Ionic Liquid / Electrode Interface

Differences in Structure as a Function of Ionic Liquid Species

Ionic liquids exhibit a remarkably diverse interfacial chemistry. Recent theoretical and experimental results show that conventional double layers do not form on metal electrodes in ionic liquid systems, rather a multilayer morphology is present. The number of layers and the strength of adsorption are strongly dependent on ionic liquid chemical species, solutes and applied electrode potential. Understanding of the interfacial structure is important for wider integration of ionic liquids.

Ionic Liquids in Focus of Research

Ionic liquids (ILs) are organic salts with melting points usually less than 100°C. They consist entirely of charged species (bulky organic cation and an organic or inorganic anion) and behave very differently to common molecular liquids. ILs are currently the focus of intense research activities due to their remarkable physical properties, which often include wide electrochemical windows, high conductivity, negligible vapor pressures, etc. Furthermore, all these properties can be modified by varying the cation/anion's chemical structure. A fascinating aspect of ILs is their variety: currently about 800 ionic liquids exist and around 1018 different liquids and mixtures have been predicted. IL applications encompass many areas including analytics, catalysis, chemical synthesis, separation technologies, electrochemistry, capacitors, batteries, fuel cells, solar cells, and lubrication. Many of these applications involve reactions at the IL/solid interface and a detailed understanding of the structure of this interface is important for a wider integration of ILs.

Ionic Liquids Studied by In Situ STM

The scanning tunneling microscope (STM) is a powerful tool allowing visualization of metal and semiconducting solid surfaces in real space with atomic resolution. Originally the STM was operated in ultrahigh vacuum (UHV) and air. Nowadays the STM can also be used in liquids as an in situ technique for electrochemical applications (e.g. electrochemical cells). In the electrochemical (in situ) STM the tunneling current flows between a metallic tip and a solid conductive sample, which are both immersed into the liquid solution (electrolyte).
During the measurement the sample also serves as a working electrode in a standard three electrode electrochemical cell containing a reference electrode and a counter electrode to complete the cell. The typical distance between the STM tip and the surface is about 1 nm, which means that the ions of an electrolyte adsorbed to the surface must be involved in the tunneling process. The STM tip must move through these adsorbed layers during the scanning. In this case the STM tip either images the layers, which are strongly adsorbed, or ruptures them.

During the last decade in situ STM has been extensively used to probe the IL structure at the IL/solid interface. Combined in situ STM and in situ atomic force microscopy (AFM) experiments reveal that ILs are strongly adsorbed to solid surfaces and several layers are present adjacent to surface [1-6]. The interfacial structure of ILs on metal electrodes differs depending on the IL chemical structure. The number of detectable ion layers and the strength of ion adsorption increase with increasing the electrode potential. At the open circuit potential as well as at negative electrode potentials, the innermost layer is enriched with cations, while at positive electrode potentials the anions are predominant in the innermost layer [5]. Such a strong, specific adsorption must influence electrochemical reactions [7].

**Results**

In situ STM suggests that IL ions facilitate restructuring the Au(111) surface [1-4]. At the open circuit potential (OCP) the gold surface has a worm-like appearance, when immersed in 1-butyl-1-methylpyrrrolidinium bis(trifluoromethylsulfonyl)amide ([Py$_{1,4}$]Tf$_2$N) (fig. 1a) or in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMIm]Tf$_2$N) (fig. 1b) [2], while in the case of 1-butyl-1-methylpyrrrolidinium tris(pentafluoroethyl)trifluorophosphate ([Py$_{1,4}$]FAP) the typical Au(111) surface is obtained (fig. 1c) [1]. In the cathodic regime the Au(111) surface undergoes a (22 × √3) surface reconstruction, when immersed in [Py$_{1,4}$]Tf$_2$N and [Py$_{1,4}$]FAP, leading to the herringbone superstructure (fig. 1d, f) [1-3]. However, in the case of ([EMIm]Tf$_2$N the herringbone superstructure was
not obtained (fig. 1e) [2]. These structures could be a consequence of ion adsorption, gold reconstruction or a combination of both effects. It is likely that different ions have different orientations in the interfacial layer depending on their chemical structure and the applied electrode potential, which in turn induce different surface structures. The AFM measurements revealed that both at OCP and at -1.0 V an innermost layer is enriched in cations [1, 2, 5]. However, at -1.0 V vs. Pt the width of the [Py$_{1,4}$]$^+$-ion layer becomes thinner, indicating that the cation adopts an orientation that renders it more parallel to the surface which induces the Au(111) (22 x $\sqrt{3}$) reconstruction (seen in fig. 1d, f). Gnahm et al. [8] and Su et al. [9] 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. Su et al. [9] reported the selective adsorption of imidazolium cations on the Au(100) surface but not on Au(111), suggesting that structural commensurability is required for cation adsorption to the surface.

Figure 2 represents the in situ STM images of highly ordered pyrolitic graphite (HOPG) substrate at the OCP and at cathodic polarization in 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([OMIm]Tf$_2$N) [4]. The periodic structure obtained at OCP is attributed to the superstructure of the underlying HOPG (fig. 2a). The image quality is lower compared to similar STM images in aqueous solutions that can be attributed to a stronger adsorption of the IL ions to the graphite surface. At -2.1 V vs. Pt an unusual periodic structure with semicircle-like structures of 1.2 nm in diameter forms (fig. 2b). By increasing the electrode potential a square-like structure with lattice spacing of 1.7 nm appears first at -2.0 V (fig. 2c) followed by the formation of a more complicated overstructure revealing "lines" with a spacing of 2 nm at -1.9 V (fig. 2d). These structures are correlated with adsorbed [OMIm]$^+$ cations as at this potential regime the innermost layer is highly enriched in cations and strongly bound to the graphite surface according to in situ AFM data and density functional theory (DFT) calculations [4].

Conclusions
These in situ STM results show that the IL chemical structure has a strong influence on the structure and composition of the IL/solid interface. However, solutes dissolved in ionic liquids (e.g. for the sake of electrodeposition) can also influence the interfacial structure. For instance, in situ STM measurements show that at negative electrode potentials both [Py$_{1,4}$]$^+$ and Li$^+$ ions interact with the gold surface leading to an incomplete herringbone reconstruction of Au(111) surface in [Py$_{1,4}$]FAP containing LiCl [10].
Outlook

Ionic liquids behave very differently to common molecular liquids. This remarkable difference is ascribed to higher adsorption strength of ILs onto solid surfaces compared to typical organic solvents or water. This might be due to specific ion/ion and ion/surface interactions that are strongly dependent on the type of the functional groups and therefore will be different for various ILs. Therefore, the structure and composition of the interfacial layer can be tuned by varying the surface potential and the ionic structure, and by addition of solutes. Such interfacial effects have to be considered for all applications that involve reactions at the IL/solid interface. Further studies of this interface both in the pure IL and in the presence of solutes are essential for better understanding of the IL's complex surface chemistry.

References

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