421a Microscopic Structure of the Electric Double Layer at the Cassiterite Surfaces

Lukas Vlcek and Peter T. Cummings

To develop a realistic model and usable theory of the electric double layer (EDL) at metal oxide – water interfaces, detailed and unambiguous information on the structure and dynamic properties at the molecular level is needed. In this study, we use molecular dynamics simulations to obtain data on the microscopic structure of the EDL formed at the interface between various types of cassiterite (α-SnO_2) surfaces and water or aqueous solutions of electrolytes at ambient and hydrothermal conditions. Cassiterite was chosen as a model system with the same structure as previously studied rutile (α-TiO_2) but with much lower dielectric constant. The results can thus provide insight into the relative importance of structure and electrostatics on the formation of the EDL. The electrolyte solution is modeled by SPC/E water and ions (Na^+, Rb^+, Ca^{2+}, Sr^{2+}, Zn^{2+}, and Cl^-) with interactions optimized for use with the SPC/E potential. For interactions of cassiterite and surface hydroxyl groups with water, we use a recently developed forcefield [1] based on ab initio calculations. To avoid the formidable complexity of simulating surface chemistry, we adopt an approach tested in the previous study of rutile surface [2] and mimic the dissociation of water by directly binding hydroxyl groups to defined places on the cassiterite surface. Guidance in the construction of the surface hydroxylation is provided by macroscopic data from titration experiments. The structure of the first two molecular layers is studied in detail including orientation of water molecules, hydrogen bonding, ion adsorption, and the formation of complexes of cations with surface oxygens. In particular, such information is needed for further development of the multisite complexation (MUSIC) theory [3]. The structural predictions from simulations are compared to data from X-ray experiments. Further, we study electrostatic properties of the EDL and dynamic properties such as diffusivity with the aim of identification of the shear plane and calculation of the ζ potential.

References:

[1] Bandura, A. V., Sofo, J., and Kubicki, J. D., J. Phys. Chem. B, submitted.

[2] M. Předota, A. V. Bandura, P. T. Cummings, J. D. Kubicki, D. J. Wesolowski, A. A. Chialvo, and M. L. Machesky, J. Phys. Chem. B 2004, 108, 12049-12060.

[3] M. L. Machesky, D. J. Wesolowski, D. A. Palmer, and M. K. Ridley, J. Colloid Interface Sci. 2001, 239, 314-327.