ at the same AlCl₃ concentration. Differences in aluminium speciation should be revealed by this technique, as it directly probes the aluminium.

The ²⁷Al NMR spectra of the $[C_4mpyr][NTf_2]$ -AlCl₃ mixture at x_{AlCl_3} =0.24 recorded between 25 and 130 °C are displayed in Figure 8 (see data in Table 2). It can be seen that



Figure 8. a) The ²⁷Al NMR spectrum of a $[C_4mpyr][NTf_2]$ -AlCl₃ mixture at x_{AlCl_3} =0.24 acquired at 25 °C. The impact of temperature on the region of the spectrum denoted by the dotted spheres and indicative of b) 4-co-ordinate aluminium and c) 6-coordinate aluminium is shown between 25 and 130 °C at 15 °C intervals.

the ²⁷Al NMR spectra collected for the $[C_4mpyr][NTf_2]$ – AlCl₃ system are very similar to those of the $[C_3mpip]$ - $[NTf_2]$ –AlCl₃ system at x_{AlCl_3} =0.24. Most noteworthy again is the appearance of a new resonance at δ =92 ppm between 70 and 130 °C indicative of a 4-coordinate aluminium-containing species. At higher temperatures, this broad resonance appears to be comprised of more than one species as a shoulder becomes evident at δ =94 ppm. A very weak resonance at δ =-5 ppm, attributed to 6-coordinate [AlCl₂-(NTf₂)₂]⁻, also becomes apparent between 85 and 130 °C. The ²⁷Al NMR spectroscopic evidence indicates that the aluminium chemistry in the two NTf₂-based ionic liquids is essentially the same albeit that the new 4-coordinate aluminium-containing species forms at slightly lower temperatures in the [C₄mpyr][NTf₂]–AlCl₃ system than the [C₃mpip]- $[NTf_2]-AlCl_3$ system at $x_{AlCl_3}=0.24$. In turn, it implies that aluminium electrodeposition from this $[C_4mpyr][NTf_2]-AlCl_3$ mixture at $x_{AlCl_3}=0.24$ should be possible at temperatures ≥ 70 °C if the species that gives rise to the resonance at $\delta = 92$ ppm, assigned to $[AlCl_3(NTf_2)]^-$, is indeed the electroactive species as we suggest.

Aluminium electrodeposition was investigated from a $[C_4mpyr][NTf_2]$ -AlCl₃ mixture at x_{AlCl_3} =0.24 on a gold and copper electrode at various temperatures. Figure 9 shows



Figure 9. Cyclic voltammograms recorded at 21, 80 and 110 °C on a gold electrode in a $[C_4mpyr][NTf_2]$ mixture at $x_{AICl_3}=0.24$. Scan rate was 10 mVs⁻¹.

the cyclic voltammogram of the mixture recorded at 21, 80 and 110 °C on a gold electrode using a scan rate of 10 mV s^{-1} . Aluminium could not be potentiostatically electrodeposited from this solution on either substrate at 21 °C;

however, it was possible at 80 and 110 °C. An SEM micrograph of an aluminium film obtained on copper at 80 °C is shown in Figure 10. The nature of a film electrodeposited at a constant potential of -1.3 V for 25 min at 80 °C on a copper electrode was examined by XRD. Figure 11 shows the XRD pattern of the film which upon phase analysis is shown to be crystalline aluminium. The average crystallite size in this deposit was (18 ± 4) nm.



Figure 10. SEM micrograph of an aluminium film electrodeposited at 80 °C onto a copper electrode from a $[C_4mpyr]$ - $[NTf_2]$ mixture at x_{AlCl_3} =0.24.

It is not surprising that the aluminium chemistry in $[C_4mpyr][NTf_2]$ and $[C_3mpip][NTf_2]$ upon the addition of AlCl₃ is the same. In both ionic liquids, only the NTf₂⁻ anion component is expected to interact with AlCl₃. Although the NTf₂⁻ anion was initially thought to be a weakly or non-coordinating anion, several studies have shown this to be far from the truth.^[49-60] In the absence of more coordinating ligands, NTf₂⁻ can be considered a weakly coordinating ligand with four possible coordination modes. It can behave as a monodentate ligand coordinating a metal ion di-



Figure 11. XRD pattern of aluminium electrodeposited at 80 °C on a copper substrate at -1.3 V for 25 min (280 mC passed) in a [C₄mpyr]-[NTf₂] mixture at x_{AlCl_3} =0.24.

