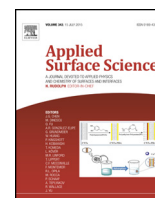




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Density-functional theory investigation of Al pitting corrosion in electrolyte containing chloride ions

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ABSTRACT

The behavior of chloride ions (Cl^-) and oxygen species (the oxygen atom, O or molecular oxygen, O_2) on Al(111) surface has been studied by density functional theory calculations in order to deepen the molecular understanding of fundamental processes leading to pitting of aluminum (Al). The adsorption behavior of individual species, Cl^- , O atom and O_2 was determined first. Subsequently, three possible scenarios in different pitting stages were modeled exploring the repassivation and dissolution of Al in neutral electrolyte containing Cl^- . In scenario i, it was found that Cl^- can hardly destroy even an O-monolayer on Al(111) surface, however may lead to the elongation of Al–O bond and the weakened binding between the first Al layer and subsequent Al layers. Both O_2 and Cl^- were simultaneously introduced onto Al(111) in scenario ii. The result showed a weakened Al–O interaction and an intensive hybridization peak at -0.18 Ha between Al-3p with Cl-3p suggesting insufficient repassivation behavior of Al under this condition. Finally, scenario iii mimicked different local environmental conditions in pits formed on Al. At low coverage of Cl^- , chloride ions had little effect on surface relaxation. The interaction among chloride ions and Al surface became stronger as Cl^- coverage increased. Surface Al atoms dissolved gradually and substructures such as AlCl_3 and Al_2Cl_5 formed when the coverage was larger than $2/3$ ML of a monolayer.

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1. Introduction

Aluminum and its alloys are one of the most important technological metals, known for their good corrosion resistance due to the effective protection of the passive film. However, Al is susceptible to the presence of aggressive ions, such as Cl^- and pitting corrosion will eventually occur as a consequence of depassivation [1]. It is believed that the initial stage of Al pitting corrosion involves at least the adsorption of aggressive ions, the incorporation of such ions in the passive film, film thinning, and Al dissolution occurring on the passive oxide surface, in the oxide, and at the Al/Al-oxide interface, respectively [1–4]. The pH_{pzc} of Al is 9–9.5, so the Al surface will be positively charged when the solution is neutral or near neutral, attracting negative ions [2]. Furthermore, experimental observations have demonstrated that Cl^- obviously accumulate on the Al surface prior to the onset of pitting [5]. XPS and XANES detections by Natishan [6–8] further illustrated that Cl^- not only adsorbed on surface but also incorporated into the aluminum oxide. When

Cl^- were presented at the Al/oxide interface, they competed with oxygen species and the repassivation was hindered when sufficient Cl^- accumulated there [9]. Cl^- also participated in the dissolution reactions at the Al/oxide interface, assisting pitting initiation [4].

The eventual breakdown of the oxide film results in the local exposure of the bare Al surface and accelerated Al dissolution at such sites (metastable pit initiation). However, not all of the metastable pits result in stable pitting. Pit propagation or repassivation depends on the local environmental conditions [10]. Though there is no experimental data for Al, it is suggested that the local concentration of Cl^- should at least be 3 M to propagate a pit in stainless steel [11]. According to the experimental results and hypotheses of Evans [12], Galvele [13] and Videm [14], it is suggested that the passivity breakdown is presumed to occur continuously even below E_{pit} . In the absence of aggressive anions, defects in the passive film are thought to be healing rapidly, while in the presence of aggressive anions and at sufficiently high potentials, the metal surface becomes activated.

Despite a considerable amount of research on Al pitting corrosion, the molecular insight into Al repassivation, passivity breakdown, and metastable pit propagation induced by Cl^- , remains to be unraveled.

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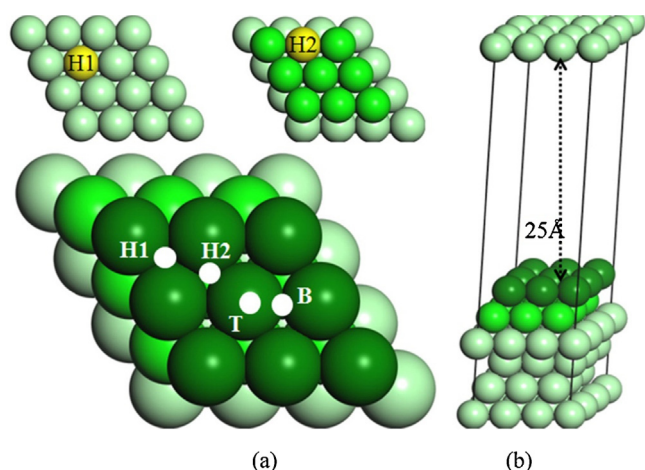


Fig. 1. Models of the (a) top view and (b) side view of Al(111) surface. The four sites considered in our study are pointed out by white dot in (a). They are top site (T), bridge site (B) and two hollow sites (H1 and H2), respectively. The insets over (a) mark the position of H1 and H2 site with yellow and different Al layers are with different colors to show where the H1 and H2 sites are. Hereinafter, Al atoms will be all displayed with light green. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

In situ atomic-scale analysis has provided insight into the mechanism of surface adsorption and reactions of Cl^- on various metals. For instances, in situ STM suggested that Cl^- adsorb and form $(\sqrt{3} \times \sqrt{3})R30^\circ$ surface structure on Cu(111) surface [15], while they form a chain-like adsorbate structure on Au(100) surface in 0.01 M HCl solution [16]. Although surface specific experimental techniques have revealed some other metal/solution interface in a rather detailed way, there are inherent challenges for atomic scale in situ experimental studies to be applied on metallic aluminum due to the difficulties to prepare single crystal aluminum surfaces that are free of oxide.

