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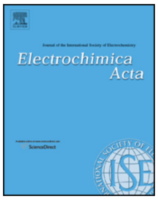

Strong correlations between structural order and passive state at water–copper oxide interfaces

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ABSTRACT

A fundamental understanding of coupled electrochemical processes including metal dissolution, structural evolution and solvation dynamics at the atomic level is of interest to corrosion research and electrochemistry in general. Using molecular dynamics (MD) simulations based on a reactive force field (ReaxFF), we evaluate the impact of non-stoichiometry in a model system of copper oxide passive films on the local fluctuation of the chloride ion density and structure and dynamics of interfacial water layers. We investigate (a) the interplay of oxygen content in the passive oxide film and the solvation dynamics of halide ions in the aqueous interfacial layers during breakdown of the oxide film, and (b) their combined effects on the dissolution kinetics of copper and adsorption of chloride ions on the copper-oxide surface. We demonstrate that the solvation behavior, particularly near the oxide/aqueous medium interface, is strongly correlated with the interfacial chloride ion concentration, which in turn is influenced by the oxygen stoichiometry in the passive oxide. Residence probability and hydrogen-bond correlations show that water present in the aqueous media forms ordered layers on oxide films with high oxygen content; and as the oxygen content is reduced, this order gets disrupted due to increased chloride ion adsorption. Interfacial molecular order is, therefore, strongly correlated with stoichiometry of the passive oxide film.

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1. Introduction

Open questions pertaining to atomistic understanding of initiation of corrosion as well as nanoscale mechanisms of breakdown of the passive metal oxide films include probing the (a) role of water and solute ions on the oxide structure, composition, and reactivity at defective surface sites, (b) interfacial distribution of cations and anions in the oxide layer as well as solution, (c) charge transfer dynamics at the passive oxide−water interface, and (d) mechanisms of ion adsorption and transport, and their effect on corrosion resistance of the passive oxide layer [1–6]. Additionally, there are several important questions pertaining to solvation dynamics near electrochemical interfaces, ionic transport across electrochemical double layers as well as interfacial molecular order in a typical electrochemical environment that are not yet well understood [7–9].

Several macroscopic theories as well as simulation and experimental reports exist in the literature, which attempt to explain the mechanistic sequence of events leading to corrosion initiation and passive oxide breakdown. The atomistic origin of these events and nanoscale pitting mechanism remain an active area of study [10,11]. Most corrosion models at continuum or atomistic scale focus on either ion adsorption or transport through passive oxides [12–14]. While the continuum scale kinetic models such as the point defect models [15–17] can capture the description of the growth and breakdown of the passive oxide film, the atomistic details involving bond formation and bond breakage in a reactive aqueous environment cannot be elucidated. There have been a few classical molecular dynamics simulations [5,6,9,18] and first-principles studies [19–21] in the past to understand the dynamics and energetics of chloride ion adsorption onto the surface of passive oxides. These studies including our recent study [5] have focused on the effect of chloride ion concentration and ambient temperature on passive oxide breakdown. A systematic evaluation of the role of oxygen non-stoichiometry on passive oxide breakdown and the interplay between the non-stoichiometric oxide composition and solvation dynamics of interfacial aqueous layers is the primary focus of this study.

The ordering of water molecules into “ice-like” layers near the interface between water (or aqueous solutions) and several oxides e.g., RuO_2 [22], mica [23], among various other minerals [24–26]

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have been investigated using specular reflectivity measurements, spectroscopic and electron diffraction experiments [27]. These reports indicate that water molecules near the oxide/water interface undergo spatial ordering to form hydration layers owing to either (a) completion of coordination shells of surface cations, or (b) interactions between surface oxygen atoms in the oxide and the water molecules [27]. Such an ordering can occur over a few layers (e.g., monolayer at RuO_2/water [22], 2–3 layers at MgO/water interfaces [28,29]); in extreme cases, weak ordering could exist over larger length scales ~1 nm from the interface, e.g., muscovite mica [23,27]. Apart from these experimental reports, researchers have also probed this ordering phenomenon using atomistic simulations [28–32]. In terms of corrosive aqueous environments, the presence of halide anions can profoundly alter the structure and dynamics of interfacial water layers [18,33]. While the solvation characteristics of interfacial layers are expected to play an important role in corrosion initiation, they have received much less attention to date [7,33]. Recently, we have shown that ionic solvation of water near passive oxides could also play an important role in influencing halide ion adsorption and transport [18]. Chloride anions beyond a certain threshold concentration can significantly alter the dynamics of re-arrangement of hydrogen bonding (HB) network and local interfacial ordering near a passive oxide such as MgO. We note that the solvated ions have important functional roles in screening or moving charge, and can thus potentially influence the kinetics of breaking and structural relaxation of ion-water and water-water HB in these solutions. These, in turn, greatly influence the mobility of both the ions and water molecules. In the case of interfacial water, it would be fair to state that the physical picture of solvation dynamics i.e. HB network connectivity and its response to aggressive anions is still emerging [34].

