

# Abstract

The oxidation of aluminum surfaces and their interactions with corrosion inhibitors is investigated with density functional theory (DFT) calculations. Surprising attractive interactions between negatively charged oxygen adatoms are identified in the earliest stage of oxidation, which involves dissociative chemisorption of oxygen. We find that they result from an interplay between simple geometric and electrostatic effects and that there exists a critical adatom height above the surface, below which lateral interactions are attractive and above which they are repulsive. This model is generally applicable, provided that the adatom–metal bond is sufficiently ionic and the adatoms are small enough to bond close to the surface, below the critical height. The oxidation of aluminum proceeds by aluminum ions migrating through the adlayer of oxygen atoms until a stable ultrathin film is formed. The dissociation of water on this film is thermodynamically favorable and the fully hydroxylated surface is the most stable even when only trace amounts of water are present.

Next the interactions of a model silanol molecule,  $\text{CH}_3\text{Si}(\text{OH})_3$ , and its oligomers (up to the trimer) with the obtained model of the oxidized aluminum surface are analyzed. The silanols bond to the surface via the condensation mechanism, where a molecule reacts with a surface OH group to form a strong SiO–Al bond and a water molecule. Forming one such bond (monodentate) is exothermic for all considered silanols. However, the formation of two such bonds (bidentate) is found to be exothermic only for the trimer and exergonic for the dimer and trimer. Therefore, only a single bond to the surface per monomeric unit of the siloxane film is plausible and some monomeric units likely act as spacers as to reduce the strain. Finally, the archetypal structure of the corrosion inhibitor as consisting of an anchor group and backbone is considered. Adsorption via condensation of five anchor groups is investigated and it is found to be considerably exothermic for the phosphonic and silanol anchor groups, marginally exothermic for the carboxylic group, and endothermic for thiol and imidazole, indicating that the last two do not “stick” to oxidized aluminum surfaces. Additionally, the effect of the backbone is analyzed and it is found that via backbone tilting cohesion in the inhibitor monolayer is increased. Tilting also increases effective coverage, which hinders the access of other species to the substrate.

**Keywords:** aluminum, DFT, silanol, corrosion inhibition