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Physical Chemistry of Ionic Liquids

Guest Editor: Frank Endres (Technical University of Clausthal, Germany)

Editorial

Physical chemistry of ionic liquids

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Do solvation layers of ionic liquids influence electrochemical reactions?

Frank Endres,^{*ab} Oliver Höfft,^a Natalia Borisenko,^{ab} Luiz Henrique Gasparotto,^{ab}
Alexandra Prowald,^b Rihab Al-Salman,^a Timo Carstens,^a Rob Atkin,^c
Andreas Bund^d and Sherif Zein El Abedin^{†ab}

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In this discussion paper we discuss our recent results on the electrodeposition of materials and *in situ* STM/AFM measurements which demonstrate that ionic liquids should not be regarded as neutral solvents which all have similar properties. In particular, we focus on differences in interfacial structure (solvation layers) on metal electrodes as a function of ionic liquid species. Recent theoretical and experimental results show that conventional double layers do not form on metal electrodes in ionic liquid systems. Rather, a multilayer architecture is present, with the number of layers determined by the ionic liquid species and the properties of the surface; up to seven discrete interfacial solvent layers are present on electrode surfaces, consequently there is no simple electrochemical double layer. Both the electrodeposition of aluminium and of tantalum are strongly influenced by ionic liquids: in 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide, [Py_{1,4}]TFSA, aluminium is obtained as a nanomaterial, whereas in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, [EMIm]TFSA, a microcrystalline material is made. Tantalum can be deposited from [Py_{1,4}]TFSA, whereas from [EMIm]TFSA only non-stoichiometric tantalum fluorides TaF_x are obtained. It is likely that solvation layers influence these reactions.

Introduction

In recent times, ionic liquids have proved to be promising electrolytes for the electrodeposition of metals and semi-conductors. Their physical properties, such as *e.g.* wide electrochemical windows, high conductivities and low vapour pressures, have led to a vast number of articles in which ionic liquids are employed as electrolytes for electrodeposition (see for example ref. 1). However, so far little is known about the structure of the metal/ionic liquid interface and there are no satisfactory descriptions of the arrangement of ions at the interface. Quite recently Kolb *et al.*² and Mao *et al.*³ independently investigated the electrochemical interface between gold single crystal electrodes and imidazolium based ionic liquids with PF₆⁻ or BF₄⁻ anions to explore the double layer structure on gold surfaces. Mao *et al.*³ reported the selective adsorption of an imidazolium cation on the Au(100) surface (less pronounced on Au(111)) which revealed the necessity of the adsorbed cation being structural commensurate with the surface. This means that the adsorption of the imidazolium cation at gold single crystal electrodes

depends strongly on the structure of the surface. Furthermore, they also observed that Au(111) exhibits long-range restructuring as a result of the interaction of imidazolium cations in a certain potential range.⁴

Baldelli⁵ investigated the Pt/[BMIm]BF₄ interface using surface-specific sum frequency generation spectroscopy (SFG) and electrochemical impedance spectroscopy (EIS). He reported that ions organize in a Helmholtz-like layer at the interface, where the potential drop occurs over a range of 0.3–0.5 nm from the metal surface into the liquid. Furthermore the structure of the interface is potential dependent, since at potentials positive to the potential of zero charge (PZC) anions are adsorbed to the surface and the imidazolium ring is repelled to orient more along the surface normal, while at potentials negative to PZC the cation is oriented more parallel to the surface plane and the anions are repelled from the surface.

We ourselves (the Clausthal group) have intensively studied electrochemical processes at electrode/ionic liquid interfaces by *in situ* STM (scanning tunneling microscopy) for the last 10 years. According to our studies it is obvious that ionic liquids influence electrochemical processes; however, the mechanism of such an influence is not yet fully understood. We have investigated the potential dependent restructuring/reconstruction of Au(111) in the presence of ionic liquids. It was found that [Py_{1,4}]TFSA induced a restructuring/reconstruction of Au(111), most likely due to adsorbed ionic liquid.⁶ Prior to the cathodic decomposition of the [Py_{1,4}] cation, the TFSA anion seems to be subject to a cathodic breakdown leading to surface films which can be probed by *in situ* STM. Cathodic breakdown of the TFSA anion was

^a Institute of Particle Technology, Arnold-Sommerfeld-Strasse 6, D-38678 Clausthal-Zellerfeld, Germany.

E-mail: frank.endres@tu-clausthal.de

^b EFZN Goslar, Am Stollen 19, D-38640 Goslar, Germany

^c Centre for Organic Electronics, Chemistry Building, The University of Newcastle, Callaghan, New South Wales 2308, Australia

^d Institute of Physical Chemistry and Electrochemistry, Dresden University of Technology, D-01062 Dresden, Germany

[†] Permanent address: National Research Centre, Dokki, Kairo, Egypt.

previously reported⁷ although more recent results show that when recrystallized there does not seem to be a cathodic breakdown.⁸ It seems that impurities, even in the low concentration regime, have an influence on the electrochemical stability of ionic liquids; this shows that for any fundamental studies ionic liquids should ideally be free of any impurity.

In this discussion paper we aim to stimulate other groups to fundamentally study the processes at the metal/ionic liquid interface and their subsequent influence on electrochemical reactions. It is not intended to present a comprehensive review, therefore we rather present and discuss our recent results on the electrodeposition of Al, Ta and $\text{Si}_x\text{Ge}_{1-x}$ in ionic liquids, taking into consideration the formation of solvation layers at the electrode/ionic liquid interface which can significantly influence the electrochemical processes. Until recently we have been unable to satisfactorily explain the following results:

1. Despite our efforts we have not yet succeeded with *in situ* STM atomic resolution of Au(111) in ionic liquids. There are only hints in the literature showing Fourier filtered AFM images of single crystalline gold electrodes⁹ as well as adsorbed anion layers.³

2. In some liquids, *e.g.* $[\text{Py}_{1,4}]\text{TFSA}$ and $[\text{EMIm}]\text{TFSA}$, it is surprisingly difficult to achieve atomic resolution even of HOPG (highly oriented pyrolytic graphite), which otherwise is a standard substrate and is even used for education purposes.

