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***In situ* STM, AFM and EQCM studies of the electrochemical deposition of
tantalum in two different ionic liquids with the
1-butyl-1-methylpyrrolidinium cation**

Timo Carstens¹, Adriana Ispas², Natalia Borisenko¹, Rob Atkin³, Andreas Bund²,
Frank Endres¹

¹ Institute of Electrochemistry, Clausthal University of Technology, Arnold-
Sommerfeld-Str. 6, 38678 Clausthal-Zellerfeld, Germany

² Technische Universität Ilmenau, FG Elektrochemie und Galvanotechnik, Gustav-
Kirchhoff Str. 6, 98693 Ilmenau, Germany

³ Newcastle Institute for Energy and Resources, The University of Newcastle, Callaghan
2308, NSW, Australia

Abstract

The electrochemical reduction of 0.1 M TaF₅ in two hydrophobic ionic liquids (1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate ([Py_{1,4}]FAP) and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ([Py_{1,4}]TFSA) is probed using three *in situ* techniques: scanning tunneling microscopy (STM), atomic force microscopy (AFM), and electrochemical quartz crystal microbalance (EQCM). These techniques reveal that under similar conditions TaF₅ is more easily reduced in the liquids with [TFSA][−] than [FAP][−] anions. Increasing the temperature reduced the viscosity and density of the ionic liquids which facilitates TaF₅ electroreduction, in particular, in [Py_{1,4}]TFSA. A herringbone reconstruction of the Au electrode was observed by STM for both ionic liquids with and without TaF₅. Ta deposition was proved by STM and EQCM in [Py_{1,4}]TFSA. Cracked layers,

with ionic liquid trapped inside, were obtained by direct plating from the [TFSA]⁻ ionic liquid. No Ta containing deposits could be obtained in the liquid with the [FAP]⁻ anion.

1. Introduction

Air- and water-stable ionic liquids (ILs) often have wide electrochemical and thermal windows, good ionic conductivities, usually negligible vapor pressure at room temperature, have high solubility for a variety of compounds and are therefore interesting solvent media for the electrodeposition of refractory metals. The widespread use of ILs in applied electrochemistry is currently impeded by the lack of understanding of the solution chemistry and especially of the interfacial properties.

The interface IL / electrode is considerably more complicated than in aqueous electrolytes. [1] The ionic atmosphere is not diluted by neutral solvent molecules, thus leading to highly effective charge screening in ILs, with calculated Debye lengths of the order of the size of the solvent ions. In general, IL ions are large and asymmetric, with the charge delocalized over one or more functional groups. Therefore, they should not be described as neutral solvents. Theoretical studies show that ILs have a complex structure in the bulk phase and at interfaces, and simple double layers do not form on metal surfaces. [2] *In situ* scanning tunneling microscopy (STM) and atomic force microscopy (AFM) studies reveal that a multilayer arrangement is present at electrode surfaces. [3-7, 10] A model for the IL interfacial structure could be developed by dividing the interface into three key regions: the innermost layer, the transition zone, and the bulk liquid. [4] The innermost layer is composed of the IL layer adsorbed to the electrode surface. Ions in the innermost layer in direct contact with the electrode show the highest order. In the transition zone the innermost layer structure decays to the bulk morphology.

An applied electrode potential has a strong effect on the interfacial nanostructure. At open circuit potential (ocp) and at negative electrode potentials the innermost layer is usually enriched with cations, whereas at more positive potentials anions are enriched. At more negative or positive electrode potentials both the number of layers that are measured with AFM and the force to push through them increase. [1, 3, 5-12]

Interfacial properties, including adsorption/co-adsorption of ions at the interface, are determined by the nature of the electrode and the electrolyte. Even a small variation in the electrolyte composition, e.g. due to impurities [13] or dissolved solutes [14], may drastically influence electrochemical reactions. For example, ultrapure [EMIm]TFSA can show unexpected behavior at the electrode/electrolyte interface if it is treated with Al_2O_3 to remove organic impurities post synthesis. Al_2O_3 seems to dissolve in the IL in low (ppm) concentrations and is deposited at the electrode surface [13]. The effect of dissolved LiCl has also been probed [14, 47]; the repulsive interaction measured at OCP becomes attractive when LiCl is present.

Tantalum, in its elemental or in its oxidized form, is one of the key elements in many applications due to its special anticorrosive properties and inertness in aggressive electrolytes. For example, it is used in integrated circuit interconnects as a barrier layer against the diffusion of copper into silicon, [15] and in combination with hydroxyapatite it forms a coating with good bioactivity and compatibility [16, 17]. It is also used in insoluble anodes [18, 19] or can protect different materials against corrosion [20, 21].

Our previous studies showed that Ta can be deposited from a TaF_5 precursor in a series of air and water stable room temperatures ILs [20 - 25]. The type of the ionic liquid, the temperature and electrodeposition technique strongly influence the composition, uniformity and homogeneity of the deposited layers. In these studies a concentration of 0.5 M TaF_5 was used for Ta electrodeposition. The best quality deposits were obtained in 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ([Py_{1,4}]TFSA). In the present paper

we investigate the reduction mechanism of Ta from a lower concentration of TaF₅ (0.1 M) in two ILs with [Py_{1,4}]⁺ cations and the [TFSA]⁻ and [FAP]⁻ anions.

The properties of [Py_{1,4}]TFSA in relation with the electroreduction of TaF₅ were discussed in our previous studies, [22, 23, 24] as well as in [26]. ILs containing [FAP]⁻ anions were first reported in [27]. They have a higher viscosity and density, as well as a lower conductivity, compared to ILs containing [TFSA]⁻ anions [26, 28]. However, the electrochemical window of ILs with the same cation, for example, the 1-ethyl-3-methylimidazolium, [EMIm]⁺, having [FAP]⁻ or [TFSA]⁻ anions is similar, as well as their hydrolytic stability [26, 29]. Both anions are hydrophobic, but [FAP]⁻ more so. [FAP]⁻ ILs have been employed as lubricants, i.e., to steel-steel contacts [30, 31, 32, 33, 48], for analytical measurements [34], to determine the activity coefficients of volatile organic compounds at infinite dilution [35], to extract polycyclic aromatic hydrocarbons, [36] for building membrane-free amperometric O₂ sensors [37] and as possible biosensors for the electrochemical reduction of guanine and adenine [38]. Different ILs with the [FAP]⁻ anion have already been used for the electrodeposition of poly(p-phenylene) and of poly(p-phenylene)/TiO₂ nanowires [39, 40, 41], Si_xGe_{1-x} [42], and poly(3,4-ethylenedioxythiophene) [41, 43]. However, no published study could be found in the literature on the electrochemical reduction of Ta in an ionic liquid with the [FAP]⁻ anion.

2. Experimental

1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate, [Py_{1,4}]FAP, purchased from Merck KGaA (EMD), was used in custom-made quality. All detectable impurities were guaranteed by the supplier to be below 10 ppm. 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide, [Py_{1,4}]TFSA, was purchased from IOLITEC in the highest available quality. Prior to use, the liquids were dried under vacuum at 100 °C to water contents of below 1 ppm and stored in a closed bottle in an argon-filled glove

box with water and oxygen contents below 2 ppm (OMNI-LAB from Vacuum-Atmospheres). TaF₅ (99.99 %) purchased from Alfa Aesar was first purified by sublimation and then added to the ionic liquids.

All STM experiments were performed at 23 °C using in-house-built STM heads and scanners under inert gas conditions with a Molecular Imaging / Agilent PicoScan 2500 STM controller in feedback mode. Assembling of the STM head and filling of the electrochemical cell were performed in an argon-filled glove box solely reserved for assembling of STM heads. The STM head was placed inside of an argon filled vacuum-tight stainless steel vessel, to ensure inert gas atmosphere during the STM experiments, transferred to the air-conditioned laboratory (T = 23 °C) and placed on a vibration damped table from IDE (Germany). STM tips were made by electrochemical etching of Pt–Ir wires (90/10, 0.25 mm diameter) with a 4 mol/L NaCN solution and subsequently electrophoretically coated with a cathodic electropaint (BASF GY85-0030). During the STM experiments the potential of the working electrode was controlled by the PicoStat from Molecular Imaging/Agilent. In all experiments the STM images were obtained by scanning from the bottom to the top with a scan rate of 2 Hz and a resolution of 512 pixels per line.