rectly through either an N or O atom or it can behave as a bidentate ligand coordinating the metal ion through O,O or O,N pairs of atoms. Furthermore, NTf₂⁻ displays high conformational flexibility and can adopt either a transoid or cisoid conformation whereby the CF3 groups lie on the opposite or the same side of the S-N-S plane, respectively. The transoid conformation is the energetically more stable conformation for the free anion.^[51,58] The NTf₂⁻ ligand will adopt the coordination and conformational mode that best accommodates the electronic and steric preference of the metal ion. In terms of aluminium, in our previous study,^[36] and that of Eiden et al.,^[37] it was shown using Raman and NMR spectroscopy and also DFT calculations that the NTf₂⁻ anions of [C₄mpyr][NTf₂] and [C₂mim][NTf₂] interact with added AlCl₃ to form several different aluminium complexes in solution such as [AlCl₃(NTf₂)]⁻, [AlCl₂(NTf₂)₂]⁻ and Al(NTf₂)₃. The NTf₂⁻ acts as a monodentate ligand in $[AlCl_3(NTf_2)]^-$ and a bidentate ligand in Al $(NTf_2)_3$. There is, however, divergence on the most favourable structure for $[AlCl_2(NTf_2)_2]^-$. We predicted that the energetically more favourable structure of $[AlCl_2(NTf_2)_2]^-$ was that in which both NTf₂⁻ ligands are bound to Al³⁺ in a bidentate fashion through O,O atoms, thus yielding a 6-coordinate species, whereas Eiden et al. predicted that the most favourable structure was a 4-coordinate configuration in which both NTf₂⁻ ligands are bound in a monodentate fashion through an O atom.

In the [C₄mpyr][NTf₂]–AlCl₃ and [C₃mpip][NTf₂]–AlCl₃ systems at x_{AlCl_3} =0.24, the formation of the species with an ²⁷Al chemical shift of δ =92 and 94 ppm, respectively, assigned to electroactive [AlCl₃(NTf₂)]⁻, appeared to be a temperature-dependent phenomenon rather than an AlCl₃-concentration-dependent phenomenon. This is not the case in the [C₄mpyr][NTf₂]–AlCl₃ system at x_{AlCl_3} =0.32, since aluminium can be electrodeposited at 25 °C.^[34,35] At this AlCl₃ concentration, the mixture is biphasic and aluminium electrodeposition is only possible from the upper phase, as the lower phase is the [C₄mpyr][AlCl₄] chloroaluminate melt

whereby the Lewis basic AlCl₄⁻ species is not reducible within the electrochemical window of the melt. Due to the biphasic nature of the mixture, the chemical composition of the upper electroactive phase is therefore different to what the overall mixture composition suggests. Most of the NTf₂⁻ resides in the upper phase, hence the NTf₂⁻/Al³⁺ ratio in the upper phase is higher than that in the monophasic mixture at x_{AlCl_3} =0.24. As a consequence, it is possible that different equilibria are established in the mixture at x_{AlCl_3} = 0.24 and the upper phase at x_{AlCl_3} =0.32, thereby allowing for the formation of the electroactive species at room temperature in the latter.

Although the $[C_4mpyr][NTf_2]$ -AlCl₃ mixture at x_{AlCl_2} = 0.50 is a solid at room temperature, it becomes a biphasic liquid upon heating to 80°C. In this instance, aluminium electrodeposition is only possible from the lower phase, as the upper phase is the electrochemically inactive [C₄mpyr]-[AlCl₄] chloroaluminate melt.^[36] The ability to electrodeposit aluminium at different AlCl₃ concentrations and temperatures and from different phases raised the question of whether or not the electroactive species was the same in each scenario. To determine whether the electroactive species in the lower phase at $x_{AlCl_3} = 0.50$ is the same as that from the monophase at $x_{AlCl_3}=0.24$, and most likely the upper phase at $x_{AICI_3} = 0.32$, the upper and lower phases at $x_{AlCl_2} = 0.50$ were examined by ²⁷Al and ¹³C NMR spectroscopy between 80 and 130°C. As expected, the ²⁷Al NMR spectrum of the electrochemically inactive upper phase in this temperature range only displayed a major resonance at $\delta =$ 103 ppm attributed to AlCl₄⁻ and a minor resonance at $\delta =$ 97 ppm, which is assigned to a product of the reaction with residual water, most likely a hydrolysis product of AlCl₃ (Figure 12a). The presence of this latter resonance in the electrochemically inactive upper phase is further verification that the species that gives rise to this resonance is not the electroactive species. Temperature had little impact on the ²⁷Al spectrum of the upper phase. A quartet centred around $\delta = 119$ ppm due to the CF₃ groups of NTf₂⁻ was observed in the ¹³C NMR spectrum of the upper phase, which indicated that NTf_2^- was still present in the upper phase (Figure 12b). The presence of only one CF_3 quartet indicates that the two CF_3 moieties of NTf_2^- are chemically equivalent and that the NTf₂⁻ exists in one chemical environment, which is the "uncoordinated" state, that is, ion-paired to [C4mpyr]+. Thus, the upper inactive phase is in fact a mixture of [C₄mpyr][AlCl₄] and [C₄mpyr][NTf₂]. It is difficult to say whether the presence of [C₄mpyr][NTf₂] in the upper phase is due to poor phase separation or due to the solubility of $[C_4mpyr][NTf_2]$ in the chloroaluminate $[C_4mpyr][AlCl_4]$ melt.