3. The deposition of Al from AlCl_3 in $[\text{Py}_{1,4}]\text{TFSA}$ leads to nanocrystalline deposits, whereas in $[\text{EMIm}]\text{TFSA}$ a microcrystalline deposit is obtained; the Al-species in both liquids are practically the same.^{10,11} In ref. 10 we have shown that the addition of AlCl_3 to both liquids first leads to a complexation with $[\text{TFSA}]^-$ and disproportionation of the initial $[\text{AlCl}_x(\text{TFSA})_y]^-$ complexes giving $\text{Al}(\text{TFSA})_3$ and $[\text{AlCl}_4]^-$. At high concentrations of AlCl_3 , leading to a biphasic regime, the lower phase consists almost completely of $\text{Al}(\text{TFSA})_3$, whereas in the upper phases $[\text{AlCl}_4]^-$ is the dominant species. Electrodeposition of Al in the upper phase occurs *via* mixed $\text{AlCl}_x(\text{TFSA})_y$ species, presumably *via* $[\text{AlCl}_2(\text{TFSA})_2]^-$ and $[\text{AlCl}_3(\text{TFSA})]^-$ formed in small concentrations at the phase boundary between the $[\text{AlCl}_4]^-$ and the $\text{Al}(\text{TFSA})_3$ layers. Thus, different Al species cannot be the reason for the different grain sizes.

4. The deposition of tantalum from TaF_5 in thin layers is possible in $[\text{Py}_{1,4}]\text{TFSA}$, but not in $[\text{EMIm}]\text{TFSA}$ (at least not near room temperature).¹²

5. The composition and thickness of electrochemically made $\text{Si}_x\text{Ge}_{1-x}$ is influenced by the ionic liquid species.¹³

Some of these effects can be explained on the basis of interfacial solvation layers, which is the focus of the following section. The possible influence of solvation layers, or more generally of adsorbed ionic liquids, on electrochemical processes has hitherto been neglected in literature.

Solvation layers

In 2007 Atkin and Warr reported force profiles for the approach curves of an AFM tip to a substrate.¹⁴ Forces were only measured at discrete distances, suggesting that well formed ionic liquid layers are present adjacent to the surface.

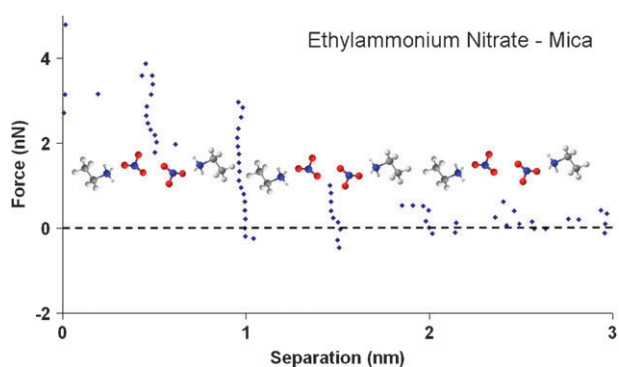


Fig. 1 Force *versus* distance profile for an AFM tip (Si_3N_4) approaching the surface of a mica substrate in ethylammonium nitrate (EAN).¹⁵

The force to rupture a layer increases closer to the surface, as order is stronger near the substrate. On account of the AFM tip's relative roughness and low surface charge, it was argued that the forces measured are mainly due to solvent layers associated with the substrate under investigation. Force profiles for the $[\text{EMIm}]\text{acetate}$ /graphite system revealed six or seven solvation layers and that $[\text{EMIm}]^+$ cations in the surface layer have a rather flat orientation relative to the substrate. Similar results were found for ethylammonium nitrate on mica.¹⁵ Fig. 1 shows an approach curve as well as a sketch for the adsorbed liquid. These results were, in principle, confirmed using tris(pentafluoroethyl)trifluorophosphate ionic liquids.¹⁶ The authors write in ref. 16: “*In this high-energy X-ray reflectivity study, the temperature-dependent structures of three ionic liquids with the tris(pentafluoroethyl)trifluorophosphate anion in contact with a charged sapphire substrate were investigated with submolecular resolution. All three RTILs show strong interfacial layering, starting with a cation layer at the substrate and decaying exponentially into the bulk liquid. The observed decay length and layering period point to an interfacial ordering mechanism, akin to the charge inversion effect, which is suggested to originate from strong correlations between the unscreened ions.*” Since then Atkin *et al.* have shown that $[\text{EMIm}]\text{TFSA}$ and $[\text{Py}_{1,4}]\text{TFSA}$ are adsorbed differently on mica.¹⁷ Finally, the primary conclusion from a series of papers by Kornyshev based on a simple theoretical model was: “*The plots for the distribution of ions near the electrode at different electrode charges show that for the considered system, unlike it is often assumed, the double layer is not one layer thick.*”[‡]

Thus, published data clearly show that ionic liquid cations are strongly adsorbed on solid surfaces. Adsorption is driven by electrostatics on charged surfaces and by van der Waals interactions between the surface and the cation alkyl chain on hydrophobic surfaces. (To date, ionic liquid interfacial structures present on an anionic surface have not been reported.) The adsorbed cation layer and the inherent nanostructure of the bulk ionic liquid lead to the formation of several well formed interfacial layers. These concepts are addressed in the article by Hayes *et al.* in this Themed Issue.¹⁸ These facts motivated our study of the interaction of $[\text{Py}_{1,4}]\text{TFSA}$ and

[‡] From ref. 31.