Force curves were collected using a Molecular Imaging Pico Plus AFM in contact mode. A silicon SPM-sensor from Nano World was employed for all experiments presented in this study. The spring constant was 6 N/m as given by the supplier. All force curves were acquired at room temperature in an argon-filled glove box. Previous studies have shown that the low surface charge and roughness of the AFM tip will prevent IL layer formation around the tip; [5] the push throughs in the force curve are therefore primarily associated with the gold substrate.

Electrochemical quartz crystal microbalance (EQCM) measurements were carried out simultaneously with the classical electrochemical measurements, such as potentiodynamic, chronoamperometric or chronopotentiostatic experiments. A network analyzer (Agilent

E5100A) connected to a PC via a GPIB card was used for recording the resonance frequency of quartz crystals and the full width at half maximum of their resonance curves. An in house made EQCM cell which can be heated up to 250°C by resistive elements was used.

All electrochemical experiments were performed inside of an argon filled glove box using a PARSTAT 263A potentiostat/galvanostat. The electrochemical cell was made of polytetrafluoroethylene (Teflon) and clamped over a Teflon-covered Viton O-ring onto the substrate, thus yielding a geometric surface area of the working electrode of 0.3 cm² (in the STM experiments) and 0.22 cm² (in the EQCM experiments). Au(111) substrates and Au thin layers sputtered onto quartz substrates served as working electrodes in STM and EQCM experiments, respectively. Platinum wires were used as quasi-reference and counter electrodes.

Scanning electron microscopy combined with EDX (energy dispersive X-Ray) measurements were performed with a Hitachi S4800 system.

3. Results and Discussion

3.1 *In situ* STM measurements at the [Py_{1,4}]TFSA / Au(111) interface

In ultra pure [Py_{1,4}]TFSA Au(111) undergoes a herringbone-like reconstruction at negative electrode potentials [44, 45]. At -1.6 V the Au(111) surface exhibits a long-range superstructure pattern that is preserved until about -2.1 V where the adsorption of the organic cation begins [44]. AFM experiments reveal that multiple near surface ion layers are present at the IL / gold interface [8]. The interaction strength of the innermost layer and the charged substrate is dependent on the cation type. The required force to rupture interfacial IL layers for [Py_{1,4}]TFSA is greater than for [EMIm]TFSA and can be attributed to stronger cation surface interactions [8].

In previous studies we could show that the electrodeposition of tantalum at room temperature in [Py_{1,4}]TFSA occurs only in a very narrow potential window and is preceded by the formation of various non-stoichiometric tantalum subhalides. Attempts to deposit micrometer thick tantalum layers at room temperature failed, presumably because of kinetic reasons [22].

The typical cyclic voltammogram of 0.1 M TaF₅ in [Py_{1,4}]TFSA on Au(111) at 25 °C is presented in Fig. 1. The potential was initially swept cathodically from the open circuit value (ocp, -0.15 V vs. Pt) at a scan rate of 10 mV s⁻¹. In the cathodic regime a series of reduction processes (C₁-C₄) is obtained. C₂ is correlated with the bulk deposition of Ta, while C₁, C₃ and C₄ are attributed to the formation of various non-stoichiometric tantalum subhalides. It was found that the irreversible reduction of the organic cation occurs at slightly more negative electrode potentials (at -3.4 V) than the formation of tantalum subhalides (C₄) [22].

Fig. 1 Cyclic voltammogram (10 mV/s) of 0.1 M TaF₅ in [Py_{1,4}]TFSA on Au(111) at 25 °C.

In the following we present *in situ* STM results of the electrochemical reduction of 0.1 M TaF₅ in [Py_{1,4}]TFSA on Au(111) at room temperature. The tip approach was done at

ocp, subsequently the working electrode potential was very slowly changed during scanning towards more negative electrode potentials.

During the first STM scan the *in situ* images of Au(111) in [Py_{1,4}]TFSA containing 0.1 M TaF₅ and 0.5 M TaF₅ [22] look quite similar. At ocp (-0.15 V) a thin layer, which might be the result of the adsorbed TaF₅ [22], is present on the gold surface (Fig. 2a). The image quality decreases when the electrode potential is reduced. However, at -0.9 V (C₁) small islands start growing out of this layer (Fig. 2b). Between -1.3 V and -2.2 (C₂) a clear deposit forms on the gold surface (Fig. 2c,d). The *in situ* current/voltage tunneling spectra of this deposit exhibit metallic behavior. The CV/EQCM measurements show that at C₂ elemental Ta forms. Interestingly, if the electrode potential is set to -2.9 V, the morphology of the deposited layer changes again (Fig. 2e) and with time “chopstick like” structures of 50-60 nm in height and of about 18 nm in width can be observed (Fig. 2f). *Ex situ* SEM/EDX and XPS measurements reveal that at these electrode potentials subvalent non-stoichiometric tantalum fluorides like TaF_x can be formed [22, 23]. The differences in surface morphology as a function of the potential are thus attributed to the specific interaction of the IL species as well as the tantalum subhalides with the Au(111) surface.

Fig. 2 Sequence of *in situ* STM images representing the electrochemical behavior of 0.1 M TaF₅/[Py_{1,4}]TFSA on Au(111) at various electrode potentials during the 1st scan.

An interesting observation is that the “herringbone” reconstruction can also be probed in a certain potential regime in [Py_{1,4}]TFSA containing TaF₅ if the electrode potential is reduced extremely slowly over 48 hours (Fig. 3). At the ocp the thin layer shown in Fig. 2a is present on the gold surface. However, the roughness of this layer decreases by slowly reducing of the electrode potential (Fig. 3a). Between the ocp and -0.9 V the surface gets smoother and at -1.0 V instead of a Ta electrodeposit (Fig. 2b, c) the typical Au(111) surface with a terrace-like structure is obtained (Fig. 3b). At -1.4 V some vacancies with depths between 250 pm and 500 pm are probed (Fig. 3c). Their number may decrease with time by decreasing the electrode potential (Fig. 3d) and then the gold surface remains stable until the irreversible reduction of the organic cation begins at -2.9 V. Ultra-slow formation of vacancies in the herringbone structure in a similar potential regime was also identified for pure [Py_{1,4}]FAP [46] and pure [Py_{1,4}]TFSA. Furthermore, similar vacancies were obtained at -1.4 V in non-reconstructed surface for [Py_{1,4}]FAP containing LiCl [47]. Unlike in pure

[Py_{1,4}]FAP, the (22 x $\sqrt{3}$) reconstruction of the gold surface was not complete in the presence of LiCl. However, we have not yet been able to probe such vacancies for Au(111) in ILs with imidazolium cations. The surface becomes very smooth if the electrode potential is set back to -1.4 V (Fig. 3e). Furthermore zooming in (40 x 40 nm² area) shows that with time the terraces exhibit a long-range ("herringbone") superstructure pattern (Fig. 3f). In the presence of 0.1 M TaF₅ the reconstruction of the gold surface is not as stable and as pronounced as in the case of pure [Py_{1,4}]TFSA [44].

Fig. 3 *In situ* STM images of the Au(111) surface obtained in 0.1 M TaF₅/[Py_{1,4}]TFSA during extremely slow cathodic polarization in the 1st scan.

