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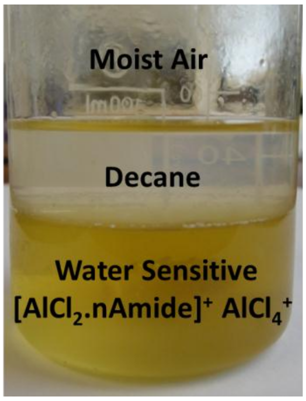
## Graphical Abstract

The electrodeposition of aluminium is demonstrated using a eutectic mixture of aluminium chloride and urea and the use of a protective alkane layer enable aluminium to be deposited under ambient conditions.



# Aluminium Electrodeposition under Ambient Conditions

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## Abstract

The electrodeposition of aluminium is demonstrated using a eutectic mixture of aluminium chloride and urea. The mixture is shown to be conducting through the formation of both cationic ($[AlCl_2.urea_n]^+$) and anionic ($AlCl_4^-$) species and electrodeposition is achieved through the cationic species. The use of a biphasic system with the ionic liquid and a protective hydrocarbon layer allows metal deposition to be carried out in an environment with ambient moisture without the need for a glove box. A direct comparison is made between the $AlCl_3$: urea and imidazolium chloride: $AlCl_3$ systems and the differences in speciation and mass transport manifest themselves in different deposit morphologies. Brighteners which work in the chloroaluminate system such as toluene and LiCl are shown to be ineffective in the urea based system and the reasons for these differences are ascribed to the mechanism of the anodic reaction which is rate limiting.

Key words: Aluminium, electrodeposition, eutectic, urea, speciation

## Introduction

A facile, low temperature and moisture insensitive route to the electrodeposition of aluminium remains a key technological goal. Aluminium remains an elusive coating material due to the sensitivity of most precursors to hydrolysis. To date only the SIGNAL process has been operated under commercial conditions. This was ultimately discontinued due to the pyrophoric nature of triethyl aluminium.[1,2]

Numerous groups have studied the electrodeposition of aluminium using ionic liquids. Most of these have used eutectic mixtures of quaternary ammonium chloride with aluminium chloride. These studies have shown that the metal can only be electrodeposited using Lewis acidic mixtures ($x_{AlCl3} > 0.5$). Many papers have been published on the electrodeposition of aluminium and its alloys from chloroaluminate, so-called first generation ionic liquids.[3,4,5,6] These liquids are easy to synthesize by simple addition of the Lewis acidic $AlCl_3$ to a 1, 3-dialkyl-imidazolium chloride, alkyl-pyridinium chloride or quaternary ammonium compound under an inert atmosphere. The liquids are however still relatively moisture sensitive and it has recently been shown that the morphology of the deposit is sensitive to parameters such as the nature of the Lewis acidity, cationic additives and diluents.[7] It was shown that toluene could act as a good brightener and mirror bright deposits could be obtained. This was ascribed to an increase in the rate of the anodic reaction brought about by a decrease in the viscosity of the liquid. The addition of LiCl was also found to significantly affect deposit morphology through changes to the double layer structure.

We have recently shown that the addition of a simple amide to $AlCl_3$ causes the formation of a liquid of the form $[AlCl_2.nAmide]^+$ $AlCl_4^-$. The material thus produced is liquid over a wide temperature range, is relatively insensitive to water and has the properties of an ionic liquid.[8] In the current study it is shown that mixtures of $AlCl_3$ and urea can be easily handled under a layer of decane in a normal humidity environment. Relatively thick adherent aluminium layers can be deposited using this liquid.