[EMIm]TFSA with Au(111). It was found that both [EMIm]⁺ and [Py_{1,4}]⁺ are adsorbed on Au(111), and 3–5 subsequent layers were noted.¹⁹ Fig. 2 shows the force curves published in ref. 19 and Fig. 3 shows a sketch of these results summarizing the overall picture for these 2 liquids. As a result [Py_{1,4}]⁺ is approximately 4 times more strongly adsorbed on Au(111) than [EMIm]⁺, and a force between 5 and 20 nN for rupturing the last ionic liquid layer has to be regarded as considerable. It should be mentioned that these results were obtained with a commercial AFM without lock-in amplification. Since in molecular solvents such curves are only measurable with lock-in AFM devices, at a minimum it can be concluded that ionic liquids are more strongly adsorbed on surfaces than molecular solvents. In ref. 19 we also presented potential dependent *in situ* STM results for Au(111) electrodes immersed in [Py_{1,4}]TFSA and in [EMIm]TFSA. In [Py_{1,4}]TFSA the gold surface appears strongly structured (in part wormlike), and more than 1600 mV of cathodic polarization are required to transform the surface to a flat one. In [EMIm]TFSA Au(111) is also structured, but much more weakly, and less than

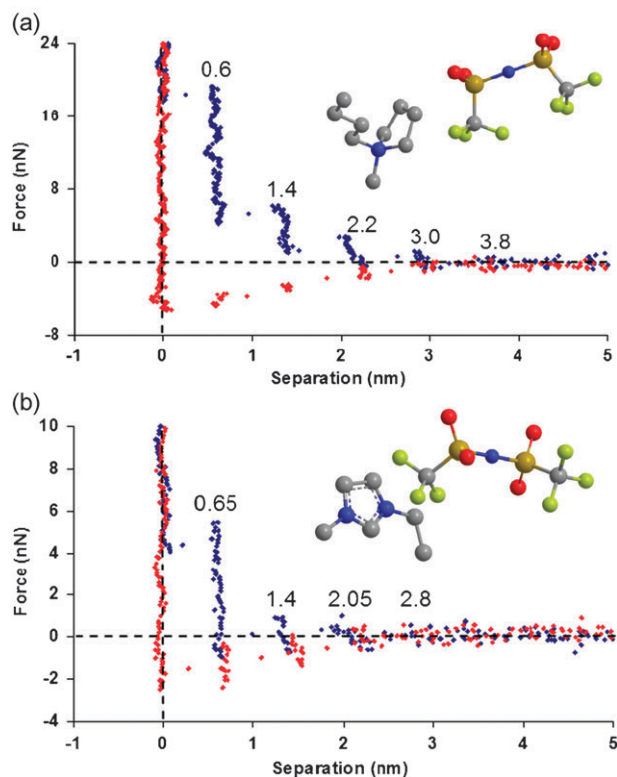


Fig. 2 (a) Force *versus* distance profile for an AFM tip (Si₃N₄) approaching (blue) and retracting from (red) a gold (111) surface in [Py_{1,4}]TFSA. At least five steps in the force curve can be seen, extending to a separation of 3.8 nm. The force required to rupture the innermost layer and move into contact with the gold surface is 20 nN. The separation distances for each layer prior to push-through are given on the plot. (b) Force *versus* distance profile for an AFM tip approaching (blue) and retracting from (red) a gold (111) surface in [EMIm]TFSA. At least three steps in the force curve can be seen, extending to a separation of 3 nm. The force required to rupture the innermost layer and move into contact with the gold surface is 5 nN. The separation distances for each layer prior to push-through are given on the plot.

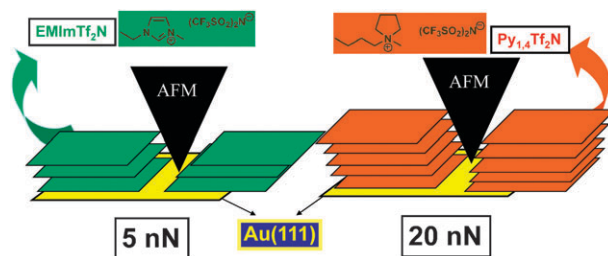


Fig. 3 A sketch of AFM tips pushing through solvation layers of ILs on Au(111) surface. The force values indicate that [Py_{1,4}]TFSA is 4 times more strongly adsorbed on Au(111) than [EMIm]TFSA.

500 mV of cathodic polarization are required to transform the surface to a flat one. From these results we conclude that adsorption of the ionic liquid cations leads to a restructuring of the gold surface, and that this adsorption seems to be dependent on the electrode potential. This raises the issue of the nature of the interaction of the ionic liquids with the STM tip, and how the tunneling process can be understood. Ouchi and Katayama presented a poster entitled “Electrochemical interface structure of neat ionic liquids on metal electrode studied by *in situ* sum frequency generation” at the 3rd conference on ionic liquids (COIL-3) in Cairns, Australia.²⁰ The principle was published in ref. 21. Briefly, sum frequency generation is sensitive to interfacial molecules whose orientation is different to that of the bulk liquid. For an introduction into the prospects of this technique for ionic liquids science we would like to refer to recent papers from Baldelli.^{5,22} Ouchi and Katayama²⁰ probed both the 1-butyl-3-methylimidazolium ion and the bis(trifluoromethylsulfonyl)amide ion, and found potential dependent adsorption of the ions on a platinum surface. Starting from a neutral layer, cation adsorption prevails in the cathodic regime, whereas in the anodic regime anion adsorption prevails. Furthermore, there seems to be a strong hysteresis when the potential window is passed from the anodic to the cathodic regime and *vice versa*.

These results suggest that ionic liquid layers form adjacent layers to metal surfaces; the potential dictates whether cations or anions are bound to the substrate. As *in situ* scanning tunneling microscopy probes local variations in surface density of states, it is possible that the slight variations in the electronic density of states of the investigated surface are masked by adsorbed liquid/ions, perhaps in all but the most pure aqueous systems. If this adsorption is not ordered, it would at least be difficult (if not impossible for some ionic liquids) to probe single crystal metal electrodes atomically with the STM. Hitherto there is only one paper available in literature that suggests Au(100) might be probed with AFM quasi-atomically.⁹ However, details on the quality of the liquid and the experiment were not given in that paper. The results of Mao *et al.*³ showed that an ordered adsorption of the BF₄⁻ anion, if carried out on Au(100) in a certain potential regime, leads to a quasi-atomic resolution with the *in situ* STM.

