A combined STM, AFM and DFT study of the HOPG / 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([OMIm]Tf$_2$N) Interface

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Abstract

The highly ordered pyrolytic graphite (HOPG) / 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([OMIm]Tf$_2$N) interface is examined by ultrahigh vacuum scanning tunneling microscopy (UHV-STM) and atomic force microscopy (UHV-AFM), and as a function of potential by in situ scanning tunneling microscopy (STM), in situ atomic force microscopy (AFM) and density functional theory (DFT) calculations. In situ STM and AFM results reveal that multiple ionic liquid (IL) layers are present at the HOPG / electrode interface at all potentials. At open circuit potential (OCP), attractions between the cation alkyl chain and the HOPG surface result in the ion layer bound to the surface being cation rich. As the potential is varied, the relative concentrations of cations and anions in the surface layer change: as the potential is made more positive anions are preferentially adsorbed at the surface, while at negative potentials the surface layer is cation rich. At -2 V an unusual overstructure forms. STM images and AFM friction force microscopy measurements both confirm that the roughness of this overstructure increases with time. DFT calculations reveal that [OMIm]$^+$ is attracted to the graphite surface at OCP, but adsorption is enhanced at negative potentials due to favorable electrostatic interactions, and at -2 V the surface layer is cation rich and strongly bound. The energetically most favorable orientation within this layer is with the [OMIm]$^-$ octyl chains
aligned “epitaxially” along the graphitic lattice. This induces quasi-crystallization of cations on the graphite surface and formation of the overstructure. An alternative explanation may be that, because of the bulkiness of the cation sitting along the surface, a single layer of cations is unable to quench the surface potential, so a second layer forms. The most energetically favourable way to do this might be in a quasi-crystalline / multilayered fashion. It could also be a combination of strong surface binding / orientations and the need for multilayers to quench the charge.

**Keywords:** Ionic liquid, gold, potential, STM, AFM, DFTB.

**Introduction**

Wide electrochemical and thermal windows, good ionic conductivities, acceptable viscosities, extremely low vapor pressures and the ability to solubilize many chemical species make Ionic Liquids (ILs) interesting solvents for electrochemical applications. However, the structure of the electrode / IL interface is still poorly understood, particularly as the potential is varied. Models of the solid liquid interface for molecular solvents are not appropriate for ILs because they are pure salts, meaning that concepts including the Debye length and diffuse layers have little meaning. In contrast to molecular solvents, most ILs are nanostructured in the bulk due to solvophobic effects. The solvophobic effect in ILs is due to electrostatic attractions between anions and cation charged groups leading to the formation of charged domains in the liquid. Incorporation of cation alkyl chains into these charge regions is energetically unfavorable because electrostatic attractions would be disrupted. Thus, alkyl side groups are solvophobically repelled from the charged regions and cluster together in a structure that is sponge-like for both protic and aprotic ILs. The presence of a solid surface flattens this sponge structure into layers, similar to surface induced sponge to lamellar phase transitions in aqueous surfactant systems.
ILs are inherently structured, and simple double layers do not form on metal surfaces.\textsuperscript{13} However, electrochemical processes in ILs depend on the structure of the interface, and optimizing IL performance in electrochemical processes requires knowledge of ion organization close to the electrode interface. AFM and STM are techniques capable of performing a local characterization of the electrical double layer (EDL). AFM and/or STM have been used to probe the structure of various ionic liquids at different interfaces like mica, silica, Au(111) and graphite.\textsuperscript{8,10,14-20} This has enabled a model for the IL-interfacial structure to be developed which divides the interface into three key regions: the interfacial layer, the transition zone and the bulk liquid.\textsuperscript{21} The interfacial or innermost layer is composed of the IL layer adsorbed to the electrode surface. In a recent discussion paper\textsuperscript{1} it was summarized that the interfacial structure of ILs on metal electrodes differs depending on the IL and that such layers can influence electrochemical reactions. For example, AFM force curves reveal that 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide (\([\text{EMIm}]\text{Tf}_2\text{N}\)) and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide (\([\text{Py1,4}]\text{Tf}_2\text{N}\)) both form 3 - 5 near surface layers near a gold surface, but that the \([\text{Py1,4}]^+\) is about four times more strongly adsorbed to the surface in the interfacial layer than the \([\text{EMIm}]^+\) cation.