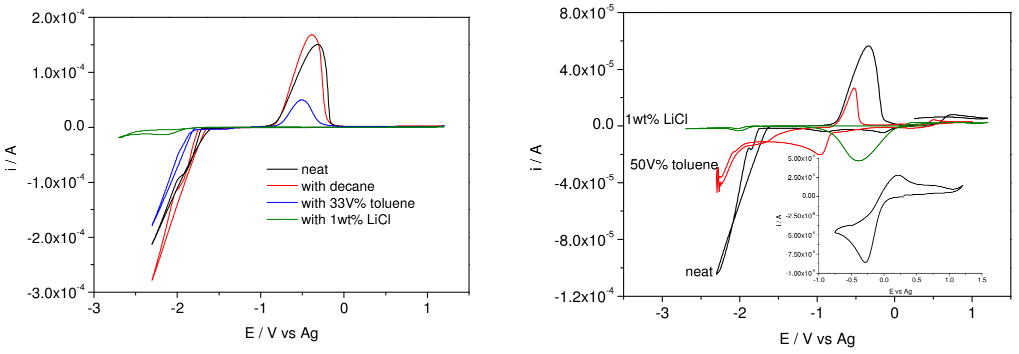
## Experimental

The liquid was synthesized by slowly mixing aluminium chloride (Fluka >99%) and urea (Fisher Scientific analytical reagent grade) together at room temperature under a dry nitrogen atmosphere. A homogeneous straw-brown liquid was formed. All electrochemical studies were carried out using an Autolab PGSTAT 12 potentiostat controlled by GPES software with a three-electrode system. Glassy carbon (1.5 mm radius), Pt disc (1 mm radius), and Al disc (0.5 mm radius) working electrodes, Pt foil counter electrode (area = 1 $cm^2$), and a silver wire reference electrode (area = 0.9 $cm^2$) were used. The working electrodes were polished with 0.3 μm alumina paste, washed by deionised water, and dried prior to all measurements. All voltammograms were performed at 25 $^oC$ and scan rate of 20 $mVs^{-1}$.

Electroplating experiments were carried out in two-electrode system. The decane layer (Fluka analytical) was on the top of the eutectic solvent to avoid contact with the air. Different volume ratios of toluene (Fisher Scientific laboratory reagent grade) were added. The cathodes were mild steel sheets, and the anode was an Al mesh. The cathodes were abraded by using the sand paper followed by rinsing with deionised water, then dipped into 10V% HCl, deionised water and acetone for 5 min, respectively. The anode was cleaned by dipping into 50V% HCl, deionised water and acetone. After deposition, samples were rinsed in i-propanol followed by deionised water and then dried in air before characterization. The morphologies of the deposits were visualized using scanning electron microscopy (Philips XL30 ESEM) and energy dispersive analysis by X-ray (EDX). The phase compositions were characterized by X-ray diffraction (XRD). NMR characterisation was carried out by the process described in the literature.[9] An electrochemical quartz crystal microbalance consisting of an Agilent HPE5061A network analyser with a 10 MHz AT-cut gold quartz crystal (International Crystal Manufacturing Co., Oklahoma City, USA) was used. A three-electrode compartment cell was constructed from PTFE, with an unpolished gold coated crystal working electrode, a silver wire reference electrode and a Pt flag counter electrode. The electrodes were connected to a potentiostat (Autolab 263A) in order to record voltammetric data. The quartz crystal had a piezoelectrically active area of 0.23 $cm^2$. Current efficiency was measured at -2 V vs Ag.

## Results

**Fig. 1** shows the voltammetry of an equimolar mixture of $AlCl_3$: urea mixture on a glassy carbon electrode. A clear signal for the reduction of aluminium is observed at -1.6 V and the anodic dissolution is also observed at -0.9 V. In the Lewis acidic mixtures of $AlCl_3$ and ethyl-methyl-imidazolium chloride ($C_2$mimCl) the reduction and oxidation onset potentials differ by less than 0.1 V whereas in the systems shown in **Fig. 1** show a difference of *c.a.* 0.7 V.



*a* *b*

***Fig.1**: Cyclic voltammograms recorded on GC disc electrode in 1-1 $AlCl_3$-urea neat, with decane, with 33V% toluene, and 1wt% LiCl. a) GC electrode b) Pt electrode The inset shows the under-potential deposition on Pt electrode in the neat liquid.*

Previously we have shown that $AlCl_3$ cannot be reduced in mixtures where $x_{AlCl3} < 0.5$ because the primary species, $AlCl_4^-$, cannot be reduced.[7] We have therefore previously concluded that reduction of the metal occurs from the cationic species $[AlCl_2.urea]^+$. The double layer at the deposition potential is dominated by cations and this should change significantly the deposition characteristics compared to the $AlCl_3$: $C_2$mimCl system where the metal species are predominantly $Al_2Cl_7^-$ and the layer adjacent to the electrode is dominated by $C_2$mim cations.

