

ADSORPTION OF SULFONYL-GROUP BASED ANIONS FROM IONIC LIQUIDS: AN *IN SITU* STM AND IMPEDANCE STUDY

Georg Gorbatovski, Ove Oll, Jinfeng Zhao and Enn Lust

Institute of Chemistry, University of Tartu

Ravila 14A, 50411 Tartu, Estonia

georg.gorbatovski@ut.ee

Adsorption of particles, such as molecules or ions, is an important basis for many everyday phenomena, such as corrosion inhibition or chromatographic separation. Although the formation of the EDL in ILs has been in the scientific focus for over a decade, there is still a lack of understanding with regard to the specific interaction of ions at IL|metal interfaces [1].

To overcome these problems, both classical electrochemical methods (cyclic voltammetry and electrochemical impedance spectroscopy) as well as *in situ* scanning tunneling microscopy (STM) method have been applied to observe the interfacial structuring at electrode|IL interfaces. Three sulfonyl-group based anions - triflate (OTf), mesylate (Mes) and bistriflimide (TFSI) have been chosen for their potential ability to chemically bond to the surface through the sulfonyl groups, which has been demonstrated in aqueous solutions, but not ILs. These anions have been combined with aliphatic imidazolium cations that are generally thought to not specifically adsorb at the metallic electrodes. It is observed that sulfonyl-group anions show a largely different adsorption behavior at Bi electrodes compared to that of halide anions studied in our previous paper: adsorption of OTf, Mes and TFSI anions is a very slow process and the adsorbed layer acts as a dielectric at the surface, therefore considerably lowering the amount of charge that can be stored. OTf and TFSI anion containing ILs also demonstrated wider electrochemical stability ranges compared with halide ion based ILs, which averaged to 2.3V opposed to the 1.4V of halide-based systems, while Mes anion based ILs did not.

It should be noted that adsorbed sulfonyl-anions form two stable polarization regions (electrostatic and dielectric chemisorbed regions) that can be switched between by varying the applied potential value, possibly contributing to a new electronic memory type system.

References

1. M.V. Fedorov, A.A. Kornyshev, Ionic liquids at electrified interfaces, *Chem. Rev.* 114 (2014) 2978–3036.
2. O. Oll, C. Siimenson, K. Lust, G. Gorbatovski, E. Lust, Specific adsorption from an ionic liquid: impedance study of iodide ion adsorption from a pure halide ionic liquid at bismuth single crystal planes, *Electrochimica Acta*. 247 (2017) 910–919



Euroopa Liit
Euroopa
Regionaalarengu Fond



Eesti
tuleviku heaks