*In situ* STM suggests that IL cations facilitate restructuring of the Au(111) surface\textsuperscript{14}. When immersed in \([\text{Py1,4}]\text{Tf}_2\text{N}\) the gold surface has a worm-like appearance at OCP. The worm-like structures could be a consequence of ion adsorption, gold restructuring, or some combination of both effects. The gold surface becomes flat, however, when the potential is reduced. In \([\text{EMIm}]\text{Tf}_2\text{N}\) the gold surface is less structured at OCP but, like \([\text{Py1,4}]\text{Tf}_2\text{N}\), flattens when the potential is varied. *In situ* STM experiments show that in the cathodic regime the Au(111) surface undergoes a (22 x \(\sqrt{3}\)) surface reconstruction when immersed in 1-butyl-1-methylpyrroloidinium tris(pentafluoroethyl)trifluorophosphate (\([\text{Py1,4}]\text{FAP}\)), leading to the herringbone superstructure.\textsuperscript{15} Kolb *et al.*\textsuperscript{22} and Mao *et al.*\textsuperscript{23} have independently investigated the electrochemical interface between gold single crystal electrodes and ionic liquids with imidazolium ions and either PF\(_6^–\) or
BF$_4^-$ anions by *in situ* STM. Mao *et al.*$^{23}$ reported the selective adsorption of imidazolium cations on Au(100) surface, but not on Au(111), suggesting that structural commensurability is required for cation adsorption to the surface.

For electrochemical capacitors, highly porous carbon-based materials are typically used as electrode material with ions from the electrolyte adsorbing and arranging at the carbon surface to form the EDL. Optimization of IL based electrochemical systems requires a deep understanding of the interface structure when the ion structure and the electrode potential are varied. There are few studies of the structure of the interface between ILs and carbon based substrates. In 2007, Atkin and Warr showed with AFM force curves that six or seven near surface layers are present for the [EMIm]acetate / graphite system. The distance between steps in AFM force curves suggested that the [EMIm]$^+$ cation is orientated flat across the substrate,$^{10}$ in contrast to the gold surface where a more upright orientation was favored.$^{14}$ More recently combined AFM force curves and molecular dynamic simulations$^{20}$ have been used to probe the structure of the [EMIm]Tf$_2$N / graphite surface as a function of potential. The results obtained are consistent with those described previously: slight enrichment of cations in the surface bound layer at OCP, counterions enrichment at the surface as the potential is changed, and interfacial structure that is most pronounced at the surface, decaying with distance.

In the present work we report on the interfacial structure HOPG/ [OMIm]Tf$_2$N by cyclic voltammetry (CV), Ultraviolet Photoelectron Spectroscopy (UPS), *in situ* and UHV STM, AFM and DFT calculations.

**Experimental**

[OMIm]Tf$_2$N was purchased from Iolitec in the highest available quality (99.9%). Prior to use, the liquid was dried under vacuum at 120 °C to water contents well 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).

The UHV experiments were carried out in an ultra-high vacuum apparatus with a base pressure of $5 \times 10^{-9}$ Pa (Omicron MULTIPROBE System). Electron spectroscopy was performed using a hemispherical analyzer (EA125, Omicron) detecting electrons under an angle of $45^\circ$ to the surface normal. In the case of ultraviolet photoelectron spectroscopy an ultraviolet photon source (HIS 13) was applied, using a cold gas discharge for generation of He (I/II) radiation.

The UHV STM / AFM measurements were performed with a variable temperature device (VT-STM / AFM, Omicron) under ultra-high vacuum conditions. Etched tungsten tips were used for STM. AFM was carried out using silicon AFM probes with a tip radius $< 7$ nm and a force constant of 0.2 N/m.

The HOPG crystal was initially treated ex situ using adhesive tape to prepare a fresh and smooth surface. The sample was subsequently heated in situ at 600 K for at least 30 min to remove residual surface contaminants.

Monolayers of [OMIm]Tf$_2$N were prepared in situ using an UHV molecular evaporator (TCE-CS, Kentax). The ionic liquid was evaporated at 400 K from a quartz crucible. The deposition rate was previously determined by analyzing the attenuation of emitted electrons of the Au4f orbital of an Au(111) substrate due to the ionic liquid, supposing the mean free path to be 3 nm.$^{24}$

All in situ STM experiments were performed at 23 °C using in-house-built STM heads and scanners under inert gas conditions (H$_2$O and O$_2$ below 2 ppm) 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 \((T = 23 ^\circ C)\) 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 a cathodic electropaint (BASF GY85-0030). In all STM experiments HOPG substrates served as a working electrode and platinum wires were used as quasi-reference and counter electrodes, respectively. During the STM experiments the potential of the working electrode was controlled by the PicoStat from Molecular Imaging / Agilent.

