

SPECIFIC ADSORPTION FROM AN IONIC LIQUID: IN SITU STM AND IMPEDANCE STUDY OF THE INTERFACIAL STRUCTURING AT BI SINGLE CRYSTAL PLANES

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Ionic liquids are versatile solvents and electrolytes for many electrochemical applications, such as secondary batteries, capacitors, solar cells and electrochemical deposition[1]. In order to rationally design and further develop such systems, however, a detailed understanding of the processes that govern the interfacial processes and stability of ionic liquid interfaces is required. It is thus the focus of this work to provide detailed understanding of the concentration dependent activity of halide ions in an ionic liquid and to explore the effect of ion activity on the nanoscale stability of Bi(*hkl*) electrode surfaces.

Potentiometry, cyclic voltammetry, electrochemical impedance spectroscopy and *in situ* scanning tunneling microscopy (STM) have been applied to explore the concentration dependent activity of halide ions and to demonstrate how the activity of halides affects the electrochemical stability and 2D layer formation at Bi(*hkl*) electrode surface in ionic liquids. It is shown that, different from aqueous and organic electrolyte solutions, the ionic liquid media promote ion aggregate formation and complex cations can exist in many different valence states, dependent upon the concentration of complex forming ions. The effects of the ion activity are evident from *in situ* STM measurements, as the surface of a Bi(111) electrode is stable in both ionic liquids that contain no halide additions as well as those with a saturated amount of halide ionic liquids, but is unstable in mixtures containing a small or medium amount of halide ionic liquid additions. Electrochemical measurements show that different processes and mechanisms are required to describe the concentration dependence of the specific adsorption of halide ions at a Bi(*hkl*) electrodes. *In situ* STM measurements demonstrate that the formation of a tightly packed 2D layer of specifically adsorbed ions is only formed in concentrated mixtures of halide ionic liquids thus determining the corrosion behaviour of the interface.

Acknowledgements

This work was supported by the Estonian Ministry of Education and Research (projects no. IUT 20-13, PUT55, PUT1033 and PUT1107) and Estonian Centres of Excellence project TK141.

References

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