Atkin's results¹⁴ for ionic liquid adsorption on a graphite surface might explain why the apparently trivial substrate HOPG is also not easy to probe atomically with *in situ* STM. Fig. 4 shows a sequence of STM images of freshly cleaved HOPG in [Py_{1,4}]TFSA. At the 300 nm × 300 nm scale

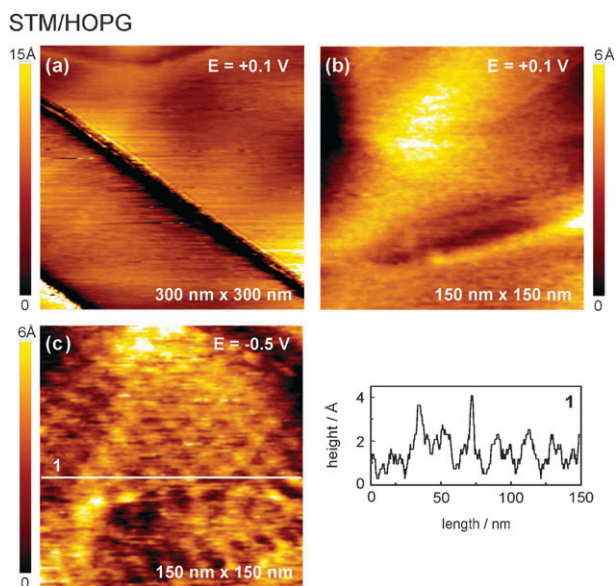


Fig. 4 A sequence of *in situ* STM images of HOPG in [Py_{1,4}]TFSA. At +0.1 V vs. Pt quasi ref. a typical surface structure of HOPG is obtained (a). A higher resolution shows that an adsorbed layer seems to be present (b). On decreasing the electrode potential a type of ordering is observed (c). The individual islands are of about 20 nm in width with a height of less than 0.5 nm (height profile, bottom right).

(Fig. 4a) the typical surface structure of HOPG is probed at +0.1 V vs. the Pt quasi reference electrode. With a higher resolution (Fig. 4b), however, it is clear that the surface is not probed that well and rather an adsorbed layer seems to be present. If the experiment is done under air or in aqueous solution under what are otherwise the same conditions, the surface of HOPG is easily probed, even with atomic resolution. Quite interestingly, when the electrode potential is set to -0.5 V, suddenly a type of ordering is observed (Fig. 4c). The ordered structure, which is difficult to probe in high quality with *in situ* STM, appears hexagonal; the individual islands have a width of around 20 nm with a height of less than 0.5 nm (Fig. 4, height profile, bottom right). A likely explanation is that in this case the STM probes the HOPG surface in or under a solvation layer, and that by variation of the electrode potential an ordering of the liquid is observed. When setting the electrode potential back to the more positive regime it is difficult to get back the original topography. At this point the question remains of what it is the STM probes and how reliably the height of such structures can be measured in this way, as the tunneling gap might be influenced by the adsorption of the ionic liquid species. It cannot currently be determined to what extent the tunneling current, and thus the image quality, are influenced by such adsorbed layers. This example shows that even such an apparently trivial substrate like HOPG can have some challenges for the experimenter. Nevertheless, we do not exclude atomic resolution of single crystalline metal surfaces with STM in ionic liquids. However, in any case, such approaches will be much more difficult than in aqueous solutions and one should not expect to see atoms “at the push of a button”.

From the aforementioned results another question arises: do these solvation layers influence electrochemical reactions?

A further complication is that currently there is no information available in the literature suggesting to what extent these solvation layers are influenced by dissolved salts. We have found the first hints that the restructuring of Au(111) in [Py_{1,4}]TFSA in the presence of LiTFSA is different from the restructuring which occurs in the pure ionic liquid.²³ We also have to mention that impurities in ionic liquids are still a concern, and in our experience surface reactions are strongly influenced by impurities in ionic liquids. In ref. 6 we have shown that even apparently ultrapure ionic liquids can contain diminutive amounts of inorganic impurities leading to unanticipated behavior on the single crystalline surface of Au(111). A further open question is: how are solvation layers built up if mixtures of ionic liquids are employed? Apart from a fundamental interest, such variable solvation layers might have an influence on the bulk deposition of materials. Therefore, from our point of view, a deep understanding of such layers and of their influence on chemical and electrochemical reactions is required.

Aluminium deposition

A key motivator of our studies of Al electrodeposition from AlCl₃ in [Py_{1,4}]TFSA and [EMIm]TFSA was to use *a priori* water-free liquids, as water reacts irreversibly with AlCl₃ to produce HCl and oxo-chloroaluminates, which can be adsorbed on the working electrode. Although an ionic liquid made of [EMIm]Cl and AlCl₃ is well suited to Al electrodeposition, preparing the organic halide to be water-free is difficult. Apart from the interesting phase behaviour of AlCl₃ in [EMIm]TFSA and in [Py_{1,4}]TFSA leading to 2 immiscible phases we found that—surprisingly—the electrodeposition of Al from [Py_{1,4}]TFSA always led to a nanocrystalline deposit with grain sizes between 10 and 40 nm,²⁴ whereas deposits from [EMIm]TFSA were always microcrystalline. *In situ* STM investigations reveal that in [EMIm]TFSA there is clearly an underpotential deposition of Al on Au(111), but not in [Py_{1,4}]TFSA, from which we suggested that the [Py_{1,4}]⁺ cation might be adsorbed on the surface of growing Al nuclei, thereby hindering growth beyond nanocrystalline sizes. Detailed spectroscopic measurements and calculations confirmed that the Al-species in both liquids are practically the same.¹⁰ As described in detail in ref. 25 the *in situ* STM probes a structured surface in AlCl₃/[Py_{1,4}]TFSA which transforms to a flat one before the bulk deposition of aluminium starts. We did not observe an underpotential deposition of Al. In AlCl₃/[EMIm]TFSA from the beginning there was a flat surface, followed by the underpotential deposition of aluminium before the bulk growth of aluminium set in. In the first case a nanocrystalline deposit is obtained, in the second case a microcrystalline deposit, in the bulk phase. As the Al-species are the same^{10,11} it is likely that both the underpotential deposition and the bulk deposition are influenced by the solvation layers discussed for pure liquids. The underpotential deposition of Al in [Py_{1,4}]TFSA does not occur and obviously the growth of the nuclei is also hindered in this liquid. Although it is an open question to what extent the Al-species influence the solvation layers themselves, it is obvious that the ionic liquid must be so strongly adsorbed that

