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Structure and Dynamics of the Interfacial Layer between Ionic Liquids and Electrode Materials

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Abstract

In this paper we present a combined *in situ* STM, AFM and EIS study on the structure and dynamics of the interfacial layers between Au(111) and two extremely pure ionic liquids, namely [Py_{1,4}]FAP and [EMIM]FAP. The combination of these methods provides valuable information for both neutral and electrified interfaces. *In situ* STM and AFM results reveal that multilayered morphology is present at the IL/Au(111) interface, with stronger near surface layering detected at higher electrode potentials. The *in situ* STM measurements show that the structure of the interfacial layers is dependent on the applied electrode potential, the number of subsequent STM scans and the scan rate. Furthermore, in the case of [Py_{1,4}]FAP, the Au(111) surface undergoes herringbone reconstruction, Au(111)(22 × √3), in the cathodic potential regime, and the ultra-slow formation of vacancies in the herringbone structure is probed with *in situ* STM. EIS measurements reveal the presence of two distinct capacitive processes at the interface taking place on different time scales. The time scale of the fast process is typically in the millisecond range and is governed by the bulk ion transport in the IL, which exhibits a Vogel-Fulcher-Tammann-type temperature dependence. The slow process takes place on a time scale of seconds and is Arrhenius activated. The contribution of this process to the overall interfacial capacitance is

particularly large in the potential regime where the herringbone structure is probed. Furthermore, we analyze the temperature dependence of the interfacial capacitance.

Introduction

Modern ionic liquids (ILs) possess fascinating properties, including large electrochemical and wide thermal windows, good ionic conductivities, negligible vapor pressures and the ability to solubilize many chemical species, which are difficult or impossible to dissolve in conventional solvents. Another remarkable advantage of ILs is that all these properties are tunable by varying cation/anion's chemical structure. For these reasons, ILs are becoming especially attractive as solvents for electrochemistry (e. g. electrodeposition¹, capacitors², dye sensitized solar cells³, corrosion inhibition⁴, lithium batteries⁵, etc.). However, wider integration of ILs in electrochemistry is hindered by limited understanding of IL's complex physical and surface chemistry; replacing a traditional electrolyte with an IL often results in lower process efficiencies or departures from expected behavior.⁶ Thus, an improved understanding of the structure and dynamics of the IL-electrode interface structure is required as this dictates electrochemical performance for all of these applications.⁷

During the last 5 years it has been found that ILs have interesting surface chemistry, quite distinct from molecular liquids.⁸ The key differences in are related to the level of solvent structure. Molecular solvents form solvation layers at simple solid-liquid interfaces,⁹⁻¹¹ characterized by an oscillatory density profile that extends a few molecular diameters from the interface.⁸ Solvation layers form because of geometric packing constrain the arrangement of solvent molecules near a smooth solid surface. The molecules in these layers have no preferred orientation, except the surface layer in some cases, and the bulk liquid is unstructured. Oscillatory density profiles has been detected in ILs,^{8,12-17} IL interfacial structure is stronger than that of molecular liquids because the ions often self-assemble into

well-defined nanostructures in the bulk, and this structure becomes *stronger* near a solid surface. Bulk ionic liquids often have a sponge-like nanostructure due to segregation of charged and uncharged groups into separate domains. The presence of a solid surface usually leads to enrichment of either the cation or anion in the surface layer and flattens the bulk nanostructure. At the ethylammonium nitrate (EAN) – mica interface, this leads to structural transition from sponge-like¹⁸⁻²¹ far from an interface to a more layered arrangement^{8,12} close to the interface, and finally a worm-like morphology in the surface bound layer.²² The degree of interfacial nanostructure can be tuned by changing the ion structure, which has implications for the controlling the structure-property relationships at IL-electrode interface.

The IL-electrode interface is more complex than in aqueous systems. The interface of a dilute electrolyte solution with a metal electrode is well-described theoretically by considering electrostatic interactions of ions with the electrode and specific interactions (e.g. van-der-Waals interactions). The electrostatic interactions give rise to the formation of a rigid outer Helmholtz layer and a diffuse layer, whereas the specific interactions result in the formation of an inner Helmholtz layer of adsorbed ions and molecules.

In the case of an IL, both solvent-solvent and ion-surface interactions are considerably different. An IL consists only of cations and anions with no other solvent. This leads to highly effective charge screening in ILs; calculated Debye lengths of order of the size of individual ions. IL ions are large and asymmetric, with the charge delocalized over one or more functional groups, which means that the system cannot be modeled as a continuum of spherical point charges because the electrostatic charge is not localized on one atom. This weakens electrostatic interactions – hence the low melting points for a pure salt – allowing effects of between ions, such as H-bonding²³ or solvophobic interactions, to assert themselves. Ion-surface interactions are strong in ILs, driven by electrostatic attractions (via charged groups) or van der Waals forces (via uncharged groups) between ions and the surface respectively²⁴⁻²⁸.

The IL-electrode interface is not a simple double layer like that formed by aqueous electrolyte solutions. This means classical models for electrical double layer (EDL) structure (Gouy-Chapman model and Stern model) are not appropriate for IL-electrode interface, as these do not describe IL ion arrangements close to the electrode surface. In the case of ILs, the concentration of ions is high and relatively uniform. Therefore, the ion–surface interactions are not strong enough to induce distinct regions of ion excess and ion depletion close to the interface analogous to Stern and diffuse layers in classical theories for aqueous electrolytes. Recent experimental measurements reveal that ILs display ion layering (multilayers) at electrode interfaces, similar to that described previously for other surfaces.^{6-8,13-17,29-36} Atomic force microscopy (AFM) measurements have shown that this layering is strongly influenced by the ion type,⁶⁻⁸ and is strongly influenced by changes in surface potential;^{33-35,37} the number of interfacial layers and their composition varies from anions-rich (at positive potentials) to cation-rich (at negative potentials). Finally, small amounts of IL impurities strongly influence on the IL-electrode structure.^{7,34}