According to AFM data presented below the surface layering gets more pronounced both in the pure IL and in the presence of TaF₅ upon applying negative electrode potentials. Furthermore, in the case of the pure IL the width of the ion layer in contact with the gold surface becomes thinner indicating that the cation adopts an orientation more parallel to the surface, which induces the herringbone reconstruction. However, at negative electrode

potentials tantalum compounds (TaF_5 and TaF_3) will also participate in the surface process. If the electrode potential is reduced quickly, the tantalum compounds will be preferentially adsorbed to the electrode surface and then reduced to metallic Ta leading to the formation of Ta electrodeposit. However, if the electrode potential is reduced rather slowly, the large and bulky IL cations, which are already adsorbed at the ocp, will change their orientation blocking the surface and permitting the Au(111) ($22 \times \sqrt{3}$) reconstruction.

The appearance of the Au(111) surface is different during the second STM scan. The electrode potential was increased from -1.4 V to the former ocp (-0.15 V) and then reduced again. In the 2nd scan between -0.15 V and -0.4 V the typical gold terraces separated by steps of 250 pm in height occur. However, when the electrode potential is reduced to -0.5 V the surface starts to grow rapidly (Fig. 4a-d). Between -0.6 V and -1.2 V the surface continues to grow, the growth rate significantly decreases with decreasing electrode potential (Fig. 4e). Between -1.3 V and -2.9 V the surface remains almost stable (Fig. 4f) until the decomposition of the IL occurs.

As there are several IL layers on the Au(111) surface and possibly also on the tip, the layers on the surface surely hinder a good tunneling contact between the tip and the surface, and might also hinder the deposition of Ta in the first scan if the electrode potential is reduced extremely slowly. Electrochemical reactions require that the interfacial IL structure is disrupted to allow charge transfer. Subsequent scanning seems to “soften” the adsorbed layers, as the typical distance between tip and sample is 0.2 - 1 nm, the tip must move laterally through these layers, meaning that ions are pushed away. This often leads to a “blurred” image quality in the 1st scan as the tip disrupts the layers to allow electrochemical reactions on the surface. In the 2nd scan the typical terraces of gold separated by steps of 250 pm in height can be probed already at -0.15 V as the adsorbed layers have been disrupted by the tip during the 1st scan. Therefore, the surface growth at more negative electrode

potentials might be attributed to an underpotential deposition of Ta as the surface becomes “free” for electrochemical reactions.

Fig. 4 The sequence of STM images represents the electrochemical behavior of 0.1 M TaF₅/[Py_{1,4}]TFSA on Au(111) in the 2nd scan.

3.2 *In situ* AFM measurements at the [Py_{1,4}]TFSA / Au(111) interface

Fig. 5 shows normal force versus separation for an AFM tip approaching the Au(111) surface at the ocp, -0.5 V and -1.0 V in [Py_{1,4}]TFSA in the presence (red) and absence (black) of 0.1 M TaF₅. The steps in these AFM force curves are due to expulsion of the interfacial liquid layers from between the gold substrate and the AFM tip. The step width usually corresponds to the dimension of the individual ionic species or ion pairs. The "push-through" force required to rupture the layer is a function of the strength of cohesive interactions between the ions within the layer [5-8, 10, 48, 49]. The absolute separation between the AFM tip and the surface is unknown in contact mode AFM experiments. The "zero" position corresponds to the AFM tip in contact with material that it cannot displace, which may be the

surface or strongly adsorbed material. For solid IL interfaces, often it is possible to determine whether the tip is in contact with the substrate or a layer of strongly bound ions from the width of the step closest to the surface [50, 51, 52].

Fig. 5 Force versus separation profiles for an AFM tip approaching a Au(111) surface in [Py_{1,4}]TFSA in the presence (red) and absence (black) of 0.1 M TaF₅ at the ocp (a), -0.5 V (b) and -1.0 V (c).

AFM results show that at least 4 layers (at 0.64 nm, 1.47 nm, 2.3 nm and 3.2 nm) can be detected in pure [Py_{1,4}]TFSA at ocp, which is in good agreement with previous AFM data [8]. For all except the innermost layer the measured spacing of layers is 0.8 nm consistent with the IL ion pair diameter. However, at ocp the innermost layer is only 0.64 nm indicating that the IL cation adopts an orientation more parallel to the surface due to

maximize electrostatic attractions between the surface and the cation aromatic ring [8]. At negative electrode potentials five layers can be detected at the surface (Fig. 5, black curves). However, the width of the innermost layer decreases by reducing of the electrode potential (0.53 nm at -0.5 V and 0.47 nm at -1.0 V) indicating that the cation in the IL ion pair adopts a flatter surface conformation, which in turn induces the $(22 \times \sqrt{3})$ reconstruction of the gold surface.

The appearance of the force curves changes markedly when 0.1 M TaF₅ is added (Fig. 5, red curves). At ocp there are only two steps at 0.27 nm and 0.54 nm (Fig. 5a, red curve), while at -0.5 V three narrower steps are detected at 0.24, 0.49 nm and 1.05 nm (Fig. 5b, red curve), and the force required to rupture the layers is greatly reduced. These results indicate that a different, weaker near surface structure is present, in line with previous results for added LiCl [14]. Further reducing the potential to -1.0 V the strength of the surface layering increases the number of steps in the force curve (Fig. 5c, red curve). The three narrow steps near the surface are retained but additional steps are noted at wider separations superimposed on a weakly attractive background, and the push through force for the 0.25 nm step closest to the surface is markedly increased. The 0.25 nm step that is present at both -0.5 V and -1.0V is too narrow to be due to expulsion of the cation or the anion, and is not present in the absence of TaF₅. It is therefore possible that this narrow step near the surface is due to TaF₅ species, similar to recent results for solvate ionic liquids where lithium ions produced a similar small step [49].

These STM and AFM results show that the [Py_{1,4}]TFSA/Au(111) interface becomes more complex with the addition of TaF₅ due to specific interaction of the IL species as well as the tantalum subhalides with the Au(111) surface. This interaction is strongly dependent both on the applied electrode potential and the scan rate. Between -1.3 V and -2.2 V a tantalum deposition is probed if the electrode potential is reduced relatively fast. However, by slow decreasing of the electrode potential the Au(111) $(22 \times \sqrt{3})$ reconstruction occurs in the

similar potential regime. Furthermore, the appearance of the Au(111) surface is markedly different in the second STM scan, attributed to the STM tip disrupting the surface bound ionic liquid layer and thereby permitting electrochemical reaction with the solute.

3.3 *In situ* STM measurements at the [Py_{1,4}]FAP / Au(111) interface

The structure of the interfacial layers at the electrified [Py_{1,4}]FAP / Au(111) interface with no added solutes has been thoroughly studied by our groups using *in situ* STM and *in situ* AFM [1, 3, 10]. The [Py_{1,4}]FAP / Au(111) interface is complex with both the cation and anion adsorbed on the electrode surface. This adsorption becomes stronger and the number of the interfacial layers increases at higher electrode potentials. Preceding *in situ* STM experiments showed that in the cathodic regime the Au(111) surface undergoes a (22 x $\sqrt{3}$) surface reconstruction in pure [Py_{1,4}]FAP leading to the herringbone superstructure [3]. Similar to pure [Py_{1,4}]FAP, the (22 x $\sqrt{3}$) reconstruction was also probed in the presence of 0.1 M LiCl during cathodic polarization [47]. However, unlike the pure IL, the reconstruction of the gold surface was not complete. Furthermore, in the presence of LiCl the dissolution of the gold surface was obtained at negative electrode potentials. Here we present *in situ* STM results of the electrochemical reduction of 0.1 M TaF₅ in [Py_{1,4}]FAP on Au(111) at room temperature.

Fig. 6 Cyclic voltammogram (10 mV/s) of 0.1 M TaF₅ in [Py_{1,4}]FAP on Au(111) at 25 °C.

