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In-situ STM and AFM Studies on Electrochemical Interfaces in Imidazolium-based Ionic Liquids

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Abstract

Voltammetric responses, adsorption behaviors and layered structures of 1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide (EMMITFSI) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI) at Au(111) have been investigated by cyclic voltammetry, in-situ STM and in-situ AFM force curve measurements, respectively. Cyclic voltammetry measurements pointed out that two pairs of sharp redox peaks are located at around 0.1 and 0.7 V in EMMITFSI, but not in EMITFSI. In-situ STM studies revealed no etching of the Au(111) surface in the investigated potential region in EMMITFSI, but an etched Au(111) surface was observed in EMITFSI in the same potential region, indicating that the interaction between EMITFSI and the Au(111) surface is much stronger than that between EMMITFSI and the Au(111) surface. In-situ AFM force curve measurements showed three layered structures at Au(111)/EMITFSI interface, but no force curves with saw-toothed feature can be

obtained when the potential is higher than +0.5 V, which implies the disappearance of layered structures. In EMMITFSI, force curves with saw-toothed feature can be obtained even at +1.2 V. The fact that layered structures can form in a broader potential region indicates that a stronger interaction exists between the EMMI cation and the TFSI anion. It is inferred that the methylation of the hydrogen position provides a configuration for EMMI cations with an increased hydrophobic interaction, which maintains the layered structure in wider potential region. As a consequence, the electrode potential may induce structural transition of the layered structures, which is responsible for the origin of the voltammetric features.

Keywords: Ionic Liquids; Electrochemical Interface; STM; AFM; Force curve

1. Introduction

Ionic liquids (ILs) are a type of molten salt composed of entirely organic cations and organic or inorganic anions with a melting point around room temperature [1-5]. Due to their wider electrochemical window, low vapor pressure, good conductivity and other designable properties, ionic liquids have been extensively used in electrochemical research [6-11]. However, high ionic strength and asymmetric structures of large organic cations make ionic liquids involve multi-natured interactions including columbic interaction, Van de Waals molecular interaction and hydrogen bonding [12]. The multi-natured interactions lead to the complexity of electrode/ILs interface, and thus ion adsorption on electrode surface, surface restructuring and particularly layered structure near electrode surface should be investigated to understand the structure of the interface [13-21].

A variety of techniques that can provide complementary information have to be employed to better characterize these complicated interfaces, preferably on well-defined model electrode surfaces, such as in situ scanning tunneling microscopy (STM) [22-25], atomic force microscopy (AFM) [26-30], vibrational spectroscopies (sum frequency generation [31, 32], Raman [33-35], and infrared spectroscopy [36, 37]), surface force apparatus [38, 39], X-ray reflection [40, 41] and electrochemical impedance spectroscopy (EIS) [42-45]. Recently, laser temperature jump method combined with well-defined single crystal electrodes was used to investigate the electrochemical interface in ionic liquids [46-49]. For Au(111) single crystal electrode in 1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide (EMMITFSI), the characteristic sharp spikes were observed on cyclic voltammograms [48, 49]. The sharp current peaks found in EMMITFSI have not been reported previously for other ionic liquids, and thus two plausible explanations, phase transition and ionic layer reorganization, were proposed. Therefore, further studies using techniques with high spatial resolution are desirable to provide additional information to discriminate the two explanations.

In this work, we investigated adsorption behaviors of EMMITFSI on Au(111) surface by in-situ

STM and layered structures of EMMITFSI at the interface by in-situ AFM force curve measurements. Since the chemical characteristic of EMMI cation is that the hydrogen position in C-2 of imidazolium ring is methylated, the comparative studies on 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI) without the corresponding methylation were also performed as control experiment. By comparing adsorption behaviors and layered structures of EMMITFSI and EMITFSI under potential control, a better understanding of the role of the methylation in the electrochemical structure of Au(111)/IL interface could be achieved.

