

Probing atomic charges at the electrochemical interface through Resonant Surface X-Ray diffraction

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An unsolved and crucial question in electrochemistry is the issue of charge transfer between the metal electrode and the adsorbate as this defines the nature of the bonding. Although there have been several theoretical studies of the charge transfer mechanism, initially in ideal UHV conditions but recently with extension to the electrochemical interface, there have been few experimental electrochemical studies due to the complexity of the electrochemical environment which is inaccessible to electron-based surface probes of charge transfer. A fundamental understanding of the nature of the charge transfer, especially the influence of the applied potential and the screening by the electrolyte, is a major goal in electrochemistry. We performed in-situ resonant surface x-ray scattering experiments for the halide Cu(001) system to investigate the suitability of this technique to probe the charge transfer and nature of the chemical bonding in-situ for such systems and to give detailed information of the atomic subsurface charge at the interface.

Halide adsorption onto a Cu(001) electrode is an ideal system in which to attempt this measurement, as the halides, Br and Cl, both form simple ordered $c(2 \times 2)$ adlayers on the Cu(001) surface. These are simple square structures with a coverage of 0.5 halide atoms per surface Cu atom and adsorption uniquely into the 4-fold Cu hollow site. The $c(2 \times 2)$ cell gives rise to additional surface scattering that is independent from the Cu crystal truncation rods (CTR's). In the experiment it is therefore possible to probe the surface Cu atoms, by performing resonant measurements at the 'anti-Bragg' positions of the Cu CTR's and at the $c(2 \times 2)$ superstructure positions. A shift in the adsorption edge is then indicative of a change in the charge state of the surface Cu atoms. More detailed information can be obtained by modelling the experimental data through single atomic charges.

This is the first direct experimental proof of partial charge transfer and subsurface charge distribution at the electrochemical interface. These measurements show that resonant x-ray scattering is an excellent tool to investigate the charge transfer at an electrochemical interface and will shed light on the nature of the chemical bonding at the interface and the role of the double layer.