underpotential deposition is totally hindered and the growth of the nuclei slowed down. In [EMIm]TFSA, on the other hand, there seems to be a much weaker adsorption leading to a upd of Al and a less hindered growth of the nuclei. In our opinion such effects have to be expected for all ionic liquids and the deposition of metals can be totally altered if just another liquid is employed. If Al deposition is *e.g.* performed in [EMIm]Cl/AlCl₃ Al can be deposited in high quality even for technical purposes. If Al is deposited in [Py_{1,4}]Cl/AlCl₃ only a loosely adhering deposit is obtained. Thus, ionic liquids can lead to totally different results if just one ion is replaced by another one. One should also be prepared for the possibility that the variation of the metal salt concentration influences the solvation layers; furthermore there should be a temperature dependence of the solvation layers. These are all open questions that should be in the mind of any electrochemist if less reproducible or “unexpected” results are obtained. It should not be forgotten that ionic liquids, unless extremely pure, can contain numerous impurities like Li⁺, halide, alumina, silica or organic compounds that might segregate at the interface and consequently influence the solvation layers and thus the whole of the interface chemistry. A paper from Abbott *et al.* for this Themed Issue also shows that the deposition of Al is strongly influenced by Li⁺ and organic co-solvents.²⁶ In our opinion the ionic liquid/electrode interface is also influenced by these additives

Tantalum deposition

In 2005 we reported our first results on the electrodeposition of tantalum from [Py_{1,4}]TFSA in *PCCP*.²⁷ We showed that the electrodeposition of tantalum is highly complicated. From TaCl₅ only non-stoichiometric TaCl_x can be obtained whereas from TaF₅ tantalum can—in principle—be electrodeposited.

In contrast to the main group metals, d-orbitals are filled in the case of the reactive transition elements and consequently bonds to halides and other elements can be formed. Ta/Cl clusters of the formula [Ta₆Cl₁₂]²⁺ are known, whereas for fluorides there is in general a less rich cluster chemistry of transition metals. Our results also showed that the addition of LiF to TaF₅/[Py_{1,4}]TFSA facilitated the electrodeposition of thin crystalline tantalum layers. We investigated the tantalum deposition in more detail recently and found that the deposition of Ta from TaF₅ is influenced by the ionic liquid.¹² Fig. 5 compares the electroreduction of TaF₅ in [Py_{1,4}]TFSA with that in [EMIm]TFSA. Both voltammograms have the common feature that the first reduction process (C1) is not correlated with any deposition. Thus it must be due to a solution process, possibly the reduction of TaF₅ to TaF₃ as TaF₄ is usually not stable. At lower electrode potentials in both liquids the deposition of black layers starts. At the peaks labelled C2 in both cases non-stoichiometric TaF_x compounds are formed. In the case of [Py_{1,4}]TFSA there is a narrow potential regime between -2000 and -2300 mV on this potential scale where the quartz crystal microbalance shows the deposition of elemental tantalum. With pulsed deposition tantalum can indeed be deposited in micrometre thick layers (around peak/shoulder C3). In the case of [EMIm]TFSA we could not get elemental tantalum under the same conditions and at around -2500 mV on this potential scale the decomposition of the organic cation starts. The [EMIm]⁺ cation is known to be cathodically about 700 mV less stable than the [Py_{1,4}]⁺ cation. Surprisingly in the case of TaF₅/[Py_{1,4}]TFSA there is one more reduction process (C4) at which, after the deposition of elemental tantalum, again the deposition of non-stoichiometric TaF_x compounds sets in. At the first glance this observation does not seem to make any sense. How can TaF_x form if there was already a depletion of