With the recent advances in computation capability, new chances are offered for researchers to study corrosion phenomena theoretically with electronic and molecular calculation methods, which take various chemical and physical processes at atomic scale into account [17]. Of these theoretical methods, DFT (density functional theory) has been demonstrated to be a high-quality approach for the investigation of the surface adsorption and diffusion of atoms, molecules or ions on metals [18–22] or metal oxides [23–25], as well as at the metal/solution interface [26–28]. Most theoretical studies that have explored the interaction of halide atoms and metal surface have focused on those noble metals, such as Au [20], Ag [21] and Cu [22], or transition metals [29]. Very few DFT studies have focused on interaction of Cl^- with bare Al. An exception is a study on Cl^- adsorption on different sites of Al_{31} cluster as part of an Al(111) surface, but its main emphasis was on the influence of an inhibitor on the corrosion behavior of Al in HCl and NaOH [30]. Besides, DFT calculations have been performed by Grassman et al. to explore the Cl_2 etching reactions on Al(111) surface [31]. To the authors' knowledge, no DFT studies have so far been concerned with the adsorption competition between Cl^- and O_2 (or O atoms) that may occur on a bare Al surface.

The objective of this work is to reveal a deeper molecular insight into fundamental processes that may eventually lead to pitting of Al through a DFT investigation of the interactions between Cl^- and/or oxygen species on locally exposed aluminum metal. Three possible scenarios will be considered, representing different stages of Al pitting: (i) oxygen species in the solution reach the bare Al first, forming an oxide monolayer after which Cl^- reach the same surface; (ii) oxygen molecules and Cl^- reach the bare Al surface simultaneously; (iii) the pit is exposed to a chloride-dominated

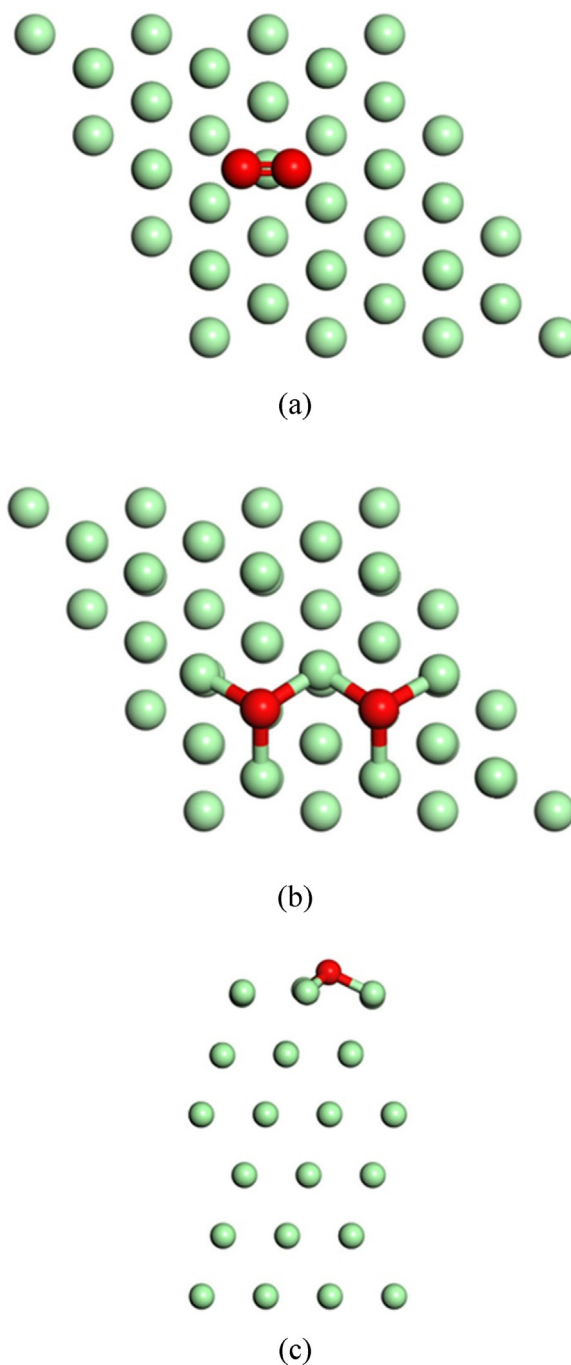


Fig. 2. Single O_2 adsorption on Al(111) surface. (a) Initial position of oxygen before optimization; Top view (b) and side view (c) of oxygen adsorption structure after optimization. Oxygen atoms are displayed with red balls. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

solution with no oxygen species present, representing a scenario after the initiation of metastable pitting.

2. Computational models and methods

In this work, Al(111) was modeled using a 3×3 or 4×4 supercell containing six or four layers where periodic boundary conditions were applied parallel to a slab surface. The height of the vacuum was set to 25 Å. The reliability of the slab model was verified by comparing the surface energies in the case of 3–10 layers of

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