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### Abstract

The electro-deposition of titanium from two different classes of ionic liquids has been studied. Gold ions in solution have been used as an additive in order to provide a stable nucleation site for titanium to deposit on *via* a co-deposition process. Despite evidence from previous literature, it was found that it was not possible to reduce titanium from the +4 state to titanium (0) due to problems of redox cycling and solubility of reduced titanium species in the various ILs trialled. It was however found that gold was a very effective nucleating agent for these reduced titanium species and that successful mixed  $Ti^{n+}$ /gold electro-deposits were obtained. The content of titanium in these species could be varied according to the conditions and IL used.

### Keywords

Electrochemical, deposition, phases, gold, ionic, liquids

### Disciplines

Life Sciences | Physical Sciences and Mathematics | Social and Behavioral Sciences

### Publication Details

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# Electrochemical co-deposition of $Ti^{n+}$ phases with gold in ionic liquids

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The electro-deposition of titanium from two different classes of ionic liquids has been studied. Gold ions in solution have been used as an additive in order to provide a stable nucleation site for titanium to deposit on *via* a co-deposition process. Despite evidence from previous literature, it was found that it was not possible to reduce titanium from the +4 state to titanium (0) due to problems of redox cycling and solubility of reduced titanium species in the various ILs trialled. It was however found that gold was a very effective nucleating agent for these reduced titanium species and that successful mixed  $Ti^{n+}$ /gold electro-deposits were obtained. The content of titanium in these species could be varied according to the conditions and IL used.

## Introduction

Titanium is an industrially important metal used in many applications due to its physical and corrosion properties. Current processing of titanium rich ores to obtain the metal involves high temperature molten salts as the most efficient media for titanium electro-deposition.<sup>1–4</sup> Such media and conditions are problematic and corrosive. Past attempts to use other organic<sup>5,6</sup> or aqueous<sup>7</sup> media have not been very successful. In recent years, the increasing interest and availability of room temperature ionic liquids (IL) has led to a growing literature on the electro-deposition of metals from these novel media.<sup>8–18</sup>

This success, due to the many desirable properties of IL, such as wide electrochemical windows, good conductivity and wide liquid temperature range,<sup>15,19</sup> has led a number of groups to investigate the potential for using IL to produce titanium. However, to date reports of the direct electro-deposition of titanium from a range of ionic liquids at room temperature have not been convincing or successful. Attempts have been hampered by difficulties in eliminating redox cycling of multi-valent titanium ions, formation of titanium sub-halide species and handling very reactive dendritic products.<sup>20</sup> It is believed that titanium is deposited in a very reactive form, which may be subsequently chemically attacked. The titanium electro-deposits can only be obtained by producing large nuclei, which affect either the nucleation kinetics or the chemical reactivity of the growing surface, and hence induce adherent titanium deposition.<sup>21</sup> Other work has reported that the titanium was electro-deposited<sup>22</sup> on Au(III) and the step edge of HOPG (highly oriented pyrolytic graphite)<sup>23</sup> from ionic liquids although only a trace amount of titanium metal was obtained. Abbott and co-workers have reported that titanium electro-deposition has been achieved using a foreign metal (such as

silver) as an additive in several kinds of aromatic solvent, which nucleates readily, allowing growth of titanium on these nuclei.<sup>21</sup> Shinsaku has shown that titanium electro-deposition has occurred on an aluminium cathode in propylene carbonate, with Ti forming an alloy with Al.<sup>24</sup>

A recent paper<sup>22</sup> describes the deposition of Ti from  $TiCl_4$  in butyl methyl imidazolium bis(trifluoromethanesulfonyl)amide (bmim NTf2) at a gold electrode. This paper uses cyclic voltammetry, chronoamperometry and *in situ* scanning tunnelling microscopy (STM) to follow the reduction process of  $Ti(IV)$  to  $Ti(II)$  and then deposition of  $Ti(0)$  at a potential of around  $-1.8$  V (vs. a ferrocene/ferrocenium  $Fc^+/Fc$  reference) onto a Au(111) substrate surface. The amounts of deposit formed are very small, being just a few monolayers thick and essentially this work looks at the nucleation process. In addition, definitive evidence for the presence of Ti metal is lacking.

This work though does provide a parallel to our own investigations which have been aimed at trying to produce titanium *via* an ambient temperature electrochemical method using ionic liquids as a viable alternative to current high temperature methods such as the Kroll process used industrially.<sup>25</sup> Part of this work has involved studying the redox chemistry of titanium in ionic liquids and the problems of redox recycling of the species between the electrodes and the solubility of these species. This included a detailed *in situ* EC-STM study of the electro-deposition process, where the difficulties of trying to deposit titanium from  $TiCl_4$  solutions in room temperature ionic liquids are described.<sup>26</sup> The main conclusion from this work was that we were unable to convincingly show that  $TiCl_4$  in ionic liquids was reduced to  $Ti(0)$  by chemical or electrochemical reduction. Rather the presence of non-stoichiometric halides, such as  $TiCl_{0.2}$  and  $TiCl_{1.1}$  were detected in deposits. In addition it was shown that the lack of solubility of  $Ti(II)$  and possibly  $Ti(III)$  chloro species was a major stumbling block to further reduction.