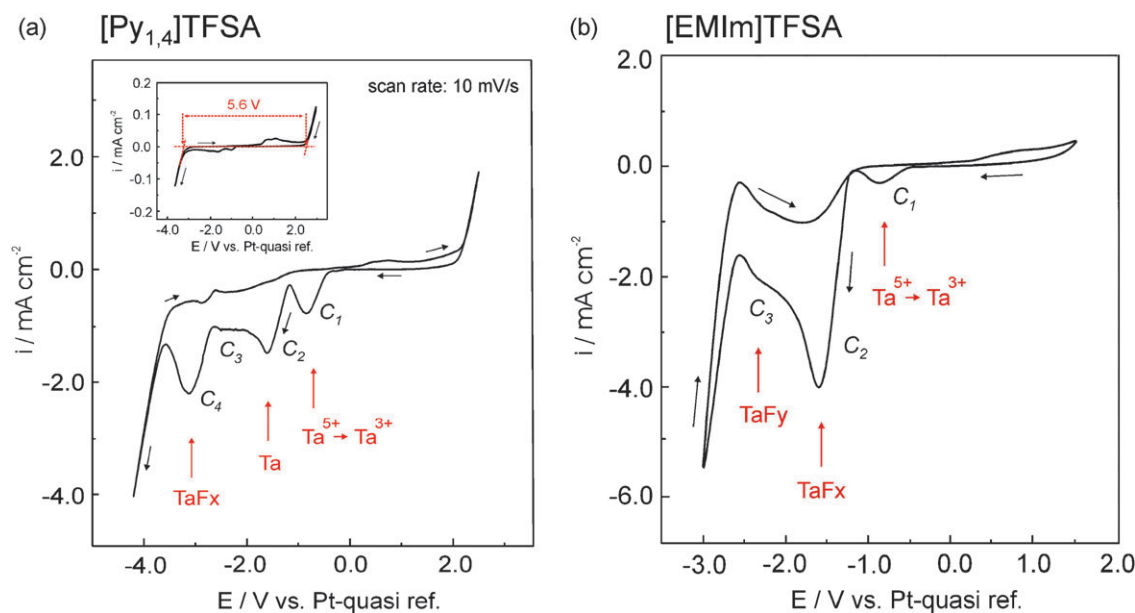


Fig. 5 (a) Cyclic voltammogram of 0.5 M TaF₅ in [Py_{1,4}]TFSA on Au(111) at 25 °C. Inset: cyclic voltammogram of ultrapure [Py_{1,4}]TFSA on Au(111) at 25 °C. The electrochemical window is of about 6 V limited by the irreversible reduction of the organic cation and gold oxidation. The scan rates are 10 mV s⁻¹. (b) Cyclic voltammogram of 0.5 M TaF₅ in [EMIm]TFSA on Au(111) at 25 °C.

TaF₅ near the electrode surface leading to elemental Ta? In the following we give a possible explanation. We found with *in situ* STM that Au(111) can be probed in high quality in [Py_{1,4}]TFSA. If TaF₅ of the highest quality is added, the surface looks “contaminated”.¹² Nevertheless, in the regime of peak C2 we could clearly observe with the STM that a well defined deposit starts growing out of this “contamination layer” which can be well probed with the STM. In ref. 12 we interpreted the initially bad surface with possible contaminations from our commercial TaF₅. A further explanation, which—of course—will have to be proved in further experiments, is that the addition of TaF₅ alters the solvation layer forming a type of solid/electrolyte interface. In this case the electrochemical reduction would require the diffusion of TaF₅ through this layer. It has to be expected that the solvation layer will change as soon as the first tantalum layer has been deposited. Furthermore, the applied electrode potential will influence the solvation layer. If we consider all this, it is possible to make a preliminary conclusion that the reduction process C4 is induced by a less strongly adsorbed solvation layer that allows the direct diffusion of TaF₅ to the electrode surface and consequently a further deposition of non-stoichiometric TaF_x compounds. In our opinion in all electrochemical studies on the electrodeposition of metals from ionic liquids, the influence of solvation layers on the electrochemical processes has to be considered. In pure liquids the solvation layer of [EMIm]TFSA is less strongly adsorbed on the surface and as a consequence it disturbs the electrodeposition less. We can currently not explain why we do not get elemental tantalum in [EMIm]TFSA. Either there is a further interaction between the ions of the liquid and TaF₅ destabilizing the Ta–F bond in the case of [Py_{1,4}]TFSA or the mass transport is different. A final answer to this question, which is of relevance to all reactive elements, will require further experiments.

Si_xGe_{1-x}

As a final example in this discussion paper we would like to summarize recent results on the electrodeposition of Si_xGe_{1-x} from [Py_{1,4}]TFSA and from [EMIm]TFSA. In ref. 28 we showed that during the codeposition of Si and Ge from equimolar SiCl₄ and GeCl₄ in [Py_{1,4}]TFSA a coloured deposit is obtained with roughly an equimolar composition in the deposited material. During deposition we observed a change in colours which we explained as one possibility on the basis of quantum size effects. Fig. 6 shows the cyclic voltammograms of SiCl₄/GeCl₄ in [Py_{1,4}]TFSA and in [EMIm]TFSA.¹³ The cyclic voltammograms of Si_xGe_{1-x} in both liquids look similar, apart from the different relative positions of the peaks *vs.* the silver pseudo reference electrode. First the reduction of Ge(IV) to Ge(II) is observed in the cathodic regime, followed by the deposition of germanium. The deposition of Si_xGe_{1-x} is observed as a shoulder in [Py_{1,4}]TFSA, whereas in [EMIm]TFSA only a belly in the decreasing part of the reduction peak is obtained. Both Si and Ge are indirect semiconductors with band gaps of 1.1 and 0.7 eV in the microcrystalline bulk phase, respectively, near room temperature. Thus they should, to some extent (depending on their thicknesses), absorb visible light in any case and both Si and Ge indeed have a dark colour

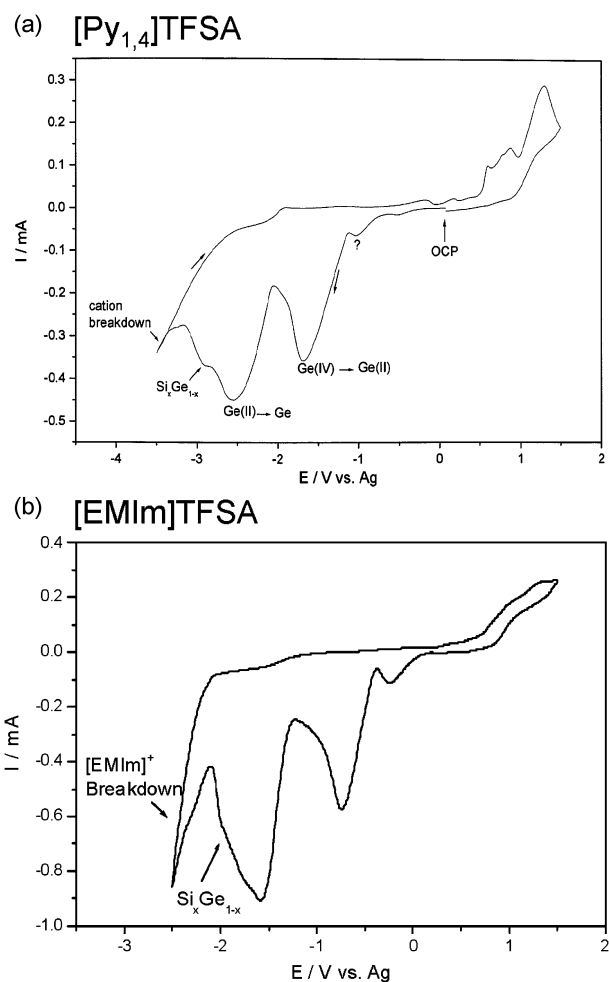


Fig. 6 (a) Cyclic voltammogram of SiCl₄:GeCl₄ (1:1 molar ratio) in [Py_{1,4}]TFSA on Au(111) at 25 °C. (b) Cyclic voltammogram of SiCl₄:GeCl₄ (1:1 molar ratio) in [EMIm]TFSA on Au(111) at 25 °C.

