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Book of abstracts

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Bonding of Silanols to Oxidized Aluminum Surfaces: an insight from DFT modeling

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Silane based sol-gel coatings are a promising alternative for the replacement of toxic chromate conversion coatings used to protect aluminum and its alloys against corrosion. It is well known that sol-gel synthesis occurs via a hydrolysis/condensation mechanism and a similar mechanism is proposed for the reaction of silanols with the surface. In order to test this hypothesis a model silanol molecule, $\text{CH}_3\text{Si}(\text{OH})_3$, was chosen and the bonding of it and its oligomers (up to the trimer) with the aluminum surface was investigated by means of density-functional-theory (DFT) calculations. According to our thermodynamic calculations, oxidized Al surfaces are fully hydroxylated, even in the presence of traces of water vapor and correspondingly a model of the fully hydroxylated surface was used. We find that the formation of a monodentate bonding mode with the hydroxylated surface via the condensation mechanism is exothermic by ≥ 0.5 eV in all considered cases. In contrast, the formation of a bidentate bonding mode is exothermic only for the trimer. These results reveal that after the formation of a single molecule-surface bond for the monomer and dimer, additional molecule-surface bonds do not form via condensation mechanism most likely due to the strained configurations the adsorbates have to adopt. This indicates that the commonly used scheme of silanol-surface bonding where each monomeric silanol subunit in a polymer binds to a surface metal atom may not be generally applicable; according to our calculations there has to be at least one subunit acting as a “molecular spacer”, connecting two monomeric subunits bonded to the surface.

Poster Session / 1

Corrosion inhibitors for aluminium investigated using integrative experimental-modeling approach: A DFT modeling study

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In the search for new ways of how to achieve efficient corrosion inhibition, the knowledge about the interaction between the substance acting as an inhibitor and the metallic substrate is useful. To this end, Density Functional Theory (DFT) based modeling is a convenient tool for providing new insights, hence it has been utilized to complement the experimental characterization of several molecules as potential corrosion inhibitors of aluminium in chloride media [1]. Two basic constituents of the archetypal structure of corrosion inhibitor—the reactive anchor group, which interacts with the surface and the less reactive backbone, which governs lateral cohesion within the inhibitor layer—were varied in order to disentangle and scrutinize the interactions within the inhibitor–substrate system.

The phosphonic, silanol, carboxylic, imidazole, and thiol functional groups were chosen as model anchors. Adsorption of inhibitors was modeled via two different mechanisms, i.e., plain (non-dissociative) adsorption and a dissociative condensation mechanism, but strong molecule–surface bonds are formed only in the latter mode. This mode is found to be considerably exothermic for the phosphonic and silanol anchor group, marginally exothermic for the carboxylic anchor group, and endothermic for the thiol and imidazole anchor groups. This indicates that molecules containing the phosphonic and silanol anchor groups will “stick” to the surface regardless of the backbone, whereas for the carboxylic anchor group additional stabilization is required for a stable layer to form and such stabilization can be provided by a backbone. In contrast, the thiol and imidazole groups are unlikely to “stick” to the surface. These predictions conform well with the experimental measurements performed in our groups [1].

Since additional stabilization is required for the carboxylic anchor group, it was chosen as a representative anchor while the length and type of backbone was varied. Alkyl and perfluoroalkyl backbones of lengths ranging from 2 to 17 carbon atoms were considered. In order to maximize the lateral cohesive interactions within the adsorbed inhibitor layer both types of chains were found to be tilted with respect to the surface normal. For the bulkier fluoroalkyl chains the tilting angle was found to be smaller. An additional effect of tilting is that it increases the effective coverage, preventing aggressive species from accessing the substrate.

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[1] I. Milošev et al., in preparation.

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Electrostatic stabilization and geometric effects lead to attractive interactions between oxygen adatoms on Aluminum surfaces

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When electronegative atoms adsorb on an electropositive metal surface, charge transfer occurs and the adatoms become negatively charged. Due to this charge accumulation, repulsive lateral interactions are expected between them, and according to the classical method of images they can be treated as dipole-dipole interactions that scale as $\Theta^{3/2}$, where Θ is the surface coverage of adatoms. This dependence is typical for chemisorbed atomic oxygen on transition metal surfaces and it is depicted in Figure 1a for atomic oxygen on Cu(111). However, in the case of O on Al(111) and Al(100) surfaces the opposite occurs and the magnitude of binding energy increases with increasing coverage (see Figure 1b). Analysis of the electronic structure with DFT calculations reveals that the attractive interactions are a consequence of a simple electrostatic stabilization. Namely, at full monolayer coverage the O adatoms are located close to the surface and together with positively charged surface Al atoms form an electrostatically stable interlaced layer of anions and cations. This is evident from Figure 1c which shows the charge density difference for O on Al(111) (note the alteration of positive (blue) and negative (red) regions). We conclude that the attractive interactions between negatively charged O adatoms at high-coverage stem from an interplay between Coulombic interactions and geometric effects (height of the adatoms), i.e. there exists a critical adatom height below which the lateral interactions are attractive and above which they are repulsive. We propose that this picture is generally applicable for electronegative adatoms on metal surfaces provided that (i) the adsorption bonding is sufficiently ionic and (ii) the adatoms are sufficiently small to come close enough to the surface.