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On the electrodeposition of titanium in ionic liquids

Abstract

The ability to electrodeposit titanium at low temperatures would be an important breakthrough for making corrosion resistant layers on a variety of technically important materials. Ionic liquids have often been considered as suitable solvents for the electrodeposition of titanium. In the present paper we have extensively investigated whether titanium can be electrodeposited from its halides (TiCl_4 , TiF_4 , TiI_4) in different ionic liquids, namely 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMIm] Tf_2N), 1-butyl-1-methylpyrrolidinium bis(trifluoromethyl-sulfonyl)amide ([BMP] Tf_2N), and trihexyltetradecyl-phosphonium bis(trifluoromethylsulfonyl)amide ([P_{14,6,6,6}] Tf_2N). Cyclic voltammetry and EQCM measurements show that, instead of elemental Ti, only non-stoichiometric halides are formed, for example with average stoichiometries of $\text{TiCl}_{0.2}$, $\text{TiCl}_{0.5}$ and $\text{TiCl}_{1.1}$. In situ STM measurements show that—in the best case—an ultrathin layer of Ti or TiCl_x with thickness below 1 nm can be obtained. In addition, results from both electrochemical and chemical reduction experiments of TiCl_4 in a number of these ionic liquids support the formation of insoluble titanium cation–chloride complex species often involving the solvent. Solubility studies suggest that TiCl_3 and, particularly, TiCl_2 have very limited solubility in these Tf_2N based ionic liquids. Therefore it does not appear possible to reduce Ti^{4+} completely to the metal in the presence of chloride. Successful deposition processing for titanium in ionic liquids will require different maybe tailor-made titanium precursors that avoid these problems.

Keywords

electrodeposition, titanium, ionic, liquids, CMMB

Disciplines

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On the electrodeposition of titanium in ionic liquids

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The ability to electrodeposit titanium at low temperatures would be an important breakthrough for making corrosion resistant layers on a variety of technically important materials. Ionic liquids have often been considered as suitable solvents for the electrodeposition of titanium. In the present paper we have extensively investigated whether titanium can be electrodeposited from its halides (TiCl₄, TiF₄, TiI₄) in different ionic liquids, namely 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMIm]Tf₂N), 1-butyl-1-methylpyrrolidinium bis(trifluoromethyl-sulfonyl)amide ([BMP]Tf₂N), and trihexyltetradecyl-phosphonium bis(trifluoromethylsulfonyl)amide ([P_{14,6,6,6}]Tf₂N). Cyclic voltammetry and EQCM measurements show that, instead of elemental Ti, only non-stoichiometric halides are formed, for example with average stoichiometries of TiCl_{0.2}, TiCl_{0.5} and TiCl_{1.1}. *In situ* STM measurements show that—in the best case—an ultrathin layer of Ti or TiCl_x with thickness below 1 nm can be obtained. In addition, results from both electrochemical and chemical reduction experiments of TiCl₄ in a number of these ionic liquids support the formation of insoluble titanium cation–chloride complex species often involving the solvent. Solubility studies suggest that TiCl₃ and, particularly, TiCl₂ have very limited solubility in these Tf₂N based ionic liquids. Therefore it does not appear possible to reduce Ti⁴⁺ completely to the metal in the presence of chloride. Successful deposition processing for titanium in ionic liquids will require different maybe tailor-made titanium precursors that avoid these problems.

1. Introduction

Titanium owes its great importance to its excellent mechanical and corrosion performance. Many attempts have been made to electrodeposit titanium from organic,^{1,2} and even aqueous^{3,4} media without success as mainly titanium subhalides TiX_y (X = F, Cl, Br, I) are formed. Abbott *et al.*⁵ have tried to electrodeposit titanium from aromatic solvents by seeding the electrolyte with traces of Ag to act as islands for the titanium to grow on. Coordination compounds of Ti(III) and Ti(IV) with long chain amines and nitriles were used as sources of Ti. There were some hints on the formation of some isolated patches on the electrode surface, however no significant deposits of metallic titanium were obtained.⁵ However, high temperature molten salts have been considered as the most efficient media for titanium electrodeposition.^{6–14} As an example, alkali halide melts containing TiCl₂/TiCl₃ mixtures were used to electrodeposit Ti at temperatures between 450

and 850 °C.⁶ Despite this success the deposits obtained are often brittle and, in general, high temperature molten salts are difficult to handle and to some extent corrosive. The rise in interest in, and the availability of, a wide range of ionic liquids with interesting physicochemical properties presents an attractive alternative route for the electrodeposition of metals. Room temperature ionic liquids have, in some cases, wide electrochemical windows of up to ±3 V vs. NHE, good ionic conductivity, and wide thermal windows of ~300 °C combined with extremely low vapour pressures. These properties make them promising solvents for a wide variety of fundamental and applied studies, and they have been extensively studied over the last fifteen to twenty years with a number of good reviews being available.^{15–18} Based on this information one might argue that the wide electrochemical windows available, making available redox processes otherwise inaccessible, should make the deposition of reactive elements like Ti, Ta, W, V and others technologically attainable. Recently, there was an attempt to electrodeposit titanium at room temperature in the air and water stable ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide [BMIm]Tf₂N containing TiCl₄ as a source of titanium. Using *in situ* STM there were some hints that titanium might be electrodeposited in ultra-thin layers.¹⁹ Our own experience has shown, however, that attempts to deposit micrometer thick titanium deposits fail completely. We have also recently investigated the use of pyrrole as a nucleating agent to induce titanium deposition.²⁰ Instead of elemental titanium it is believed that the reduction to Ti(III) and Ti(II) takes place, but that there is

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little evidence of the reduction to titanium metal. Instead, we postulate that polymeric subvalent titanium halide species are obtained, initially soluble but rapidly precipitating. *In situ* EQCM measurements show (see below) that there is a tremendous increase in viscosity during TiCl_4 electroreduction, furthermore Tf_2N breakdown^{21,22} might further alter titanium deposition. Abbott has proposed in ref. 18 that the apparent increase in viscosity during electrolysis is due to changes in the double layer structure. Thermodynamically, Ti deposition should be quite simple in thick layers in ionic liquids, as its electrode potential is -1.63 V vs. NHE . Aluminium, which can be electrodeposited quite easily in different ionic liquids, has practically the same electrode potential for reduction ($\sim -1.7\text{ V vs. NHE}$). As we will demonstrate in this paper the right ionic liquid and especially the right titanium precursors still have to be found to allow titanium electrodeposition from ionic liquids.

The objective of this study was to investigate the electroreduction of several titanium compounds in ionic liquids in order to investigate if titanium can be deposited. Three air and water stable ionic liquids, namely, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMIm] Tf_2N), 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ([BMP] Tf_2N), and trihexyltetradecyl-phosphonium bis(trifluoromethylsulfonyl)amide ([P_{14,6,6,6}] Tf_2N) in ultrapure form were employed for this purpose. There is no deposition of elemental titanium and we discuss why Ti deposition fails at low temperatures in ionic liquids.