A complete theoretical description of the IL-electrode interface does not yet exist. The mean field models by Kornyshev³⁸, Oldham³⁹ and Henderson et al.²⁸ give general predictions for potential-dependent differential capacitance curves (“bell” and “camel-shaped” curves). Kornyshev’s models stress two additional factors for ion organization: overscreening and lattice saturation effects^{38,40}. Overscreening predicts an alternating anion-cation layered framework, however the electrode polarization is overcompensated in the ion layers; strong, short-range ion–surface interactions induce a slight excess of ions of opposite charge to arrange immediately adjacent the electrode such that there is more charge in the layer flanking the surface than on the electrode itself. This leads to an excess of counter-charge (compared to the electrode surface) in the second ion layer and so on away from the interface. This overcompensation of charge is reduced towards the bulk liquid and is similar to findings for molten salt interfaces.⁴¹ Lattice saturation^{38,40} occurs at high surface potentials and is a

consequence of the finite size of the IL ions; as IL ions are not point charges, at high polarizations they are unable to pack densely enough at the surface to quench the electrode's charge. This leads to multiple layers with the same ion type close to the surface and hence an effective increase in the IL double layer thickness.

Molecular dynamics and Monte Carlo computer simulations also reveal the existence of oscillating ion density profiles at the electrode surface^{24,25,42-53} and the formation of ion ad-layers^{42,44,49} and thus confirm the experimental findings. A theoretical model suggested in²⁴ shows that the charged heads and neutral counterparts of the ions interact with the electrode surface resulting in potential-dependent capacitance curves with various shapes. At the open circuit potential, both the charged groups and neutral groups of the ions interact with the electrode surface. With the increasing cathodic or anodic electrode potentials a reorientation takes place: the neutral groups can be replaced by charged groups via translations and rotations of ions until the saturation is reached at high electrode potentials, increasing the double layer capacitance. A recent theoretical study shows that multilayer arrangement of ILs can be described.⁴⁰

We have developed a model for the IL-electrode interface structure¹² that divides this interface into three key regions: the innermost layer, the transition zone and the bulk liquid. The innermost layer is composed of the IL-ions in direct contact with the electrode surface. This layer is one ion diameter thick and enriched in the ion that mirrors the surface charge of the underlying substrate (i.e. anions over positive surfaces and cations over negative surfaces).⁵⁴ For uncharged substrates, ion adsorption still occurs, but proceeds through solvophobic interactions between non-polar alkyl groups (usually on the cation) and the surface. Ions in the innermost layer are the most spatially organized and have preferred orientation⁵⁵ due to electrostatic or solvophobic interactions with the electrode surface. The transition zone is the region over which the more pronounced interfacial (innermost) layer structure decays to the bulk morphology. Layering in the transition zone occurs over 2-7 ion pairs, until it

decays into the bulk liquid structure. The transition zone structure principally arises from the templating effect of ion ordering in interfacial layer, but is also influenced by molecular flexibility^{8,14,35}, ion charge localization/delocalization^{8,14,35}, surface roughness^{8,14}, temperature^{8,36}, electrode charge^{33,35} and dissolved solute^{7,34}. The bulk zone refers to the bulk of the liquid and encompasses the remaining volume of liquid beyond the influence of the electrode surface. AFM is insensitive to bulk structure but probes IL structure in the innermost layer and transition zone. The push-through forces for these layers increase closer to the surface suggesting that ordering is more pronounced close to the interface. X-ray reflectivity studies^{30,31} and sum frequency generation (SFG) measurements⁵⁵⁻⁵⁷ have confirmed these results.

Over the last 15 years, *in situ* STM has been extensively used for investigations of well-defined single crystalline metal electrode surfaces in ILs, and has elucidated potential dependent long-range restructuring of electrode surfaces as well as the formation of anion/cation adsorption layers^{6,7,33,58-60}. The Endres group has pioneered the use of *in situ* STM of the IL–electrode interface to probe surface reconstructions. In 2006 it was reported that the adsorption of IL cations causes Au(111) surface restructuring⁶¹. More recently, it has been shown that at cathodic potentials, the kinetically hindered formation of the herringbone reconstruction, Au(111)($22 \times \sqrt{3}$), has been imaged for a single-crystalline Au(111) surface in contact with neat 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF₄]⁵⁸, 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF₆]⁶⁰, 1-butyl-1-methylpyrrolidinium bis[(trifluoromethyl)sulfonyl]amide [Py_{1,4}][TFSA]⁶ and 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate [Py_{1,4}][FAP]³³. Recent results from Mao et al.⁶² suggest that such structures can be due to cation adsorption in the case of imidazolium cations, as the worm-like structure depends on the length of the alkyl chain in the imidazolium ion. Furthermore, Mao et al.⁵⁹ have found a cation adsorption layer showing a well-ordered zig-zag-like super structure when they investigated the interface between [BMIM][BF₄] and Au(100) at negative

electrode potentials. The formation of $[\text{PF}_6]^-$ anion adsorption layers showing a potential-dependent 2D phase transition from a moiré-like structure to a $(\sqrt{3} \times \sqrt{3})$ phase has been observed for $[\text{BMIM}][\text{PF}_6]$ at Au(111) by Pan and Freyland⁶⁰. Kolb et al.⁶³ have performed similar *in situ* STM investigations of gold single crystal electrodes and ILs with imidazolium ions and either $[\text{PF}_6]^-$ or $[\text{BF}_4]^-$ anions. It is important to mention that the interface IL-electrode is influenced by even low (ppm regime) amounts of impurities⁶¹. Therefore, only ILs of the highest available quality should be employed for the measurements to reduce the risk of misinterpretations. It is problematic to use liquids with $[\text{PF}_6]^-$ or $[\text{BF}_4]^-$ anions, since these are subject to hydrolysis and practically not stable during the experiment⁶⁴.