All electrochemical experiments were performed inside of an argon filled glove box (Vacuum Atmospheres OMNILAB) with water and oxygen below 2 ppm using a PARSTAT 263A potentiostat/galvanostat controlled by PowerSuite software. 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 cm\(^2\). In all electrochemical experiments HOPG substrates served as a working electrode and platinum wires were used as quasi-reference and counter electrodes, respectively.

Both normal and lateral force measurements were performed using a Digital Instruments NanoScope IV Multimode AFM with an EV scanner in contact mode. Two sharp silicon tips from the same batch (model NSC36, Mikromasch, Tallinn, Estonia) were used over the course of the investigation. The procedures used to setup the AFM electrochemical cell are exactly as described in Ref.\(^2\) HOPG surfaces were freshly cleaved before experiments. They were used as both the working electrode and the solid substrate for force and friction measurements. A thin cylindrical strip of Cu metal and 0.25 mm Pt wire were used as the counter and “quasi” reference electrodes, respectively.

Normal force curves were collected by moving the surface towards the tip and detecting the cantilever deflection as a function of separation. The ramp size was 30 nm and the scan rate was
0.1 Hz. Standard methods were used to convert deflection vs. separation data to normal force vs. apparent separation curves.\textsuperscript{25} Lateral force measurements were acquired by performing lateral AFM scans with a scan angle of 90° (with respect to the cantilever long axis) with the slow scan axis disabled.\textsuperscript{2} The scan size was 100 nm x 100 nm, and the scan rate was 30 Hz. The lateral deflection signal (i.e., cantilever twist) was converted to lateral force using a customized function produced in Matlab 7.0 which takes into account the torsional spring constant and the geometrical dimensions of the cantilever.\textsuperscript{26} Repeat experiments revealed that the features of the normal and lateral forces were constant.

The interaction between [OMIm]Tf$_2$N and HOPG was analysed using DFT calculations. The M06-2X functional in conjunction with a 6-31G(d) basis set was employed. M06-2X is a member of the Minnesota family of functionals developed by Truhlar \textit{et al.}\textsuperscript{27} Through its explicit inclusion of long-range correlation effects, it produces accurate thermochemistry for non-covalent interactions, such as those at the ionic liquid HOPG interface. Moreover, the accuracy of M06-2X in the context of aprotic ionic liquids has been demonstrated on a number of occasions.\textsuperscript{28, 29} Adsorption energies of individual [OMIm]$^+$ and Tf$_2$N$^-$ ions bound to a model graphite surface have been calculated at 0 K. Adsorption energies of all possible conformers of [OMIm]$^+$ and Tf$_2$N$^-$ ions were calculated, so that the most stable adsorbed conformer was identified. Adsorption energy $E_{\text{ads}}$ of a species $X$ is defined here as,

$$E_{\text{ads}} = E(X + \text{graphite}) - [E(X) + E(\text{graphite})]$$

where $E$ denotes the optimised energy of each individual species.

The influence of positive and negative external potentials on adsorption energies was investigated via an electric dipole field normal to the graphite surface (Fig. 11). To approximate the HOPG surface, we employed a hexagonal C$_{96}$H$_{24}$ graphene flake, \textit{ca.} 2 nm in diameter. All calculations were performed using the Gaussian09 software package.\textsuperscript{30}
Results and Discussion

Results for two different interfaces are presented in this work. In the first section *in situ* CV, STM and AFM measurements for the bulk IL interface are presented. As has been reported before for other substrates, atomic resolution images of the IL on the surface could not be obtained for [OMIm]Tf₂N on graphite. To gain further insight into the structure of the interface, experiments on a liquid monolayer under UHV were performed using UPS, STM, AFM, supported by DFT simulations. These results are presented in the second section, and provide further insight into the precise arrangement of the ions at the surface, and the origin of some of the unusual results revealed for the bulk liquid interface. In the final part, results for the bulk IL interface and thin IL films are correlated and summarized, to provide as well as currently possible an understanding of the structure of the [OMIm]Tf₂N interface, and how this structure varies with the electrode potential.