2. Experimental

The ionic liquids 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMIm] Tf_2N), 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ([BMP] Tf_2N) and trihexyltetradecyl-phosphonium bis(trifluoromethylsulfonyl)amide ([P_{14,6,6,6}] Tf_2N) were obtained from Merck KGaA in the highest available (ultrapure) quality. The liquids were dried under vacuum for 12 h at a temperature of $100\text{ }^\circ\text{C}$, to a water content below 3 ppm (by Karl–Fischer titration) and stored in an argon filled glove box, with water and oxygen levels below 1 ppm (OMNI-LAB from Vacuum-Atmospheres). TiCl_4 (Alfa, 99.5%), TiF_4 (Alfa, 99.9%), TiI_4 (Alfa, 99.2%) and Ti-isopropanolate (Alfa, 99.995%) were used without further purification. Pure samples of titanium(II) chloride and titanium(III) chloride, both 99%+, were obtained from Sigma-Aldrich, handled in a glove-box and used as received.

In situ STM experiments were performed using in-house designed STM heads and scanners under inert gas conditions (H_2O and $\text{O}_2 < 1\text{ ppm}$) with a Molecular Imaging PicoScan 2500 STM controller in feedback mode. The STM experiments were performed in an air-conditioned laboratory with $\Delta T < \pm 1\text{ }^\circ\text{C}$. STM tips were prepared by electrochemical etching of platinum–iridium wires (0.25 mm diameter) and electrophoretically coated with an electropaint (BASF ZQ 84-3225 0201). During the STM experiments the electrode potential was controlled by the PicoStat from Molecular Imaging.

All electrochemical measurements were performed in the glove box using a VersaStatTM II Potentiostat/Galvanostat

(Princeton Applied Research) controlled by PowerCV and PowerStep software. Gold substrates from Arrandee (gold films of 200–300 nm thickness deposited on chromium-covered borosilicate glass), Au(111) (gold on mica, purchased from Molecular Imaging) and platinum sheets of thickness 0.5 mm (Alfa, 99.99%) were used as working electrodes, respectively. Directly before use, the gold substrates were very carefully heated in a hydrogen flame to red glow, and Pt-substrates were cleaned for 10 min in an ultrasonic bath in acetone, then heated in a hydrogen flame to red glow for a few minutes. Pt-wires (Alfa, 99.99%) were used as quasi-reference and counter electrodes, respectively. Pt-quasi reference electrodes were employed for *in situ* STM measurements, also defined reference electrodes in ionic liquids, especially for *in situ* STM, are still not available. A quartz round bottom flask was used as the electrochemical cell. Prior to use, all parts in contact with the solution were thoroughly cleaned in a mixture of 50/50 vol% $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ followed by refluxing in bidistilled water.

Gold coated quartz crystals (10 MHz AT-cut) were purchased from Vectron International (Neckarbischofsheim, Germany). The electrochemical cells were cleaned in a mixture of concentrated sulfuric acid/30% aqueous hydrogen peroxide and subsequently refluxed in *aqua destillata ad iniectionem*. The quartz crystal was cleaned with isopropanol and dried under air at $100\text{ }^\circ\text{C}$. A cylindrical (home-built) PTFE cell—pretreated as described above—was used for EQCM measurements. The quartz crystal was placed at the bottom of this cell and was held between two O-rings. On the ionic liquid side it is essential to use a perfluoroelastomer such as Kalrez (Dupont Dow Elastomers L.L.C., Newark, Delaware, USA) since swelling of the gasket can lead to considerable signal drifts. The cell was operated under argon in an inert gas glove box in which deposition experiments were performed. The potential of the Au electrode facing the ionic liquid was controlled with a Versastat II potentiostat/galvanostat, the other electrode of the quartz crystal faced the inert gas atmosphere of the glove box. The potentials were measured *versus* Pt quasi-reference electrode. A platinum wire was used as the counter electrode. The electrical admittance curve of the quartz crystal near its resonance frequency (*i.e.* 10 MHz) was measured in parallel to the electrochemical experiments with a network analyzer (Agilent E5100A) and transferred to a PC compatible computer *via* GPIB interface. Lab-made software (Visual C++) was used to extract the resonance frequency and the damping of the quartz crystal.²³

Experiments designed to study the products of the chemical reduction of TiCl_4 were carried out adapting a method by Katayama and coworkers.²⁴ 100 mg of TiCl_4 was added to 2 ml of [BMP] Tf_2N in a test tube with a tightly fitted screw top cap. A deep orange/yellow solution formed. This mixture was warmed to $130\text{ }^\circ\text{C}$. A separate experiment used a stoichiometric amount (15 mg) and an excess (50 mg) of clean bright Li ribbon was added to the IL mixture. The orange solution slowly turned deep brown over 3 days. The lithium became heavily encrusted with a brown solid. This solid was washed clean of IL with $2 \times 5\text{ ml}$ aliquots of THF. The remaining lithium was carefully dissolved with dry methanol and the brown solid was then filtered and washed with methanol and

then water. A similar experiment was carried out at room temperature.

3. Results and discussions

3.1 Electrodeposition experiments in [EMIm]Tf₂N and [P_{14,6,6,6}]Tf₂N

Fig. 1a shows the cyclic voltammogram of the ionic liquid [EMIm]Tf₂N containing 0.25 M TiCl₄ recorded on Au(111) at 25 °C (first cycle). The electrode potential was scanned from the open circuit potential in the negative direction at a rate of 10 mV s⁻¹ until -2.5 V (vs. Pt). The corresponding changes in frequency and mass with the potential sweep are displayed in Fig. 1b and c, respectively.

It is clearly seen from Fig. 1a that at room temperature, the cathodic branch of the cyclic voltammogram exhibits at least two different cathodic processes suggesting that the electrochemical reduction of Ti(IV) occurs in at least two steps. The first reduction peak at 25 °C is observed at a potential of about -650 mV, the second much weaker peak is located at a potential of about -1950 mV. Here we had to rely on Pt quasi reference electrodes as the addition of ferrocene leads to a deep blue solution, probably a type of a titanocene was formed. The first process at around -650 mV is shown to be a two electron reduction of titanium(IV) to titanium(II). Experiments studying cyclic voltammetry of TiCl₃ in [EMIm]Tf₂N support this conclusion as there are indications of an initial reduction of Ti³⁺ to Ti²⁺ followed by full reoxidation of Ti²⁺ to Ti⁴⁺. This is discussed further in section 3.3.

The quartz crystal microbalance shows a frequency decrease and a damping increase associated with the peak at -650 mV. Interestingly, the damping increase is almost twice the frequency decrease (Fig. 1b and c). Such behaviour is characteristic of a Newtonian viscosity change.²⁵ If the measured frequency change is assumed to be the sum of a viscous contribution and a mass contribution, $\Delta f = \Delta f_{\text{vis}} + \Delta f_{\text{mass}}$, the mass induced frequency decrease can be obtained by adding half of the damping change to the frequency shift, $\Delta w_{\text{vis}} = -2\Delta f_{\text{vis}}$. This correction procedure has been applied in Fig. 1b. Applying the Sauerbrey equation the mass induced frequency change (Δf_{mass}) can be converted to the mass density, $\Delta m/A$, at the quartz crystal surface.

$$\Delta f_{\text{mass}} = [2f_0^2/(\mu\rho)^{0.5}] \Delta m/A = -K \Delta m \quad (1)$$

where f_0 is the resonant frequency of the quartz crystal, A is the mass-sensitive area, μ is the shear modulus of the quartz, ρ its density and K a constant relating the frequency shift to a mass change.