In this current study, we look at the role of gold in being able to facilitate the electro-deposition of titanium species from a number of different ionic liquids including imidazolium based

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types. The use of gold as a substrate was shown to be useful by Mukhopadhyay and co-workers<sup>22,26</sup> for titanium and by El Adebini *et al.* for a range of metals being electro-deposited from ionic liquids.<sup>10,11,13</sup> The electrochemistry of gold chloride solutions in the common ionic liquid 1-butyl-methyl-imidazolium bis(trifluoromethanesulfonyl)amide (bmim NTf<sub>2</sub>) has recently been comprehensively studied.<sup>27</sup> For our study a solution containing gold was trialled to first deposit gold to provide a stable nucleation site for titanium to deposit on.

## Experimental

### Chemicals

Ethyl-methyl-imidazolium bis(trifluoromethanesulfonyl)amide (emim NTf<sub>2</sub>) and methyl-propyl-pyrrolidinium bis(trifluoromethanesulfonyl)amide (C<sub>3</sub>mpyrNTf<sub>2</sub>) were prepared using an existing method.<sup>28</sup> Titanium tetrachloride and gold chloride were obtained from Sigma-Aldrich and used as purchased.

### Apparatus and electrochemical measurements

All experiments involving the ionic liquids were performed in a nitrogen-filled glovebox to exclude water and oxygen. Cyclic voltammetry and electro-deposition (under potentiostatic conditions) were carried out using a three-electrode system. A piece of platinum mesh was used as the auxiliary electrode; a glassy carbon disk was used as the working electrode and an Ag/Ag<sup>+</sup> was used as the reference electrode. This pseudo reference electrode was calibrated against the ferrocene/ferrocenium ion redox couple. The Ag/Ag<sup>+</sup> reference is +0.45 V vs. Fc/Fc<sup>+</sup>. More details are given in the discussion later.

Three different concentrations of Au(III) were prepared (0.01 M, 0.05 M, and 0.1 M) by adding AuCl<sub>3</sub> to 5 ml emim NTf<sub>2</sub> solutions containing 0.59 M TiCl<sub>4</sub>. Experiments to investigate potentiostatic electro-deposition were carried out on these three different solutions giving varying molar ratios of Au(III) to Ti(IV) (Au:Ti, 1:59, 1:12, 1:5.9). The deposition time used was 3 h. Electrodeposition by potentiostatic reduction were carried out at -1.8 or 2.5 V (vs. Ag/Ag<sup>+</sup>).

A second ionic liquid, methyl-propyl-pyrrolidinium bis(trifluoromethanesulfonyl)amide (C<sub>3</sub>mpyrNTf<sub>2</sub>) was trialled for the co-deposition of titanium. This ionic liquid has a substantially larger potential window. It was hoped that it might be feasible to extend the redox chemistry possible using the available potential range of ± 3 V vs. Ag/Ag<sup>+</sup> using this system. Growth of Au-Ti deposits were then followed by studying both CV and potentiostatic reduction at -3.0 V.

### Electron microscopy and XPS measurements

The deposits obtained on a GC electrode and were stored in the ionic liquid and analysed by both SEM and XPS, the latter being carried out at the University of New South Wales, Sydney. Prior to both XPS and SEM work samples were washed to remove residual TiCl<sub>4</sub>/IL solution that may have been attached to the surface of the film. The XPS data were acquired using a monochromatic Al K-alpha X-ray source on an ESCALAB220i-XL photoelectron spectrometer (VG Scientific, UK) at pass energy of 100 eV for wide scans and 20 eV for narrow scans. The step size for narrow scans was 0.1 eV.

The analysis area was about 1 mm<sup>2</sup>. Data files were collected and processed using Eclipse software.

The morphology and microstructure of the Ti-Au co-deposit prepared in this work were investigated using SEM. The images obtained were recorded using a Leica Model Stereoscan 440 scanning electron microscope. The SEM images were taken at different magnifications, varying between ×500 and ×30 000, in order to obtain detailed information on the samples.

