Structural Investigation of Adsorption at the Liquid Mercury-Electrolyte Interface by X-Ray Reflectivity

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The interface between the liquid mercury electrode and an electrolyte solution has been extensively studied with electrochemical methods. It has been central for the verification of traditional and modern theories of the electrochemical double layer [1]. Although the contribution of the metal interface structure to the double layer capacity is known [2], a verification of this structure is very challenging as most experimental techniques can not be applied to liquid interfaces.

In a first atomic resolution X-ray reflectivity study of liquid mercury electrodes in a simple electrolyte solution (0.1M NaF), our group had clarified the interfacial layering of the Hg atoms [3]. By reproducing these experiments at our recently developed dedicated Liquid Surface Diffractometer LISA [4] at the PETRA III beam line P08 we have demonstrated the ability to record high quality X-ray reflectivity curves at a liquid-liquid interface with LISA (Figure 1). Additionally due to the novel setup of the diffractometer, which avoids the movement of the sample during the reflectivity, we were able to reduce the measurement time by 20%.

![Figure 1](image)

Figure 1: a) X-ray reflectivity of the Hg-0.01M NaF interface (red) and Fresnel reflectivity with added roughness of 1.2 Å (black). This experiment was carried out at LISA at the beamline P08 at PETRA III at a photon energy of 22 keV; b) Corresponding electron density profile in the direction normal to the interface.

By using a more complex electrolyte solution the adsorption of molecules at the liquid mercury electrode can be studied. Electrochemical methods can give quantitative information about the adsorbed molecules but not directly on the structure of the adsorbed layer whereas X-ray reflectivity can provide structural information up to the atomic scale. For this experiment the electrolyte was changed to a mixture of 0.01M NaF, 0.01M NaBr and 0.1mM PbBr₂. X-ray reflectivity measurements have been carried out to reveal structural information perpendicular to
the interface on an atomic scale. During the X-ray reflectivity measurements the interface was held under electrochemical control to create a defined electrochemically adsorbed layer on the mercury electrode and to be able to investigate a possible effect of the applied potential on the adsorbed layer. Our measurements show that we can reversibly adsorb PbBr\textsubscript{2} at the Hg-electrolyte interface.

![Figure 2](image.png)

Figure 2: Structural investigation of the Hg-0.01 M NaF + 0.01 M NaBr + 0.1 mM PbBr\textsubscript{2} interface: a) X-Ray reflectivity curves of the mercury-electrolyte interface at different applied potentials: -0.75 V (green), -0.28 V (red) and -0.589 V (black). Inset: Cyclic voltammogram of the investigated system, potentials of X-ray reflectivities are marked. All potentials are given relative to the Hg/Hg\textsubscript{2}SO\textsubscript{4} electrode; b) Diffuse scattering at different q\textsubscript{z} values at a potential of -0.75 V. This experiment was carried out at LISA at the beamline P08 at PETRA III at a photon energy of 25 keV.

At potentials negative of the adsorption peak at -0.7 V (relative to the Hg/Hg\textsubscript{2}SO\textsubscript{4} reference electrode) in the cyclic voltammogram (figure 2, inset) the reflectivity reveals no significant differences compared to the Hg-0.01M NaF interface. Whereas at potentials positive of -0.7 V oscillations are found in the reflectivity, indicating the formation of an adsorbate layer with a thickness of 7-8 Å. In addition the structure of the adsorbate layer has been found to be influenced by the applied potential as can be seen by the black and red curve in figure 2a).

By use of X-ray reflectivity we were able to investigate the interfacial structure of the mercury-electrolyte interface and the thickness of a layer adsorbed at the interface. We plan to use Grazing Incidence Diffraction to study the in-plane structure of the 2 dimensional adsorbate layer in the next phase of this investigation.

The project was funded by the BMBF projects 05 KS7FK3 and 05 K10FK2.

References