By combining eqn (1) with Faraday's law ($\Delta Q = z\Delta m F/M$) the relation between frequency change and charge is obtained:

$$\Delta f_{\text{mass}} = -(KM/Fz) \Delta Q \quad (2)$$

where, ΔQ is the charge consumed during the deposition, z is the number of electrons involved in the reaction, F is the Faraday constant and M is the molar mass of the deposit. The slope of the curve of Δf_{mass} vs. ΔQ can be used to determine the

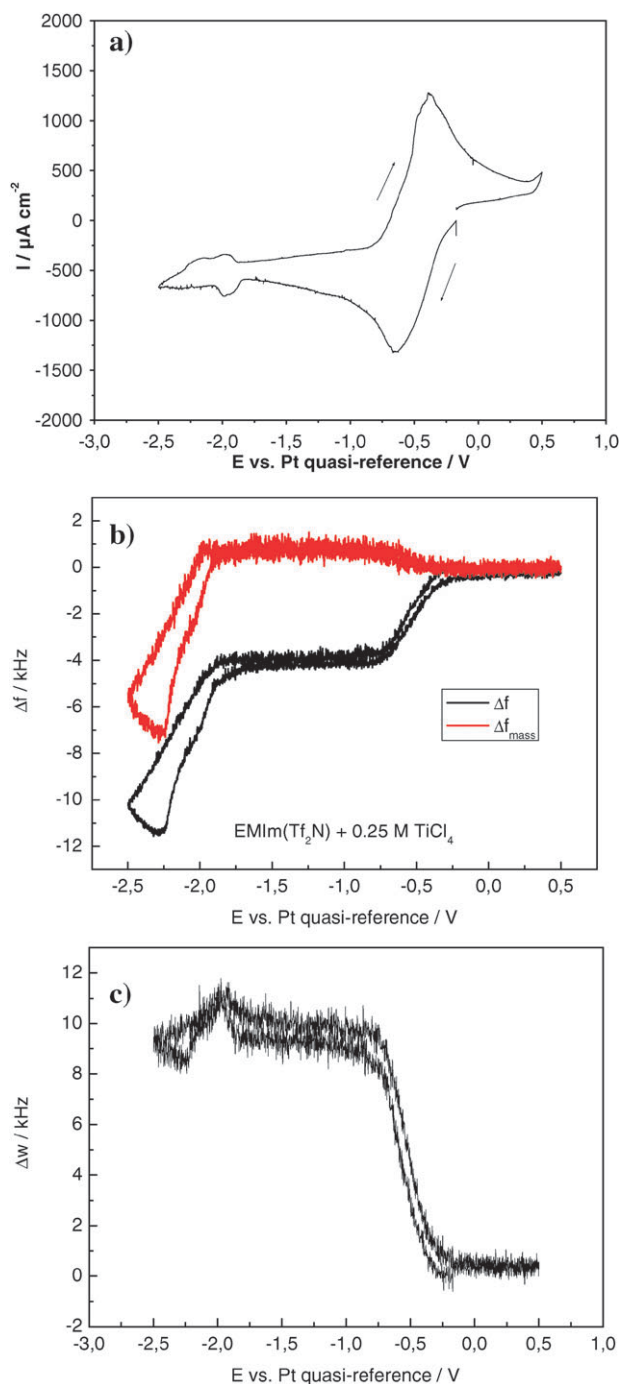


Fig. 1 (a) Cyclic voltammogram of [EMIm]Tf₂N containing 0.25 M TiCl₄ on Au(111) substrate vs. Pt at a scan rate of 10 mV s⁻¹ at room temperature, (b) the corresponding changes in frequency and (c) the damping of the quartz crystal. The mass induced frequency shift shown in (b) has been calculated according to $\Delta f_{\text{mass}} = \Delta f + \Delta w/2$ (for details see text).

ratio M/z from eqn (3). The value M/z can be termed the apparent molar mass of the deposited species.²⁶

$$M/z = \text{slope} \times (F/K) \quad (3)$$

Fig. 1b shows that there is no mass increase in the cathodic sweep until -2.0 V. This is supported by *in situ* STM studies, as discussed later. Below -2.0 V a species with an apparent

molar mass of 65 g mol^{-1} is deposited which can only be explained with the formation of a subhalide species, e.g. $\text{Ti}^{+} + 0.8\text{e}^{-} + 0.2 \text{Cl}^{-} = \text{TiCl}_{0.2}$ ($M/z = 69 \text{ g mol}^{-1}$). The deposition continues after reversal of the sweep (-2.5 V) until -2.2 V . Above -2.2 V stripping of the previously deposited mass sets in, which is finished at -1.9 V . The M/z value for the stripping reaction is 197 g mol^{-1} which would be in agreement with the formation of a soluble subhalide species, like $\text{TiCl}_{0.2} + 0.3 \text{Cl}^{-} = \text{TiCl}_{0.5} + 0.3\text{e}^{-}$ ($M/z = 183 \text{ g mol}^{-1}$). At this electrode potential there is visually the formation of a brownish film surrounding the working electrode which spreads in the solution as soon as the potential control is stopped. It should be stressed that the above discussed stoichiometries are integral estimates of the real picture, as only average M/z values can be obtained from EQCM. Such non-stoichiometric subhalides are well known, and they are made up of both Ti–Ti bonds and Ti–Cl bonds. Therefore, it is difficult to make exact suggestions about the stoichiometry of the involved subhalides, and the values given are best thought of as illustrative examples of the types formed. Nevertheless, their formation is clearly shown by the EQCM data and definitely no elemental titanium is deposited. From *in situ* STM measurements it can not be excluded totally that ultra-thin layers in the subnanometer regime on Au(111), described in ref. 19, maybe consist of elemental titanium. Their formation might be induced by surface alloying between Ti and Au. However, at present, this is only a speculation and even so, such thin layers are rather of academic interest only.

The next obvious step was to investigate whether an increase in temperature has an effect on the reduction of TiCl_4 . Kinetic barriers are much easier to overcome at elevated temperature and in high temperature molten salts Ti can be deposited. The effect of increasing temperature, from 25 to 100°C , on the cyclic voltammetry behaviour of the ionic liquid $[\text{EMIm}]\text{Tf}_2\text{N}$ containing 0.25 M TiCl_4 is displayed in Fig. 2. 100°C was selected as an upper limit as at this temperature there is already some TiCl_4 evaporation which gets more distinct at even higher temperature. Similar to the results described above, the cathodic branch of the cyclic voltammograms exhibits at least two cathodic processes suggesting that the

electrochemical reduction of Ti(IV) occurs in more than two steps. However, there are also no hints for the electrodeposition of elemental titanium down to -3000 mV . On increasing the temperature from 25 to 100°C , the currents of the reduction peaks increase but there was no observable deposition on the substrate surface, too. This is also true when the gold substrate is replaced by Pt. As shown in Fig. 3, there are two reduction peaks at -600 mV and at -2100 mV on Pt and two subsequent oxidation peaks at -2000 mV and at -600 mV around room temperature. However, again there was no visible deposition. The quartz crystal microbalance experiments also confirmed that there was no deposition at all. Besides the already discussed subvalent TiCl_x species TiCl_4 might also form complexes with the Tf_2N^{-} anion—especially at elevated temperature—thus lowering the potential for titanium deposition below the cathodic decomposition limit of the ionic liquid.