2. Experimental

EMITFSI (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) and EMMITFSI (1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide) were purchased from IoLiTec in the highest available quality (99%). Prior to each measurement, 0.3 nm molecular sieve was added into ionic liquids and then the ionic liquids were vacuum-dried for 8 hours at 80 °C in a glovebox filled with ultra-pure Ar (99.999%) to remove the absorbed water and other impurities [50]. Au(111) single crystal electrodes were prepared following a modification of Clavilier's method [51-53]. The electrodes were subjected to electrochemical polishing and flame annealing in H₂ followed by cooling under a N₂ atmosphere prior to each experiment.

Cyclic voltammetry measurements were performed on an Autolab electrochemical workstation (Eco Chemie, The Netherlands) in a glovebox filled with ultra-pure Ar (99.999%). In-situ STM measurements were carried out on a Nanoscope E STM instrument (Veeco, Santa Barbara, CA) under constant-current mode and under the protection of N₂ atmosphere. Mechanically cut Pt/Ir tips were used, which were insulated by thermosetting polyethylene to reduce the faradaic current. A silver wire was used as a reference electrode, and a platinum wire was used as a counter electrode.

AFM force curve measurements were performed on Agilent 5500 SPM in ECAFM mode under the protection of N₂ atmosphere. Gold-coated silicon probes (NT-MDT, cantilever force constant 0.4 N/m calibrated by a thermal noise method) were employed. A Ag wire and a Pt wire were used

as reference and auxiliary electrodes, respectively. All potentials reported in this paper are versus Ag quasi-reference electrode. AFM force curve measurements obtain the vertical force that the tip applies to the sample. Then the acquired force-distance curves were converted to force-separation curves. Briefly, when tip contacts sample, the deflection of the cantilever is coupled with the movement of the piezo. The deflection signal is converted into units of distance. Hookes' law then translates the scaled deflection into units of force. The two-dimensional (2D) histograms were calculated using 50 measured force separation curve. The color represents the probability of a point of the force-separation plot. The red represents high probability, and the blue represents low probability.

3. Results and Discussion

Cyclic voltammetry measurements. Illustrations of chemical structures of two ionic liquids used in this work are shown in Figure 1. It can be clearly seen that the only difference between the two ionic liquids is that a H atom of the imidazolium ring at 2 position is substituted by a methyl group. Therefore, the effect of the alkyl side chain substitution on the electrochemical behavior and the interfacial structure can be studied by performing a comparative study on the two ILs. A cyclic voltammogram of Au(111) in EMMITFSI is shown in Figure 2 (see the solid line), and two pairs of sharp redox peaks can be clearly observed, which are superimposed on two capacitive processes. The two pairs of redox peaks are located at around 0.1 and 0.7 V, and marked by A1/C1 and A2/C2, respectively. In Feliu's work, the two pairs of redox peaks were also observed in the investigated potential region [48]. However, in EMITFSI no sharp current peaks appear in the same region, only a small charging current with current density lower than $15 \mu\text{A cm}^{-2}$ can be observed (dashed line in Figure 2). Therefore, the methylation indeed causes quite different voltammetric responses of the two ILs.

In-Situ STM Characterization. To compare the adsorption behavior of the two ionic liquids on Au(111) surface, in-situ STM experiments were carried out in the aforementioned potential

region. The STM images showing the evolution of adsorbed structures on the Au(111) electrode in EMMITFSI are shown in Figure 3. It can be seen that a clean Au(111) surface with three monoatomic steps separating wide terraces is observed at -0.1 V (Figure 3a). No adsorption of EMMITFSI appears on the surface until the potential is anodically increased to +0.7 V (Figure 3b and c). With a further positive potential increase, the surface terraces are gradually covered by disordered structures. Finally, a poorly ordered film layer is formed, coating the whole surface of the terraces with (111) orientation at 1.3 V (Figure 3d). It is worth noting that no etching of Au(111) surface occurs during the process.