## Results and discussion

The potential window of emimNTf<sub>2</sub> at a glassy carbon disk electrode was found to be between about ±2 V vs. Ag/Ag<sup>+</sup>. This was calibrated against the reference standard Ferrocene/Ferrocenium ion (Fc/Fc<sup>+</sup>). For solutions of 0.001–0.02 M Fc/Fc<sup>+</sup> the redox couple was found to be at 0.45 (±0.01) V vs. Ag/Ag<sup>+</sup> and independent of scan rate (10–100 mV s<sup>-1</sup>). Upon addition of 10% w/w TiCl<sub>4</sub> the solution quickly turned yellow. This colour change, we believe, is due to the chloro-titanium complexes formed in solution. The water content (as measured by Karl Fischer titration) of the ionic liquid used is approximately 100 ppm. The change in colour also occurs for batches of ionic liquid that have been prepared under much more stringent conditions (water content less than 10 ppm). Given this concentration of water and that of the TiCl<sub>4</sub> (10% w/w), it is very unlikely that there is a significant role being played by the residual water in hydrolysing the Ti species present in the solution. Whether the residual water plays any other role in the electrochemistry particularly in relation to the stability of the ionic liquid at deeply reductive potential is an interesting matter beyond the scope of this paper but is currently being investigated. Cyclic voltammetry (CV) obtained at a glassy carbon disk electrode of a solution containing 10% w/w TiCl<sub>4</sub> shows a large redox couple centred on 0.4 V with no large tail toward the cathodic limit (Fig. 1). The electrochemistry observed for a solution of emimNTf<sub>2</sub> containing TiCl<sub>4</sub> is almost identical to that seen for a solution of bmimNTf<sub>2</sub> containing TiCl<sub>4</sub> by Mukhopadhyay and co-workers.<sup>22</sup> We have also repeated this experiment using bmimNTf<sub>2</sub> and obtained a similar result (data not shown). The reduction peak at

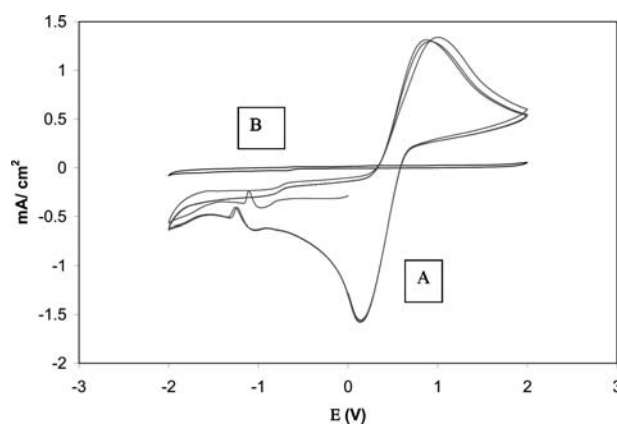
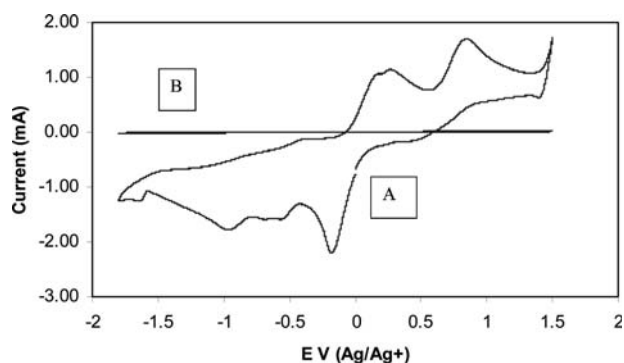
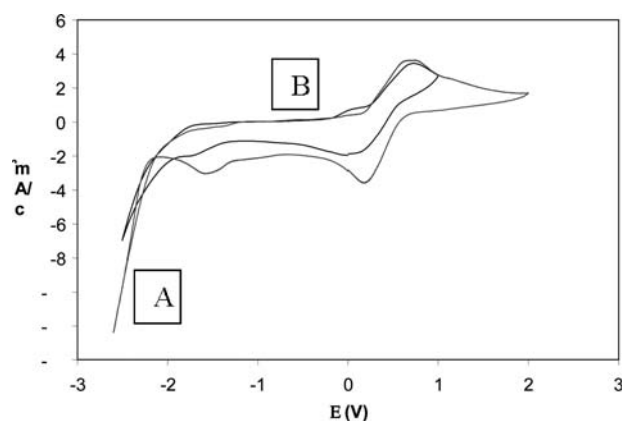


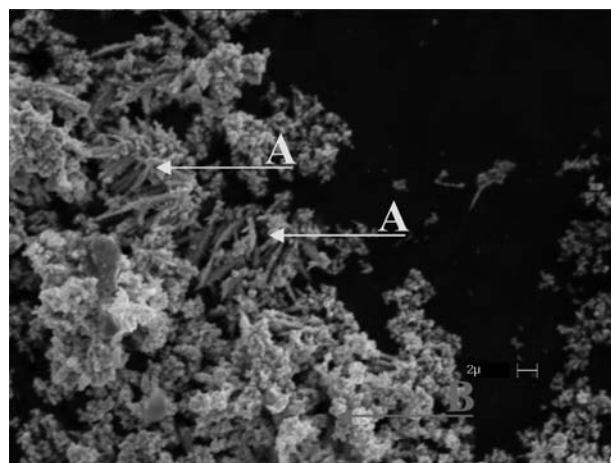
Fig. 1 CV of emim NTf<sub>2</sub> with (A) and without TiCl<sub>4</sub> (B) at a glassy carbon disk working electrode, scan rate: 100 mV s<sup>-1</sup>.