As a further attempt, the electrodeposition of titanium from TiI_4 and TiF_4 in $[\text{EMIm}]\text{Tf}_2\text{N}$ at different temperatures, was also investigated, as shown in Fig. 4. The motivation for doing this was that previous work²⁷ showed that electrodeposition of tantalum in ionic liquids was only successful with TaF_5 , but not with TaCl_5 . It is known that fluoride has a lower tendency to make halide-bridged subvalent clusters. As the binding energies Ti–Cl and Ti–I are different, it was also thought that Ti-deposition may be successful with TiI_4 . However, in case of TiI_4 , although there are at least two reduction and two oxidation waves, there is again no evidence for the electrodeposition of titanium from both titanium compounds even at elevated temperatures, up to 200°C .

From the above experiments, it appears that the deposition of titanium from its halides is at least not straightforward. It was therefore decided to investigate the electrodeposition of titanium from titanium isopropanolate in the ionic liquid trihexyltetradecyl-phosphonium bis(trifluoromethylsulfonyl)amide ($[\text{P}_{14,6,6,6}]\text{Tf}_2\text{N}$). The idea was that it might be easier to electrodeposit titanium from Ti(IV) species involving organic anions/ligands. Furthermore, liquids with the $\text{P}_{14,6,6,6}$ cation have even wider electrochemical windows compared to liquids with imidazolium cations. Fig. 5 shows the cyclic

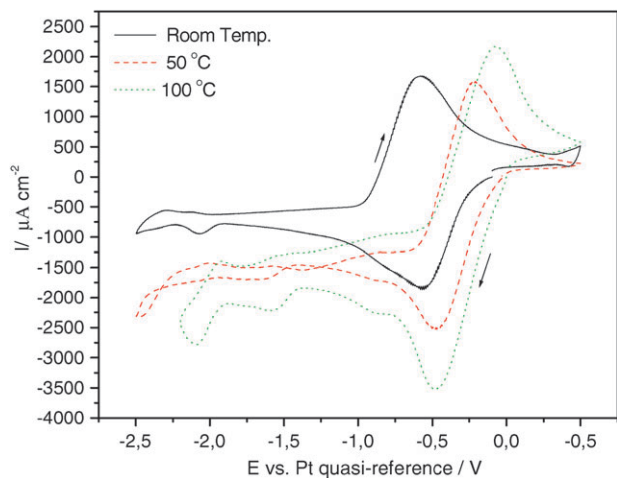


Fig. 2 Cyclic voltammograms of $[\text{EMIm}]\text{Tf}_2\text{N}$ containing 0.25 M TiCl_4 on Au(111) at different temperatures. Scan rate: 10 mV s^{-1} .

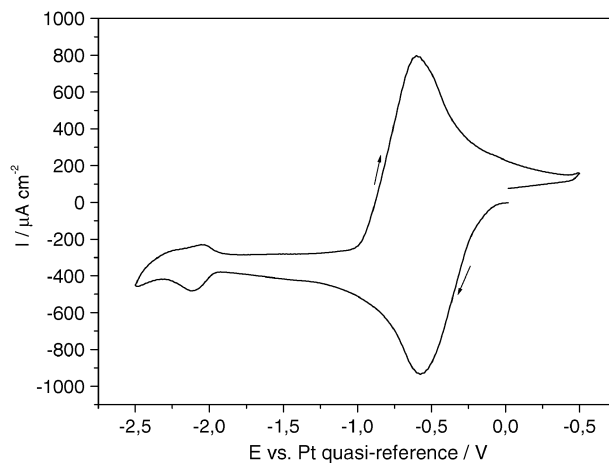


Fig. 3 Cyclic voltammogram of $[\text{EMIm}]\text{Tf}_2\text{N}$ containing 0.25 M TiCl_4 on platinum at room temperature. Scan rate: 10 mV s^{-1} .

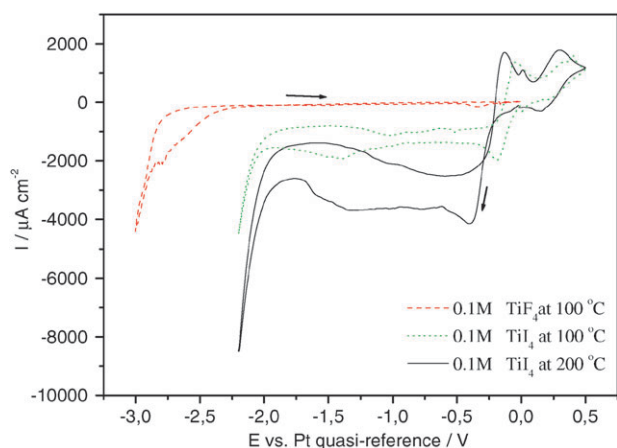


Fig. 4 Cyclic voltammograms of [EMIm]Tf₂N containing 0.1 M TiCl₄ and 0.1 M TiF₄ on platinum at different temperatures. Scan rate: 10 mV s⁻¹.

voltammograms of (P_{14,6,6,6}-Tf₂N) containing 1.0 M Ti-isopropanolate on Au(111) at 25 and 50 °C. Unfortunately, as shown in Fig. 5, there is no reduction peak even with increasing temperature. In addition, it seems that reduction of the ionic liquid starts to become a problem around a potential of -2000 mV at both room temperature and 50 °C. Furthermore, there are two oxidation peaks recorded at -1500 mV and -400 mV which could be attributed to the re-oxidation of cation decomposition products of the ionic liquid. We can conclude that titanium isopropanolate is thermodynamically too stable to allow Ti deposition.

The next approach was to check if maybe at the interface Au(111)/IL ultrathin layers of titanium can be deposited, probed by *in situ* STM. Previous studies using *in situ* STM suggested¹⁹ that titanium can be electrodeposited in ultra-thin layers in 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)amide [BMIm]Tf₂N containing TiCl₄. However, as shown above from the EQCM results, it seems extremely difficult to get elemental titanium using TiCl₄ as a source of titanium. Instead of elemental titanium initially soluble, polymeric subvalent titanium halide species are obtained. Therefore, it was decided to investigate the electrodeposition of Ti

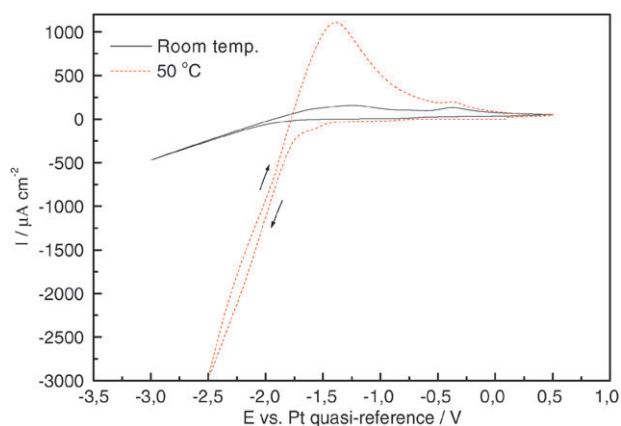


Fig. 5 Cyclic voltammograms of (P_{14,6,6,6}-Tf₂N) containing 1.0 M Ti-isopropanolate on Au(111) at different temperature. Scan rate: 10 mV s⁻¹.

from the ionic liquid [EMIm]Tf₂N containing 0.25 M TiCl₄ on Au(111) by means of *in situ* scanning tunnelling microscopy (STM) to get further information.