However, in the presence of EMITFSI, an etched Au(111) surface is always observed in the investigated potential region as shown in Figure 4a-d. The etching leads to the existence of a worm-like network on the whole Au(111) surface. The inset in Figure 4a shows that the depth of etched surface is around 0.305 nm and the characteristic width of top strips ranges from 2 to 6 nm. The depth of the etched surface is larger than the height of monoatomic step of Au(111). Therefore, we infer that TFSI anions adsorbed on the upper part of the etched region in a flat configuration, but not on the lower part. Even when the potential is positively shifted to +1.1 V, the worm-like network still remains on the surface as shown in Figure 4d. In order to exclude a simple worm-like network of adsorbate layer and prove the etching of Au surface, an STM image is shown in Figure 4d as an inset. The STM image was obtained after the potential was moved negatively to +0.3 V, in which we can see that the etched Au surface restored to some extent after TFSI anions desorbed. The surface etching indicates that ion entity of EMITFSI has a very strong interaction with Au(111) surface [54-56].

Based on the adsorption behaviors of EMMITFSI and EMITFSI on Au(111) surface, it can be concluded that the interaction between EMITFSI and Au(111) surface is much stronger than that between EMMITFSI and Au(111) surface.

In EMMITFSI, in-situ STM experiments showed that no ordered adsorptive structure could be observed within the investigated potential region, indicating that the origin of sharp current peaks

A1/C1 and A2/C2 in Figure 2 would not be usual disorder/order 2D phase transitions. Generally adsorbates with ordered structures on single crystal surfaces present similar sharp peaks like ordered adsorption of ions on Au(111) and Pt(111) in aqueous solution [57-59]. It was suggested that these peaks might be due to the reorganization in the ionic layer near electrode surface, and the structure of the ionic layer keeps changing due to the scanning of the applied potential. On the other hand, it is well known that STM works based on the detection of tunneling current, so the information acquired by STM imaging was usually limited to species directly adsorbed on electrode surfaces. Therefore, it is meaningful to use AFM measurements to obtain the information of interfacial structures [60], which may be several nanometers or even further away from the electrode surface [61].

In-Situ AFM force curve measurements. AFM force curve measurements were conducted in the two ILs within potential region from -0.1 to +1.2 V. The potential region was chosen in order to cover the current peaks appeared on the CV of Au(111) in EMMITFSI. Fifty force curves were collected at each potential, which allows the preparation of two dimensional histograms of the force curves to demonstrate the fluctuation of these curves at the specified potential, and thus reasonably obtain the values of thickness and rupture force. The rupture force is the applied force by AFM probe to break through the solid-like layered structure. The larger rupture force is, the more stable layered structure is. Force-separation 2D histograms of Au(111) in EMMITFSI at -0.1 V and +0.5 V are shown in Figure 5. The two potentials are located at two sides of the first redox peaks of CV of Au(111) in EMMITFSI, see A1/C1 peaks in Figure 2. Force-separation 2D histograms at these two potentials present similar characteristics. Three layered structures at the interface can be observed from the Force-separation 2D histograms. The three layered structures were marked by L1, L2 and L3, which are three molecular layers (ion pairs) near the surface. The three molecular layers are detected via sequential rupture by the AFM tip. The rupture force and layer thickness of each layered structure may be read from the Force-separation 2D histograms. The thicknesses for the first layer at the two potentials are around 0.95 nm, which is larger than the length of individual

anion or cation, so we infer that the detected layered structure should be attributed to a molecular layer. Rupture forces of the first layer at the two potentials are also similar, and they are around 0.8 nN in both cases. The above results demonstrate that the stability of the layered structures in EMITFSI is similar in the investigated potential region. It is worth noting that when the potential is positive than +0.5 V, no force curves with saw-toothed feature can be obtained, which indicates the disappearance of layered structures. In our previous work, force curves with the saw-toothed feature were also unavailable when measurements were conducted in relatively positive potential region at the interface between Au(111) and other ILs including BMIPF₆ and BMPTFSI [29, 61].

