



Short communication

# Potential-dependent condensation of Water at the Interface between ionic liquid [BMIM][TFSA] and an Au electrode

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## ABSTRACT

Surface-enhanced infrared absorption spectroscopy (SEIRAS) at the interface between humid 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([BMIM][TFSA]) and an Au electrode reveals that water molecules strongly interact with the anion and are condensed at the interface at high potentials where the anion is the major adsorbate.

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Interfacial water

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## 1. Introduction

Room temperature ionic liquids (RTILs) are promising electrolyte materials for electrochemical devices owing to their fascinating properties such as high thermal and electrochemical stabilities [1–5]. For such applications, it is essential to uncover the structures and dynamic behavior of RTILs on electrode surfaces [6,7]. The conventional Gouy–Chapman–Stern (GCS) model of electric double layer is not directly applicable to RTILs that are full of ionic species [8–10]. Multiple layer-by-layer stacking of cation and anion has alternatively been proposed as a model for the RTIL/electrode interfaces [11–13]. Various surface-sensitive vibrational spectroscopy techniques have revealed potential-dependent reorientation and adsorption/desorption of ions at the interface [14–19]. By using surface-enhanced infrared absorption spectroscopy (SEIRAS) [20], one of the most powerful tools for probing RTIL/electrode interfaces [21,22], we have shown that the cation dominates the negatively charged surface and the anion dominates the positively charged surface, and that the exchange of ions at the interface exhibits a hysteretic behavior against potential excursions due to the coulombic interactions among the ions [23].

Most RTILs are hygroscopic and absorb a large amount of water from the atmosphere. Water molecules form hydrogen-bonded (H-bonded) network in bulk RTILs as in aqueous solutions at high concentrations, while at sufficiently low concentrations they are free from H-bonding [24,25]. They exist near ionic parts of nano-segregations in bulk RTILs [26,27], and interact with two anions or with the aromatic hydrogen of cations [24,25,28]. Even at small contents, water reduces the viscosity of RTILs [29] and accelerates self-diffusion of ions [30].

An open question is how water molecules behave and affect the arrangement of ions in RTILs in the vicinity of the electrified interfaces. Because of the different structures of RTILs in the bulk and near the interfaces, solvation states of water are also expected to be different. Recent molecular dynamics (MD) simulation suggested that water molecules are condensed near charged carbon electrode [31]. The condensation of water at the interfaces can affect electrochemical reactions, such as CO<sub>2</sub> reduction in which water act as hydrogen source [32,33], and degradation of both RTILs and electrodes which may result in narrower electrochemical windows [34]. However, such behavior of water near the electrode has not been confirmed experimentally yet. Since the complete removal of water from RTILs is difficult and costly, it is essential for practical applications of RTILs to electrochemical devices to examine the effect of low contents of water on the structure and dynamics of RTILs at the electrode surface at the molecular scale.

In this communication, we will provide the first experimental evidence for water condensation and H-bonding formation at an Au

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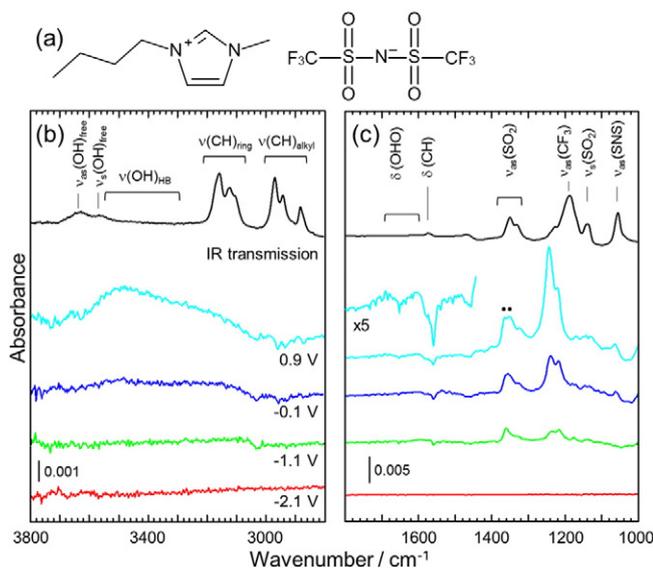
electrode in [BMIM][TfSA] even at low concentrations where water molecules in the bulk are free from H-bonding.