**Fig. 2** CV using GC electrode in emim NTf<sub>2</sub> (A) with and (B) without 0.01 M AuCl<sub>3</sub>.



**Fig. 3** CV of GC electrode in emim NTf<sub>2</sub> containing 0.59 M TiCl<sub>4</sub> with (A) and without (B) 0.01 M AuCl<sub>3</sub>.

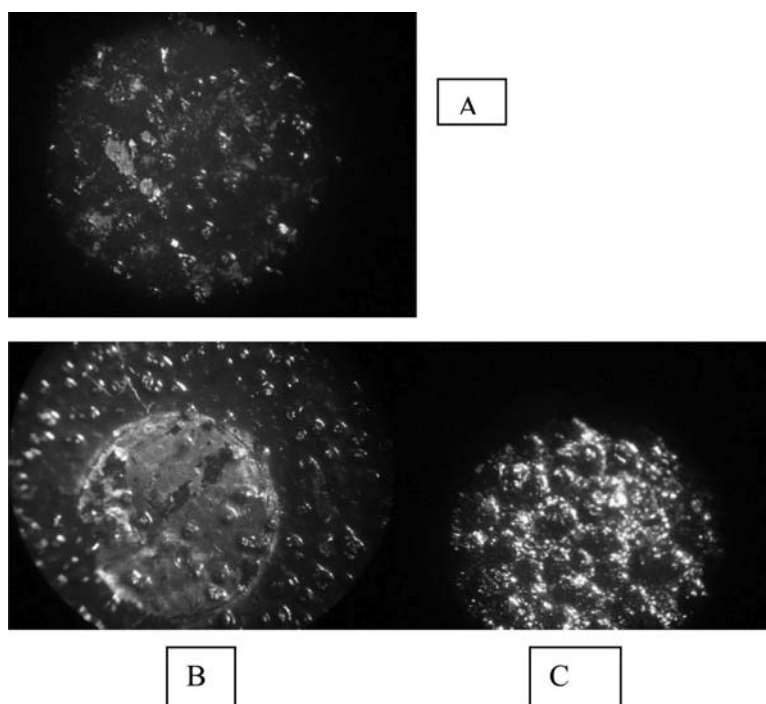


**Fig. 4** SEM of Au/Ti deposit on glassy carbon electrode deposited at  $-2.5$  V for 3 h from a solution of emim NTf<sub>2</sub> containing 0.01 M AuCl<sub>3</sub> and TiCl<sub>4</sub>.

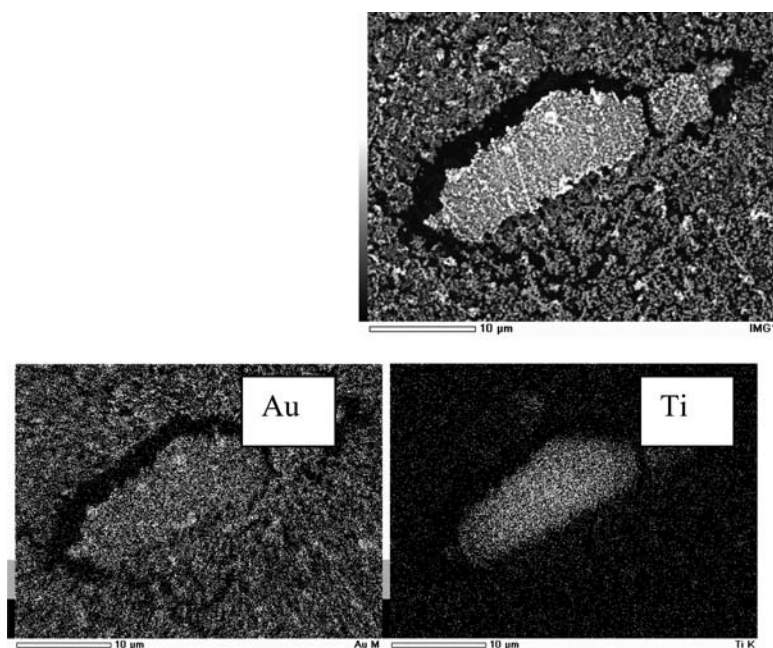
**Table 1** Effect of gold concentration on Ti deposition

AuCl <sub>3</sub> /M	Molar ratio Ti: Au in deposit
0.01	1: 1.76
0.05	1: 6.32
0.10	1: 9.89