The electrochemical behavior of 0.1 M TaF₅ in [Py_{1,4}]FAP on Au(111) at room temperature is presented in **Fig. 6**. At least four cathodic processes are seen within this potential range (C_1 - C_4). However in comparison to TaF₅ / [Py_{1,4}]TFSA, the current densities are very low for electrodeposition processes. Furthermore, EQCM measurements presented below do not indicate any deposition of elemental Ta in this IL even at elevated temperatures. These processes are likely correlated with different surface processes that occur upon IL adsorption, which are quite different in the presence of TaF₅ (**Fig. 11**). *In situ* STM reveals that between C_1 and C_3 the Au(111) surface undergoes several restructurings. At C_1 an initial "wormlike" surface modifies to a smooth one. At C_2 the $(22 \times \sqrt{3})$ reconstruction begins and at C_3 the gold surface shows the herringbone superstructure pattern. The oxidation peak A^* is directly correlated with the reduction processes C_3 and C_4 as this peak appears only if the scanning reaches potentials required for C_3 and C_4 .

Fig. 7 shows *in situ* STM images of Au(111) in [Py_{1,4}]FAP containing 0.1 M TaF₅ between the ocp (-0.2 V vs. Pt) and -0.4 V. At the ocp, instead of large flat terraces typical for Au(111) in [Py_{1,4}]FAP [3], a rough gold surface with wormlike structures is obtained (Fig. 7a). The Au(111) steps can be recognized and the average step height is 250 pm. The depth of the defects in the surface seems to be ~ 250 pm. Similar wormlike structures were also obtained at the ocp for pure [Py_{1,4}]TFSA [8, 44] and [HMIm]FAP [53]. *In situ* AFM results show that at the ocp a strong adsorption of the [Py_{1,4}]⁺ and [HMIm]⁺ occurs for [Py_{1,4}]TFSA and [HMIm]FAP, respectively, which facilitates the gold reconstruction leading to a wormlike pattern [8, 53]. If the electrode potential is slightly decreased (the potential regime of C₁) the surface becomes smoother and the holes disappear (Fig. 7b). By further reducing of the electrode potential to -0.5 V the surface modification occurs again (Fig. 8). After about 1 hour many islands and vacancies can be probed on the gold surface (Fig. 8). With time these islands slowly disappear and simultaneously the (22 x √3) reconstruction appears (Fig. 8b, c). By further reducing the electrode potential (potential regime of C₂) the reconstruction becomes more pronounced (Fig. 8d, e). However, the vacancies can still be seen on the surface. Interestingly, in the case of the pure [Py_{1,4}]FAP IL, the herringbone reconstruction is first noted in a similar potential regime [3]. By further decreasing of the electrode potential (C₃) the vacancies disappear completely and the Au(111) surface exhibits a beautiful herringbone superstructure pattern, which remains stable until -2.0 V (Fig. 8f). *In situ* STM reveals that the Au(111) surface is subject to a restructuring/reconstruction both in the case of pure [Py_{1,4}]FAP IL and in the presence of 0.1 M TaF₅.

Fig. 7 *In situ* STM images of the Au(111) surface obtained in 0.1 M TaF₅/[Py_{1,4}]FAP between the ocp and -0.4 V.

Fig. 8 *In situ* STM images of the Au(111) surface obtained in 0.1 M TaF₅/[Py_{1,4}]FAP during cathodic polarization.

In situ STM images of Au(111) in 0.1 TaF₅ / [Py_{1,4}]FAP during anodic polarization are presented in Fig. 9. The electrode potential was initially changed from the ocp (-0.2 V vs. Pt) to +1.4 V. At higher electrode potentials dissolution of gold sets in and the STM images are

not stable. At ocp the gold surface exhibits a wormlike structure shown in Fig. 7a. Between the ocp and +1.4 V the quality of the STM images is rather low. According to AFM data, at ocp the innermost layer is enriched in cations, however at higher electrode potentials anions are present in the innermost layer [10]. Thus there must be a transition between these states, which might be different in the presence of TaF₅, hindering a clear image at lower positive potentials. If the electrode potential is slowly reduced to +1.0 V the gold surface is very rough with some islands/defects (Fig. 9a). The height/depth of these structures is between 0.6 and 1.2 nm. *In situ* AFM reveals that at +1.0 V a strong adsorption of IL anions occurs [10]. The structures grow in width and decrease in height with reducing the electrode potential (Fig. 9b, c). The height of the structures shown in Fig. 9c is up to 0.6 nm. Similar structures were also obtained for pure [HMIm]FAP during anodic polarization [53]. The surface hardly changes by further reducing the electrode potential to +0.1 V (Fig. 9d). However, if the electrode potential is kept at +0.1 V for several hours, the surface modifies (Fig. 9e) and after 18 hours a wormlike surface structure with 0.3-0.5 nm deep vacancies (typical for the ocp) occurs again (Fig. 9f).

Fig. 9 The sequence of STM images represents the electrochemical behavior of 0.1 M TaF₅ / [Py_{1,4}]FAP on Au(111) during anodic polarization. .

The AFM data below suggests that at the ocp the interfacial layer is enriched in cations, which are covered by an anion layer [10], while *in situ* STM images show a wormlike surface structure with 0.3-0.5 nm deep vacancies (Fig. 7a). At -0.5 V the innermost layer is enriched in cations both in the pure IL and in the presence of TaF₅, however, the addition of the Ta salt decreases the force required to rupture the innermost layer indicating that the layer becomes less strongly bound to the surface (Fig. 11a). *In situ* STM shows that first the wormlike structure closes completely (Fig. 7b) and then the (22 x √3) reconstruction of the gold surface begins (Fig. 8a-c). Between -1.0 V and -2.0 V the gold surface is completely reconstructed (Fig. 8f), the cation layer is more strongly bond to the surface both in the pure IL and in the presence of TaF₅ (Fig. 11b-d). At +0.4 V, instead of the wormlike structure typical for the ocp, the surface structure with ~0.6 nm high islands is obtained (Fig. 8c), while at +1.0 V a rough surface with 0.6-1.2 nm high island is probed (Fig. 8a). At +1.0 V the AFM

suggests an anion-rich innermost layer [10]. According to *in situ* AFM and STM data, the variation in interfacial structure between -2.0 V and +1.0 V suggest that at negative electrode potentials (-2.0 V, -1.0 V) the innermost layer is enriched in cations strongly bound to the surface, which induces the herringbone reconstruction. At the ocp, both cations and anions are present in the interfacial layer leading to a wormlike surface structure. At higher electrode potentials anions are enriched in the interfacial layer resulting in the structure shown in Fig. 9c. The transition between these two states is presented in Fig. 9d-f.

Recently, we reported that the gold surface dissolves at negative electrode potentials in [Py_{1,4}]FAP containing LiCl [47]. Interestingly, a similar dissolution of the gold surface can also be obtained at -0.6 V in [Py_{1,4}]FAP in the presence of TaF₅ (Fig. 10). In another STM experiment the electrode potential was decreased relatively fast (within 1.5 hour) from the ocp to -0.6 V. At the ocp the wormlike surface structure shown in Fig. 7a is obtained. By decreasing the electrode potential the holes disappear and the surface becomes flat. Then at -0.6 V a fast dissolution of the surface occurs (Fig. 10). Within just 1 hour a ~3 nm deep hole has formed.

Fig. 10 Dissolution of the gold surface at -0.6 V in 0.1 M TaF₅ / [Py_{1,4}]FAP.

These results show that the addition of TaF₅ to [Py_{1,4}]TFSA and [Py_{1,4}]FAP has a certain influence on the interfacial structure. The observations made are not trivial to explain, but are clearly considerably different to corresponding results in aqueous solutions. However, the interfacial structure *vice versa* has also a strong influence on the electrochemical reduction of Ta compounds.

3.4 *In situ* AFM measurements at the [Py_{1,4}]FAP / Au(111) interface

Fig. 11 shows normal force versus separation curves for an AFM tip approaching the Au(111) surface at negative potentials in [Py_{1,4}]FAP in the presence (red) and absence (black) of 0.1 M TaF₅.

Fig. 11 Force versus separation profiles for an AFM tip approaching a Au(111) surface in [Py_{1,4}]FAP in the presence (red) and absence (black) of 0.1 M TaF₅ at ocp (a), -0.5 V (b), -1.0 V (c), -1.5 V (d) and -2.0 V (e).

