

***In Situ* Surface-Enhanced Infrared Absorption Study of Protic Ionic Liquids/Pt Interfaces**

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Protic ionic liquids (PIL) have emerged as promising electrolytes for various future applications, *e.g.*, polymer electrolyte fuel cells (PEFC), because of their intrinsic proton activity, low volatility and high thermal and chemical stability [1]. Since electrochemical performance is governed by processes at electrode/electrolyte interfaces, a molecular level understanding of the interfacial structure during operation is essential.

Unlike diluted aqueous electrolytes, ionic liquids (IL) exhibit a high density of charge carriers in the bulk as well as at the electrode interface, without screening by a dielectric solvent. In the last years, significant progress has been made in studying IL interface, but almost all of the studies have focused on aprotic ionic liquids (AIL) on model electrode surfaces such as Au, Ag or highly oriented pyrolytic graphite (HOPG). In contrast, the interfacial structure of PILs, particularly on catalytic active electrodes such as Pt is far less explored. In PILs, the presence of proton donors and a network of hydrogen-bonds further increase the interfacial complexity. The ion adsorption behavior on Pt in PILs has been investigated by infrared reflection absorption spectroscopy (IRRAS) in a preceding study [2]. However, there are some intrinsic limitations on the IRRAS configuration such as restricted mass transport in a thin electrolyte layer and a slow response to the applied potential. To avoid these issues, an alternative approach is made by employing attenuated total reflectance surface enhanced infrared absorption spectroscopy (ATR-SEIRAS).

An in-house built spectro-electrochemical cell with a micromachined silicon ATR wafer with a thin Pt electrode layer is used for *in situ* SEIRAS measurements. Various PILs are investigated, composed of the cations, diethylmethylammonium [Dema]⁺ and 1-ethylimidazolium [EIm]⁺ and the anions, bis(trifluoromethanesulfonyl)imide [TFSI][−] and triflate [TfO][−]. As the hydrogen bonding between the active proton of the cation and the anion strongly influences the N–H stretching mode, leading to an overlap with the O–H and C–H stretching modes, also deuterated PILs were prepared for comparison.

The measurements reveal a potential-dependent interfacial rearrangement, evidenced by intensity changes of the ion-specific vibrational bands. As expected, the anions are exchanged by cations at increasingly negative potentials, *i.e.*, towards potentials below the point of zero charge (PZC). However, a hysteresis of the adsorption/desorption is observed. The TFSI-based PILs exhibited a more pronounced hysteresis, suggesting slower interfacial restructuring due to stronger interaction between [TFSI][−] and the Pt surface. In contrast to previous IRRAS results [2], the intensity of the O–H stretching mode due to interfacial water is increasing during a scan towards positive potentials. This observed water accumulation at high potentials is consistent with theoretical predictions for AILs. An interesting discrepancy revealed by simulations is that for hydrophobic AILs the adsorption of water is also enhanced, as the potential shifts to more negative values relative to the PZC [3]. Extending the upper potential limit into the Pt oxidation region reveals, that the water consumption and generation during Pt oxidation and reduction also contributes to the intensity variations of the O–H stretching band. Furthermore, an ultraslow relaxation of band intensity occurs during the potential step measurement. The implications of this slow response as well as time scales of multiple processes at PILs/Pt interfaces still remain to be explained by comparing with the results from other experimental techniques (*e.g.*, impedance spectroscopy) and theoretical studies.

References

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