As shown in the STM image of Fig. 6a, at the open circuit potential (-0.65 V) the Au(111) surface consists of atomically flat terraces with some monoatomically deep vacancies. At a potential of -1.0 V, some of these vacancies completely disappeared and the others decreased in size, as shown in Fig. 6b. With increasing reduction time at -1.0 V all vacancies completely disappeared and, as shown in Fig. 7a, at -1.25 V there was evidence of some deposition at the surface. At more negative values ($E = -2.5$ V) the formerly observed deposit disappears and a secondary surface layer is obtained as depicted in Fig. 7b. This may be attributed to the initiation of cathodic decomposition of the imidazolium cation. At -2.9 V, the roughness of the surface increased due to cation decomposition products at the electrode/electrolyte interface, (Fig. 7c and d). The “deposit” in 7c and d is not due to Ti deposition.

These *in situ* STM results in ultrapure ionic liquids reveal that it is extremely difficult, or even impossible, to obtain elemental titanium by electroreduction of titanium halides. It is possible that the titanium subhalides described above are not probed by the *in situ* STM. In contrast to the results described in ref. 19, the current results give no evidence for any deposition that could be interpreted as elemental titanium. It is possible that this is due to the ultrapure nature of the ionic liquids utilised here. These were made by an acid/base routine from H-Tf₂N and diluted [EMIm]OH and contained therefore no inorganic impurities. Prior to about 2004, these liquids were exclusively made *via* a metathesis method from LiTf₂N and [EMIm]Cl. Previously the authors have shown²² that liquids made from LiTf₂N can contain extremely low concentrations of Li⁺ that can only be probed by *in situ* STM.

3.2 Electrodeposition experiments in [BMP]Tf₂N

In comparison to [EMIm]Tf₂N, [BMP]Tf₂N has an electrochemical window which in the cathodic regime is approximately 700 mV wider. However, a cation effect also has to be considered, which maybe alters the electrochemical reaction. The cyclic voltammogram of 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide containing 0.5 M TiCl₄ on Au(111) at room temperature is shown in Fig. 8a. It is clearly seen that the cathodic branch of the cyclic voltammogram exhibits at least two cathodic processes and it is obvious that the cyclic voltammograms have a different shape than those shown for [EMIm]Tf₂N/TiCl₄. The first reduction peak is observed at a potential of about -800 mV, and at a potential of about -1300 mV a very weak wave is recorded. One possible explanation is that the reduction leads first to Ti(III), then to Ti(II). There is no clear hint for the electrodeposition of titanium down to -2500 mV. Two subsequent oxidation waves were recorded at -700 mV and at -200 mV, before the surface oxidation of gold begins at 250 mV on this potential scale.

As in the case of [EMIm]Tf₂N, the quartz crystal microbalance results were corrected for viscosity effects, see Fig. 8b and 8c. In the cathodic sweep deposition starts at -500 mV

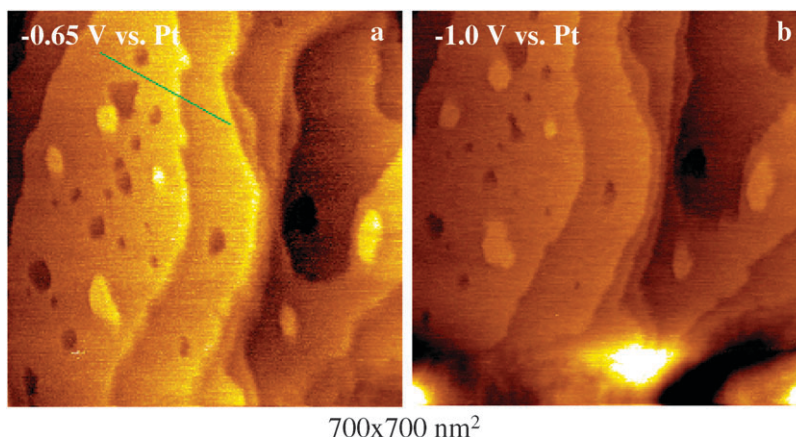


Fig. 6 STM images of Au(111) in [EMIm]Tf₂N containing 0.25 M TiCl₄ at room temperature, (a) $E = -0.65$ V and (b) $E = -1.0$ V.

with a species with an apparent molar mass of *ca.* 5 g mol⁻¹. Until -1.1 V this value increases to 97 g mol⁻¹. After that M/z goes quickly down to 5 g mol⁻¹ again, until stripping of the layer starts in the anodic scan at -0.59 V. Stripping is finished at -0.34 V. The M/z value of the stripped species is 85 g mol⁻¹. Again, the M/z values above the molar mass of titanium (47.9 g mol⁻¹) indicate the formation of subhalides, such as $\text{Ti}^+ + 0.6\text{e}^- + 0.4\text{Cl}^- = \text{TiCl}_{0.4}$ ($M/z = 104$ g mol⁻¹). If it is assumed that the phase formation starts from a divalent titanium species, a possible reaction would be $\text{Ti}^{2+} + 0.9\text{e}^- + 1.1\text{Cl}^- = \text{TiCl}_{1.1}$ ($M/z = 97$ g mol⁻¹). At the moment we cannot offer a sound explanation which reaction is associated with the M/z values of *ca.* 5 g mol⁻¹. A tentative explanation would be that the depositing subhalides replace a pre-adsorbed

species, so that this low M/z value is the difference of the apparent molar mass of the adsorbate and the subhalide. The clusters seen in the STM images below would then consist of insoluble Ti subhalides with maybe some elemental titanium. We have to also consider the possibility that TiCl₄ forms complexes with the Tf₂N⁻ anion, as discussed further below, thus pushing the electrode potential for titanium deposition below the cathodic decomposition limit of the ionic liquid.

In order to investigate the processes occurring on the nanoscale *in situ* STM experiments were performed. Fig. 9 shows a set of STM images of the Au(111) surface in [BMP] Tf₂N containing 0.25 mol l⁻¹ TiCl₄. As shown in the STM image of Fig. 9a the gold surface is characterized by the presence of tiny pits all over the surface, similar to what was

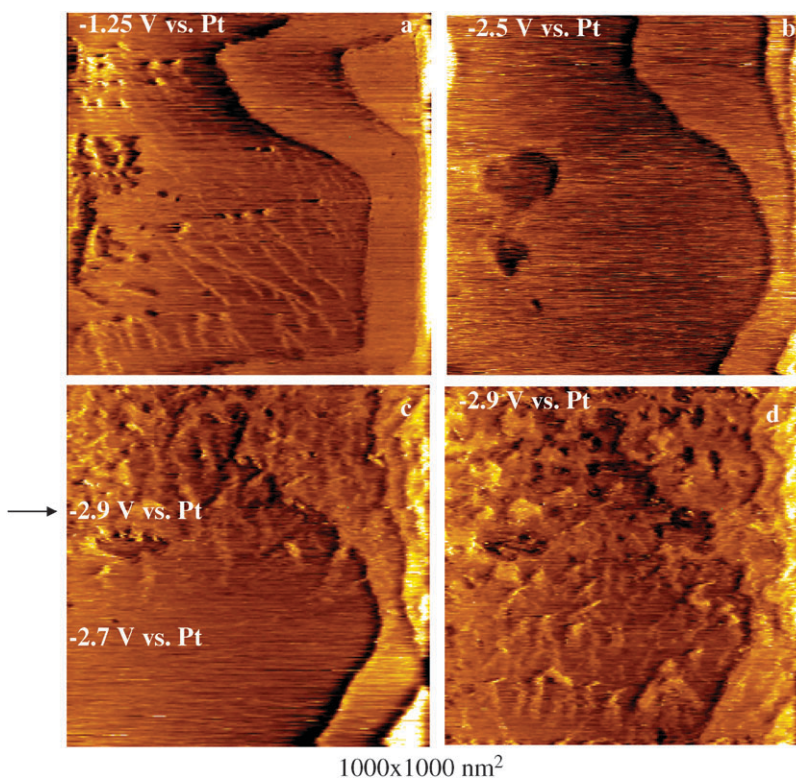


Fig. 7 STM images of Au(111) in [EMIm]Tf₂N containing 0.25 M TiCl₄ at different potentials.