In this work, we use a model system consisting of copper oxide thin film on copper interacting with chloride ions in aqueous media to gain a comprehensive understanding of representative processes that occur at the interface of passive film and aqueous media. We utilize reactive molecular dynamics simulations and investigate the temporal evolution of copper oxides and surface properties of the passive oxides in an aqueous media containing halide ions. We chose an alkaline environment with excess hydroxyl ions since it is known to show a more aggressive corrosion behavior that can be captured within MD timescales [5,6]. We evaluate the role of oxygen non-stoichiometry in the passive oxide and focus on the early stages of chemical failure. In addition, we demonstrate how oxide non-stoichiometry profoundly affects the solvation dynamics of water proximal to a passive oxide. We elucidate the atomistic level correlation between the oxide non-stoichiometry, concentration of chloride ions as well as the molecular order, diffusional characteristics and HB characteristics of interfacial water. To the best of our knowledge, this work represents the first large scale reactive atomistic scale simulations that provides fundamental insights into the interplay between the oxide non-stoichiometry and interfacial solvation behavior during aqueous corrosion of copper oxides.

2. Computational details

We performed reactive molecular dynamics (MD) simulations in the canonical ensemble (NVT) to systematically investigate the effect of surface oxide stoichiometry on the corrosion behavior of copper in an aqueous environment. The interactions between the Cu, O, H, and Cl atoms were modeled by a general bond-order based reactive force field (ReaxFF), which is known to describe accurately the formation and dissociation of chemical bonds [35–38]. In the framework of ReaxFF, the total energy of the system is composed of several contributions arising from connectivity-dependent interactions such as, bond stretching, angle bending, dihedral twisting, lone pairs, and under/over coordination. All these short-range interactions are functions of bond orders that are derived from instantaneous interatomic distances; the bond order for each pair of atoms depends strongly on its local environment, and thereby, accounts for many-body effects [35–37]. Additionally, long-range interactions (i.e., Coulomb and van der Waals) are computed for every atom-pair regardless of their connectivity. The temporal evolution of atomic charges is evaluated using electronegativity equalization method [39]. This approach enables ReaxFF to describe metallic, covalent, and ionic systems equally well [35–38]. ReaxFF has been successfully employed to study a wide range of materials, including metals [40,41], metal oxides [41–43], mixed ceramic oxides [44,45], hydrocarbons [35,37], chlorides and aqueous solutions [5,6,38]. The ReaxFF parameters used in this study were taken from Ref. [38]. These parameters were found to accurately predict formation energies of Cu oxides [41] and Cu—Cl clusters [38]; in previous works, we have employed these parameters to identify atomic-scale mechanisms of aqueous corrosion of Cu, and investigate Cl^- ion interaction with copper oxide surfaces [5,6].

All the MD simulations were performed using the classical MD simulation package LAMMPS [46] with a timestep of 0.5 fs. Following our earlier works [5,6], we employed a slightly larger timestep than that usually used for ReaxFF MD study of hydrocarbon/water systems (0.25 fs; e.g., Ref. [38]) to make longer MD runs (2 ns) tractable whilst capturing the dynamics accurately. In our MD simulations, using the larger timestep, the fluctuations in the total energy of the equilibrated configurations were found to be within 0.06 eV/atom. The computational supercell consisted of a base metal substrate containing 2048 Cu atoms (~2.6 nm × 3.6 nm × 2.5 nm) configured with (1 1 1) orientation along the surface normal. Periodic boundary conditions were employed in the plane of the substrate (i.e., along x- and y- directions). The top 2–3 layers of this Cu slab (~0.5 – 0.6 nm) were first oxidized by exposing it to an oxygen environment in a NVT MD run at 300 K for 1 ns. The constant temperature conditions were maintained using the Nosé–Hoover thermostat as implemented in LAMMPS [46]. Representative structures were then chosen from different stages of this oxidation run such that the top oxide layer CuO_x possessed the desired oxygen stoichiometry x_O. A wide range of values of x_O from 0.16 (oxygen deficient) to 0.79 (oxygen enriched) was considered in this study. We note that for cuprous oxide with ideal stoichiometry, i.e., Cu_2O, that value of x_O is 0.5. At each value of x, the Cu slab with surface oxide film was relaxed in vacuum (supercell dimensions: ~2.6 nm × 3.6 nm × 6.5 nm; ~4 nm vacuum normal to the surface) for 100 ps at 300 K prior to exposing them to aqueous conditions. After thermal relaxation of the slab with surface oxide film, the empty space above the slab was filled with 714 H_2O, 238 OH^- ions, and 169 Cl^- ions (equivalent to 10 M Cl^- concentration) at random locations as shown in Fig. 1. The number of water molecules was evaluated assuming a density of 1 g/cc, while the excess hydroxide and Cl^- ion concentration was chosen to mimic marine environment such as seawater [5,6]. The system was allowed to equilibrate at 300 K using NVT-MD simulation for 1.5 ns; a subsequent production run of 0.5 ns was used to investigate dynamical and structural properties. It is important to note that in the initial configurations, the charges on all the atoms (including hydroxyl and chloride ions) were set to zero to avoid introduction of any bias. The temporal evolution of the atomic charges was determined via the electronegative equalization method, which is incorporated in the ReaxFF framework. During the MD runs, irrespective of the value of x_O, the Cu/CuO_x slab exhibits a slight positive charge (e.g., ~0.01 e^-/atom at $x_O = 0.16$ after 0.1 ns), while the aqueous solution possesses a slight negative charge (e.g., ~ −0.01 e^-/atom at $x_O = 0.16$ after 0.1 ns); the overall system, however, remains neutral.

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