One of the limitations of aluminium deposition using ionic liquids is the moisture sensitivity. One simple method to decrease the absorption of water into the ionic liquid is to float a layer of a hydrophobic liquid on top of the ionic liquid. We have used a variety of saturated hydrocarbons which are functional but decane has a relatively wide liquid range and shows relatively low volatility and has been used throughout this study. **Fig. 2** shows a photograph of the neat liquid with a decane upper phase. This was taken under ambient humidity conditions *c.a.* 50% and no fuming of the aluminium-based liquid is observed. The advantage of this configuration is that pieces can be simply immersed through the bilayer and direct plating can take place without purging the environment surrounding the cell first. There appears to be negligible mutual solubility of the two layers (as detected by nmr) and **Fig. 1** shows that there is negligible difference between the voltammetry of the cell in glove-box conditions compared to that in ambient conditions with a protective decane layer. The lack of solubility may seem unusual given that urea forms adducts with decane[10] however these adducts form because the urea produces hydrogen bonded cages around the alkane and the strong complexation with the aluminium prevents it from doing so with these eutectic mixtures. No discoloration of the aluminium layer is noted up to approximately 1 week. Thereafter some cloudiness is observed and there is a marked decrease in the deposit quality presumably due to the slow ingress of water from the atmosphere. The same result can be obtained through the deliberate addition of small quantities of water to the liquid. While one week is insufficient longevity for a practical electroplating bath it is a significant improvement over operating in a strict glove-box environment. It could be possible to put a water scavenger in the oil phase however much of the extraneous water probably enters the ionic liquid phase with the immersion of the electrodes.

***Fig. 2****: Photographs of phase behaviour of decane with a) [$AlCl_2$. urea]$^+$ $AlCl_4^-$ b) as (a) with 20 vol % toluene.*

**Fig. 1** also shows the voltammetry of the 1:1 $AlCl_3$: urea liquid in an ambient humidity environment with a protecting layer of decane. It can be seen that the results are extensively the same as those obtained using a glove-box demonstrating the efficacy of this methodology.

It was previously shown[7] that the addition of LiCl to the Lewis acidic mixtures of $AlCl_3$ and $C_2$mimCl did not significantly change the voltammetry but it did have a marked effect upon the morphology of the deposit. This was a complimentary result to that of Endres[11] who showed that the cation from the ionic liquid could also change morphology. Endres also showed that the effect was due to the adsorption $Li^+$ at the electrode surface.[12]

The addition of 1 wt% LiCl to the $AlCl_3$: urea eutectic causes the current for deposition and stripping to decrease significantly and this is thought to arise from the liquid becoming more Lewis basic with the aluminium cation reacting with LiCl forming $AlCl_4^-$.

$[AlCl_2.nAmide]^+ AlCl_4^+ + 2\ LiCl \leftrightarrows 2[Li^+.\ nAmide\ .AlCl_4^-]$

Since no aluminium is deposited when LiCl is added to the liquid this tends to confirm that the aluminium is deposited from the $[AlCl_2.nAmide]^+$ species.

**Fig. 3** shows the voltammetry of various $AlCl_3$/urea mixtures with different compositions between 1:1 and 1:2. It can be seen that there is relatively little difference in the stripping voltammetry but the onset voltage for the 1:1 mixture is shifted significantly in the cathodic direction. This could be due to changes in speciation. It was previously shown[8] that in the 1:1 mixture there is more $[AlCl_2.urea]^+$than $[AlCl_2.urea_2]^+$which we assume changes the relative ability of the species to be reduced. It should not, however affect its ability to be oxidised and therefore the oxidation potential does not change. There is a large increase in the current as the liquid becomes more Lewis acidic due to more aluminium species in the liquid (see Table 1 for compositional changes). This is despite a significant increase in the solution viscosity.