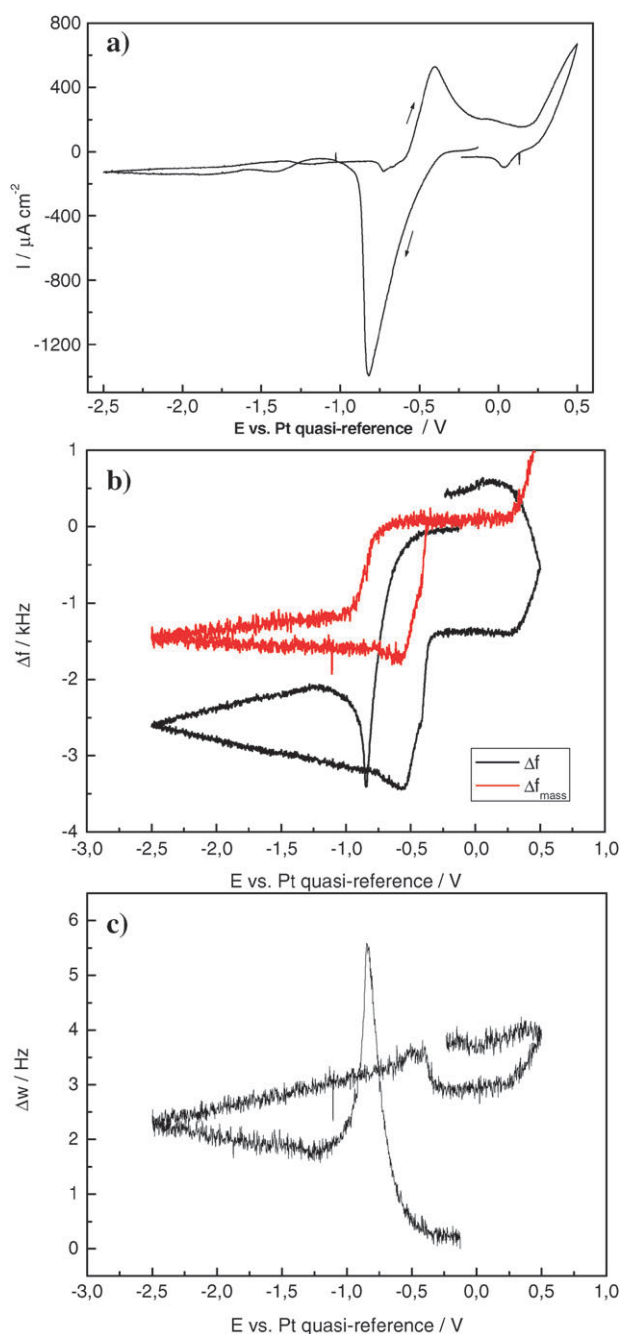


Fig. 8 (a) Cyclic voltammogram of [BMP]Tf₂N containing 0.5 M TiCl₄ on Au(111) at room temperature, (b) the corresponding changes in frequency and (c) the damping of the quartz crystal. Scan rate: 10 mV s⁻¹. The mass induced frequency shift shown in (b) has been calculated according to $\Delta f_{\text{mass}} = \Delta f + \Delta w/2$ (for details see text).

observed for the pure ionic liquid and for the upper phase of the biphasic mixture of AlCl₃/[BMP] Tf₂N on Au(111).^{22,28} Therefore, it can be concluded that the Au(111) surface is also restructured in the mixture of [BMP] Tf₂N/0.25 mol l⁻¹ TiCl₄. Such effects are known and adsorption of ions can be responsible for the formation of vacancies and pits as a result of their interaction with the gold surface leading to increase in the mobility of gold atoms which can be

ejected from the gold surface forming pits.^{29,30} Furthermore, the presence of Cl⁻ ions can weaken the Au–Au bond at the surface and consequently lead to an increased mobility of gold atoms.³¹

By shifting the electrode potential to more negative values, quite a nice Au(111) surface with monoatomically high terraces is obtained, see Fig. 9b. At –1.8 V, the STM image appears reproducibly noisy, Fig. 9c. This noise may be attributed to the beginning cathodic breakdown of the Tf₂N anion.^{22,28} By switching the electrode potential to –2.2 V, one can observe the formation of some islands on the Au(111) terraces and step edges, Fig. 9d. These islands may be attributed to the formation of metallic titanium and/or insoluble titanium sub-chloride, TiCl_x. The number and size of these islands increase preferentially at the step edges by switching the potential to more negative values (–2.5 – –2.7 V) as shown in Fig. 9e.

The dissolution process of the deposited film was also investigated by a stepwise shift of the potential in the anodic direction. Fig. 10 shows a set of *in situ* STM images obtained during the dissolution of a film deposited at a potential of –2.2 V. At –1.5 V the deposited layer starts to dissolve, Fig. 10a. At –1.0 V, some distinct monoatomically high islands are clearly seen all over the surface. Furthermore, some vacancy islands are formed on the Au(111) surface, as shown in Fig. 10b. With ongoing time the number of these islands decreases considerably, Fig. 10c. When the dissolution process is continued by switching the potential to –0.7 V, the original surface of Au(111) becomes visible with the presence of a small number of islands and small tiny pits. When the electrode potential is set to –0.26 V the number and size of these pits increase as shown in Fig. 10d. This indicates the formation of a surface alloy, presumably between Au and Ti at the early stages of deposition. It is therefore possible that an ultrathin surface alloy film of Ti–Au is possibly obtained in the ionic liquid [BMP]Tf₂N containing TiCl₄ preceding the formation of very thin layers of titanium subhalides. We observed similar STM-behaviour with TiF₄, where in the best case, islands of 1 nm in height were obtained on Au(111). From the experiments described in this paper it may be concluded that the deposition of titanium from halides in ionic liquids is at least extremely difficult. In our opinion, it is hopeless to try to deposit bulk layers of titanium in ionic liquids from titanium halides. In order to further investigate the reasons for the failure to deposit elemental titanium from ionic liquids, electrochemical reduction experiments were carried out using both TiCl₄ and TiCl₃ as the starting material.