In recent years, several groups have used AC voltammetry and electrochemical impedance spectroscopy (EIS) to measure the differential capacitance of various IL-electrode interfaces⁶⁵⁻⁷⁸. However, it is not easy to extract general trends from the data, as the results are in part contradictory. The appearance of capacitance curves for similar IL-electrode combinations range from pseudo-parabolic, to “bell-” and “camel-” shaped, each of which suggest different IL-electrode interfacial structure. Possible reasons for this were discussed by Lockett et al.⁶⁸ who considered the IL purification procedure, the reference electrode stability, the surface of electrode materials and the methods for extracting capacitance data from EIS results. Broadband EIS employed by Paykossy, Kolb and coworkers and by Roling and coworkers clearly reveal the existence of distinct processes at the IL/electrode interface taking place on different time scales^{63,71,72,79}. At least two capacitive processes, one on millisecond time scales and one on second time scales, can be distinguished. Furthermore, ultraslow processes can be detected, which seem to be Faradaic or pseudo-capacitive in nature. While ms time scales are expected for double layer charging at IL/electrode interfaces in typical electrode setups with mm distances between working and counter electrode, the nature of the slower processes has not yet been clarified unambiguously. However, it is clear that the existence of slower processes can lead to hysteresis effects in the capacitance of the fast ms process^{71,80}.

Consequently, a careful analysis of broadband electrochemical impedance spectra is important for obtaining reliable values for the time scales of the different processes and for their contributions to the interfacial capacitance. In this context, single-frequency measurements^{74-76,81} and fits of impedance spectra with a single constant-phase element^{76,78} are problematic. The application of different methods of analysis is certainly one reason that published experimental results are in part contradictory. Therefore, a general discussion about the best suited methods for analyzing impedance spectra of IL/electrode interfaces with respect to capacitive processes is urgently needed.

Quite recently, ultrathin films of two imidazolium-based ILs, 1,3-dimethylimidazolium bis(trifluoromethyl)amide and 1-methyl-3-octylimidazolium bis(trifluoromethyl)amide were prepared on Au(111)⁸² and Ni(111)⁸³ single-crystal surfaces by physical vapor deposition in ultrahigh vacuum. The adsorption behavior, orientation, and growth were studied via angle-resolved X-ray photoelectron spectroscopy (ARXPS). It was found that for both ILs, the first layer is formed from anions and cations directly in contact with the Au surface in a checkerboard arrangement. For higher coverages, both ILs grow layer-by-layer up to thicknesses of at least 9 nm⁸². On clean Ni(111), the initial growth occurs in a layer-by-layer mode⁸³. At submonolayer coverages, a preferential arrangement of the IL ions in a bilayer structure, with the imidazolium cations in contact with the Ni surface atoms and the anions on top of the cation, is obtained. For higher coverages, a transition to a checkerboard-type arrangement occurs.

In this paper, we review recent studies on the structure and dynamics of the interface **between two ultrapure ILs (c.f Figure 1)** and a well-defined Au(111) surface. In these studies, broadband EIS is combined with *in situ* STM and AFM measurements. The results are critically discussed and compared to the results of other groups in this field.

Experimental

[Py_{1,4}]FAP and [EMIM]FAP were purchased from MERCK in highest available quality. The liquids were custom-made, and the purity protocol delivered by Merck showed that all detectable impurities were below 10 ppm. HF and oxide levels were below the detection limit of 10 ppm. It is important to mention that impurities in ILs, which are observed too often in commercial ILs (even in apparently ultrapure quality), can strongly alter the surface processes leading to misinterpretations⁶¹. If the liquid is synthesized for example via a metathesis reaction from a metal salt and an organic halide, organic impurities (decomposition products of anions and / or cations, side products) and Li⁺, Na⁺, K⁺ and halides can be found in the 1000 ppm range even in apparently ultrapure ILs. Furthermore, purification procedures may introduce SiO₂ or Al₂O₃ particles, which can accumulate at the interface and influence bulk or interfacial properties. Prior to use, all ILs were analyzed using CV, XPS and *in situ* STM to ensure the purity. Additionally, the IL was dried under vacuum (10⁻³ mbar) at 100 °C to H₂O contents well below 1 ppm and stored in a closed bottle in a desiccator (at Newcastle), in an Ar-filled glove box with H₂O and O₂ contents of below 2 ppm (OMNI-LAB from Vacuum-Atmospheres) (in Clausthal) and in a N₂-filled glove box with H₂O and O₂ contents of below 1 ppm (LABstar from MBRAUN GmbH) (in Marburg). *In situ* STM, AFM and EIS measurements were carried out using samples of the same IL, which were sent in sealed ampoules to the partners. The substrates for AFM and STM experiments and the working electrode (WE) were Au(111) (a 300 nm thick film on mica) purchased from Agilent. Directly before use, the substrates were carefully heated in a H₂-flame to minimize possible surface contaminations. CV measurements were carried out in the glove box using a Parstat 2263 potentiostat / galvanostat (Princeton Applied Research) controlled by a PowerCV software. The electrochemical cell connected to the in-situ STM setup (Clausthal) 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 WE of 0.3 cm². Pt wires (Alfa Aesar, 99.99 %) of 0.5 mm diameter were applied as quasi-reference (RE) and counter (CE) electrodes, respectively. From our experience, Pt has a sufficiently stable electrode potential under *in situ* STM conditions.

Directly before use, the Pt wires were cleaned for 15 min in an ultrasonic bath in acetone followed by heating in a H₂-flame to red glow for a few minutes to minimize surface contaminations.

STM experiments were performed at 23 °C using in-house-built STM heads and scanners under inert gas conditions (H₂O and O₂ < 2 ppm) with a Molecular Imaging PicoScan 2500 STM controller in feedback mode. Assembling of the STM head and filling of the electrochemical cell were performed in an Ar-filled glove box solely reserved for assembling of STM heads. The STM head was placed inside an Ar-filled vacuum-tight stainless steel vessel, to ensure inert gas atmosphere during the STM experiments, transferred to the air-conditioned laboratory (T = 23 ± 1 °C) and placed onto 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 an electropaint (BASF ZQ 84-3225 0201). During the STM experiments the potential of the WE was controlled by the PicoStat from Molecular Imaging / Agilent.