A detailed *in situ* AFM study of the electrified [Py_{1,4}]FAP / Au(111) interface has been presented in [10]. There are at least 5 IL layers (at 0.30 nm, 0.95 nm, 1.83 nm, 2.9 nm and

3.8 nm) in pure $[\text{Py}_{1,4}]\text{FAP}$ at the ocp (Fig. 11a, black curve). The innermost layer is 0.30 nm consistent with the size of the $[\text{Py}_{1,4}]$ cation [10]. At lower electrode potentials the number of layers increases (Fig. 11b-e, black curves). At -0.5 V and -1.0 V a small step at 0.31 nm indicates that the layer is cation-rich. The force required to rupture this layer increases by reducing the electrode potential (Fig. 11b,c, black curves). At -1.5 V and -2.0 V the innermost layer is 0.61 nm wide (Fig. 11d,e, black curve). At these electrode potentials the innermost layer must be composed of cations, as the surface is strongly negatively charged. However, at such a negative electrode potential the cation layers become so strongly bound to the surface that the AFM tip cannot displace them [10], thus AFM probes the anion layer. The small compression noted at high force for the -1.5 V data is a consequence of rearrangements in the anion layer. These do not occur at -2.0 V because the layer is more strongly formed.

As opposed to the $[\text{Py}_{1,4}]\text{TFSA}$ data above, the form of the data for the $[\text{Py}_{1,4}]\text{FAP}$ / Au(111) interface is quite similar with and without added 0.1 M TaF_5 . While the push through forces are generally slightly reduced, indicating reduced cohesion between near surface ion layers, the width of the near-surface layers barely changes upon addition of TaF_5 , *especially* for the ion layer nearest the surface. We conclude that in $[\text{Py}_{1,4}]\text{FAP}$ TaF_5 is expelled from the the IL / Au interface whereas in $[\text{Py}_{1,4}]\text{TFSA}$ TaF_5 rather disturbs the interfacial layers. This shows that the anion plays a key role in directing surface behavior, even at negative potentials.

3.5 Characterization of the electrolyte properties by EQCM

As a by-product of the EQCM measurements we determined the viscosity and the density of our electrolytes in the temperature range 20-170°C. This is relatively straightforward because the shift of the resonance frequency of a thickness shear mode quartz crystal is proportional to the square root of the viscosity-density product of the contacting liquid (Eq. 1) [54].

$$\Delta f = -f_0^2 \sqrt{\frac{n \rho \eta}{\pi \rho_q \mu_q}} \quad \text{Eq. 1}$$

where n is the overtone number ($n = 1, 3, 5, \dots$), ρ and η are the density and the viscosity of the liquid, and ρ_q and μ_q are the density and shear modulus of the quartz crystal.

The advantage of the EQCM over commercial viscosimeters or densitometers is that small amounts of liquids can be accurately measured, while in commercial devices, relatively large amounts of liquids are needed. The temperature dependence of the viscosity-density product will reflect mainly the exponential temperature dependence of the viscosity. The temperature dependence of the density is much weaker. From the experimental data (Fig. 12) it is obvious that below 100 °C the mass transport of the tantalum species in [Py_{1,4}]FAP will be more sluggish compared to [Py_{1,4}]TFSA. This is in perfect agreement with the lower current densities in [Py_{1,4}]FAP observed above (Fig. 6). Above 100 °C, the differences in the viscosities reduce and in a first naive approach one would expect that tantalum deposition should be possible in both ILs at elevated temperatures

Fig. 12 The viscosity-density product of the electrolytes used as a function of temperature.

(■) for 0.1 M TaF₅ in [Py_{1,4}]TFSA and (●) for 0.1 M TaF₅ in [Py_{1,4}]FAP

3.5.1 *Voltammetry and in situ microgravimetry at polycrystalline gold electrodes*

The electrochemical behaviour of polycrystalline gold in the pure ILs, as well as in the ILs containing 0.1 M TaF₅, in the temperature range between 18 °C and 170 °C was analyzed. The results obtained at room temperature and 100°C are presented in Fig. 13.

At 100 °C the partial decomposition of [Py_{1,4}]TFSA occurs at electrode potentials more negative than -2.7 V (notice the strong increase of the cathodic current at lower potentials, (Fig. 13a)). However, no significant peaks are observed in the cyclic voltammograms at low temperatures, or at higher temperatures at potentials above -2 V. The pristine [Py_{1,4}]FAP shows an anodic and a cathodic wave (Fig. 13b). With increasing the temperature, the amplitude of these waves increases which is in accordance with the viscosity discussed above. The peak position changes slightly with temperature, fact that can be partially attributed to the potential drift of the Pt quasi reference electrode with the temperature.

When TaF₅ is added, the current densities in the voltammograms change drastically (Figs. 13c and 13d). A cathodic wave appears and its position changes to more positive values with increasing the temperature. In both ILs used in this study the maximum current at 100°C is reached at ca. -1.25V. With further increase of the temperature, a second cathodic peak appears. At the same time, an anodic peak can be found, that indicates a partial stripping of the deposited layer. When the scan rate is low (e.g. 10 mV/s), some noise often occurs in the current response during the CVs experiments, if the potential is more cathodic than -2V and the temperature is above 100°C. Some irreversible changes occur on the surface of the polycrystalline Au electrode under these conditions, which disappears afterwards in the consecutive cycles (not shown). One interesting fact to mention here is that the shapes of the cyclic voltammograms obtained on polycrystalline gold electrodes (Figs. 13 c and d) are quite

similar to those obtained on single crystalline Au electrodes (Figs. 1 and 6). Thus, it seems that the process of Ta deposition in the two ILs investigated here does not depend on the crystallinity of the substrate (poly- or single crystalline).

Fig. 13 Cyclic voltammograms(10 mV/s) in the electrolytes used in this study at 21°C and 100°C. (a) [Py_{1,4}]TFSA; (b) [Py_{1,4}]FAP; (c) 0.1M TaF₅ in [Py_{1,4}]TFSA; (d) 0.1M TaF₅ in [Py_{1,4}]FAP;. Working electrode was polycrystalline Au, while counter and reference electrodes were Pt wires. Here just the first cycles are presented.

EQCM measurements were performed parallel to the CVs experiments. By using the EQCM technique one can get *in-situ* information on the moment when an electrodeposition process occurs. This is possible as the frequency shift of an oscillating quartz crystal during electrodeposition can be transformed into deposited mass based on the Sauerbrey's equation (Eq. 2):

$$\frac{\Delta m}{A} = -\frac{\Delta f}{2f_0^2} \sqrt{\mu_q \rho_q} \quad \text{Eq. 2}$$

where Δm represents the deposited mass, A the active area, Δf the shift of the resonance frequency, f_0 the frequency of the unloaded quartz, μ_q the shear modulus of the quartz and ρ_q is the density of the quartz.

Thus, based on Faraday's law, which gives the deposited mass as a function of the passed charge, and Sauerbrey's equation (Eq. 2), one can calculate *in situ* the apparent molar mass of the deposited species [22, 23]. In this way, one can get information on the nature of the deposited layer before spectroscopic measurements (EDX, XRD or XPS) are performed *ex-situ*.