in the microcrystalline bulk phase. The situation, however, seems to be more complicated here. During the deposition of Si and Ge alone we have hitherto not yet observed a colour change during deposition. In both cases, the material turns brownish upon deposition, then black. In the case of Si_xGe_{1-x} deposition a colour change is clearly observed which can be explained by the direct band gap behaviour of the deposit. In both liquids a colour change from orange to green is observed (Fig. 7a and b). The colours started to appear after roughly 30 s and under the given conditions the material changes, in both cases, from colour to colourless. The sequence of the colours was repeated up to 3 times until finally a brown–black deposit was obtained. In our opinion the material shows a transition from direct to indirect behaviour with increasing particle size followed by the further deposition of new nuclei that start growing. It is surprising that the Si_xGe_{1-x} deposit obtained from [EMIm]TFSA after applying a constant potential of –1.9 V for 1 h showed a lower Si content than that obtained from [Py_{1,4}]TFSA under the same conditions (about 1–1.5:1 overall Si/Ge ratio from [Py_{1,4}]TFSA *vs.* about 1:3 from [EMIm]TFSA). As the molar ratios of the precursors were the same in both liquids the results must be due to kinetic phenomena. In most of the cases we have obtained

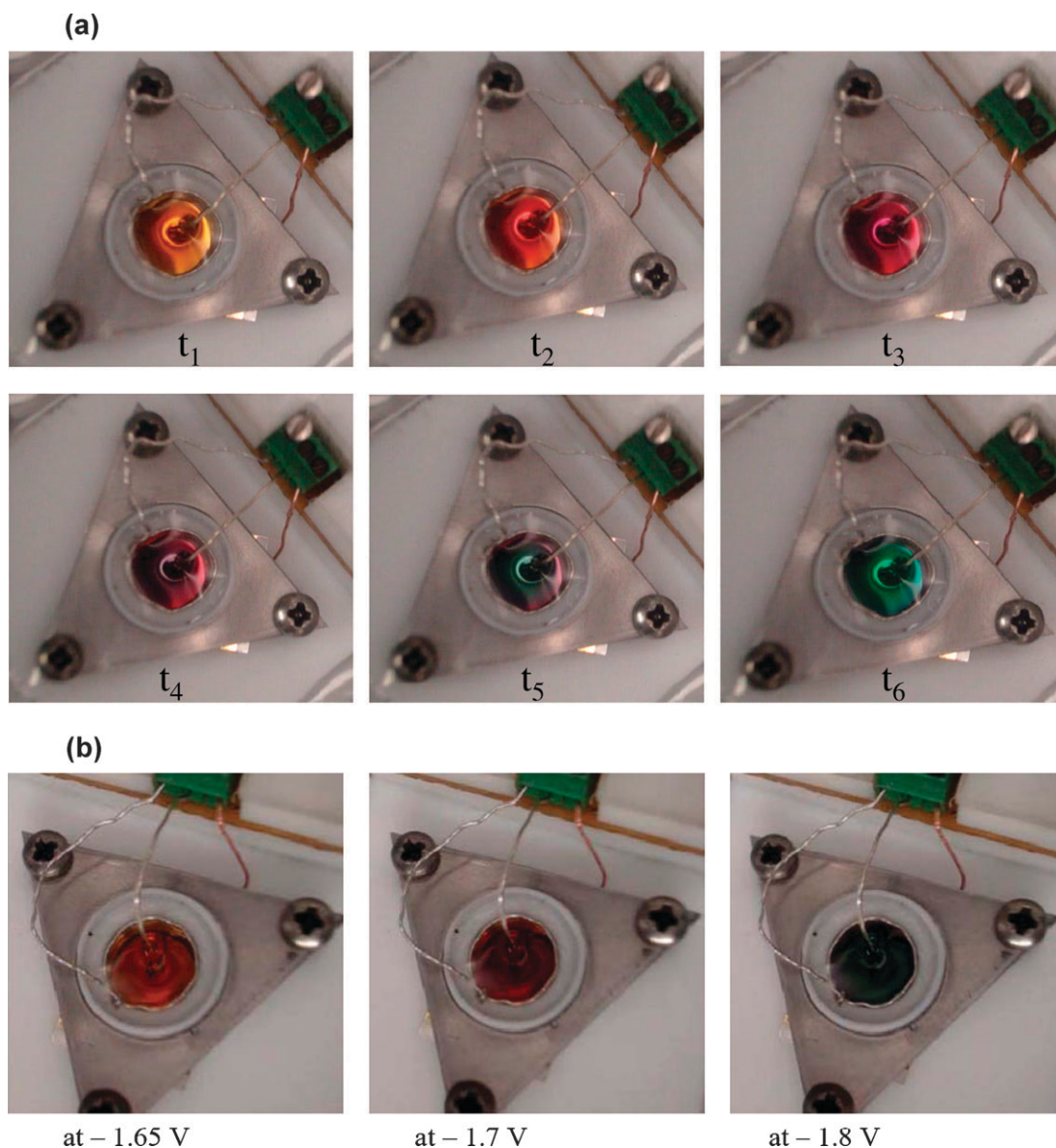


Fig. 7 (a) Colour sequence of $\text{Si}_x\text{Ge}_{1-x}$ deposition in $[\text{Py}_{1,4}]\text{TFSA}$. (b) Colour sequence of $\text{Si}_x\text{Ge}_{1-x}$ deposition in $[\text{EMIm}]\text{TFSA}$. In both cases during $\text{Si}_x\text{Ge}_{1-x}$ deposition a sequence of colours is observed during growth.