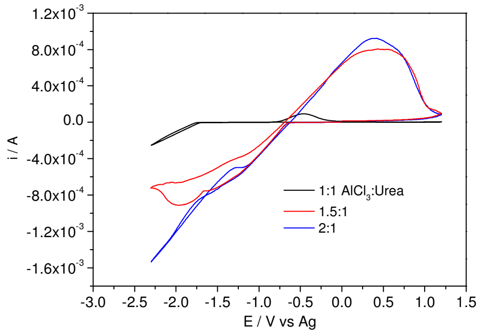


***Fig. 3***: *Cyclic voltammetry of various $AlCl_3$/urea mixtures as a function of composition on a GC disc electrode*

It has previously been shown that $^{27}$Al NMR can be used to identify and quantify speciation in ionic liquids.[8,9] The three peaks in the $AlCl_3$: acetamide system have direct analogues in the $AlCl_3$: urea systems which occur at almost exactly the same δ values and so these have been ascribed to δ = 102 ($[AlCl_2(urea)_2]^+$ ), 88 ($AlCl_4^-$ ) and 74 ($[AlCl_2(urea)]^+$) ppm. **Fig. 4** shows the $^{27}$Al NMR spectra as a function of $AlCl_3$ composition. Qualitatively it can be seen that the proportions of the cationic species vary with composition although as more $AlCl_3$ is added to the system the signals become very broad and quantification becomes difficult due to an increase in viscosity. **Table 1** shows that at a 1:1 composition, $AlCl_4^-$ makes up approximately half of the aluminium species and the two cationic aluminium species have approximately equal content. If all of the urea was bound to aluminium then a 1:1 mixture would be expected to contain just $[AlCl_2(urea)_2]^+$. This suggests that either the urea is "free" in solution, or more likely it is hydrogen bonded to the aluminium containing anion.

| Sample $AlCl_3$: urea | Chemical shift δ/ppm | Line width σ/ppm | $T_2$/ms | Integral /% |
|---|---|---|---|---|
| 1.0: 1.0<br>Liquid neat | 73.03 | 6.372 | 0.38 | 22 |
| | 88.95 | 3.187 | 0.77 | 51 |
| | 102.30 | 1.912 | 1.28 | 27 |
| 1.0: 1.0<br>Liquid + 33 V%<br>toluene | 73.96 | 1.521 | 1.61 | 22 |
| | 89.70 | 0.760 | 3.21 | 54 |
| | 102.81 | 1.520 | 1.61 | 24 |
| 1.0: 1.0<br>Liquid + 50 V%<br>toluene | 74.60 | 1.569 | 1.56 | 18 |
| | 90.35 | 1.884 | 1.30 | 55 |
| | 103.06 | 6.591 | 0.37 | 27 |

***Table 1:*** *Chemical shift, line width and relaxation time data for $^{27}$Al NMR spectra of 1-1 $AlCl_3$ : urea eutectic mixture with and without addition of toluene.*

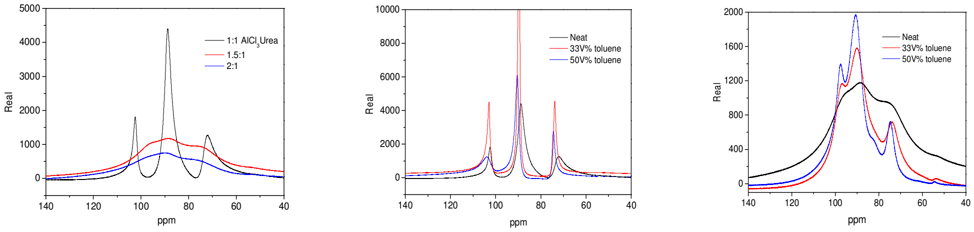


***Fig.4:*** *$^{27}$Al spectra of (left) $AlCl_3$-urea mixtures in different molar ratios (middle) 1-1 $AlCl_3$-urea as a function of added toluene content and (right) as (middle) but for 1.5-1 $AlCl_3$-urea*

Bulk electrolysis experiments carried out for 1 hour at constant current yielded metallic aluminium films, albeit relatively dull in appearance (**Fig. 5**). During bulk deposition at constant current the cell voltage was generally about -1V due to using an aluminium anode and this did not lead to appreciable ohmic heating of the liquid.