$-0.4$  V (vs. Fc/Fc<sup>+</sup>) has been assigned to the Ti(IV) to Ti(II). The available literature also assigns the reduction peak at  $-1.3$ – $1.5$  V (vs. Fc/Fc<sup>+</sup>) to the under potential deposition (UPD) of Ti(II) to Ti metal,<sup>22,23</sup> with 3D deposition of Ti being observed around  $-1.9$  V (vs. Fc/Fc<sup>+</sup>). It is observed here that



**Fig. 5** Photos of the deposits on the glassy carbon disk electrode after deposition at  $-2.5$  V for 3 h from a solution containing A, B or C in emim NTf<sub>2</sub>, A: 0.01 M AuCl<sub>3</sub> + 0.59 M TiCl<sub>4</sub>, B: 0.05 M AuCl<sub>3</sub> + 0.59 M TiCl<sub>4</sub>, C: 0.1 M AuCl<sub>3</sub> + 0.59 M TiCl<sub>4</sub>.

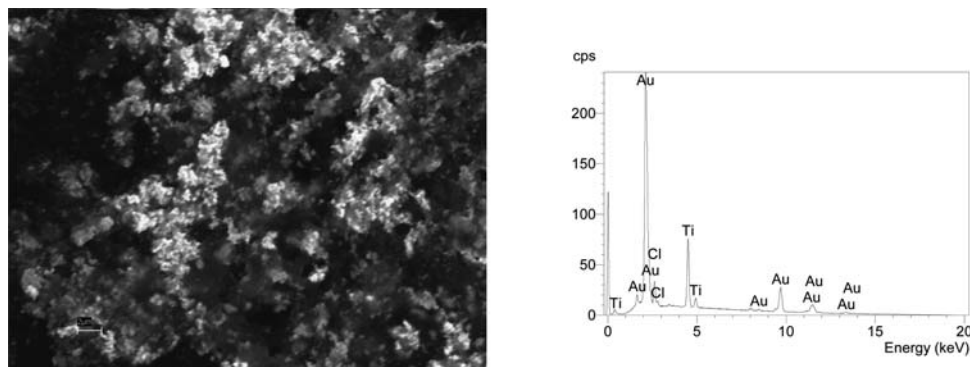


**Fig. 6** X-Ray mapping of Ti–Au deposits. The deposits obtained from a solution containing 0.01 M  $\text{AuCl}_3$  and 0.59 M  $\text{TiCl}_4$  in emim  $\text{NTf}_2$ .

this couple is much less well defined. We have also repeated the CV experiment using a gold working electrode with the  $\text{TiCl}_4/\text{emimNTf}_2$  system and obtain similar reproducible results. The nature of this redox peak at this more negative potential and its assignment is discussed further in another paper.<sup>26</sup> Our investigation here now focuses on the role that gold might play in the redox chemistry and deposition of Ti species in ionic liquid by considering gold as  $\text{AuCl}_3$  in the ionic liquid in addition to  $\text{TiCl}_4$ .

Fig. 2 shows the CV characterisation of the emim  $\text{NTf}_2$  electrolyte in the presence and absence of gold. Characteristic gold redox peaks are observed and a gold metallic deposit was readily obtained at the working electrode. This is consistent with work by Aldous *et al.* who showed<sup>27</sup> that  $\text{AuCl}_4^-$  is initially reduced to  $\text{AuCl}_2^-$  prior to deposition as  $\text{Au}(0)$ . In the presence of both  $\text{TiCl}_4$  and  $\text{AuCl}_3$  the redox peaks for titanium are still clearly seen by comparing Fig. 1 with Fig. 3A and B.

The deposits obtained on the electrodes with varying concentrations of gold(III) showed a similar visual appearance. SEM images revealed two types of deposit, a dendritic growth (Type A) and more uniform patches of growth (Type B) as shown in Fig. 4. EDS was performed to assist in the elucidation of the chemical composition of the deposition. The Au–Ti deposition results are summarized in Table 1. The amount of Titanium in the film is clearly affected by the ratio of Au : Ti in solution. The larger mole ratio of gold in the deposit compared with Ti, in spite of the large Ti : Au molar ratio in solution, is indicative of the more facile reduction process for Au and the more accessible reduction potential. The highest Ti : Au in solution ratio (590 : 1) does enable substantially more titanium in the deposit. EDS however, does not give any details of the nature or speciation of the titanium in the deposit. Fig. 5 shows photographs of the electrode deposits taken through a standard light microscope, which were obtained from the three



Element analysis Ti, Au, Cl

Ratio (am%) Ti 38.89, Au 43.83 Cl 17.28

**Fig. 7** Au–Ti co-deposition onto glassy carbon electrode from 0.01 M  $\text{AuCl}_3$  and 0.59 M  $\text{TiCl}_4$  containing emim  $\text{NTf}_2$  solution, using 16 h potentiostatic reduction conditions ( $-1.8 \text{ V vs. Ag/Ag}^+$ ). Left: SEM; Right EDS result.

different solutions of varying molar ratios of Au(III). The metallic lustre, due to the presence of Au(0) is clearly visible in the deposits. The presence of gold as Au(0) was unequivocally confirmed by XPS.