For EIS measurements, a temperature-controlled microcell HC (rhd instruments) was used which was placed inside the glovebox. The measurements were carried out at temperatures ranging from 0 °C to 90 °C. Heating and cooling was done by means of a Peltier element controlled by a Eurotherm 2416 thermostat with an accuracy of 0.01 °C. A three-electrode configuration was used for all measurements with a polycrystalline Pt disc (Goldschmiede Meusser, Marburg, Germany) acting as the counter electrode (CE), a mica-supported Au film with a thickness of 200 nm (Agilent Technologies or phasis) acting as the working electrode (WE) and a Ag/Ag[TFSA]/[EMIm][TFSA]-based micro reference electrode (RE). The micro reference electrode consists of a Ag wire (99.999 % from Alfa Aesar) in contact with a 100 mmol/L solution of Ag[TFSA] in [EMIm][TFSA]⁸⁴. To keep the ionic liquid in the measurement cell, a polyether ether ketone mould was clamped over a Viton O-ring onto the Au on mica substrate, resulting in a WE surface area of 0.38 cm². Directly before use, the Au film on mica substrates was carefully annealed for 30 s at 700 °C while being held under an Ar atmosphere or

vacuum in a quartz tube. This ensures a better quality of the Au(111) surface, which had been epitaxially grown on mica during the production procedure⁸⁵⁻⁸⁷, and leads to much broader Au(111) terraces⁸⁶. Furthermore, any possible surface contamination was minimised by the annealing process. The potential of the RE was tested and adjusted before and after each measurement against the ferrocene/ferricinium redox-couple, Fc^0/Fc^+ , using a separate measurement setup and was found to be relatively stable over several weeks⁸⁴.

The microcell HC was connected to a Novocontrol modular measurement system consisting of an Alpha-AK high-resolution impedance analyser and a POT/GAL 15V/10A electrochemical interface. Before carrying out an EIS measurement, a cyclic voltammogram with a scan rate of 100 mV/s was recorded in order to determine the electrochemical window. The EIS experiments were carried out at different WE dc potentials which were superimposed by a small ac voltage signal of $U_{\text{ac,rms}} = 10 \text{ mV}$. The frequency range typically extended from 10 mHz to 0.1 MHz. In the case of a single-frequency measurement, a frequency was chosen at which the phase angle was as close as possible to -90° . Usually after changing the temperature, the system was given an equilibration time of 10 min before starting a new EIS measurement. The recorded EIS data were fitted by means of the WinFit software (Novocontrol Technologies).

AFM force measurements were acquired continuously using a Digital Instruments NanoScope IIIa Multimode AFM in contact mode in an incubator at 21°C . The scan rate and scan size were kept between 0.1 and 0.5 Hz and 10 and 50 nm, respectively. One standard sharpened tip Si_3N_4 cantilever (Digital Instruments, CA) was used for all measurements. The spring constant was measured to be $0.07 \text{ N/m} \pm 0.005$ (thermal noise method)⁸⁸. The tip was carefully rinsed in Milli-Q H_2O and irradiated with ultraviolet light for 40 min prior to use. The IL was held in an AFM fluid cell, sealed using a silicone O-ring. Both of these were cleaned by sonication for 30 min, rinsed copiously in distilled ethanol and Milli-Q H_2O , and then dried using filtered N_2 . A modified AFM cell setup was used to

acquire force curves as a function of potential. The changes made were inspired by a design proposed by Wanless *et al.*⁸⁹. A thin cylindrical strip of Cu metal and 0.25 mm Pt wire were used as the CE and RE, respectively. The CE and RE were cleaned firstly in diluted HCl acid solution and then washed with distilled ethanol and Milli-Q H₂O and dried using filtered N₂. The CE was mounted with the O-ring in the groove of the fluid cell. This was to ensure that the effective area of the CE is relatively large and axially symmetric with respect to the WE and to establish an equipotential WE surface. The RE was located directly above the centre of the WE surface by securing the Pt wire through the outlet valve of the fluid cell. This configuration enabled the RE to be positioned as close as possible to the WE (minimizing ohmic losses) and thus enable the potential difference between the two electrodes to be readily controlled. The electrodes were connected to an EG & G Princeton Applied Research Model 362 Scanning Potentiostat. The features of the AFM force curves at a given surface potential did not alter over a 48 h period. Typical start distances for force scans were 30-50 nm from the Au(111) surface. The maximum applied force in contact was between 30 and 500 nN. However, no evidence for structure was detected at forces greater than 30 nN in any system. Repeat experiments revealed that the number and period of the steps was constant. Every surface potential was studied over three or more separate experiments.

Results and Discussion

a) Cyclic voltammetry

Typical cyclic voltammograms of the custom-made [EMIM]FAP and [Py_{1,4}]FAP ILs on Au(111) at 25 °C are presented in **Fig. 2**. Scans were initially swept cathodically from the ocp (-0.2 V) with a scan rate of 10 mV s⁻¹. This is the potential regime in which the EIS, STM and AFM measurements were performed. Both ILs exhibit wide electrochemical windows (5.1 V and 5.9 V for [EMIM]FAP^{33,90} and [Py_{1,4}]FAP³³, respectively) limited by the irreversible reduction of the organic

cation and gold oxidation. At the cathodic limit two processes (C_1 and C_2 , **Fig. 2**, 1st scan) can be obtained in [EMIM]FAP, while in the case of [Py_{1,4}]FAP at least four cathodic processes (C_1 - C_4 , **Fig. 2b**) can be identified. Furthermore, in [EMIM]FAP the second scan shows considerably different behavior with a huge anodic process A_2 is obtained while the cathodic process C_2 seems to disappear (**Fig. 2a**, 2nd scan). This behavior is consistent over repeat scans (**Fig. 2a**, 3rd scan). As in these ILs all impurities (including halides and water) were guaranteed by the supplier to be below 10 ppm, it is unlikely that these alterations, and peaks in the voltammograms, are due to impurities. These processes are likely correlated with different interfacial processes. For further details we would like to refer the reader to Ref.^{33,90}