1. Bulk [OMIm]Tf₂N / HOPG Interface

Cyclic Voltammetry

Representative cyclic voltammograms for [OMIm]Tf₂N / HOPG are presented in Fig. 1. In the cathodic regime, the electrochemical window is limited by the reduction of the organic cation at -2.3 V, whilst the anodic limit is marked by graphite oxidation above +1.5 V (inset in Fig. 1). A broad anodic peak at -0.7 V is correlated with the cathodic breakdown observed at -2.3 V as it only appears if the cathodic scan exceeds the cathodic decomposition limit of the organic cation. This explains the absence of an anodic peak at -0.7 V in the cyclic voltammogram (Fig. 1). Three cathodic processes are noted at -1.0 V, -1.7 V and at -2.0 V. The cathodic peaks are likely correlated with different surface processes that occur upon IL adsorption. The *in situ* STM results presented below reveal several unusual overstructures at ~ -2 V. For the first two cathodic peaks, until a potential of ~ -2 V is reached, no significant changes could be probed with STM. The AFM results described below indicate that strong cation adsorption occurs.
**Fig. 1** Cyclic voltammograms of [OMIm]Tf$_2$N recorded on HOPG. Scan rate: 10 mV s$^{-1}$.

**In situ STM**

*In situ* STM measurements were used to evaluate the morphology of the [OMIm]Tf$_2$N / HOPG interface at different electrode potentials. The structure at -0.4 V vs. Pt (~OCP) is presented in Fig. 2. The image is somewhat unclear due to the presence of the IL, but the periodic structure can be attributed to the superstructure of underlying HOPG. The lattice spacing found is about 0.26 nm. The low image quality on the IL covered HOPG compared to similar STM images in air$^{31,32}$ and water$^{33}$ is attributed to a stronger (compared to aqueous solutions) binding of the IL ions to the graphite surface as well as to some thermal drift of the STM tip. Nonetheless, because of this strong binding, it is not clear what the STM tip exactly probes in these experiments, or how reliably the structure height can be measured as the tunneling gap might be influence by adsorbed ions. These issues are the subject of continued study.
This structure did not vary until a potential of ~ -2 V is reached. When the potential of the graphite surface is reduced to -2.1 V a marked change in the appearance of the interface occurs (Fig. 3a). At this potential the surface layer is highly enriched in cations according to AFM data. A periodic structure forms initially at -2.1 V. After about 80 min. at -2.1 V a more dense structure evolves revealing semicircle-like structures with a diameter of 1.2 nm (Fig. 3b). After changing the potential to -2.0 V (3c) within 30 min, a square-like structure with lattice spacing of 1.7 nm can be probed. At -1.9 V, a more complicated overstructure was found revealing “lines” with spacing of 2 nm (Fig. 3d, e). The lattice space of the periodic structure in image 3b and following images 3c-e is about 6-8 times “larger” than the structure of the underlying HOPG in Fig. 2. Such structures at slightly different cathodic potentials must be correlated with adsorbed [OMIm]$^+$ cations; the lattice dimension of an [OMIm]$^+$ cation arranged parallel is about 1.7 nm (DFT supporting information), and therefore of the same dimension as these features.

It is possible that more than one layer of cations gives rise to the structure imaged using STM. To probe this, Fast Fourier Transformations (FFT) of key images were performed. Fig. 4 presents the FFT of Fig. 3e, and an inverse FFT image calculated from the strongest FFT peaks. The FFT post processing reveals a complex overstructure (Fig. 4) which cannot be rationalized by a single ion layer from geometric considerations, thus it must be the result of a superposition of at least two ordered monolayers at the HOPG / [OMIm]Tf$_2$N interface.

**Fig. 2** STM images of HOPG surface in [OMIm]Tf$_2$N at -0.4 V vs. Pt quasi-reference electrode.
Fig. 3 STM images of HOPG surface in [OMIm]Tf$_2$N at different electrode potentials and times.

Fig. 4 FFT of the STM images in Fig. 3e and inverse FFT images calculated from the most distinctive peaks from FFT images.

