

Gold electrodes emersed from aqueous electrolytes: A Kelvin probe and infrared spectroscopy approach

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The study of the electric double layer (solid/liquid interface) is of crucial importance for an in-depth understanding electrochemical processes. However, the electrochemical interface (or interphase) is usually buried under a barrier of bulk water which is blocking direct access for most analytical tools. One way to enable direct access is e.g. the emersed electrode concept. For this, electrodes are emersed under potential control from the electrolyte into an inert atmosphere. It was shown in prior works for emersion into UHV [1] and into humid nitrogen [2] that the electrochemical double layer seems to be kept more or less intact during this process. However, thus an electrochemical double layer is obtained that is vertically confined to just one or two monolayers, depending on the humidity of the environment. The Kelvin probe technique can be employed for measuring the resulting electrode potential of such emersed electrodes [3], often providing a linear correlation between applied potentials during the electrochemical polarization and the potentials determined after emersing the sample from the electrolyte [2]. An open question is the role of the amount of water molecules in the double layer on the electrode potential [1,2]. A powerful technique for the investigation of the structure of the water molecules in the double layer region is infrared spectroscopy. Since infrared spectroscopy techniques (using an ATR set-up) can also be applied for characterization of the electrode immersed bulk electrolyte [4], a direct comparison between these two cases is possible.

For this work, NaClO₄ and H₂SO₄ diluted aqueous solutions were used as electrolytes, which both present anions with similar specific adsorption [5]. The Kelvin probe tip was calibrated against an Ag/AgCl/KCl homemade reference electrode [6]. Different atmosphere conditions (relative humidity) were used and their effect on the emersed electrode was investigated by Kelvin probe and IR spectroscopy. Furthermore, studies employing Near Ambient Pressure X-Ray Photoelectron Spectroscopy (NAP-XPS) technique have been conducted in order to detect the presence of anions and cations in the electrochemical double-layer and also for *in operando* studies with different atmosphere conditions.

Literature:

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