The AFM measurements of the IL/Au(111) interface indicate that strong ion adsorption can occur³⁵. Already at ocp a multilayered morphology is present and at least four and five layers can be identified for [EMIM]FAP and [Py_{1,4}]FAP, respectively. Upon applying higher electrode potentials, a stronger near surface structure is found and both the number of ion layers and the force required to rupture these layers increase for both ILs. Furthermore, in [Py_{1,4}]FAP the Au(111) surface undergoes potential dependent restructuring³³. *In situ* STM reveals the formation of herringbone superstructure in the regime of C_1 and C_2 . In the regime of C_3 the herringbone structure disappears. The *in situ* STM and AFM measurements show that the IL/Au(111) interface is quite complex and strong ion adsorption occurs.

b) Electrochemical impedance spectroscopy

(i) Analysis of broadband impedance and capacitance spectra

Fig. 3 shows an exemplary impedance Nyquist plot for the system [Py_{1,4}]FAP/Au(111) at a WE potential of -0.2 V (open circuit potential)³³. In this representation, ideal capacitive behavior

$\hat{Z}(\nu) = 1 / (j2\pi\nu \cdot C)$ would manifest in a line parallel to the $Z''(\nu)$ axis. While the data in **Fig. 4** clearly reveal deviations from an ideal capacitive behavior, this Nyquist representation is not well suited for resolving different capacitive processes. A plot of the data in the complex capacitance plane is much better suited for this, see **Fig. 4a** and b. The complex capacitance $\hat{C}(\nu)$ is calculated from the complex impedance $\hat{Z}(\nu)$ via $\hat{C}(\nu) = 1 / (j2\pi\nu \cdot \hat{Z}(\nu))$. At all dc potentials, a slightly suppressed high-frequency semicircle due to electrical double layer formation is detected. This semicircle starts from the bulk capacitance of the IL, C_{bulk} , and would intersect with the $C'(\nu)$ axis at the double layer capacitance C_{EDL} , if there were no additional capacitive processes at the interface. The time scale of the double layer formation is determined by the bulk resistance of the IL. Typical values for double layer formation $\tau_{\text{EDL}} = R_{\text{bulk}} C_{\text{EDL}}$ are in the range of 1 ms. Thus, the fast process should encompass all interfacial charge redistributions, which do not require an activation energy in excess of that for charge transport in the IL. The data in **Fig. 4a** and b clearly reveal the existence of additional processes in the anodic and cathodic regimes³³. The time scale of underlying capacitive process is in the range of seconds, i.e. much slower than the fast process. The contribution of the slow process to the overall capacitance is similar to that of the fast one.

For a quantitative analysis, complex impedance data are often fitted to equivalent circuits. Here, we used a different approach. Since we were mainly interested in the capacitance relaxation strengths and the time scales of the different processes at the IL/Au(111) interface, we used an empirical Cole-Cole type expression to fit the slightly suppressed semicircles in the complex capacitance plane:

$$\left(\hat{C}(\nu) - C_{\infty}\right) = \sum_{i=1}^n \frac{\Delta C_i}{1 + (j2\pi\nu\tau_i)^{\alpha_i}} \quad (1)$$

Here, C_∞ is the bulk capacitance of the IL, while ΔC_i and τ_i denote the capacitance relaxation strength and the relaxation time of process i , respectively. This kind of approach is well known from the analysis of dielectric relaxation processes in supercooled liquids and polymers.

In **Fig. 5a**, the capacitance relaxation strength of the fast capacitive process, ΔC_{fast} , is plotted versus the electrode potential. A broad peak in ΔC_{fast} is detected around -0.4 V. At -1.0 V, there is a local minimum of the capacitance followed by a slight increase towards more negative potentials. Thus, even up to highly negative electrode potentials of -2.0 V, positive counter charge can be accumulated closely to the Au(111) surface. We do not find evidence for lattice saturation effects at highly negative potentials as predicted by Kornyshev's theory³⁸. In the cathodic regime, the slow capacitive process is detected in a potential window from -0.84 V to -1.04 V, see **Fig. 5b**. In this potential window, the herringbone reconstruction of the Au surface is seen by *in situ* STM³³ (see next subsection). In the anodic regime, ΔC_{slow} exhibits a capacitance maximum, which may be related to latent voids at the electrode surface created by alkyl chains of cations⁹¹. When these alkyl chains are removed from the surface with increasing anodic potential so that the voids can be occupied by anions.

(ii) Temperature dependence of capacitive processes

In several recent publications, it was claimed that the differential capacitance of IL/electrode interfaces increases with increasing temperature^{65,77,92}. In contrast, most theoretical models developed so far predict a decrease of the differential interfacial capacitance with increasing temperature^{38,93}.

We found that a careful analysis of broadband capacitance spectra results in a weak temperature dependence of the differential capacitance values⁹⁴. In the following, we present the results of potential-dependent EIS measurements on the interface [Py_{1,4}][FAP]/Au(111) at temperatures ranging from 0 °C to 90 °C. In **Fig. 6**, the relaxation strength of the fast capacitive process, ΔC_{fast} , is plotted versus the WE potential. It is obvious that the differential capacitance shows a rather complicated

potential and temperature dependence. Overall, there is a weak tendency for a decrease of the differential capacitance decreases with increasing temperature.

Next we consider the temperature dependence of the relaxation times of the two capacitive processes τ_{fast} and τ_{slow} . In **Fig. 7**, we show an Arrhenius plot of the relaxation times and of the ionic liquid conductivity. A detailed analysis reveals that the ionic conductivity σ_{dc} and the relaxation time τ_{fast} exhibit a Vogel-Fulcher-Tamann-type (VFT-type) temperature dependence, while the temperature dependence of τ_{slow} is better described by an Arrhenius law. The results confirm that the time scale of the fast capacitive process is governed by bulk ion transport in the IL. The Arrhenius-type temperature dependence of the slow process suggests that the dynamics of strongly bound ions in the innermost ion layers and/or structural rearrangement of the electrode surface are responsible for this process.