It was also found that X-ray mapping results gave qualitatively consistent results to the EDS (Fig. 6). The deposit was compositionally heterogeneous with islands of high Ti content being present. XPS confirmed the clear presence of titanium; however, energy of the titanium peaks were found to be characteristic not of Ti(0) but of higher oxidation states, predominantly Ti(IV) (Ti 2p<sub>3/2</sub> 459.2 eV). The samples for XPS were not exposed to air to any significant extent and the transfer into the spectrometer was rapid. While some surface oxidation may be possible during transfer, it is unlikely that there were significant changes sufficient to convert all of the deposit from Ti(0) to higher oxidation states. It was not possible to relate this specifically back to the presence of non-stoichiometric halides found in our previous paper.<sup>26</sup> These were found using in-situ techniques and only with a few layers of atoms deposited rather than with the bulk films produced here. However, the key finding from this experiment again is that titanium was not present as Ti(0).

In a longer term (16 h) experiment the result of electro-deposition at  $-1.8$  V from a  $0.01$  M  $\text{AuCl}_3$  and  $0.59$  M  $\text{TiCl}_4$  solution (Fig. 7) showed a large amount of deposition with a distinctly porous structure. EDS data indicated the relatively high amount of titanium and strong titanium peaks in the spectrum, again the main characteristic peak being consistent with Ti(IV) and not Ti(0).

Similar electro-deposition experiments were carried out using a different ionic liquid, C<sub>3</sub>mpyrNTf<sub>2</sub>. C<sub>3</sub>mpyr NTf<sub>2</sub>

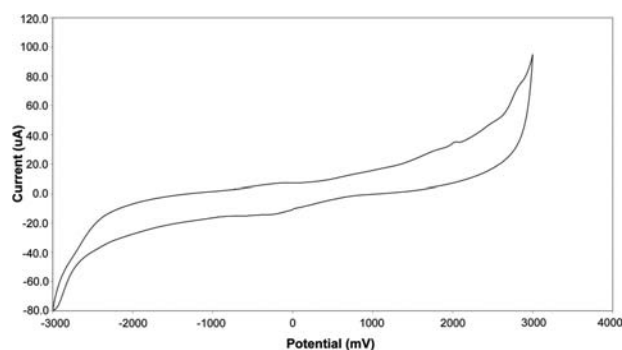


Fig. 8 Typical CV of C<sub>3</sub>mpyr NTf<sub>2</sub> at a scan rate of  $50 \text{ mV s}^{-1}$ .

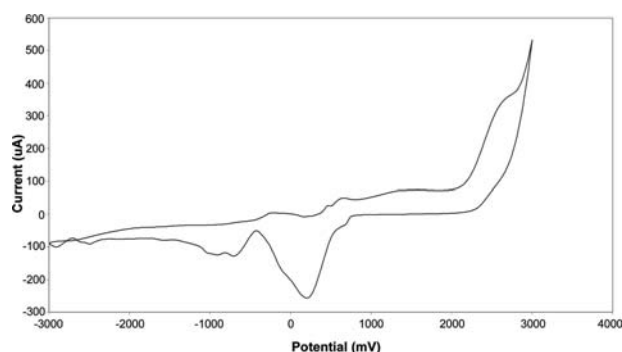
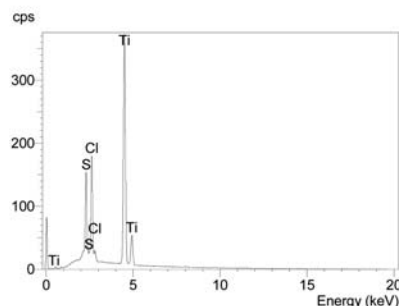
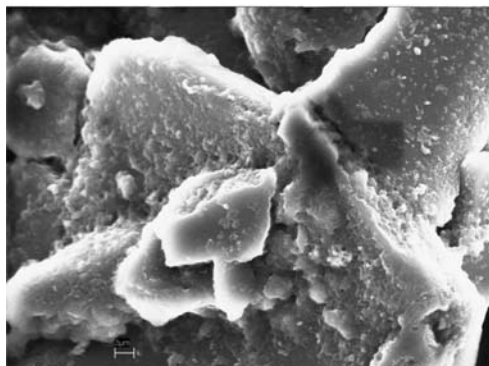
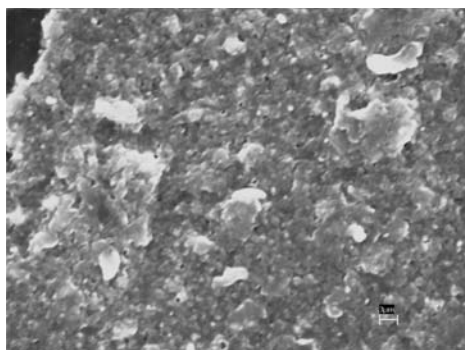