**AFM Normal and Friction Forces**

Whereas STM probes the structure of the IL adsorbed to the surface laterally, AFM can probe the structure of the interface in the normal direction, thus providing indirect evidence regarding the composition of interfacial layers. Fig. 5a shows the chemical structures of [OMIm]$^+$ cation and Tf$_2$N$^-$ anion and their approximate dimensions in nm calculated from the van der Waals radii. Fig. 5b-f show AFM force-distance profiles for [OMIm]Tf$_2$N confined between a sharp tip and an
HOPG surface at different applied potentials within the electrochemical window. Two key features are observed in all the force curves presented: (1) a series of steps at discrete separations; (2) an increasing repulsive force with decreasing tip-surface separation. Both features indicate that [OMIm]Tf$_2$N arranges into layers near the graphite surface for all potentials investigated, consistent with previous investigations on Au(111).$^{11,17,26,34}$ More layers are detected and higher forces are required to push through each layer at a more polarized surface, which indicates a more strongly layered structure with better ion ordering.

Over a range of studies it has been shown that in most cases the AFM tip is unable to rupture the final, strongly bound, ion layer and move into contact with the surface.$^{11,17,26,35}$ Thus, in general, a “zero” apparent separation corresponds to the tip in contact with a layer of ions that is unable to penetrate, and the final step corresponds to the last layer of ions that can be displaced. Provided there is an appreciable difference between the expected [OMIm]$^+$ cation ($\sim$0.28 nm with the imidazolium ring lying flat on the graphite surface) and the Tf$_2$N$^-$ anion ($\sim$0.47 nm with the flat orientation) dimensions as shown in Fig. 5a, the width of the final step provides an indication of the composition of that layer. At 0 V, the final pushed-through layer is $\sim$0.44 nm (Fig. 5b), corresponding to a mixed layer slightly enriched in Tf$_2$N$^-$ anions ($\sim$0.47 nm). The DFT results below, and other studies,$^{36,37}$ show that the cation binds much more strongly to the graphite surface than the anion. We therefore conclude that at 0 V (OCP) there is a cation rich layer strongly bound to the graphite, followed by a layer enriched in anions, which is the last measured layer. These calculations do not discount the possibility that anions are present in the surface layer, as observed in previous studies of related IL-HOPG interfaces.$^{38,39}$ The width of subsequent layers corresponds to the ion pair, as noted in our prior investigations.$^{8-11,17}$ The composition of subsequent layers becomes more mixed with distance from the surface until the bulk liquid composition is reached.
At -1.0 V the width of the final pushed-through layer is ~0.5 nm (Fig. 5c), essentially equal to the Tf₂N⁻ anion. This indicates that the layer is rather anion-enriched. As it is physically unreasonable that ions of the same charge as the surface are enriched in the interfacial layer, this suggests that a cation-enriched layer is strongly bound to the negatively charged graphite surface, as per 0 V. The final step at -1.5 V is ~0.36 nm (Fig. 5e), corresponding to a cation-enriched layer, with the ring orientated slightly away from the surface. Given that at lower potentials the results indicate that the final ion layer could not be ruptured, it must be concluded that at -1.5 V an ion layer remains between the tip and the surface up to high forces. There, the high surface charge density at -1.5 V cannot be quenched by a single cation layer, so a second layer(s) of cations forms on top of the surface bound layer, in accordance with theoretical studies by Bazant et al.¹³ and Kirchner et al.⁴⁰

At positive potentials, the final steps (~0.30 nm at +1.0 V and ~0.24 nm at +1.5 V) are closer to the dimensions of [OMIm]⁺ cations (~0.28 nm) with the ring adsorbed flat along the graphite surface (Fig. 5d, f). This indicates an anion rich layer bound to the graphite substrate that the tip cannot penetrate with a cation layer above it. The fact that the dimension of this final measured layer is smaller than expected for the cations means that cations are orientated rather parallel to the surface.

Slightly attractive forces (~ 3 nm to 1 nm) are observed at 0 V and at +1.0 V (Fig. 5b, d). Similar effects have also been seen at other graphite-IL⁸, ²⁰ and alumina-IL⁴¹ interfaces. The origins of these short-range attractions are not clear at this stage. They could be due to van der Waals forces⁸, structural forces¹¹, electrostatic attractions (e.g. ion-ion correlations and image forces)⁴² or some combination of these effects. From these force curves it cannot be discerned which of these effects, or another as yet unidentified force, actually operates. The origin of this force has been the topic of some debate in the literature⁴³, ⁴⁴ and we are currently conducting further experiments on similar systems in an attempt to resolve this issue. However, at more biased
potentials the push-through forces are generally higher and more repulsive. This means the stronger IL layering induced by a more polarized surface is more effectively screening the attractive forces between the AFM tip and the HOPG surface.