(iii) Comments on other methods of analysis

Traditional methods for probing the double layer capacitance of electrode interfaces are problematic when applied to ILs systems. In the following section, we explain why analysis of impedance / capacitance spectra with equivalent circuits containing a constant phase element or single frequency plots of capacitance are unsuitable for ILs.

In the literature, the charging of a non-ideal layer capacitance through the bulk resistance of the electrolyte is often described by an equivalent circuit shown in **Fig. 8a**. In **Fig. 8b**, the complex capacitance of this semicircle is plotted in the complex capacitance plane for different values of the CPE exponent α . As clearly seen, when $\alpha < 1$, the low-frequency limiting behavior is not capacitive, but both the real and imaginary part of the capacitance diverge as the frequency goes to zero⁷². When this behavior is formally described by a distribution function of parallel ideal capacitances, the

distribution function cannot be standardized and thus its first moment, the average capacitance, is infinite. We note that although Brug et al. derived a mean value for the double layer capacitance

$$\langle C_{EDL} \rangle = \sqrt[\alpha]{\frac{Q}{R_{bulk}^{\alpha-1}}} \quad (2)$$

by means of an analogy observation⁹⁵, the physical meaning of $\langle C_{EDL} \rangle$ is unclear, since it is not the first moment of a well-defined capacitance distribution function. This makes the usage of the CPE for deriving interfacial capacitance values problematic.

In **Fig. 9a**, we show the potential-dependent capacitance data of the [Py_{1,4}]FAP/Au(111) interface in a constant-frequency plot. The real part of the capacitance measured at 10 Hz was taken for this plot⁹⁴. This frequency was chosen, since at room temperature (20 °C), the impedance phase angle at 10 Hz is close to -90°. In contrast to the capacitance of the fast process as shown in **Fig. 7**, the $C'(10 \text{ Hz})$ data exhibit a quite strong increase with increasing temperature. A further analysis reveals that this increase is an artefact caused by the existence of different capacitive processes with temperature-dependent relaxation times. To demonstrate this, broadband capacitance data (0.1 MHz to 10 mHz) at a WE potential of -0.92 V *versus* Fc⁰/Fc⁺ are shown in **Fig. 9b** for several temperatures extending from 0 °C to 60 °C. The filled spheres mark the position of the data points obtained at 10 Hz. At 0 °C, the 10 Hz data point is part of the high-frequency semicircle due to the fast capacitive process, while at higher temperatures, the 10 Hz data point shifts into the second semicircle caused by the slower capacitive process. Thus, the increase of $C'(10 \text{ Hz})$ does not reflect an overall increase of the interfacial capacitance with increasing temperature, but is caused by a frequency window effect⁹⁴.

c) In situ STM and AFM studies

In 2006 the Clausthal group found that even small variations in the cation/anion combination can drastically influence electrochemical process⁹⁶. We assumed that the interfacial behavior of ILs is complicated and the kinetics of metal and semiconductor deposition seems to depend on the structure and dynamics of the interfacial layers between the IL and solid surface⁹⁷. In 2007 Atkin et al.¹⁴ used AFM to show that ILs form several remarkably strongly interfacial layers on solid surfaces. Two years later a combination of *in situ* STM and AFM was used to study IL/Au(111) interface for [Py_{1,4}]TFSA and [EMIM]TFSA. These ILs with the same anion but different cations, which revealed structure / function relationships relating to the cation in particular⁶. AFM experiments reveal that multiple solvation layers (3 – 5 layers) are present at the gold interface for both ILs at open circuit potential (ocp). Furthermore, the strength of the interaction between the innermost layer and the substrate is dependent on the cation type; the force required to rupture the innermost solvation layer is about 4 times greater for [Py_{1,4}]TFSA than for [EMIM]TFSA. *In situ* STM results show that in the presence of [Py_{1,4}]TFSA the gold surface appears strongly structured (in part worm-like), while in [EMIM]TFSA Au(111) is also structured, but much more weakly. This remarkable difference in electrochemical behavior is ascribed to the greater strength of the interaction of [Py_{1,4}]⁺ compared to [EMIM]⁺ with the Au(111) surface.

In situ STM, AFM and DST experiments completed over the last 5 years have provided unprecedented insight into the interfacial structure of the electrified IL/solid interface.³⁷ In this publication recent results obtained for two ILs based on tris(pentafluoroethyl)trifluorophosphate (FAP⁻) anion and two different cations, namely [Py_{1,4}]⁺, [EMIM]⁺, have been summarized. These liquids have wide electrochemical windows (up to 6 V). Furthermore the liquids with FAP⁻ anion are the purest commercially available ILs that reduces risk of misinterpretations.

(i) [EMIM]FAP / Au(111) interface

In situ STM images of the Au(111) surface in [EMIM]FAP show that at the open circuit potential (ocp) the typical Au(111) surface with the step height of about 250 pm is obtained (**Fig. 10a**). However, something like a “layer” is present at the electrode surface leading to an imperfect image quality. Furthermore the roughness of this “layer” increases (**Fig. 10b**) at more negative electrode potentials (the potential regime of C₁ in **Fig. 2a**)⁹⁰. The AFM measurements reveal that at the ocp (-0.2 V vs. Pt) at least 4 layers are present at the interface (**Fig. 11a**). Furthermore, two small steps, 0.3 nm and 0.5 nm wide are detected that is likely correspond to cation (0.3 nm) and anion (0.5 nm) sublayers. Their sum (0.3 nm + 0.5 nm) gives the [EMIM]FAP ion pair dimension (0.83 nm)³⁵. The innermost 0.3 nm thick layer at the ocp is enriched in cations and a force of about 7 nN is required to rupture this layer. The next 0.5 nm thick layer corresponds to an anion layer. *In situ* distance tunneling spectroscopy (DTS) measurements in **Fig. 10c** allow us to estimate the distance between the tip and the sample in an STM experiment.