However, in EMMITFSI, force curves with saw-toothed feature can be still obtained even when the potential is positively moved to +1.2 V, which means that the layered structures still exist. The fact that layered structures can be formed within a broad potential region implies that a stronger interaction exists between EMMI cation and TFSI anion, compared with that between EMI cation and TFSI anion. Force-separation 2D histograms of Au(111) in EMMITFSI at four different potentials are shown in Figure 6. The four potentials were selected according to the peaks A1 and A2 in Figure 2, i. e., the first potential is negative than peak A1, the second potential is positive than peak A1 but negative than peak 2, and the other two potentials are positive than peak A2. Different from those in EMITFSI, the characteristics of force-separation 2D histograms in EMMITFSI change significantly with the positive shift of potential. Firstly, the number of layered structures changes with the potential, i.e. three layers at 0.0 V and two layers at 1.0 V. At 0.5 and 0.7 V, the force curves fluctuate intensely although two layers possibly exist. The thicknesses of the first layer at 0.0 and 1.0 V are around 0.95 nm, which should be attributed to the existence of a molecular layer. Secondly, when the potential is positive than the peak potential of A1, the rupture force of the first layer decreases rapidly from 4.2 nN to a value less than 0.5 nN (Figure 6b). The fluctuation and the smaller rupture force suggest the non-uniformity and instability of the layered structures in the potential region where the redox peaks appear, that may have a tendency to result in structural transformation.

From the above results obtained by STM and AFM, it can be seen that the interaction between EMITFSI and Au(111) surface is quite strong and thus leads to the surface etching. In contrast, the interaction between EMMITFSI and Au(111) surface is not strong, but the layered structures at Au(111)/EMMITFSI interface are stable and can be detected by AFM in a wide potential region. The stability of the layered structure originated essentially from ions arrangement and the interactions among the ions, so we may correlate the stability with the structure. In EMITFSI, the rupture force (stability) of the first layered structure stays around 0.8 nN in the investigated potential region, which means very little changes for the layered structure with the potential. However, in EMMITFSI, the rupture force (stability) of the first layered structure changes from 4.2 to 0.5 nN in the investigated potential region, indicating that the layered structure varies greatly. Considering the fact that the only difference between the two ILs is the methylation at C-2 of imidazolium ring, it is reasonable to infer that the methylation has significantly influenced the interaction between the cations and the anions. The hydrogen bond plays an important role in the interaction in ILs. When a H atom of the imidazolium ring is substituted by a methyl group, the interaction between the cation and the anion, even the arrangement of all ions at the interface, might be significantly altered possibly due to the decrease of hydrogen bonding interaction and the increase of hydrophobic interaction. In the investigated potential region, the layered structures exist in EMMITFSI, but the structures are not stable enough and inclined to change under the driving of the potential change. The reorganization of the layered structures may include the number of the layers, the number of ions for each layer and the arrangement of ions. We infer that the reorganization of the layered structure leads to the change of capacitance and thus presents capacitive current, which was observed on cyclic voltammograms.

4. Conclusions

Studies on Electrochemical Interfaces between a Au(111) electrode surface and two ionic liquids, EMMITFSI and EMITFSI, have been carried out by cyclic voltammetry, in-situ STM and

in-situ AFM. Cyclic voltammetry measurements present two pairs of sharp redox peaks in EMMITFSI, which are located at around 0.1 and 0.7 V. However, no sharp current peaks appear in the same potential region in EMITFSI. In-situ STM studies revealed that an etched Au(111) surface was observed in EMITFSI in the investigated potential region, but not in EMMITFSI, which indicates that the interaction between EMITFSI and the Au(111) surface is much stronger than that between EMMITFSI and the Au(111) surface. In-situ AFM force curve measurements showed that three layered structures at Au(111)/EMITFSI interface were observed from the Force-separation 2D histograms. However, no force curves with saw-toothed feature can be obtained when the potential is positive than +0.5 V, which suggests the disappearance of layered structures. In EMMITFSI, force curves with saw-toothed feature can be obtained even when the potential is positively moved to +1.2 V. The presence of the layered structures in a broader potential region indicates that a stronger interaction exists between the EMMI cation and the TFSI anion. It is reasonable to infer that the methylation at C-2 of imidazolium ring provides a configuration for EMMI cations with an increased hydrophobic interaction and thus maintains the layered structure in wider potential region, which makes structural transitions possible, i. e., the electrode potential may induce structural transition of the layered structures, that is responsible for the origin of the voltammetric features. In brief, a stronger interaction between Au(111) surface and EMITFSI and a more stable layered structure in EMMITFSI were revealed by complementary in-situ STM and AFM, respectively, which provide a more complete picture of the interfacial structure in the two ILs and help to understand the origin of the two sharp current peaks of the cyclic voltammogram in EMMITFSI. Further research, such as theoretical calculation about the effect of the methylation on the interactions among ions and between ions and the electrode surface, is highly desirable to fully understand these complex interfaces.

