

## Effect of Solvation dynamics and Local Ordering on Chloride Ion Transport Near a Passive Oxide Surface

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Pitting corrosion refers to localized degradation of metals when they are exposed to aggressive halide ions such as chlorides. These are typically initiated at the defect sites such as oxygen vacancy. Understanding the mechanism of pit initiation and propagation is an active area of corrosion research. Specifically, the mechanistic details of the sequence of steps which lead to the onset and propagation of pitting corrosion on metal surfaces is the most important issue which remains to be addressed. Towards this end, solvation dynamics and local ordering of the aqueous electrolyte is of the critical factors that might influence ion transport mechanisms and thereby the material stability in electrochemical environment. At the atomistic level, the correlation between solvation dynamics, local ordering and chloride ion transport is not completely understood.

We use molecular dynamics simulations with polarizable potentials to understand the correlation between adsorption behavior of halides such as chloride ion and local ordering of water molecules near the surface of metal oxides. We study the variation of the thermodynamic, structural, and transport properties of solvent molecules as a function of chloride ion concentration. A shell-model water potential, compatible with Catlow's core-shell potential models for metal oxide surfaces would be used to study the interaction of water molecules with metal oxide surfaces. This polarizable water potential model is used to model the interaction of liquid water with the metal oxide surfaces obtained in the MD simulations.

In the initial molecular dynamics simulations involving surface hydration, we equilibrated the oxide surfaces in the presence of water with no chloride ions. The dynamical simulations were performed in a canonical ensemble. In subsequent simulations, incremental amounts of chloride ions would be added to the surface of each system to

investigate a range of chloride ion concentration in aqueous media. We examined the oxygen, hydrogen and chloride distribution on the metal/metal oxide surfaces based on the simulation trajectories. The orientational order parameters are used to identify local ordering of the hydration layers formed around the solvated ions and near the oxide interfaces. The orientational preferences of the water molecules in the various hydration layers are known to depend on their local environment and the same would be investigated to study the adsorption of water molecules on metal/metal oxides. Preliminary simulations with Catlow's core-shell model have been carried out to study aqueous media interaction with MgO surface. The results indicate density differences to exist between bulk water and water monolayers closer to the oxide surface. We find that water density is greatest near the MgO surface, and that there is a clear preferred orientation on the surface.

The introduction of chloride ions appears to disrupt the ordering of water molecules. At low chloride ion concentrations, the ordering is less affected as indicated by a clear preferred orientation on the surface. At much higher concentration, the ordering of water molecules is strongly disrupted. Bond orientational order parameters are used to provide quantitative estimates of the extent of change in the local ordering near passive oxide-electrolyte interface. The site specific adsorption behavior of the solute molecules such as aggressive halide ions would be investigated. The surface coverage would be calculated by determining the number of adsorbed water molecules relative to the number of surface sites or surface hydroxyl groups. These simulation results would help understand both the near-surface water structure and the effects of halide ion adsorption and are expected to provide new insights into the corrosion phenomena in aqueous media.

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