In DTS measurement the tunneling current (I_t) is recorded as a function of the distance between the tip and the surface (d). The zero distance is chosen at the point where the tunneling current reaches 100 nA. At this value the tip is usually less than 0.1 nm above the surface. As can be seen in **Fig. 10c**, the typical tunneling current of 2 nA in the present experiment corresponds to a distance of about 1 nm. According to the AFM data (**Fig. 11a**) there is at least one IL layer between tip and sample, which means that the ions of the IL adsorbed to the surface must be involved in the tunneling process and the STM tip must move through these adsorbed layers during scanning.

At higher electrode potentials both the number of detectable layers and the push-through forces increase³⁵. In the cathodic regime the first layer close to the surface is more compressed compared to the ocp conditions. For instance, at -1.0 V the width of the innermost cation layer decreases to 0.28 nm (in contrast to 0.30 nm at the ocp) and the push-through force increases to 25 nN (from 7 nN at the ocp) (**Fig. 11b**). This indicates that the layers become more strongly adsorbed to the surface and the innermost layer gets a flatter orientation that influences the quality of STM images. In the anodic

regime at least 5 layers of [EMIM]FAP can be probed and the innermost layer is enriched in anions. According to these results the cation-rich layer adsorbed at negative electrode potentials and the transition to the anion-rich layer adsorbed at positive electrode potentials are probed with *in situ* STM.

We should mention that the structure of the interfacial layers obtained in the 1st STM scan differs from the structure obtained in the 2nd STM scan. During the 1st scan, a layer starts to grow at -1.5 V and then the surface slowly changes (**Fig. 12a**). During the 2nd scan, 0.5 nm high islands are present at the surface already at the ocp (-0.2 V). If the electrode potential is kept at -1.5 V, these islands transform to a layer, which slowly grows during several hours (**Fig. 12b,c**).

These results show that [EMIM]FAP-Au(111) interface is highly complex and both cation and anion can alter electrochemical reactions.

(ii) [Py_{1,4}]FAP / Au(111) interface

As mentioned above the Au(111) surface is a subject of restructuring / reconstruction in [Py_{1,4}]TFSA: at ocp the STM images show a wormlike structure and by reducing the electrode potential a well known herringbone superstructure can be probed⁹⁸. Instead of [Py_{1,4}]TFSA, a flat gold surface is obtained in [Py_{1,4}]FAP at ocp³³. Apart from the typical terraces there is no striking surface structure, even if we zoom in (**Fig. 13a**). *In situ* STM experiments show that in the cathodic regime the Au(111) surface undergoes a (22 x $\sqrt{3}$) surface reconstruction leading to above mentioned herringbone superstructure (**Fig. 13b,c**). The reported distance between the rims should be 6.4 nm, but one finds slightly varying values in literature^{99,100}. With a calibrated STM tip we get a value of 5.4 ± 0.5 nm which is a bit lower than the mentioned 6.4 nm. The uncertainty arises from the noise in the STM images. EIS measurements detect a slow capacitive process at the potential regime where the (22 x $\sqrt{3}$) surface reconstruction appears³³. This capacitive process is slower than electrochemical double layer formation but faster than Faradaic processes and seems to be related to the slow charge flow to the

electrode caused by the reconstruction process. We should mention that we have not yet seen the herringbone superstructure in either [EMIM]TFSA⁶ or [EMIM]FAP⁹⁰.

The AFM also detects strong near surface structure is also detected for [Py_{1,4}]FAP/Au(111) interface³⁵. Measurements reveal that at the ocp (-0.2 V vs. Pt) at least 5 layers are present at the interface (**Fig. 14a**). A small 0.35 nm step occurs closest to the surface that is likely corresponds to an innermost layer enriched in cation. However unlike [EMIM]FAP, the next step is 0.9 nm, which is consistent with the size of an ion pair (0.89 nm). Furthermore, in the case of [Py_{1,4}]FAP a higher force is required to rupture the innermost cation layer compared to [EMIM]FAP (18 nN and 7 nN, respectively). At -1.0 V (the potential regime where the herringbone reconstruction occurs) the width of surface-adsorbed cation layer decreases from 0.35 nm to 0.25 nm, while the force required to rupture this layer increases (**Fig. 14b**). This shows that the innermost layer becomes more compressed compared to ocp conditions, probably due to a change in average cation orientation to the surface (from an almost perpendicular orientation to the surface to a tilted or even parallel orientation).

The similar trends are also observed in the anodic regime^{7,35,101}. Anions are enriched in the innermost layer, and by increasing the anodic potential, the electrostatic interaction between the surface and the anions becomes stronger and causes an increase in the force required to disrupt the innermost layer. However, in contrast to the [Py_{1,4}]⁺ cations, the [FAP]⁻ anion cannot undergo significant conformational changes and thus the thickness of the innermost anion-enriched layer is not significantly influenced by the electrode potential. Preliminary tunneling spectroscopy experiments show that the tunneling barrier is lowest in the potential regime where the herringbone superstructure is observed. The preliminary conclusion is that in this limited potential regime the STM tip is close enough to the surface to allow the electrons to tunnel through the adsorbed IL layer and make the herringbone structure visible.

In addition, we have observed the ultra-slow formation of vacancies in the herringbone structure (**Fig. 15**). This process could be responsible for the sub-Hz complex capacitance contribution probed by EIS. Depending on the applied electrode potential and depending on how long an electrode potential was applied, the herringbone structure either disappears rapidly or—with slightly different conditions—these vacancies grow, sometimes on the time scale of hours, sometimes within 10–15 min. 5 year old *in situ* STM results of Au(111) under [Py_{1,4}]TFSA also gave hints for such vacancies in the herringbone structure, but we have not yet found such vacancies for Au(111) in [EMIm][TFSA], [EMIm][FAP] or [HMIm][FAP], where the herringbone structure either does not occur or needs other tunnelling parameters to be probed. If the electrode potential is increased, the vacancies disappear. As gold dissolution in this potential regime under a considerably strongly adsorbed cation layer is rather unlikely, there might either be an “underpotential” reduction of the [Py_{1,4}]⁺ or trace amounts of e.g. water are reduced to hydrogen.