The ²⁷Al NMR spectrum of the electrochemically active lower phase at 80 °C also exhibited the resonances at $\delta = 103$ and 97 ppm due to AlCl₄⁻ and an AlCl₃ hydrolysis product, respectively, but also exhibited a resonance at $\delta = -19$ ppm and a broad resonance at approximately $\delta = 92$ ppm (Figure 13a). The resonance at $\delta = -19$ ppm has been attributed to Al(NTf₂)₃, which cannot be reduced to aluminium metal

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Figure 12. a) ²⁷Al NMR spectrum and b) the proton-decoupled ¹³C NMR spectrum for the upper phase of a $[C_4mpyr][NTf_2]$ -AlCl₃ mixture at x_{AlCl_3} =0.50 acquired at 80 °C. The CF₃ quartet is shown more clearly in the inset.



Figure 13. a) A series of ²⁷Al NMR spectra acquired at various temperatures for the lower phase of a $[C_4mpyr][NTf_2]$ -AlCl₃ mixture at $x_{AlCl_3} =$ 0.50 and b) the spectrum of the lower phase acquired at 130 °C. In a) the ²⁷Al NMR spectra at 100 and 130 °C are offset by $\delta = 5$ and 10 ppm, respectively, for clarity.

in $[C_4mpyr][NTf_2]$.^[37] The resonance at $\delta = 92$ ppm is not fully resolved and appears as a shoulder on the resonance at $\delta = 97$ ppm. It is very similar to that observed in the mono-

phasic [C₄mpyr][NTf₂]–AlCl₃ mixture at x_{AlCl_3} =0.24 and accordingly is attributed to the same 4-coordinate aluminiumcontaining species [AlCl₃(NTf₂)]⁻, and deemed to be the electroactive species in the lower phase. Increasing the temperature to 130 °C increased the intensity of the resonance at δ =92 ppm relative to the resonance at δ =103 ppm (Figure 13a). At 130 °C, the resonance at δ =92 ppm is clearly resolved and a resonance at δ =-5 ppm, attributed to 6-coordinate [AlCl₂(NTf₂)₂]⁻, is also evident (Figure 13b).

The ¹³C NMR spectrum of the lower phase at 80 °C exhibited two overlapping quartets centred around $\delta = 119$ and 118 ppm due to the CF₃ moieties of NTf₂⁻ (Figure 14). The



Figure 14. A series of proton-decoupled ¹³C NMR spectra acquired at various temperatures for the lower phase of a $[C_4mpyr][NTf_2]$ -AlCl₃ mixture at x_{AlCl_3} =0.50 that highlight the resonances due to the CF₃ moieties of NTf₂⁻.

appearance of a second CF₃ quartet is clear evidence that NTf_2^- exists in at least two different chemical environments and confirms interaction between NTf_2^- and Al^{3+} . As mentioned earlier, the quartet centred around $\delta = 119$ ppm is most likely due to "uncoordinated" NTf_2^- and that centred around $\delta = 118$ ppm is due to "coordinated" NTf_2^- , either in $Al(NTf_2)_3$ or $[AlCl_3(NTf_2)]^-$, or both. At 130 °C, the $NTf_2^$ environments are in fast chemical exchange, as the two quartets coalesced into a single quartet centred around $\delta =$ 119 ppm.