Electrochemical quartz crystal microbalance studies showed that the current efficiency of metal deposition was in the region of 95% showing that there is negligible gassing at the cathode surface. Scanning electron microscopy shows a non-macrocrystalline structure which is not dissimilar to that observed for the electrodeposition of aluminium from $AlCl_3$: $C_2$mimCl systems. There is, however a marked difference in the adherence of the aluminium deposits on mild steel. A significant issue noted with the deposition of aluminium using $AlCl_3$: $C_2$mimCl systems with steel substrates appears to be the development of dense but stressed coatings which tend to peel easily from the substrate.[7] The $AlCl_3$: urea systems have less inherent stress and do not flake away from the surface in the same way as those prepared using the imidazolium based liquids.

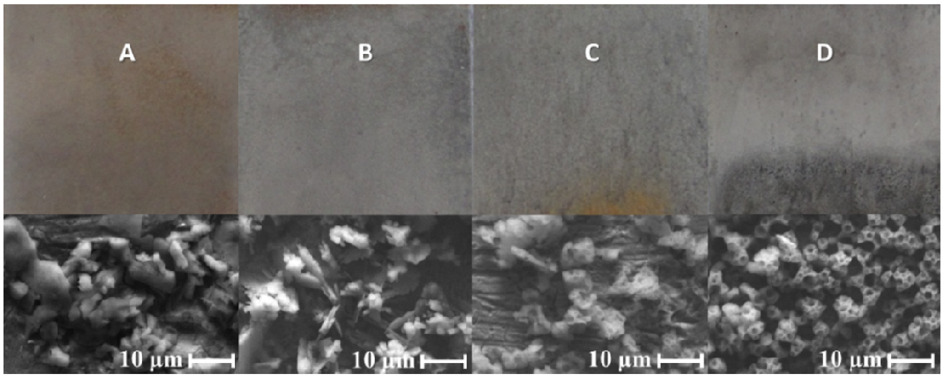


***Fig. 5****:Optical photographs (above) and SEM images (below) of aluminium deposits from a 1.5:1 $AlCl_3$-urea (A-B) and 1.5:1 $AlCl_3$-urea with 20 vol % toluene (C-D) All samples deposited for 1 hour on mild steel using an Al counter electrode. (A:3, B:3.5, C:3, D:3.5mAcm$^{-2}$.)*

### Addition of toluene

Previously[7] it has been shown that the addition of toluene to Lewis acidic mixtures of $AlCl_3$ and $C_2$mimCl leads to brighter and denser aluminium layers. The addition of toluene is known to result in a charge transfer complex,[13] but it is not known if this will also occur with a cationic aluminium containing species. **Fig. 2** shows the biphasic decane/ $AlCl_3$: urea with 20 vol% toluene added. This does not appear to affect the phase behaviour of the system, although it does make the aluminium containing phase less viscous. The aluminium layer does become very dark in appearance in an analogous way to the $AlCl_3$: $C_2mimCl$ system7 suggesting that charge transfer complexes are also formed between an aluminium containing species and the aromatic ring of toluene.

To probe this further $^{27}Al$ NMR was carried out and the results are shown in **Fig. 4** with the process parameters listed in **Table 1**. It can be seen that the positions of the peaks for the three aluminium containing species are changed slightly by the addition of toluene.[8] It is thought that these changes are due to the formation of a charge transfer complex which is characterized by an intensely coloured liquid. **Table 1** shows that the integral for the $AlCl_4^-$ species (88 ppm) is roughly equivalent to the sum of the other two cationic species when toluene is added to the system. While there are some fluctuations in the amounts of each species they remain generally similar. The line width of the ($AlCl_4^-$) and ($[AlCl_2(urea)]^+$) signals decreased as toluene was added to the mixture and this was accompanied by an increase in the $T_2$ value which is consistent with a decrease in the liquid viscosity. The line width for the ($[AlCl_2(urea)_2]^+$ ) signal increases with the addition of toluene which is consistent with this species behaving differently to that with one urea ligand. It is also worth noting that the change in chemical shift with added toluene for the species with two urea ligands is also much less than that for the other two species.