Fig. 5 Chemical structures of [OMIm]⁺ and Tf₂N⁻ and approximate dimensions in nm (a), and typical force versus apparent separation profile for a sharp silicon tip approaching from an HOPG surface in [OMIm]Tf₂N at: (b) 0 V, (c) -1.0 V, (d) +1.0 V, (e) -1.5 V and (f) +1.5 V. The insets in (b) and (d) show the slightly short-range attractive forces.
Fig. 6a-c show the force-distance profiles for [OMIm]Tf$_2$N on HOPG electrode at -2.0 V as a function of time. The width and the push-through force for the final layer change with time. At 20 min, the force distance profile (Fig. 6a) is similar to that at -1.5 V (Fig. 5e). The final step width is ~0.38 nm. As per the -1.5 V results, this suggests that two cation layers are present next to the surface; the one closest to the surface cannot be displaced by the AFM tip. The push-through force for the final step is ~5 nN higher than that at -1.5 V, consistent with stronger electrostatic attractions. At longer times, the width for the final step increases to ~0.5 nm at 40 min and 60 min (Fig. 6b, c) with a concurrent decrease in the magnitude of push-through force by 30-50%. This is likely because cations in the second last layer are incorporated into the overstructure at -2.0 V, and cannot be displaced by the AFM tip. Consequently, the last ion layer that can be displaced is anion rich, consistent with the 0.5 nm step size. This observation is consistent with the \textit{in situ} STM results presented in Fig. 3.

Friction force microscopy is highly sensitive to surface roughness \cite{45}, and thus might be used to shed more light on the overstructures identified by STM. The lateral force ($F_L$) versus normal force ($F_N$) for [OMIm]Tf$_2$N at -2.0 V for different times is shown in Fig. 6d. Two regimes are noted. The initial rapid increase regime ($F_N<10$ nN) corresponds to the AFM tip sliding against multiple ion/ion pairs, i.e. there are multiple ion layers confined between the tip and the surface. The second regime, where the increase in friction force with normal force is lower ($F_N>10$ nN), corresponds to the AFM tip sliding on the boundary layer (a single layer of ions). In this study we focus on lateral forces that occur for normal loads greater than 10 nN, as we are interested in the properties of the final ion (boundary) layer; multilayer friction has been described in detail previously.\textsuperscript{46, 47} The friction coefficient, which is the dependence of lateral force on normal force, is extracted from the gradient of the second slow increase regime ($F_N>10$ nN). The friction coefficient increases from 0.010 at 20 min to 0.027 at 60 min. As the normal force curve retractions (c.f. Supporting information Fig. S1) show no increase in adhesion, it is likely that the increase in friction is a consequence of increased surface roughness.\textsuperscript{48-50} As the tip slides over a
rougher surface, energy is lost as the tip moves in the normal direction to slide over surface asperities. This is consistent with the in situ STM images that show that the overstructure becomes rougher (Fig. 3).

![Graph showing normal force versus apparent separation and lateral force versus normal load for [OMIm]Tf₂N at -2.0 V as a function of time.](image)

**Fig. 6** Normal force versus apparent separation (a-c) and lateral force versus normal load (d) for [OMIm]Tf₂N at -2.0 V as a function of time.

**Table 1.** Friction coefficients of boundary layers ($F_N>10$ nN) for [OMIm]Tf₂N on HOPG electrode at -2.0 V for different time.

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<tr>
<th>[OMIm]Tf₂N</th>
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2. Thin [OMIm]Tf₂N / HOPG Films on Graphite

**Ultraviolet Photoelectron Spectroscopy Results**

Fig. 7 shows UPS valence band spectra of a clean (a) and of a 1.5 nm [OMIm]Tf₂N covered HOPG surface (b). The clean HOPG spectrum has 5 distinct peaks located at binding energies of...
2.7, (ii) 6.3, (iii) 8.5, (iv) 9.9 and (v) 12.3 eV. These peaks, except peak (ii), are attributed to the \( \pi \) and \( \sigma \) bands of graphite.\(^{51}\) The peak at 6.3 eV likely originates from O2p emissions, indicating the presence of minor oxygen impurities on the surface. The spectrum of [OMIm]Tf2N on HOPG in Fig. 7 b has two major peaks, a broad structure at \( \sim 6.5 \) eV and another peak at 10.1 eV. There is a small shoulder at 11.6 eV. These three peaks can be attributed to [OMIm]Tf2N valence band emissions as described in Ref.\(^{52}\) However, there are also two additional peaks at 2.8 and 8.5 eV, which probably originate from the underlying substrate. The fact that some peaks associated with the underlying graphite substrate can still be discerned when the IL is present, means that evaporation of IL onto HOPG in a very thin film under UHV conditions was successful; as the UPS penetration depth is less than 3 nm, the thickness of the IL layer must be less than this.