3.3 Extended electrochemical reduction experiments with TiCl₄ and TiCl₃ in [EMIm]Tf₂N

Preliminary solubility experiments of both TiCl₂ and TiCl₃ in [EMIm]Tf₂N showed that they both had very limited solubility at 25 °C. TiCl₂ was found to be soluble to an extent $\ll 0.001$ M with a cyclic voltammogram (not shown) of a saturated solution in EMIm Tf₂N showing no redox peaks. TiCl₃ was more soluble, with a saturated solution being around 0.001 M at 25 °C. It was still very difficult to observe reliable redox peaks. However, in the presence of a complexing agent,

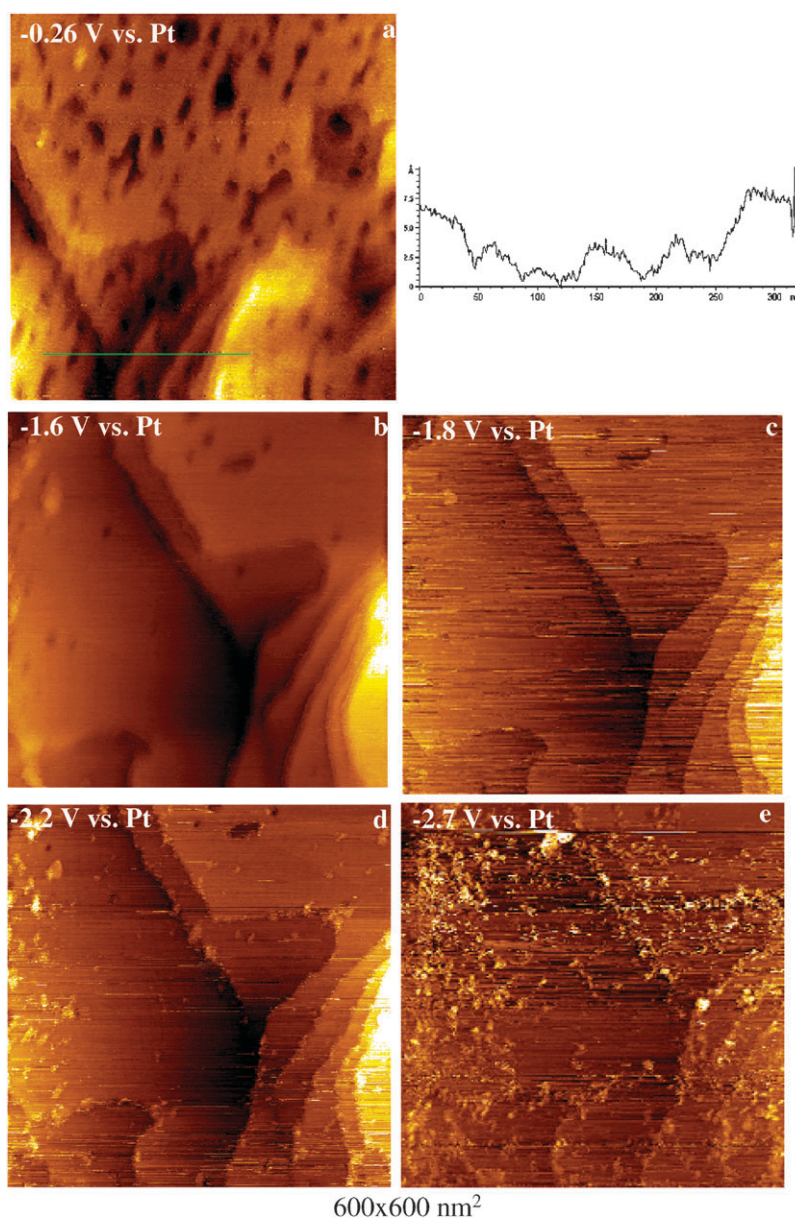


Fig. 9 A set of STM images of Au(111) in [BMP] TiF_2N containing 0.25 M TiCl_4 at different potentials.

acetylacetone (AcAc), the solubility of TiCl_3 dramatically increased (~ 0.2 M) and it was possible to obtain reproducible cyclic voltammograms. An example is shown in Fig. 11a together with the same for TiCl_4 in the presence of the complexing agent. The TiCl_3 solution in the IL showed a clear redox couple that could be attributed to initial $\text{Ti}^{3+}/\text{Ti}^{2+}$ redox couple followed by full re-oxidation to Ti^{4+} . The repetitive CV had similar characteristics to the $\text{Ti}^{4+}/\text{Ti}^{2+}$ couple observed in TiCl_4 solutions (with AcAc). Both TiCl_3 and TiCl_4 solutions showed scan rate and concentration dependence in the redox chemistry. TiCl_4 , in particular, displayed increasing peak separation with increasing scan rate and concentration.

Extended electrodeposition experiments were carried out for both the TiCl_4 and TiCl_3 solutions in [EMIm] TiF_2N . In the TiCl_3 solution (at 0.2 M) with 0.4 M AcAc, after long-term

two-stage electrodeposition (-0.6 V/21 h followed by -1.8 V/66 h), no noticeable deposition was found on the working electrode. Solution colour changes during the process, together with UV-Vis spectra analysis of solutions before and after the stages of reduction, indicated that the solution speciation of Ti had changed. In addition, CV's measured at various stages indicate substantial changes in the redox peaks with almost complete loss (or shift?) of the $\text{Ti}^{3+}/\text{Ti}^{2+}$ couple, Fig. 11b. No noticeable precipitate was observed. For a 0.2 M TiCl_4 solution with 0.4 M AcAc in [EMIm] TiF_2N colour changes were also observed and a small amount of black precipitate was found in the cell on standing after electrodeposition. No electrodeposit on the working electrode was observed. These results support the EQCM and *in situ* STM measurements above and indicate that limited solubility of titanium-halide species may be

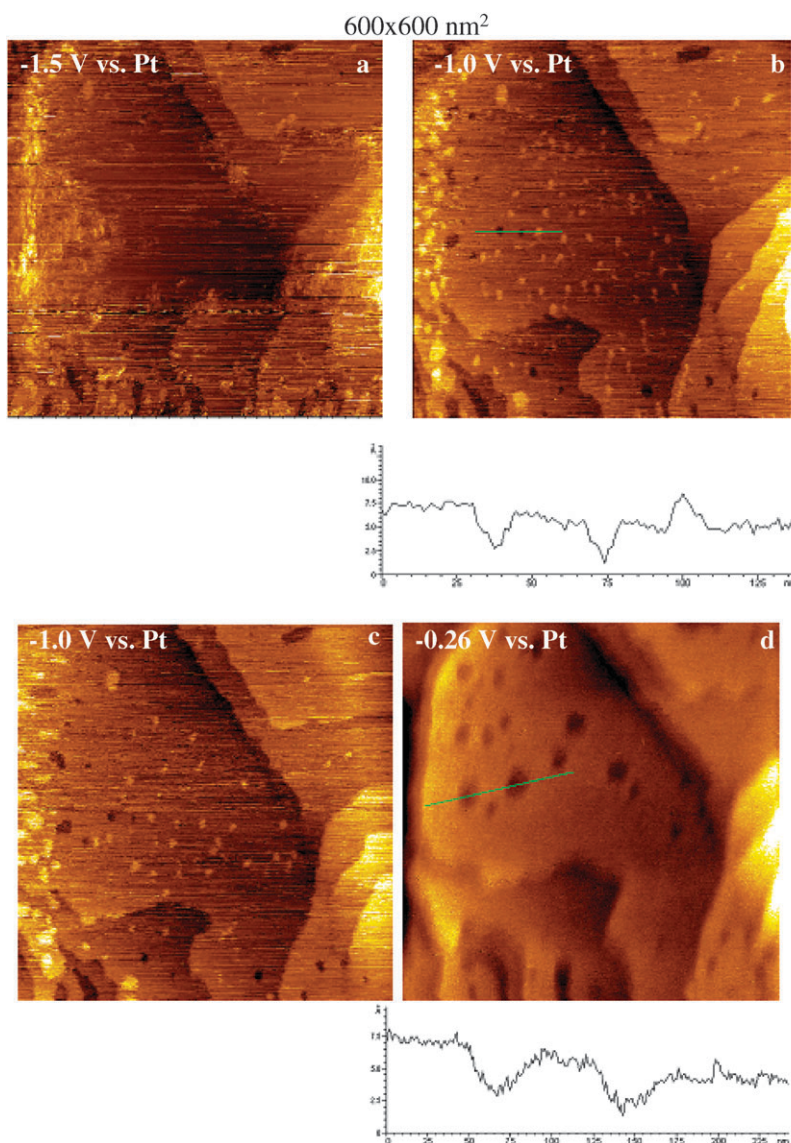


Fig. 10 A set of STM images of Au(111) in [BMP]Tf₂N containing 0.25 M TiCl₄ at different potentials.

a factor in the inability to electrodeposit titanium from halide solutions of ionic liquids.