It has been suggested that metal complexes stabilized by the NTf₂⁻ anion are rendered more electrophilic compared to analogous halide species, which has a significant impact on the reduction potential of the metal complexes in an ionic liquid. For example, it has been shown that [CoCl₂- $(NTf_2)_2]^{2-}$ is electrochemically active, whereas $[CoCl_4]^{2-}$ is not in an ionic-liquid medium.^[60] Similarly, the Ti⁴⁺/Ti³⁺ couple for an ionic-liquid solution of [(C₂H₅)₂TiCl₂] is 0.93 V more negative than $[(C_2H_5)_2Ti(NTf_2)_2]$.^[50] Our study here leads to a similar conclusion whereby substitution of a Clin electrochemically inactive AlCl₄⁻ with NTf₂⁻ to form $[AlCl_3(NTf_2)]^-$ results in the formation of a more electrophilic complex and one which has a sufficiently more positive reduction potential such that it is reducible with the electrochemical window of the ionic liquid, be it either $[C_3mpip][NTf_2]$ or $[C_4mpyr][NTf_2]$.

Conclusion

Electrochemistry combined with variable-temperature ²⁷Al and ¹³C NMR spectroscopic experiments were used to probe aluminium speciation in mixtures of [C₃mpip][NTf₂] and [C₄mpyr][NTf₂] with AlCl₃ in an effort to pinpoint the electroactive species responsible for aluminium electrodeposition in these ionic liquids. In this study we obtained spectroscopic evidence for $[AlCl_3(NTf_2)]^-$ and $[AlCl_2(NTf_2)_2]^-$, the two potential electroactive aluminium-containing species previously proposed from the study of [C4mpyr][NTf2]-AlCl₃ and [C₂mim][NTf₂]-AlCl₃ mixtures. On the basis of electrodeposition experiments, we were also able to determine which of these two species was the electroactive species. An improved understanding of the coordination chemistry that occurs in ionic liquids that contain metal ions is critical to the development of commercially attractive metal electrodeposition processes that involve ionic liquids.

Solutions that contain low concentrations of AlCl₃ from which aluminium can not be electrodeposited at room temperature can become electrochemically active by raising the temperature to approximately 80 °C. Increasing the temperature generates favourable aluminium chemistry. Only electrochemically inactive AlCl₄⁻ and Al(NTf₂)₃ are present in these solutions at room temperature by ²⁷Al NMR spectroscopy. However, between 70 and 80°C the 4-coordinate $[AlCl_3(NTf_2)]^-$ species becomes apparent in both the [C₃mpyr][NTf₂]-AlCl₃ and [C₄mpyr][NTf₂]-AlCl₃ mixtures at $x_{AlCla} = 0.24$ and 0.50. The appearance of this species coincides with the ability to electrodeposit aluminium from these solutions and is irrespective of the AlCl₃ concentration. This work therefore shows that the electroactive aluminium-containing species responsible for aluminium electrodeposition in both ionic liquids is more than likely the 4-coordinate [AlCl₃(NTf₂)]⁻ species. The 6-coordinate [AlCl₂- $(NTf_2)_2$ species is also formed in solution at slightly higher temperatures at significantly lower concentrations. It is not deemed to be the electroactive species due to the temperature at which it forms and its apparent low concentration in solution.

Identification of the electroactive aluminium-containing species in the ubiquitous NTf_2 -based ionic liquids provides valuable information on the type of coordination chemistry one should contemplate for aluminium electrodeposition applications.

Experimental Section

Chemicals: In this study, all chemicals were used as received. The highest quality $[C_4mpyr][NTf_2]$ (ultra pure >99%) was purchased from Merck. **Synthesis of the ionic liquid [C₃mpip][NTf₂]**: The precursor 1-propyl-1-methylpiperidinium iodide (C₃mpipI) was prepared by mixing 1-methylpiperidine (Aldrich, 99%) with a 5% molar excess of 1-iodopropane (Aldrich, 99%) in acetone (Merck) at ambient temperature for 48 h under a dry nitrogen atmosphere. The resultant solid was collected, washed repeatedly with acetone and dried under vacuum at 40°C. The crude product was recrystallised from acetonitrile (Aldrich) and the resultant white

solid was collected by filtration and dried under vacuum at 40 °C. The ionic liquid [C₃mpip][NTf₂] was subsequently prepared by means of an ion-exchange reaction by slowly adding an equimolar amount of LiNTf₂ (3 M, 99.5 %) to C₃mpipI in water. The lower phase of the resultant biphasic mixture that contained the crude [C₃mpip][NTf₂] was repeatedly washed with ultrapure Milli-Q water (specific resistance of >18.2 MΩ cm) until no evidence of residual iodide was detected by a AgNO₃ test. The bulk of the water was then removed in vacuo on a rotary evaporator and the product dried under high vacuum (<5× 10⁻² mbar) at 50 °C for 48 h. The product was stored in a flask equipped with a drying tube that contained lithium to remove trace amounts of residual water and kept in an argon-filled glove box.