## 2. Experimental

Pretreatment of [BMIM][TfSA] (Iolitec, Fig. 1a) and preparation of the spectroelectrochemical setup for SEIRAS have been described elsewhere [23]. The SEIRAS measurement was first performed under vacuum condition where water content  $c_w < 1$  ppm (referred to as the dry [BMIM][TfSA]) and then applied to the humid [BMIM][TfSA] where  $c_w = 700$  ppm obtained by exposing the dry [BMIM][TfSA] to the water-saturated Ar gas for 40 min. The water content was measured after SEIRAS measurements by using a Karl–Fischer titration apparatus (Mitsubishi Chemical, CA 200). The water content of 700 ppm is a possible level in real batteries and capacitors, and is comparable with the concentration used for the MD simulation [31].

## 3. Results and discussion

Fig. 1b and c shows the SEIRA spectra of the interface between humid [BMIM][TfSA] and the Au electrode collected during a potential scan from  $-2.1$  to  $0.9$  V vs  $Fc/Fc^+$  at  $2$  mV s $^{-1}$ , where the spectrum at  $-2.1$  V was used as the reference. Since the SEIRA effect is significant at the surface and fades away within a several ionic layer distance from the surface [20,23], the up-going (down-going) bands are ascribed mostly to the increase (decrease) in the concentration of the corresponding species in the near vicinity of the electrode surface. The observed spectra are nearly identical to those observed for dry [BMIM][TfSA] [23] except for the presence of the broad bands at  $3050$ – $3600$  cm $^{-1}$  and  $1600$ – $1700$  cm $^{-1}$ , and the split of the SO asymmetric stretching mode  $\nu_{as}(SO_2)$  of the anion ( $1366$  and  $1353$  cm $^{-1}$ ) in the former. The assignments of the bands are indicated on the transmission spectrum of the humid [BMIM][TfSA] (top most spectrum in Fig. 1). The significant blue-shift of the C–F stretch modes  $\nu(CF_3)$  in the SEIRA spectra compared to the transmission spectrum originates from the large dispersion of the refractive index of [BMIM][TfSA] in this spectral range [23,35,36]. As the potential is made more positive (i.e., the surface is charged more positive), the bands of the cation decrease and those of the anion increase. The same behavior has been observed also for dry [BMIM][TfSA] [23].