If Ta^0 had been deposited, the apparent molar mass calculated with the EQCM should have reached a value of ca. 36.2 g/mol for some potential regions in the CV experiments, value that corresponds to a 5 e⁻ step. When $[\text{Py}_{1,4}]\text{FAP}$ ionic liquid was used, in no experiment an apparent molar mass, indicating a total reduction of TaF_5 was obtained (Fig. 14a). One can see in Fig. 14a that at potentials which correspond to the highest peak of the CV experiments (Fig. 13d), the mass increases slightly. However, when one calculates the apparent molar mass from such graphs, values far below 36.2 g/mol are usually obtained, which indicates strongly that no elemental Ta can be obtained in this IL. These results are in perfect agreement with the STM results, described previously in Figs. 7, 8 and 9. , A maximum value of 8 g/mol was calculated from the CV experiments at 100°C in 0.1M TaF_5 in $[\text{Py}_{1,4}]\text{FAP}$ in the potential region (-1.2..-1.6V) whereas at 135°C or 170°C, values of 20 g/mol were obtained for the same potential region (not shown). At 21°C one could not calculate an accurate value for the apparent molar mass. The EQCM data obtained at room temperature in 0.1M TaF_5 in $[\text{Py}_{1,4}]\text{FAP}$ indicated that the dissipated energy is three time higher than the shift of the resonance frequency of the quartz crystal. Due to this fact, one cannot apply the

Sauerbrey's Eq. to transform the frequency shift into a deposited mass; therefore, no values of the apparent molar mass could be obtained in this case. One has to mention at this point that the shift of the resonance frequency in the experiments at temperatures above 100°C was higher than the dissipated energy and thus, Sauerbrey's Eq. could be successfully applied.

The apparent molar masses obtained during the CV experiments in 0.1M TaF₅ in [Py_{1,4}]TFSA at 10 mV/s and room temperature indicated values between 31 and 40 g/mol for a 5 electron step (not shown) in the potential region from -1.5V to -1.6V, and lower values than 30 g/mol for potentials between -1.7 and -3V. The lowest value of the apparent molar mass was obtained during the first cycle, and it increased with consecutive cycling. Until potentials of ca -1.5V vs. Pt quasi-reference electrode one could not detect any clear mass increase by the EQCM at 21°C in the CV experiments. At potentials down to -3V the mass deposited on the Au electrode increased slightly at room temperature. Here one has to mention that the STM proved the electrodeposition of Ta islands from -0.9V at room temperature (Figs. 2 and 3). The difference between the results obtained by the two *in situ* techniques can be due to the different times scales on which these experiments were performed, as well as on the sensitivity of the two methods. With EQCM one can detect average masses of ca 4 ng/ cm². However, one will not be able to detect with the EQCM the formation of few individual Ta islands that could occur at ca -0.9V onto the Au electrode. The STM is more accurate for such determinations, as it can image locally on scale of some hundreds of nanometers the occurrence and growth of Ta islands. With increasing temperature the potential at which the mass increases reduces (Fig. 14b). If the CV experiments were performed at 100°C, the following values for the apparent molar masses were obtained in the first cycle: 34.2 g/mol (E= -1.2..-1.3V), 25 g/mol (E=-1.35..-1.57V), 38 g/mol (E=-1.7..-2.1V) and 10 g/mol (E=-2.9..-3V). Starting from the second cycle values of 36 g/mol were obtained at 100°C in the potential range from -1.5V to -2V, fact that indicates that elemental Ta is then deposited. The reason why the expected ~36 g/mol are only obtained in the 2nd cycle is

unknown and might have to do with the complicated interfacial behavior. When the CVs experiments were performed at 170°C, one could identify that the apparent molar masses calculated from the EQCM results are close to those corresponding to elemental Ta starting from the first cycle, for potentials between -1.3 and -1.9V (not shown).

Fig. 14 The massograms as a function of charge density calculated from the cyclic voltammograms at 10 mV/s at 100°C in 0.1M TaF_5 in $[\text{Py}_{1,4}]\text{FAP}$ (a) and in 0.1M TaF_5 in $[\text{Py}_{1,4}]\text{TFSA}$ (b). Working electrode was polycrystalline Au, while counter and reference electrodes were Pt wires. Here just the values from the first cycles are presented.

Potentiostatic (-1.25V ; -1.4V ; -1.5V ; -1.7V ; -1.8V) and galvanostatic (0.1 mA/cm^2 , 1mA/cm^2) experiments to deposit Ta from 0.1M TaF_5 in $[\text{Py}_{1,4}]\text{FAP}$ done at temperatures between 21°C and 170°C indicated as well that no elemental Ta can be obtained in this ionic liquid. Furthermore no adherent layer could be obtained in this ionic liquid for deposition times of up to three hours.

Figure 15a presents the results obtained at 100°C for 1 h deposition at -1.8V in 0.1M TaF_5 in $[\text{Py}_{1,4}]\text{FAP}$. One can see that a deposit is obtained on the Au electrode during the first 2000s, but the deposition stops afterwards. Moreover, the calculated molar mass of the deposited species is in the beginning quite high (ca 100 g/mol), due probably also to viscoelastic

changes in the electrolyte which happens parallel to deposition. However, after some seconds it reaches again a lower value than that corresponding to Ta^0 .

Fig. 15 Mass vs. charge diagrams obtained at 100°C and -1.8V for 1 h deposition time in (a) 0.1M TaF_5 in $[\text{Py}_{1,4}]\text{FAP}$ and (b) in 0.1 TaF_5 in $[\text{Py}_{1,4}]\text{TFSA}$.

Potentiostatic depositions (-0.8V; -1.4V; -1.5V; -1.8V; -2.3V; -2.5V) were performed at RT, 100°C and 170°C in 0.1 M TaF_5 in $[\text{Py}_{1,4}]\text{TFSA}$. For all temperatures and potentials investigated in this study, the best EQCM results were obtained at 100°C and 170°C at -1.8V and -1.5V, respectively, for one hour (Fig. 15b). In this case the EQCM indicated that a relatively high mass was deposited onto the Au electrode, and an apparent molar mass close to the theoretical one. However, besides these two conditions, for the potentiostatic tests at different temperatures, the apparent molar mass indicated often values which differ from the theoretical one of elemental Ta. In many cases, especially in the measurements performed at room temperature, the damping of the quartz, which gives the dissipated energy, was similar to the frequency shift; therefore, one cannot transform directly the measured frequency shift to deposited mass via the Sauerbrey's equation. In this case, mostly viscoelastic changes in the electrolyte were detected by the EQCM.

3.5.2 Ex-situ characterizations of the deposits

SEM-EDX analyses were performed at selected deposited samples. Using direct plating, cracked layers are obtained (Fig. 16). However, there are regions on the surface of the electrode that are covered uniformly, but these are not found on the entire electrode surface. EDX analyses showed that not only pure Ta can be detected in the deposited layers. Besides Ta (ca. 72..80 at %), one detects also C (ca. 2 %) O (12..18 %) and F (ca. 6..8 %). The oxygen could be caused by the oxidation of the deposits when exposed to air, while the other elements (F and C) can come from IL remaining trapped in the layers. Therefore, despite rinsing the deposits with ethanol prior to SEM-EDX analyses, compounds of the IL are detected.

Fig. 16 SEM images of a layer deposited for 1h: (a) at 21°C and -1.4V ; (b) at -1.8 V and 100°C; (c) at 170°C and -2.3V ; in 0.1M TaF₅ in [Py_{1,4}]TFSA. Working electrode was polycrystalline Au, while counter and reference electrodes were Pt wires.

4. Conclusions

The electrochemical reduction of TaF_5 was studied in two ionic liquids, namely in $[\text{Py}_{1,4}]\text{TFSA}$ and in $[\text{Py}_{1,4}]\text{FAP}$. All three *in situ* techniques used in this study (STM, AFM and EQCM) showed that no elemental Ta can be obtained in $[\text{Py}_{1,4}]\text{FAP}$, even if the temperature of the electrolyte was increased to values higher than 100°C . The STM images and AFM force curves are quite similar both for pure $[\text{Py}_{1,4}]\text{FAP}$ and for $[\text{Py}_{1,4}]\text{FAP}$ containing 0.1 M TaF_5 . The Au(111) surface is reconstructed under electric potential in the ILs, and the well-known herringbone reconstruction that was observed before in previous studies was also obtained in this work in the presence and absence of TaF_5 .