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Author Contributions

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Figure captions:

Figure 1. Illustrations of chemical structures of (a) EMI⁺, (b) EMMI⁺, and (c) TFSI⁻. EMI⁺: 1-Ethyl-3-methyl imidazolium; EMMI⁺: 1-Ethyl-2,3-dimethyl imidazolium; TFSI⁻: bis(trifluoromethyl)sulfonyl imide.

Figure 2. Cyclic voltammograms of Au(111) electrode in EMMITFSI and EMITFSI. Scan rate: 100 mV·s⁻¹.

Figure 3. Sequence of STM images of Au(111) surface in EMMITFSI showing adsorption of EMMITFSI at (a) -0.1 V, (b) 0.3 V, (c) 0.7 V, and (d) 1.3 V. Scan size: 200 x 200 nm².

Figure 4. Sequence of STM images of Au(111) in EMITFSI showing adsorption of TFSI anions at (a) 0.6 V, (b) 0.8 V, (c) 1.0 V, and (d) 1.1 V. Inset of Figure 4a: Sectional analysis of the black line. Inset of Figure 4d: an STM image obtained after the potential was moved negatively to +0.3 V. Scan size: 200 x 200 nm².

Figure 5. Force-separation 2D histograms of 50 consecutively measured force curves of Au(111) in EMITFSI at (a) -0.1 V and (b) +0.5 V.

Figure 6. Force-separation 2D histograms of 50 consecutively measured force curves of Au(111) in EMMITFSI at (a) 0.0 V, (b) +0.5 V, (c) +0.7 V and (d) +1.0 V.

Figure 1, S. Liu

Figure 1. Illustrations of chemical structures of (a) EMI^+ , (b) EMMI^+ , and (c) TFSI^- . EMI^+ : 1-Ethyl-3-methyl imidazolium; EMMI^+ : 1-Ethyl-2,3-dimethyl imidazolium; TFSI^- : bis(trifluoromethyl)sulfonil imide.

Figure 2, S. Liu

Figure 2. Cyclic votammograms of Au(111) electrode in EMMITFSI and EMITFSI. Scan rate: $100 \text{ mV} \cdot \text{s}^{-1}$.

Figure 3, S. Liu

Figure 3. Sequence of STM images of Au(111) surface in EMMITFSI showing adsorption of EMMITFSI at (a) -0.1 V, (b) 0.3 V, (c) 0.7 V, and (d) 1.3 V. Scan size: 200 x 200 nm².

Figure 4, S. Liu

Figure 4. Sequence of STM images of Au(111) in EMITFSI showing adsorption of TFSI anions at (a) 0.6 V, (b) 0.8 V, (c) 1.0 V, and (d) 1.1 V. Inset of Figure 4a: Sectional analysis of the black line. Inset of Figure 4d: an STM image obtained after the potential was moved negatively to +0.3 V. Scan size: 200 x 200 nm².

Figure 5, S. Liu

Figure 5. Force-separation 2D histograms of 50 consecutively measured force curves of Au(111) in EMITFSI at (a) -0.1 V and (b) +0.5 V.

Figure 6, S. Liu

Figure 6. Force-separation 2D histograms of 50 consecutively measured force curves of Au(111) in EMMITFSI at (a) 0.0 V, (b) +0.5 V, (c) +0.7 V and (d) +1.0 V.