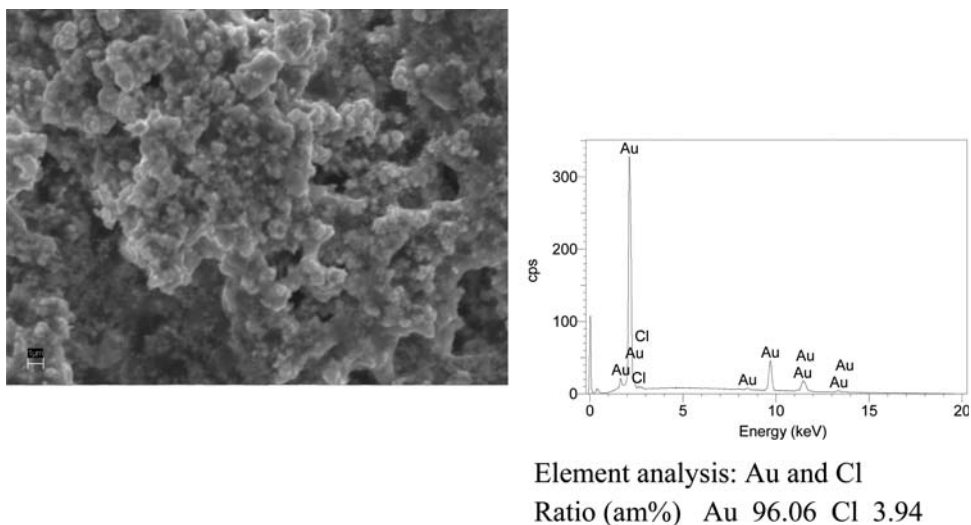
Fig. 9 Typical CV of Au ( $0.01 \text{ M}$ ) +  $\text{TiCl}_4$  ( $0.59 \text{ M}$ ) in C<sub>3</sub>mpyr NTf<sub>2</sub>.



Element analysis Ti, S, Cl

Ratio (am%) Ti 60.22, S 15.37 Cl 24.31

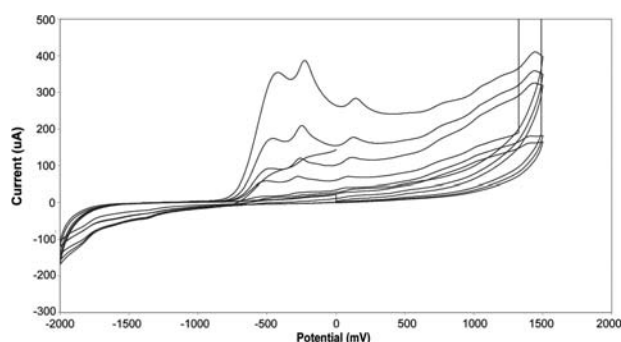
Fig. 10 Au–Ti deposition on large GC electrode from C<sub>3</sub>mpyr NTf<sub>2</sub> ( $0.01 \text{ M AuCl}_3$  and  $0.59 \text{ M TiCl}_4$ )  $-3 \text{ V}$  for  $17 \text{ h}$ . Left: SEM; right EDS result.



**Fig. 11** Typical result of Gold deposition at  $-3$  V for 17 h from a  $0.01$  M  $\text{AuCl}_3$  solution in  $\text{C}_3\text{mpyr} \text{NTf}_2$ . Left: SEM; right: EDS result.

has a substantially larger stable potential window as shown in Fig. 8. It is thus feasible to try to extend the redox chemistry possible to  $\pm 3$  V vs.  $\text{Ag}/\text{Ag}^+$ . Growth of Au–Ti deposits were then followed by studying both CV and potentiostatic reduction experiments at  $-3.0$  V. A typical CV is shown in Fig. 9. This again shows distinct redox couples attributable to both Au and Ti for an ionic liquid solution containing  $0.01$  M  $\text{AuCl}_3$  and  $0.59$  M  $\text{TiCl}_4$ .