Repeating the $^{27}Al$ NMR analysis for the non-eutectic mixtures (1.5-1 and 2:1 $AlCl_3$-urea) showed a similar trend *i.e.* a change to higher chemical shift values as toluene was added and an increase in the intensity of the peak at 102 *vs.* that at 73 ppm as more species contains 2 urea ligands. This also helps to confirm the assignment of the signals. Quantification of the effect is however not possible due to the increase in line broadening resulting from a significant increase in liquid viscosity.

The addition of toluene leads to an increase in fluidity and conductivity of the liquid. When a significant volume of toluene is added to the $AlCl_3$ system it cannot be described as an ionic liquid. **Fig. 1** shows that the addition of toluene to a 1:1 $AlCl_3$: urea eutectic leads to an increase for the deposition and stripping current for aluminium. This is despite the actual decrease in the concentration of aluminium containing species in the liquid. The same is observed for the 2:1 $AlCl_3$: $C_2mimCl$ eutectic. This is ascribed to the increase in solution conductivity (**Fig. 6**) resulting from the decreased viscosity. **Fig. 6b** shows that the molar conductivity as a function of toluene composition and it can be seen that the molar conductivity decreases as more charge carriers are added to the system, which must be a viscosity effect. A similar result has been shown for various $C_n$mim$BF_4$ salts with a variety of polar and non-polar diluents.[14] This is interesting as it shows that the polarity of the diluent has little effect upon the conductivity of the mixture which shows that mass transport is the major factor affecting charge transport.

**Fig. 1b** shows the comparative deposition of Al on a Pt electrode. It can be seen that there is a significant difference between the voltammetry of the liquid on glassy carbon and platinum. On platinum there is clear evidence of under-potential deposition at 0 V both in the neat liquid and that with toluene added. The under-potential deposition (upd) is perfectly reversible (**Fig 1b** (inset)) and is clearly affected by the addition of toluene which is presumably due to the changes in speciation. The upd signal is decreased by the addition of toluene but a signal for bulk aluminium deposition appears at -0.7 V accompanied by a fully reversible stripping peak.

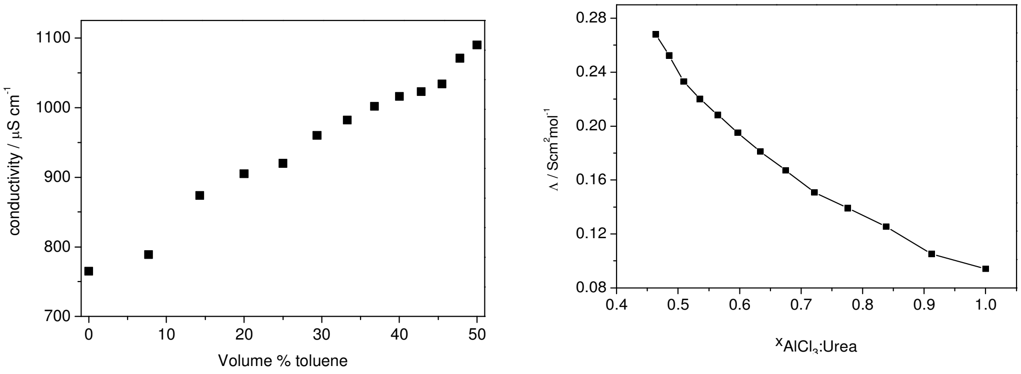


***Fig.6*** *Plots of conductivity and molar conductivity as a function of toluene content for 1-1* $AlCl_3$*-urea.*

***Nucleation and Growth***: To interrogate the mechanism by which metal films grew on the electrode surface and how these differed from the $C_2$mimCl:$AlCl_3$ system chronoamperometry and chronocoulometry were carried out. **Fig. 7** shows the chronocoulometry results for the deposition of aluminium following a potential step from 0.4 to -2.3 V in a 1:1 $AlCl_3$-urea on a glassy carbon electrode. In the absence of toluene the charge *vs.* $t^{1/2}$ plot for the $AlCl_3$/urea system is not linear suggesting that material growth is not diffusion limited which was the case for the $C_2$mimCl:$AlCl_3$

system. Interestingly the charge passed when toluene is added to the ionic liquid is lower than that without toluene, despite the current on the cyclic voltammogram being larger when toluene is added to the liquid. Chronoamperometry shows a nucleation mechanism which is close to that expected for a purely 3D instantaneous nucleation mechanism at shorter timescales but deviates at longer timescales (**Fig. 8**). The addition of toluene causes the plot of charge *vs.* $t^{1/2}$ to become more linear although it is still not what would be expected for a purely diffusion limited process. In the $C_2$mimCl:$AlCl_3$ system the addition of toluene was shown to have little effect on the chronocoulometric response which shows that the urea based system has a different growth mechanism.