Ionic liquid–AICl₃ mixture preparation: $[C_3mpip][NTf_2]$ –AICl₃ and $[C_4mpyr][NTf_2]$ –AlCl₃ samples were prepared by slow addition of weighed amounts of anhydrous AICl₃ (Aldrich, 99.99%) to weighed amounts of $[C_3mpip][NTf_2]$ and $[C_4mpyr][NTf_2]$, respectively, under constant stirring inside an argon-filled glove box in which the H₂O and O₂ levels were maintained at less than 1 ppm.

Instrumentation and analysis: The ²⁷Al NMR spectra of the [C₃mpip]-[NTf₂]–AlCl₃ and [C₄mpyr][NTf₂]–AlCl₃ mixtures were recorded using a Bruker Av400 spectrometer and a Bruker DRX500 spectrometer, respectively, operating at 104.3 and 130.3 MHz, respectively. The ²⁷Al chemicalshift values were reported relative to an aqueous solution of Al-(NO₃)₃·9 H₂O as an external reference. The ¹³C NMR spectra of the [C₃mpip][NTf₂]–AlCl₃ and [C₄mpyr][NTf₂]–AlCl₃ mixtures were recorded using a Bruker Av400 spectrometer and a Bruker DRX500 spectrometer, respectively, operating at 100.6 and 125.8 MHz, respectively.

The water content of the dried $[C_3mpip][NTf_2]$ was determined to be <10 ppm by coulometric Karl Fischer titration (Metrohm 756 KF Coulometer). The levels of residual lithium and iodide ions in the $[C_3mpip][NTf_2]$ were estimated by inductively coupled plasma mass spectrometry (Thermo Elemental X Series ICP-MS) and ion chromatography (Dionex DX 300 ion-chromatograph), respectively, and found to be <2 ppm and below the detection limit (3 ppm), respectively.

The morphologies of the electrodeposits were imaged using a FEI Quanta 400F environmental scanning electron microscope (ESEM). The elemental compositions of the electrodeposits were determined by energy-dispersive X-ray analysis using an EDS detector and control software from EDAX. X-ray diffractograms of the deposits were recorded using a PANAlytical X'Pert PRO Multi-Purpose Diffractometer with $Cu_{K\alpha}$ radiation. The deposits were examined while still attached to the working electrodes. Crystallite sizes were determined using the profile and structure analysis software DIFFRAC^{plus} TOPAS.

Electrochemistry: Cyclic voltammetry and electrodeposition experiments were performed using a VoltaLab PST050 potentiostat (Radiometer Analytical) controlled by VoltaMaster 4 software in a jacketed electrochemical cell with a standard three-electrode configuration. The temperature of the working solutions were maintained and controlled to within 0.2 °C of the set temperature by using a Julabo Labortechnik heating bath that contained silicon oil (CF350, Admil Adhesives). The jacketed electrochemical cell was designed to be used under vacuum to reduce electrochemical artefacts introduced by dissolved water or gases. The working electrodes were high-purity gold, glassy carbon, platinum and iron rods with diameters between 1 and 3 mm. The walls of the working electrodes were insulated using modified Teflon heat-shrink tubing (Tyco Electronics Corporation). The counter electrode was a 3 mm diameter glassy carbon rod. A silver wire placed inside a Luggin capillary with a glass sinter tip and containing 20 mM silver trifluoromethanesulfonate (Aldrich, >99%) in [C₃mpip][NTf₂] or [C₄mpyr][NTf₂] was used as a pseudo reference electrode. Potentials were referenced to the ferrocene/ferrocenium (Fc/Fc+) couple. The working electrodes were prepared before each electrochemical measurement by abrading their working surfaces on P2000 silicon carbide paper, rinsing them with a jet of ultrapure Milli-Q water and wiping dry on a clean long-nap polishing cloth. All voltammograms were recorded with a scan rate of either 10 or 20 mVs⁻¹. Electrodeposits recovered from the experiments were washed with acetone and ultrapure Milli-Q water to remove excess ionic liquid mixture, then air dried.

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Acknowledgements

This work was conducted under the auspices of the CSIRO Light Metals Flagship. The authors would like to thank Dr. Roger Mulder and Jo Cosgriff of CSIRO Molecular and Health Technologies for collecting the NMR spectroscopic data.

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Received: October 6, 2009 Published online: February 9, 2010