

Probing the Electrical Double-Layer Structure at the Rutile-Water Interface with X-Ray Standing Waves

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Knowledge of the ion distribution at the solid-liquid interface, generally referred to as the electrical double-layer (EDL), is fundamentally important. The current theoretical models of the EDL are generally limited by a lack of direct information about the EDL structure, particularly through *in-situ* studies. In particular, the physical significance of the distinct layers used in the context of current models (e.g. the triple layer model) has yet to be clearly established (Criscenti et al., 1999).

In this paper we demonstrate the capability to directly probe the ion distribution near the rutile-water interface using the x-ray based techniques of x-ray standing waves (XSW) and surface x-ray adsorption spectroscopy (EXAFS) (Fenter et al., 2000). Of the many surface-sensitive techniques available, X-ray based techniques are promising as a means to elucidate the structure of the EDL. The weakly interacting nature of hard x-rays makes it possible to directly probe the liquid-solid interface under the conditions of interest. The measurements are truly quantitative since the interaction of x-rays with matter is well-understood. The length scales over which x-ray scattering techniques naturally probe (from $\sim 1\text{\AA}$ to $\sim 10^4$) is also well matched to the length scales present in double layer structure.

We use the (110) surface of the TiO_2 polymorph rutile for this study since it has been extensively studied and is known to be chemically stable over a broad range of pH (Machesky et al., 1998), and the rutile (110) surface exhibits only minor structural relaxations. Finally, the surface charge behavior of rutile has been extensively studied and reveals the pH of zero surface charge, $\text{pH}_{\text{pzc}} = 5.4\text{--}5.7$ (Machesky et al., 1994; Machesky et al., 1998). Together these previous studies provide a significant database from which the present results can be interpreted. Our experimental results show that the Bragg XSW technique, using small-period standing waves generated by Bragg diffraction from the rutile substrate, can precisely and directly measure (1) the ion location within the condensed layer, and (2) the *in situ*

partitioning of ions between the condensed and diffuse layers. Differences in condensed layer ion positions were observed among the *in situ* Sr and Rb ion heights and the *ex situ* Sr ion height. Using *ex situ* measurements, the Sr adsorption site geometry was determined by combining the XSW results with polarization-dependent surface EXAFS measurements. A comparison of our results to previous potentiometric titration studies of Na, Ca adsorption to rutile (Ridley et al., 1999) suggests that the dielectric constant of the near-surface water can be directly determined through a comparison of the XSW and potentiometric titration studies (Fenter et al., 2000). We also discuss our most recent studies where XSW was used to probe the ionic strength dependence of the divalent Zn and Sr ion heights over a broad range of ionic strengths (0.001M to 3M).

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