In $[\text{Py}_{1,4}]\text{TFSA}$ one can obtain a deposit on the Au electrodes. By using direct plating, one gets usually a cracked layer, in which rests of ionic liquids are trapped. Therefore, despite the fact that EQCM indicates that elemental Ta is deposited at some potentials, the ex-situ EDX analyses proved that F, C and O are also detectable for each of the deposits. STM results show that if the electrode potential is reduced fast, TaF_5 will preferentially adsorb to the electrode surface and is subsequently reduced to metallic Ta. However, if the electrode potential is reduced extremely slowly, the large and bulky IL cations, which are already adsorbed at the ocp, will rather change their orientation blocking the surface and causing the Au(111) ($22 \times \sqrt{3}$) reconstruction.

The physico-chemical properties of the ionic liquids play an important role in the electrodeposition. Thus, even if the electrochemical window of the two ionic liquids used in this study is similar, in the $[\text{TFSA}]$ IL one can relatively easily reduce TaF_5 , while in $[\text{FAP}]$ IL this process is not straightforward. At the same time, when electrodepositing a metal from ILs, one should take into account the interaction of the IL with the substrate. Not much is known on the interaction of general ILs with metal substrates. Different ILs are differently adsorbed onto the same substrate. *In situ* techniques used in this study showed that the first cycle can be different from the consecutive one in the ionic liquids studied, and this effect is more pronounced at temperatures above 100°C . Subsequent scanning seems to “soften” the

interfacial layers. Starting with the second cycle one obtains more stable conditions, that facilitates the reduction of TaF₅.

References

- [1] F. Endres, N. Borisenko, S. Zein El Abedin, R. Hayes, R. Atkin, The interface ionic liquid(s)/electrode(s): *In situ* STM and AFM measurements, Faraday Discuss. 154 (2012) 221-233.
- [2] M. Z. Bazant, B. D. Storey, A. A. Kornyshev, Double Layer in Ionic Liquids: Overscreening versus Crowding, Phys. Rev. Lett. 106 (2011) 046102.
- [3] R. Atkin, N. Borisenko, M. Drüschler, S. Zein El Abedin, F. Endres, R. Hayes, B. Huber and B. Roling, An *in situ* STM/AFM and impedance spectroscopy study of the extremely pure 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate / Au(111) interface: potential dependent solvation layers and the herringbone reconstruction, Phys. Chem. Chem. Phys. 13 (2011) 6849–6857.
- [4] R. Hayes, D. Wakeham, R. Atkin, Interfaces of Ionic Liquids (2) In Ionic Liquids UnCOILed, John Wiley & Sons Inc.: New York 2012, 51–85.
- [5] R. Atkin, G. G. Warr, Structure in Confined Room-Temperature Ionic Liquids, J. Phys. Chem. C 111 (2007) 5162–5168.
- [6] R. Hayes, S. Zein El Abedin, R. Atkin, Pronounced Structure in Confined Aprotic Room-Temperature Ionic Liquids, J. Phys. Chem. B 113 (2009) 7049–7052.
- [7] R. Hayes, G. G. Warr, R. Atkin, At the interface: solvation and designing ionic liquids, Phys. Chem. Chem. Phys. 12 (2010) 1709– 1723.
- [8] R. Atkin, S. Zein El Abedin, R. Hayes, L. H. S. Gasparotto, N. Borisenko, F. Endres, AFM and STM Studies on the Surface Interaction of [BMP]TFSA and [EMIm]TFSA Ionic Liquids with Au(111), J. Phys. Chem. C 113 (2009) 13266–13272.

- [9] X. Zhang, Y.-X. Zhong, J.-W. Yan, Y.-Z. Su, M. Zhang, B.-W. Mao, Probing double layer structures of Au (111)–BMIPF₆ ionic liquid interfaces from potential-dependent AFM force curves, *Chem. Commun.* 48 (2012) 582–584.
- [10] R. Hayes, N. Borisenko, M. K. Tam, P. C. Howlett, F. Endres, R. Atkin, Double Layer Structure of Ionic Liquids at the Au(111) Electrode Interface: An Atomic Force Microscopy Investigation, *J. Phys. Chem. C* 115 (2011) 6855–6863.
- [11] A. Labuda, P. Grütter, Atomic Force Microscopy in Viscous Ionic Liquids, *Langmuir* 28 (2012) 5319–5322.
- [12] J. M. Black, D. Walters, A. Labuda, G. Feng, P. C. Hillesheim, S. Dai, P. T. Cummings, S. V. Kalinin, R. Proksch, N. Balke, Bias-Dependent Molecular-Level Structure of Electrical Double Layer in Ionic Liquid on Graphite, *Nano Lett.* 13 (2013) 5954–5960.
- [13] F. Endres, S. Zein El Abedin, N. Borissenko, Probing Lithium and Alumina Impurities in Air- and Water Stable Ionic Liquids by Cyclic Voltammetry and *In Situ* Scanning Tunneling Microscopy, *Z. Phys. Chem.* 220 (10) (2006), 1377-1394.
- [14] R. Hayes, N. Borisenko, B. Corr, G. B. Webber, F. Endres, R. Atkin, Effect of dissolved LiCl on the ionic liquid–Au(111) electrical double layer structure, *Chem. Commun.* 48 (2012) 10246–10248.
- [15] A. Radisic, G. Oskam, P. C. Searson, Influence of Oxide Thickness on Nucleation and Growth of Copper on Tantalum, *J. Electrochem. Soc.* 151 (6) (2004) C369-C374.
- [16] S. Ligot, T. Godfroid, D. Music, E. Bousser, J. M. Schneider, R. Snyders, Tantalum-doped hydroxyapatite thin films: Synthesis and characterization, *Acta Materialia* 60 (2012) 3435-3443.
- [17] C. Arnould, J. Delhalle, Z. Mekhalif, Multifunctional hybrid coating on titanium towards hydroxyapatite growth: Electrodeposition of tantalum and its molecular

- functionalization with organophosphonic acids films, *Electrochim. Acta* 53 (18) (2008) 5632–5638.
- [18] M. Matsuo, M. Matsunaga, Effects of Preparation Procedures and Structure of IrO₂-Ta₂O₅ Coated Insoluble Anode on Durability, *ECS Trans.* 11 (20) (2008) 67-70.
- [19] L. Schneider, J. Wurm, Reduzierung des Abbaus von Badadditiven an unlöslichen Anoden, *Galvanotechnik* 10 (2013) 1975-1981.
- [20] S. Zein El Abedin, H. K. Farag, E. M. Moustafa, U. Welz-Biermann, F. Endres, Electroreduction of tantalum fluoride in a room temperature ionic liquid at variable temperatures, *Phys. Chem. Chem. Phys.* 7 (2005) 2333-2339.
- [21] S. Zein El Abedin, U. Welz-Biermann, F. Endres, A study on the electrodeposition of tantalum on NiTi alloy in an ionic liquid and corrosion behaviour of the coated alloy, *Electrochem. Commun.* 7 (9) (2005) 941-946.
- [22] N. Borisenko, A. Ispas, E. Zschippang, Q. Liu, S. Zein El Abedin, A. Bund, F. Endres, *In situ* STM and EQCM studies of tantalum electrodeposition from TaF₅ in the air- and water-stable ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide, *Electrochimica Acta* 54 (2009) 1519–1528.
- [23] A. Ispas, B. Adolphi, A. Bund, F. Endres, On the electrodeposition of tantalum from three different ionic liquids with the bis(trifluoromethyl sulfonyl) amide anion, *Phys. Chem. Chem. Phys.* 12 (2010) 1793-1803.
- [24] A. Ispas, A. Bund, Pulse plating of tantalum from 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)amide ionic liquids, *Trans. Inst. Metal. Finish.* 90 (6) (2012) 298-304.
- [25] S. Krischok, A. Ispas, A. Zühlsdorff, A. Ulbrich, A. Bund, F. Endres, Ta and Nb Electrodeposition from Ionic Liquids, *ECS Trans.* 50 (11) (2013) 229-237.
- [26] F. Endres, A.P. Abbott, D. R. MacFarlane (Eds), *Electrodeposition from ionic liquids* Wiley-VCH, Weinheim, Germany (2008).