Conclusions

In this paper we have presented our recent results on the structure and dynamics of [EMIM]FAP/Au(111) and [Py_{1,4}]FAP/Au(111) interfaces, as probed with *in situ* STM, AFM and EIS. *In situ* AFM measurements reveal a multilayered morphology at the IL/Au(111) interface, with more near surface layers being detected at higher voltages. Overall, the adsorption strength of ions seems to be significantly higher than in aqueous and organic electrolytes. At the ocp and in the cathodic regime, the innermost layer is enriched with the cations, while in the anodic regime, an anion-rich innermost layer is detected. Furthermore, the innermost layer becomes more compressed at higher voltages compared to the ocp due to a change in the ion orientation. *In situ* STM results reveal also that the ions are strongly bound to the electrode surface. However, significant differences are found between

[EMIM]FAP and [Py_{1,4}]FAP. In the case of [Py_{1,4}]FAP, the Au(111) surface undergoes a (22 x $\sqrt{3}$) reconstruction in the cathodic regime, while in the case of [EMIM]FAP the herringbone reconstruction is not detected. Furthermore, in the case of [Py_{1,4}]FAP, the ultra-slow formation of vacancies in the herringbone structure is probed. EIS measurements reveal the existence of a fast capacitive process taking place on a time scale of milliseconds and of a slow capacitive process taking place on a time of seconds. While the fast process is detected over the entire potential range, the capacitance contribution of the slow process is particularly strong in the potential range where the herringbone reconstruction is seen via in-situ STM. The time scale of the fast process exhibits a Vogel-Fulcher-Tammann-type temperature dependence, since it is determined by bulk ion transport, while the slow process exhibits an Arrhenius-type temperature dependence. By a careful analysis of the EIS data, we were able to show that the capacitance contribution of the fast process decreases slightly with increasing temperature. In contrast, a constant frequency plot of the capacitance at different temperatures shows an apparent increase of the capacitance, which is an artefact caused by a frequency window effect. Finally, it is important to note that even slight changes in cation/anion combination of the IL may drastically influence the surface chemistry.

These results, combined with our previously published work, show ILs cannot be regarded as ‘just another’ class of solvents for electrochemistry, because the capacity for ILs to self-assemble and form ordered nanostructures at electrode interfaces influences their electrochemical behaviour.

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Figure Captions

- Fig. 2** Cyclic voltammograms of [EMIM]FAP (a) and [Py_{1,4}]FAP (b) ionic liquids on Au(111) at 25 °C and at scan rate of 10 mV s⁻¹.
- Fig. 3** Nyquist impedance plot of the [Py_{1,4}]FAP/Au(111) interface.
- Fig. 4** Complex capacitance spectra of the [Py_{1,4}]FAP/Au(111) interface
- Fig. 5** Potential-dependent capacitance of the [Py_{1,4}]FAP/Au(111) interface: (a) fast process; (b) slow process.
- Fig. 6** Potential-dependent differential capacitance of the fast capacitive process, ΔC_{fast} at the [Py_{1,4}]FAP/Au(111) interface at different temperatures.
- Fig. 7** Temperature dependence of the relaxation times τ_{fast} and τ_{slow} and of the ionic conductivity σ_{DC} at a WE potential of -0.92 V *versus* Fc⁰/Fc⁺ **for the [Py_{1,4}][FAP]/Au(111) interface**
- Fig. 8** (a) Equivalent circuit for describing the charging of a non-ideal double layer capacitance; (b) Complex capacitance plot for the equivalent circuit **for the [Py_{1,4}][FAP]/Au(111) interface**
- Fig. 9** (a) Potential-dependence of C'(10 Hz) at the [Py_{1,4}]FAP/Au(111) interface at different temperatures; (b) Complex capacitance spectra measured at -0.92 V *versus* Fc⁰/Fc⁺ and at different temperatures. The filled circles show the position of the 10 Hz data point.
- Fig. 10** *In situ* STM images of Au(111) surface in [EMIM]FAP (a, b). The current-distance tunneling spectra show that the distance between the STM tip and the surface is ~1 nm (c).

- Fig. 11** Typical force versus distance profile for an AFM tip approaching a Au(111) surface in [EMIM]FAP at ocp (a) and -1.0 V (b).
- Fig. 12** *In situ* STM images of Au(111) surface in [EMIM]FAP obtained at -1.5 V during (a) 1st and (b, c) 2nd STM scans.
- Fig. 13** *In situ* STM images of Au(111) surface in [Py_{1,4}]FAP.
- Fig. 14** Typical force versus distance profile for an AFM tip approaching a Au(111) surface in [Py_{1,4}]FAP at ocp (a) and -1.0 V (b).
- Fig. 15** The formation of vacancies at [Py_{1,4}]FAP/Au(111) interface probed with *in situ* STM.

Figures

Figure 1- Chemical structure of the two ILs examined in this study (a) [EMIm][FAP] and (b) [Py_{1,4}][FAP]. Carbon atoms are shaded gray, nitrogen are blue, fluorine are yellow, and phosphorous are pink. Hydrogens are not represented.

Figure 1- Chemical structures of (a) 1-ethyl-3-methylimidazolium [EMIm]⁺ cation (b) tris(pentafluoroethyl)trifluorophosphate [FAP]⁻ anion and (c) 1-butyl-1-methylpyrrolidinium [Py_{1,4}]⁺ cation that can be paired to form [EMIm][FAP] and [Py_{1,4}][FAP], respectively.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

a)

b)

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

(a) ocp; 250 x 250 nm²

(b) -1.2 V; 120 x 120 nm²

(c) -1.2 V; 60 x 60 nm²

Fig. 12

Fig. 13

Fig. 14