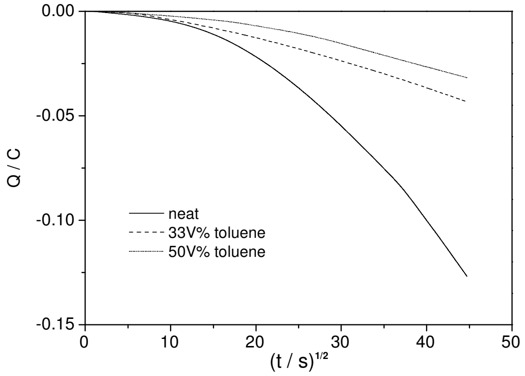


***Fig. 7:*** *Chronocoulometry of 1-1 $AlCl_3$-urea for the potential step from 0.4 to -2.3V, with and without toluene on GC electrode*

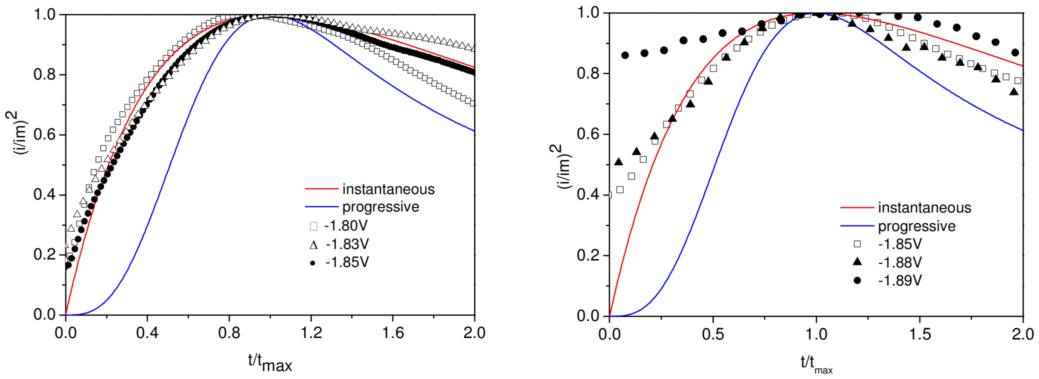


***Fig 8:*** *Chronoamperometry recorded on GC at different potentials for (left) neat 1-1 $AlCl_3$-urea and (right) with 33V% toluene.*

**Fig. 9** shows the deposits obtained with different amounts of toluene added to a 1:1

$AlCl_3$: urea mixture. The deposits are all relatively similar and the significant improvement observed previously by adding toluene to the1:2 $C_2$mimCl:$AlCl_3$ liquid is not evident with the urea-based eutectic. XRD analysis was carried out on the deposits shown in **Fig. 5** and **Fig. 9** and all were shown to have the same dominant crystal structures present; namely (100), (200), (220) and (311). These are the same responses as seen for aluminium deposited from other media.[15,16,17,18] This shows that the deposits are generally similar in their crystal structures but differ in the growth mechanism.