- [27] N. V. Ignat'ev, U. Welz-Biermann, A. Kucheryna, G. Bissky, H. Willner, New ionic liquids with tris(perfluoroalkyl)trifluorophosphate (FAP) anions, *J. Fluorine Chem.* 126 (2005) 1150-1159.
- [28] A. Guleria, A. K. Singh, S. Adhikari, S. K. Sakar, Radiation induced physicochemical changes in FAP (fluoro alkyl phosphate) based imidazolium ionic liquids and their mechanistic pathways: influence of hydroxyl group functionalization of the cation, *Dalton. Trans.* 43 (2014) 609-625.
- [29] N. V. Ignat'ev, H. Willner, P. Sartori, Electrochemical fluorination (Simons process) – A powerful tool for the preparation of new conducting salts, ionic liquids and strong Brønsted acids, *J. Fluorine Chem.* 130 (2009) 1183-1191.
- [30] F. Zhou, Y. Liang, W. Liu, Ionic liquid lubricants: designed chemistry for engineering applications *Chem. Soc. Rev.* 38 (2009) 2590-2599.
- [31] A. Garcia, R. González, A. Hernández Battez, J. L. Viesca, R. Monge, A. Fernández-González, Ionic liquids as a neat lubricant applied to steel–steel contacts, *Tribol. Int.* 72 (2014) 42-50.
- [32] J. Sweeney, F. Hausen, R. Hayes, G. B. Webber, F. Endres, M. W. Rutland, R. Bennewitz, R. Atkin, Control of Nanoscale Friction on Gold in an Ionic Liquid by a Potential-Dependent Ionic Lubricant Layer, *Phys. Rev. Lett.* 109 (2012) 155502-155507.
- [33] R. M. Espinosa-Marzal, A. Arcifa, A. Rossi, N.D. Spencer, Ionic Liquids Confined in Hydrophilic Nanocontacts: Structure and Lubricity in the Presence of Water, *J. Phys. Chem. C* 118 (2014) 6491-6503.
- [34] D. S. Silvester, Recent advances in the use of ionic liquids for electrochemical sensing *Analyst* 136 (2011) 4871-4882.
- [35] E. F. Órfão, V. Donhal, A. Blahut, Infinite dilution activity coefficients of volatile organic compounds in two ionic liquids composed of the

- tris(pentafluoroethyl)trifluorophosphate ([FAP]) anion and a functionalized cation, J. Chem. Thermodynamics 65 (2013) 53-64.
- [36] C. Yao, W. R. Pitner, J. L. Anderson, Ionic Liquids Containing the Tris(pentafluoroethyl)trifluorophosphate Anion: a New Class of Highly Selective and Ultra Hydrophobic Solvents for the Extraction of Polycyclic Aromatic Hydrocarbons Using Single Drop Microextraction, Anal. Chem. 81 (2009) 5054-5063.
- [37] X.-J. Huang, L. Aldous, A.M. O'Mahony, F. J. del Campo, R. Compton, Toward Membrane-Free Amperometric Gas Sensors: A Microelectrode Array Approach, Anal. Chem. 82 (2010) 5238-5245.
- [38] M.V. Boldrin Zanoni, E.I. Rogers, C. Hardacre, R. G. Compton, The electrochemical reduction of the purines guanine and adenine at platinum electrodes in several room temperature ionic liquids, Anal. Chim. Acta 659 (2010) 115-121.
- [39] M. Al Zoubi, F. Endres, Electrochemical synthesis of poly(p-phenylene) and poly(p-phenylene)/TiO₂ nanowires in an ionic liquid, Electrochim. Acta 56 (2011) 5872-5876.
- [40] M. Al Zoubi, R. Al-Salman, Y. Li, F. Endres, Highly Ordered 3D-Macroporous Poly(Para-Phenylene) Films Made by Electropolymerization of Benzene in an Ionic Liquid, Z. Phys. Chem. 225 (2011) 393-403.
- [41] T. Carstens, A. Prowald, S. Zein El Abedin, F. Endres, Electrochemical synthesis of PEDOT and PPP macroporous films and nanowire architectures from ionic liquids, J. Solid State Electrochem. 16 (2012) 3479-3485.
- [42] R. Al-Salman, M. Al Zoubi, F. Endres, Evidence for an influence of anodic decomposition products of ionic liquids on the electrodeposition of Si_xGe_{1-x} semiconductor, J. Molec. Liq. 160 (2011) 114-118.
- [43] S. Ahmad, T. Carstens, R. Berger, H.-J. Butt, F. Endres, Surface polymerization of (3,4-ethylenedioxythiophene) probed by *in situ* scanning tunneling microscopy on Au(111) in ionic liquids, Nanoscale 3 (2011) 251-257.

- [44] N. Borisenko, S. Zein El Abedin, F. Endres, *In Situ* STM Investigation of Gold Reconstruction and of Silicon Electrodeposition on Au(111) in the Room Temperature Ionic Liquid 1-Butyl-1-methylpyrrolidinium Bis(trifluoromethylsulfonyl)imide, *J. Phys. Chem. B* 110 (12) (2006) 6250-6256.
- [45] B. Uhl, F. Buchner, D. Alwast, N. Wagner, R.J. Behm, Adsorption of the ionic liquid [BMP][TFSA] on Au(111) and Ag(111) – Substrate effects on the structure formation investigated by STM, *Beilstein J. Nanotechnol.* 4 (2013) 903-918.
- [46] M. Drüscher, N. Borisenko, J. Wallauer, C. Winter, B. Huber, F. Endres, B. Roling, New insights into the interface between a single-crystalline metal electrode and an extremely pure ionic liquid: slow interfacial processes and the influence of temperature on interfacial dynamics, *Phys. Chem. Chem. Phys.* 14 (2012) 5090-5099.
- [47] N. Borisenko, R. Atkin, A. Lahiri, S. Z. El Abedin, F. Endres, Effect of dissolved LiCl on the ionic liquid–Au(111) interface: an *in situ* STM study, *J. Phys.: Condens. Matter* 26 (2014) 284111.
- [48] H. Li, M.W. Rutland, R. Atkin, Ionic liquid lubrication: influence of ion structure, surface potential and sliding velocity, *Phys. Chem. Chem. Phys.* 15 (2013) 14616-14623.
- [49] B. McLean, H. Li, R. Stefanovic, R. J. Wood, G. B. Webber, K. Ueno, M. Watanabe, G. G. Warr, A. Page, R. Atkin, Nanostructure of [Li(G4)] TFSI and [Li(G4)] NO₃ solvate ionic liquids at HOPG and Au(111) electrode interfaces as a function of potential, *Phys. Chem. Chem. Phys.* 17 (2015) 325-333.
- [50] H. Li, F. Endres, R. Atkin, Effect of alkyl chain length and anion species on the interfacial nanostructure of ionic liquids at the Au(111)–ionic liquid interface as a function of potential, *Phys. Chem. Chem. Phys.* 15 (2013) 14624-14633

- [51] H. Li, R. J. Wood, F. Endres, R. Atkin, Influence of alkyl chain length and anion species on ionic liquid structure at the graphite interface as a function of applied potential, *J. Phys.: Condens. Matter* 26 (2014) 284115.
- [52] T. Carstens, R. Gustus, O. Höfft, N. Borisenko, F. Endres, H. Li, R. J. Wood, A. J. Page, R. Atkin, Combined STM, AFM, and DFT Study of the Highly Ordered Pyrolytic Graphite/1-Octyl-3-methyl-imidazolium Bis(trifluoromethylsulfonyl)imide Interface, *J. Phys. Chem. C* 118 (2014) 10833-10843.
- [53] T. Carstens, R. Hayes, S. Zein El Abedin, B. Corr, G. B. Webber, N. Borisenko, R. Atkin, F. Endres, *In situ* STM, AFM and DTS study of the interface 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate/Au(111), *Electrochim. Acta* 82 (2012) 48-59.
- [54] K.K. Kanazawa, J.G. Gordon, Frequency of a quartz microbalance in contact with liquid, *Anal. Chem.* 57 (1985) 1770-1771.