X-Ray Absorption Spectroscopy Study of Water Molecules at the Water/Electrode Interfaces

Cheng Hao Wu, Juan J. Velasco-Velez, Miquel B. Salmeron
Materials Sciences Division, Lawrence Berkeley National Laboratory
1 Cyclotron Road, Berkeley, CA 94720

Most of the electrochemistry processes occur within the thin layer of water or solution at the electrolyte/electrode interfaces, commonly denoted as the electrical double layer (EDL). In spite of some classic EDL theories, very limited experimental information is available about these solvent or solute species within such EDLs.

We have developed an in-situ x-ray absorption spectroscopy (XAS) technique to characterize these species at such liquid/electrode interfaces under electrochemical conditions.[1] As an example, at the interface between gold electrode and water, it was found that without any bias, water molecules within the EDL have fewer broken hydrogen bonds compared to bulk water, which exhibits much weaker pre-peak feature in the oxygen K-edge spectrum (**Figure 1**). While applying different bias between the gold and the counter electrodes, the polar water molecules within the EDL can respond to the external electrical field and reorient at the gold surface. Under positive bias, more oxygen atoms were forced to orient towards gold, resulting in fewer broken hydrogen bonds; thus pre-peak features in the oxygen K-edge spectrum is further suppressed. Under negative bias, the oxygen atoms were forced to orient away from gold, leading to more broken hydrogen bonds and thus stronger pre-peak features.

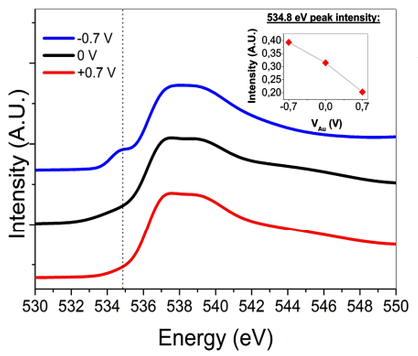

Figure 1 Oxygen K-edge spectra (total electron signal) under different bias (vs. silver wire reference electrode).

This in-situ XAS technique can be potentially applied to other electrochemical systems, to investigate the orientation, intercalation and other important electrochemical phenomena related to solvent or solute species within EDLs.

Reference:

[1]. J. J. Velasco-Velez, C. H. Wu, M. B. Salmeron, *in preparation*.