3.4 Chemical reduction of TiCl₄ in ionic liquids using lithium

When a lithium ribbon was used as a reductant for TiCl₄ in an [EMIm]Tf₂N at temperatures near 25 °C a black/brown porous precipitate formed around the lithium. Analysis of this precipitate found that it was consistent with a [Ti³⁺·(cat⁺)] [Cl⁻]₄ species being formed analogous to the reduction of Ti⁴⁺ with lithium in the presence of bipyridine in THF.^{32–34}

It may be concluded that it is not possible to reduce Ti⁴⁺ to titanium metal *via* this route at room temperature. Recently Katayama and coworkers²⁴ published a communication outlining their efforts to electrochemically reduce TiBr₄ in 1-*n*-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)-amide ([BMP]Tf₂N). The electrochemical reduction was conducted at 180 °C and at -2.3 V Ti compounds of Tf₂N were identified while at -3.0 V a Ti rich deposit was formed. In

parallel decomposition of the BMP⁺ had occurred. It was therefore decided for the present study to repeat the lithium reduction experiment at a higher temperature (130 °C) using both excess and stoichiometric amounts of Li. 100 mg of TiCl₄ was added to 2 ml of [BMP]Tf₂N in a test tube with a tightly fitted screw top cap. A deep orange/yellow solution formed. This mixture was warmed up to 130 °C. An excess (50 mg) of clean bright Li ribbon was added to the IL mixture. The orange solution slowly turned deep brown over 3 days. The lithium became heavily encrusted with a brown solid. This solid was washed clean of IL with 2 × 5 ml aliquots of THF. The remaining lithium was carefully dissolved with dry methanol and the brown solid was then filtered and washed with methanol and then water. The solid was analysed by chemical analysis, FTIR, XRD and EDS. The results of these analyses indicate the solid contained large amounts of Li, F and Ti, but IR interpretation did not show the presence of the Tf₂N anion. Rather the presence of F suggests decomposition products of the anion and mirrors the results for the electrochemical reduction

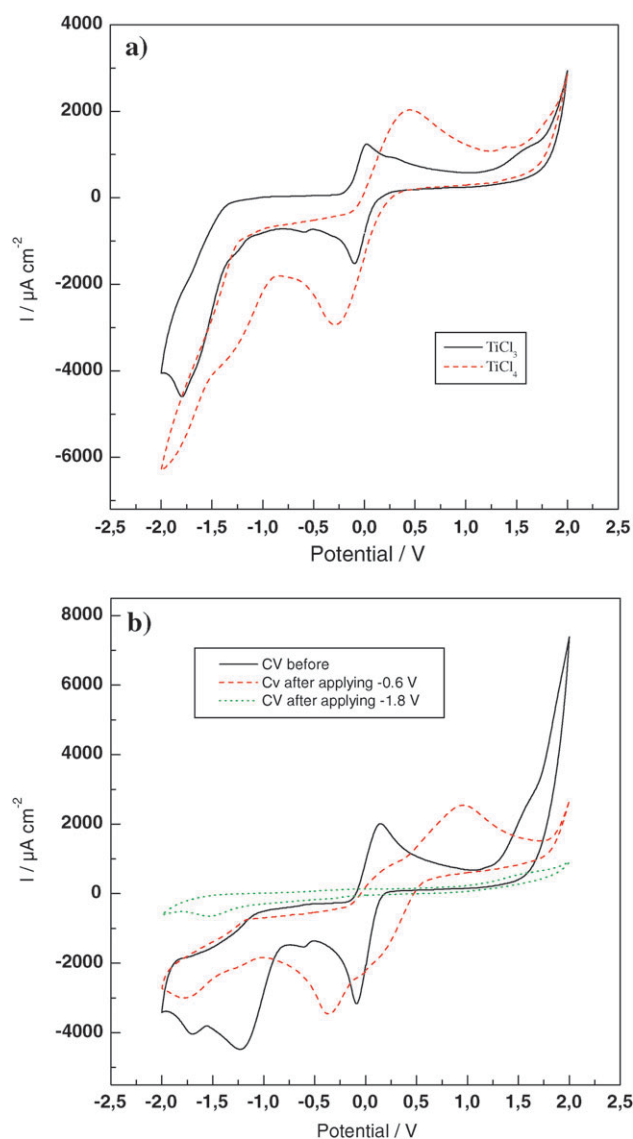


Fig. 11 (a) Comparison of CVs TiCl_3 and TiCl_4 (0.2 M) in EMIm- TiF_2N containing 0.4 M AcAc before electrodeposition. Scan rate: 50 mV s^{-1} . (b) Comparison of CVs of TiCl_3 in EMIm- TiF_2N containing 0.4 M AcAc before and after electrodeposition. Scan rate: 50 mV s^{-1} .

discussed previously, as well as other work with this anion.^{21,22,35} Clearly chemical reduction of titanium in ionic liquids is also not readily attainable even at elevated temperatures.

4. Conclusions

In this paper it has been investigated whether elemental titanium can be electrodeposited from its halides and isopropanolate in different ultrapure ionic liquids. In all cases the cyclic voltammograms do not show any indication of a defined titanium deposition. *In situ* quartz crystal microbalance experiments do not show any hint of elemental titanium deposition. Rather titanium subhalides like $\text{TiCl}_{0.2}$, $\text{TiCl}_{0.5}$ or $\text{TiCl}_{1.1}$ (as an average stoichiometry) are formed. *In situ* STM experiments reveal that there is some deposition on Au(111) leading to an ultrathin layer of titanium or titanium subhalides. In addition, long term reduction experiments to attempt to

produce bulk quantities of deposit also fail to obtain titanium metal. Rather insoluble products are formed, and it is postulated that this is caused by the poor solubility of reduced titanium (2+?)—halide complexes in the ionic liquids investigated. In addition, attempts to chemically reduce TiCl_4 using lithium did not succeed and there were distinct parallels in the formation of insoluble black/brown products with the electrochemical experiments.

Our results show without doubt that the electrodeposition of titanium from its halides in ionic liquids is at least extremely difficult if not even impossible. The wide electrochemical windows of ionic liquids alone are not sufficient to make this possible; there seem to be kinetic and thermodynamic barriers which prevent the deposition of elemental titanium at low temperatures. A successful deposition process for titanium in ionic liquids will, in our opinion, require the development of tailored titanium precursors.

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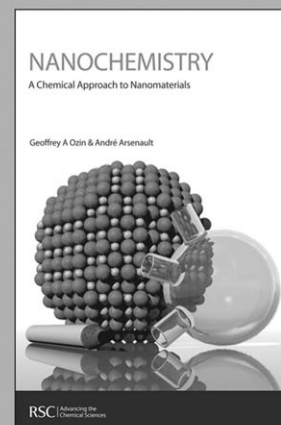
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