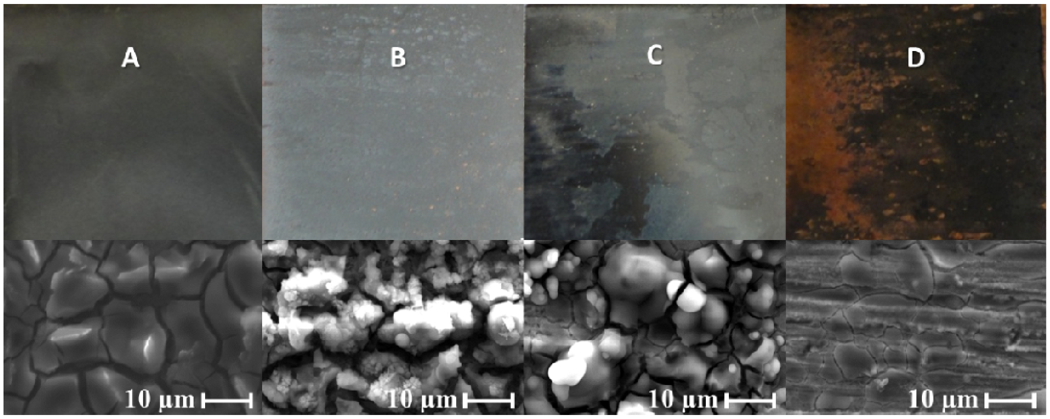


***Fig. 9****: SEM images and optical photographs of aluminium deposited from (i) 1-1 $AlCl_3$-urea (A) no additive (B) with 20V% toluene, (C) 33V% toluene, (D) 50V% toluene (All 1 V for 1 hour).*

It has previously been shown that the anodic process in the 1:2 $C_2$mimCl:$AlCl_3$ liquid is process limiting and the addition of toluene increases the rate of aluminium dissolution through improved mass transport. The dissolution of aluminium is limited by the availability of a suitable ligand and must proceed via the reaction

$Al^{3+} + 7AlCl_4^- \leftrightarrow 4Al_2Cl_7^-$

The same must be the case in the $AlCl_3$: urea system although the lack of chloride ligands will probably favour the process

$Al^{3+} + AlCl_4^- + 2\text{ urea} \leftrightarrow 2AlCl_2\text{.urea}^+$

The comparative dissolution and deposition rates were previously studied for the 1:2 $C_2$mimCl:$AlCl_3$ system using voltammetry on an aluminium working electrode and it was found that the current for the dissolution of the aluminium substrate on an anodic sweep is smaller than that for aluminium deposition on a cathodic sweep. The same experiment was repeated with the 1-1 $AlCl_3$-urea using an aluminium substrate and the result is shown in Fig. 10. The reduction of aluminium occurs below – 1.7 V and this aluminium is largely stripped off at potentials above -0.7 V. Extending the anodic sweep to + 1.2 V results in a second anodic process above +0.5 V which is the equivalent of determining the relative rate of the anodic reaction if an aluminium anode was used. It can be seen that the charge for bulk aluminium dissolution is less than that for aluminium deposition confirming as has previously be shown for DESs that the anodic reaction is rate determining. Furthermore the addition of toluene suppresses the anodic dissolution process (Fig 8) which is opposite to the effect in $C_2mimCl:AlCl_3$.[7] This suggests that it is the number of ligands which is important rather than their mass transport.

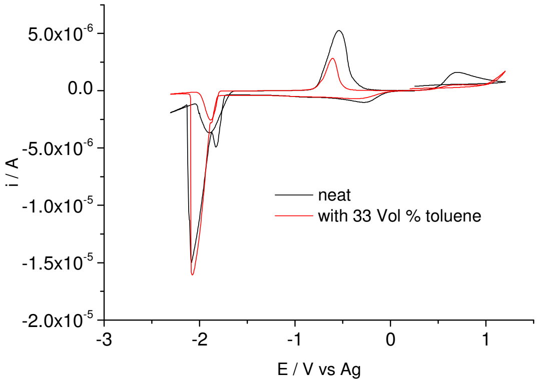


***Fig.10***: *Cyclic voltammograms recorded on Al disc electrode in 1-1 $AlCl_3$-urea neat and with 33V% toluene.*

## Conclusions

This study has shown that eutectic mixtures of urea and $AlCl_3$ can be used for the electrodeposition of aluminium. A simple but important advancement in the technology is the use of an immiscible hydrocarbon layer over the top of the moisture sensitive ionic liquid to isolate it from the atmosphere. This has allowed thick adherent pure aluminium films to be deposited on a range of substrates. The addition of toluene decreases the viscosity and increases the conductivity of the liquid but this has comparatively little effect upon the deposit morphology unlike the corresponding imidazolium chloride: aluminium chloride system where mirror bright aluminium can be deposited via the addition of toluene. It is shown that the anodic reaction is rate limiting and this is the aspect that needs to be addressed to improve the deposit quality.

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