nanomaterials from $[\text{Py}_{1,4}]\text{TFSA}$ and microcrystalline materials from $[\text{EMIm}]\text{TFSA}$. Apart from differences in the overall deposition rate due to different diffusion coefficients of SiCl_4 and GeCl_4 in both liquids it is likely to assume that the composition, the thickness and the particle size are influenced by the ionic liquid. Our first experiments on the electrodeposition of $\text{Si}_x\text{Ge}_{1-x}$ from a third different ionic liquid (1-hexyl-3-methylimidazolium tris(pentafluoroethyl) trifluorophosphate, $[\text{HMIm}]\text{FAP}$) under the same conditions showed, interestingly, no strong preference for the co-deposition of $\text{Si}_x\text{Ge}_{1-x}$, although this liquid has a comparable electrochemical window to that of $[\text{EMIm}]\text{TFSA}$.²⁹ The cyclic voltammogram (Fig. 8) of an equimolar solution (0.1 M) of SiCl_4 and GeCl_4 in the FAP-liquid showed two main reduction peaks: the first one at about -1 V is—as usual—due to the reduction of Ge(IV) to Ge(II) . The second reduction peak at about -1.75 V is mainly correlated to the reduction of Ge(II) to Ge . A potentiostatic

polarization at a potential of -1.9 V for 1 h gave, unfortunately, a Ge deposit with only 1–2 atom% of Si , as was indicated by the EDX analysis. The possibility that this quite small amount of Si is just due to adsorbed SiCl_4 , which is then converted to silicon oxide due to *ex situ* treatment, cannot be excluded. During the cyclic voltammogram there was no hint of the co-deposition of Si and Ge : first, there is no discrete peak or even shoulder for the co-deposition of Si and Ge as in the case of $[\text{EMIm}]\text{TFSA}$ and $[\text{Py}_{1,4}]\text{TFSA}$. Secondly, there was no similar colour change of the deposit during the forward scan of the cyclic voltammogram. We can currently not comment on whether this result is solely due to a different solvation layer and/or due to a different speciation in the liquid, but our results show that—in any case—different ionic liquids influence (electro-) chemical reactions differently.

An interesting aspect is now to investigate to what extent the deposition of $\text{Si}_x\text{Ge}_{1-x}$, and of semiconductors in general,

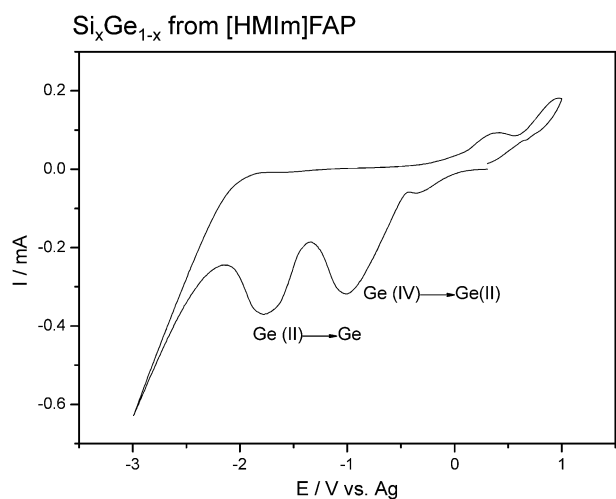


Fig. 8 Cyclic voltammogram of $\text{SiCl}_4:\text{GeCl}_4$ (1:1 molar ratio) in [HMIm]FAP on Au(111) at 25 °C.

is influenced by the solvation layers of ionic liquids. A further question that will have to be addressed by electrochemists in the future is how ionic liquids and solutes interact and to what extent solutes influence solvation layers. The whole of the solution chemistry might also be influenced by the individual ionic liquid. For example, Compton *et al.* show in this Themed Issue that different anions of ionic liquids can also influence electrochemical reactions differently.³⁰ Such effects are on the one hand a great chance for fundamental physical chemistry but on the other hand at the same time a challenge for applications if slight variations in liquid composition might alter electrochemical reactions. Similar effects are also known for high temperature molten salts but will not be considered further for the present paper as even slight variations of experimental conditions in molten salt experiments can alter the outcome considerably. This would be the topic of another discussion paper. Can we now answer the question of whether ionic liquids influence electrochemical reactions? We think that there is a lot of evidence that they do, but a final answer would require many efforts in the field.

Conclusions/outlook

In this paper we have discussed, together with the small amount of data available in the literature, our recent results on the influence of ionic liquids on the electrodeposition of metals and semiconductors. Undoubtedly solvation layers form on metal electrodes: in the case of [Py_{1,4}]TFSA five solvation layers form on Au(111), while in the case of [EMIm]TFSA at least three are present. [Py_{1,4}]⁺ is bound to the surface approximately 4 times more strongly than [EMIm]⁺. Furthermore, these solvation layers vary with the liquid species, and with the applied electrode potential. We have explained that in our opinion such solvation layers make it difficult to probe single crystalline metal electrodes with atomic resolution and they influence electrochemical reactions. Consequently, solvation layers should also influence the electrocatalytic performance of metal electrodes. To what extent these solvation layers are influenced by dissolved salts is

currently an open question. The discussed results on the deposition of Al, Ta and $\text{Si}_x\text{Ge}_{1-x}$ allow the assumption that these solvation layers are present in the case of solutes, too, and in different liquids different results are obtained. We summarize that there is substantial evidence that the solvation layers of ionic liquids influence electrochemical reactions. In our opinion, a fundamental knowledge of the interface reactions in ionic liquids is now required. A focus should from our point of view be set on the investigation of these solvation layers of different liquids under electrochemical conditions, as well as on the influence of solutes, cosolvents and temperature¹⁵ on them. In our opinion such experiments are necessary to better understand the influence of ionic liquids on electrochemical and other interface reactions.

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