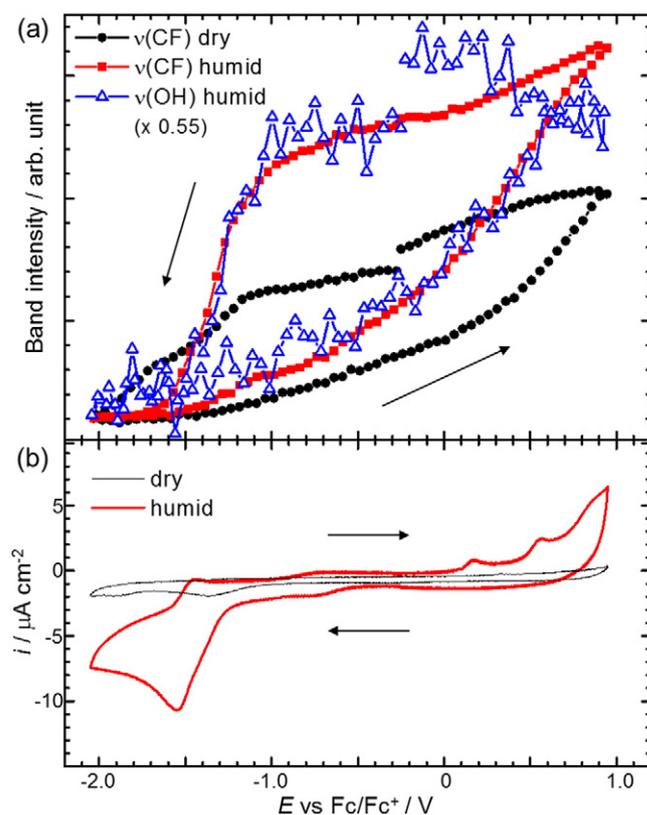
**Fig. 1.** Chemical structure of [BMIM][TfSA] (a) and SEIRA spectra of [BMIM][TfSA]/Au with  $c_w = 700$  ppm in (b)  $3800$ – $2800$  cm $^{-1}$  and (c)  $1800$ – $1000$  cm $^{-1}$  regions recorded during a positive-going scan at  $2$  mV/s. The reference spectrum was collected at  $-2.1$  V vs  $Fc/Fc^+$ . s, as,  $\nu$ , and  $\delta$  in mode assignment indicate symmetric, asymmetric, stretching and bending vibration, respectively.

An important observation in the experiment is the very broad asymmetric feature peaked at  $\sim 3500$  cm $^{-1}$  at high potentials. Similar spectral feature can be found in SEIRA spectra at the interface between acidic aqueous solutions and Au electrodes [37,38] and assigned undoubtedly to the O–H stretch mode of strongly H-bonded water  $\nu(OH)_{HB}$ . The shoulder around  $3200$  cm $^{-1}$  is assigned to either the overtone of the bending mode  $\delta(HOH)$  enhanced by the Fermi resonance with  $\nu(OH)_{HB}$  or the  $\nu(OH)$  of the so-called ice-like water.

The water spectrum at the interface is largely different from that of water dissolved in the bulk [BMIM][TfSA]: in the latter, the sharper  $\nu_{as}(OH)$  and  $\nu_s(OH)$  characteristic to free water is observed at  $3643$  and  $3580$  cm $^{-1}$ , respectively (the top most spectrum in Fig. 1). The  $\nu(OH)_{HB}$  was observed in the bulk spectrum only at much higher water contents, as has been reported in the literature [24,25].

The integrated intensity of  $\nu(OH)_{HB}$  band increases with increasing potential (vice versa) as shown in Fig. 2 (blue triangle symbols). This band was not observed when the spectrum at  $-2.1$  V for the humid [BMIM][TfSA] was referenced to that for dry [BMIM][TfSA] (not shown), indicating that the amount of interfacial water at the reference potential is negligible, if any. Accordingly, it is concluded that water molecules are condensed only at the positively charged electrode surface to form a strongly H-bonded network as in the bulk water.

It is worth noting that the band intensity of  $\nu(OH)_{HB}$  of water increases/decreases in parallel to that of  $\nu(CF_3)$  of [TfSA] and both bands show similar hysteretic behavior against the potential cycle as shown in Fig. 2a. Hysteresis of  $\nu(CF_3)$  is observed also for dry [BMIM][TfSA] and its origin has been discussed in our previous publication [23]. Briefly, cation–anion interaction stabilizes a quasi-periodic layer-by-layer arrangement of the ions at the interface; therefore,



**Fig. 2.** (a) SEIRAS band intensities as a function of potential recorded at every  $0.05$  V interval during a potential scan at  $2$  mV/s in dry ( $c_w < 1$  ppm) and humid ( $c_w = 700$  ppm) [BMIM][TfSA]. Band intensities are obtained by direct integration of the bands with respect to a local baseline. The intensity of  $\nu(CF)$  includes the bands for  $\nu_s(CF_3)$  and  $\nu_{as}(CF_3)$ . (b) CVs simultaneously measured with SEIRAS in dry and humid [BMIM][TfSA].

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