**Fig. 7** UPS HeI valence band of clean HOPG (a) and of 1.5 nm [OMIm]Tf2N evaporated *in situ* on the HOPG substrate (b).
UHV STM Results

An STM image of the clean HOPG substrate (without any IL on top), obtained at room temperature and $U_{gap} = 0.1 \text{ V}$ is shown in Fig. 8a. The hexagonal atomic structure of the HOPG surface (overstructure, every 2nd atom visible) is clearly seen. The lattice spacing is 0.25 nm, as expected. Fig. 8b shows a HOPG surface covered with 1 ML of [OMIm]Tf$_2$N at 100 K and $U_{gap} = 0.1 \text{ V}$. The appearance of the image is similar to the clean graphite surface. However the periodic structure is smaller and seems to be distorted, maybe due to an ionic liquid overlayer. As for other ionic liquid systems investigated by us, atomic resolution images of the IL layers could not be obtained under any imaging conditions.

![ STM images of clean and IL-covered HOPG surfaces ]

**Fig. 8** 25 nm x 25 nm STM image of the clean HOPG surface at RT (a) and of 1 ML [OMIm]Tf$_2$N evaporated *in situ* on the HOPG substrate at 100 K (b), ($U_{gap} = 0.1 \text{ V}$).  

UHV AFM

AFM force–distance profiles for the clean (a) and with 2, 4 and 6 nm [OMIm]Tf$_2$N covered HOPG substrate (b, c, d), are depicted in Fig. 9. The force curve for clean HOPG is consistent with strong van der Waals attractions between the tip and the surface, with an attractive jump to contact from 10 nm on approach, and a strong adhesion on retraction. When the IL is present
(Fig. 9b-d) the range and magnitude of the forces change, and the features are characteristic of liquid capillaries between the surfaces. On approach, there is a jump to contact followed by a compression region. For all liquid volumes, the jump to contact distance is about 5 nm, revealing that the range of the van der Waals attractive force is not strongly dependent on the liquid film thickness. The width of the compression region increases from 6 nm for the 2 nm and 4 nm films, to 14 nm for the 6 nm film. This increase is a consequence of an IL capillary forming between the tip and the liquid, which the tip then has to move through to contact the surface. The increase in the compression distance means that when the tip jumps towards the surface, the liquid layer also jumps towards the tip. The jumps in the retraction force curves are a consequence of multiple capillaries being present between the surfaces. As the volume of liquid in these capillaries is different, as the tip retracts from the surface they rupture at different distances. Like on approach, the range of the longest capillary bridge is similar for the 2 nm and 4 nm films at ~20 nm, but longer for the 6 nm film at 28 nm. Steps in the force data close to the surface were sometimes observed on approach (not shown), but their features between experiments were not consistent; the IL structural forces are largely masked by the much stronger and longer range capillary interactions.
Fig. 9  Typical force vs. apparent separation profile for an AFM tip approaching (blue) to and retracting (red) from (a) the clean HOPG, and from [OMIm]Tf₂N evaporated *in situ* on the HOPG substrate with different thicknesses (b) 2 nm, (c) 4 nm and (d) 6 nm, respectively.

**DFT Results**

Optimised structures of [OMIm]⁺ and Tf₂N⁻ are shown in Fig. 10, from which it is seen that the [OMIm]⁺ cation adsorbs some 70% more strongly than the anion in the absence of an electric field (representative of the scenario at OCP). The [OMIm]⁺ cation has two advantages with respect to adsorption on graphite; its extended octyl carbon tail enables significant van der Waals interactions, while the imidazolium head group enables π-π stacking directly with the graphitic lattice. The structure of Tf₂N⁻ includes neither of these attributes and so the anion can interact with the graphitic surface only weakly through limited van der Waals forces in the absence of potential. As a result, the [OMIm]⁺-graphite distance is 0.228 nm, compared to 0.3 nm for the
Tf$_2$N$^-$ graphite (at 0 K). It is clear also that the driving force behind [OMIm]$^+$ adsorption onto graphite is the presence of the imidazolium head group. Supplementary optimizations (see Supporting Information, Fig. S2) of alkyl-imidazolium cations with varying alkyl lengths show that, while $E_{ads}$ is proportional to alkyl chain length, ca. 65% of the total adsorption energy can be attributed to $\pi$-$\pi$ stacking. This is not to say that alkyl chain adsorption is insignificant, since the most preferable adsorbed [OMIm]$^+$ conformation is that in which the interaction between the alkyl chain and the graphite surface is maximized (Fig. S3). The near-epitaxial alignment of [OMIm]$^+$ induced by this conformation is evident in Fig. 10.