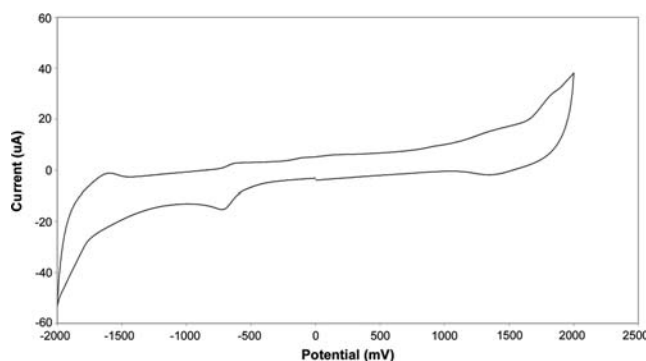
The result of potentiostatic growth at  $-3.0$  V for 17 h gave a very good uniform deposit with a bright metallic lustre. These were analysed by SEM and EDS. The most significant difference between this result and the one for  $\text{emimNTf}_2$  is the much higher amount of Ti in the EDS with little or no Au peaks at all (Fig. 10). This is surprising, given that gold by itself will readily deposit onto the GC electrode under the same conditions as shown in Fig. 11. The deposit obtained was quite thick and it is possible that in the co-deposition experiment gold was being preferentially deposited first and that a titanium rich layer is being laid down subsequently. It was not possible to carry out any depth profile studies to probe this further. It does, though, represent a very significant result. It is possible to produce films with a high Ti content but there is little evidence that the titanium has been reduced to the metallic state. It is more likely that titanium was deposited in mixed valence states. This is further developed in an accompanying



**Fig. 12** CV ( $50 \text{ mV s}^{-1}$ ) of glassy carbon electrode with Ti–Au codeposition in fresh  $\text{emim NTf}_2$  liquid.

paper.<sup>26</sup> In addition, the measurable sulfur peaks in Fig. 10 would also indicate the significant incorporation of the ionic liquid anion or its degradation product. This is again an interesting result as given the lack of sulfur in the EDS result in Fig. 7 it would suggest that when the  $\text{emim NTf}_2$  ionic liquid was used there was no measurable incorporation of it into the deposited films.

In order to test whether the co-deposits of Ti–Au were stable to reoxidation after formation the following experiment was carried out. A Ti : Au film was grown at constant potential



**Fig. 13** CV of Ti–Au deposit on glassy carbon electrode after re-oxidation ( $0.5$  V for 4 h).

at  $-1.8$  V for 17 h using emim NTf<sub>2</sub> as the solvent. This film was then placed in fresh ionic liquid and cyclic voltammetry performed as shown in Fig. 12. The CV showed 3 initial peaks located at  $-0.5$ ,  $-0.27$  and  $0.070$  V. After scanning 5 cycles, all these peaks rapidly disappeared, leaving a CV trace typical of the pure ionic liquid. This strongly suggests that the Au–Ti film is relatively stable to re-oxidation. The transient peaks observed in the initial scans are likely to be due to trace contaminants still present on/in the film that are readily returned to solution and undergo redox changes or are available on the surface of the film and re-oxidised.

Similarly, the Au–Ti co-deposit on a glassy carbon electrode was also re-oxidised at  $0.5$  V (vs. Ag/Ag<sup>+</sup>) for 4 h and then a cyclic voltammogram was run. This is shown in Fig. 13. Again the voltammogram shows little redox activity with only one or two small redox couples at around  $-1.5$  and  $-0.6$  V apparent. Both experiments suggest that the co-deposit is stable and irreversibly deposited on the electrode. There is no evidence of significant reoxidation of either gold or titanium species.

## Conclusions

Experiments to directly electro-deposit titanium from a range of ionic liquids at room temperature have not been convincing or successful. Attempts have often been hampered by difficulties of eliminating redox cycling of multivalent titanium ions and handling very reactive dendritic products. Our previous attempts have not been successful and have indicated that the solubility of Ti(II) species in the ionic liquids is an effective barrier to further reduction.<sup>26</sup> Work by Mukhopadhyay and coworkers<sup>22</sup> suggested that gold might form an effective substrate for the nucleation of titanium from these ionic liquid based solutions.

We were therefore interested in this use of gold as a possible nucleation agent and have investigated the co-deposition of titanium/gold from the solution of TiCl<sub>4</sub> and AuCl<sub>3</sub> in a variety of room temperature ionic liquids. The current results indicate that gold was able to effectively act as a nucleating agent for the electro-deposition of titanium species from TiCl<sub>4</sub> solution in two different ionic liquids. In experiments with emim NTf<sub>2</sub> films with variable Ti: Au ratio may be obtained using different molar ratio of the metal ions in solution. C3mpyrNTf<sub>2</sub> has a wide electrochemical potential window enabling potentiostatic growth of a co-deposit at  $-3.0$  V, resulting in very good uniform films with high titanium content. Stability experiments suggest that the co-deposit is stable and irreversible. This process is a good electrochemical method for obtaining thin films with controlled thickness with high levels of titanium species. This may be useful for a range of applications. However, in all our experiments<sup>26</sup> there is no convincing evidence for the reduction of Ti(IV) down to Ti(0)

and that the titanium present in the film was at a higher oxidation state with possibly mixed valence states.<sup>26</sup> This is contrary to other published literature. Further work is being carried out to look at possible ways to stabilize titanium(II) and Ti(III) species in solution in ionic liquids.

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