![M06-2X/6-31G(d) optimised structures of [OMIm]$^+$ and Tf$_2$N$^-$ ions adsorbed on a model graphite surface, shown from above and the side. The cation adsorbs more strongly due to the presence of its extended alkyl chain (see Fig. S2). Distances shown are measured between the planes of the graphite surface and the imidazole ring.](image)

Fig. 10

Upon the introduction of a negative field (i.e. negative potentials), Fig. 11 shows that [OMIm]$^+$ adsorbs more strongly to the graphite surface, as anticipated. Conversely, the interaction between the Tf$_2$N$^-$ anion and graphite becomes weaker, to the point of complete extinction. The relative magnitudes of these field-dependent adsorption energies can once again be rationalized in terms of the intermolecular interactions between both ions and the graphite surface. No significant changes within individual adsorbed ion structures were observed, irrespective of the applied field. On this basis it is proposed that at high negative potentials, [OMIm]$^+$ cations become
immobilized on the graphite surface, and this, combined with the partial exclusion of Tf₂N⁻ anions through electrostatic repulsion, facilitates the formation of a cation-rich layer at the [OMIm]Tf₂N-graphite interface. The most energetically favourable orientation within this layer is one in which [OMIm]⁺ octyl chains are aligned “epitaxially” along graphitic lattice (Fig. 10), and this induces a state akin to crystallization within the cations adsorbed on the graphite surface, the structure of which is determined by the applied potential (c.f. Fig. 3 and 4). While the adsorption energy of [OMIm]⁺ at 0 K is 40.1 kcal/mol, the Gibbs free energy of adsorption at 298 K is only 19.9 kcal/mol. Adsorption strength of this magnitude is consistent with a superstructure that rearranges over time naturally through entropic effects (c.f. Fig. 3). For Tf₂N⁻, the Gibbs free energy of adsorption at 298 K is 0 kcal/mol, with entropic effects overcoming the long-range interactions between the ion and the graphite substrate.

Fig. 11 M06-2X/6-31G(d) adsorption energies (at 0 K) of [OMIm]⁺ and Tf₂N⁻ ions on graphite in the presence of a normal dipole electric field. Negative field strengths correspond qualitatively to negative potentials in experiment.

Conclusion

In this paper we have investigated the interface HOPG / [OMIm]Tf₂N with experimental and theoretical methods. Cyclic voltammetry shows that the electrochemical behaviour is mostly
featureless but reveals 2 cathodic processes that are not due to any macroscopically visible changes on the surface. In situ scanning tunneling microscopy shows that it is difficult to probe the HOPG surface with atomic resolution in the bulk liquid at all electrode potentials. This observation is supported by UHV scanning tunneling microscopy, where the hexagonal structure of clean HOPG is easily resolved whereas only a few monolayers of the ionic liquid lead to a strongly decreased resolution. Thus, the presence of the ionic liquid disturbs the tunneling process considerably. In situ STM experiments show that close to the cathodic limit of the electrochemical window different superstructures are observed which might be the result of several cation and/or anion layers probed at the same time by the STM tip. The lateral size of these structures (between 1.2 and 1.7 nm) suggests that cations and anions form ordered layers before the liquid is decomposed at the cathodic limit. In situ AFM measurements confirm the existence of several adsorbed layers within the potential window applied, whereas STM only shows ordered layers close to the cathodic limit of the liquid. DFT calculations show that the cation is more strongly adsorbed and closer to the surface than the anion. The adsorption of the cation is favoured upon reducing of the electrode potential whereas the adsorption of the anion is weakened. Our paper shows that the combination of different techniques allows a deep insight into the processes at the interface electrode ionic liquid under electrochemical conditions.

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Supporting Information Available

Normal force curves and the results of DFTB calculations are presented in the supporting information. This information is available free of charge via the Internet at http://pubs.acs.org.
References


TOC Graphic