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.

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., RuO₂ [22], mica [23], among various other minerals [24-26] 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 RuO₂/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 ($\sim 2.6 \text{ nm} \times 3.6 \text{ nm} \times 2.5 \text{ nm}$) configured with (111) 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 ($\sim 0.5\text{--}0.6 \text{ nm}$) 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: $\sim 2.6 \text{ nm} \times 3.6 \text{ nm} \times 6.5 \text{ nm}$; $\sim 4 \text{ nm}$ 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 H₂O, 238 OH⁻ ions, and 169 Cl⁻ ions (equivalent to 10 M Cl⁻ concentration) at random locations as shown in Figure 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.

Figure 1: Side view of a typical computational supercell containing a Cu (111) substrate with an oxide thin film on top being exposed to aqueous media at 10 M Cl⁻ concentration. The spheres shown here represent copper (tan), oxygen (red), hydrogen (blue), and chlorine (green) atoms. For the sake of clarity, the atoms belonging to aqueous media are represented by smaller spheres.

3. Results and Discussion

3.1 Effect of stoichiometry on structure and density of passive oxide

The corrosion behavior of a metal (Cu in the present study) in aqueous environment is known to be highly sensitive to the structural condition of the passive surface oxide film formed on top of it [5, 47]. To characterize the structure of the oxide films prior to exposing them to aqueous media, we evaluated the pair-distribution function (PDF) for Cu-O pairs for the surface oxide films for varying oxygen stoichiometry (Fig. 2). The Cu-O PDFs show a characteristic peak at $r = 0.185$ nm – 0.190 nm corresponding to the nearest neighbor distance, which is in excellent agreement with previous x-ray diffraction measurements [48] as well as Monte-Carlo simulations [49]. As expected, the intensity of this nearest-neighbor peak decreases with reduction in O stoichiometry x_O due to the decrease in the number of O atoms (and in turn, Cu-O pairs). At higher Cu-O distances, there are no distinct peaks indicating that the Cu-oxide film is amorphous at all values of x_O . It is interesting to note that the oxide films with higher O content exhibit slightly better atomic ordering as indicated by a broad peak at $r \sim 0.41$ nm particularly at $x_O \geq 0.48$ (Fig. 2). Furthermore, a close-inspection of the nearest-neighbor peaks of the Cu-O PDFs (inset Fig. 2) shows a slight but systematic decrease in the closest Cu-O spacing ($\sim 5 \times 10^{-3}$ nm) with increasing x_O . This is understandable since the thickness of the Cu oxide films remains nearly constant ~ 0.5 nm (Fig. 1) at all values of x_O , which results in higher atomic packing in O-enriched films.

Figure 2: Pair distribution function (PDF) of Cu-O pairs in oxide films with different oxygen stoichiometry x_O . (inset) Magnified view of the nearest neighbor peaks.

3.2 Temporal evolution of passive oxide films with different O-stoichiometry upon chloride ion adsorption

The structural characterization of unexposed Cu-oxide films at different x_O indicates that these films are largely amorphous, and possess similar features irrespective of the O-content. This ensures that the aqueous corrosion behavior studied here is governed primarily by the O-content in the surface oxide film rather than any structural differences. In order to assess the corrosion resistance of the Cu-oxide films under aqueous conditions, we evaluated the temporal evolution of the number of chloride ions adsorbed on the oxide films at different x_O during our MD runs (Fig. 3(a)). We found that deficiency of O atoms in the surface oxide layer promotes chloride ion adsorption; in fact, there is a systematic increase in chlorine ion adsorption with decrease in x_O . For instance, at $x_O = 0.16$, the number of chloride ions adsorbed are nearly twice as many as that at $x_O = 0.79$. We also note that most of the chloride ions get adsorbed during the first ~ 1 ns, after which, the system is in equilibrium. The adsorbed chloride ions bind with nearby Cu atoms resulting in the dissociation of existing Cu-O bonds, which in turn, leads to chemical thinning of the oxide film. The formation of new Cu-Cl bonds also

manifests itself as a gradual increase (more negative) in the average charge on chloride ion z_{Cl} as a function of time (Fig. 3(b)). The temporal evolution of z_{Cl} shows that chloride ion charge increases gradually upto ~ 1 ns, which is consistent with the trend in number of adsorbed chloride ions. Furthermore, as expected from the chloride ion adsorption behavior in Fig. 3(a), the average charge of chloride ions in the non-stoichiometric (low x_O) cases are higher (as high as $\sim 20\%$) as compared to the more stoichiometric (high x_O) ones.

Figure 3: Time evolution of chloride ion adsorption on passive oxide films with different O-stoichiometry (a) number of adsorbed chloride ions, (b) average charge on chloride ions.

3.3 Effect of surface oxide stoichiometry on chloride ion adsorption

Figure 4 shows the snapshots of the top view of Cu-oxide films with different O-stoichiometry at different times t during our MD simulations of aqueous corrosion. Upon exposing the oxide films to aqueous media, chloride ions begin to adsorb on to the surface; consistent with Fig. 3, we observe that higher number of chloride ions adsorb on the oxide films with low O-content, and distinctly thin the passive oxide film. Chloride ions adsorbed on the oxide film facilitate the dissolution of Cu atoms from the oxide film into the aqueous media via dissociation of existing Cu-O bonds, similar to our previous

findings [5]. Furthermore, we found that an adsorbed chloride ion promotes further adsorption leading to formation of a wide range of soluble Cu-Cl complexes; these complexes subsequently dissolve into the aqueous medium. These direct observations clearly indicate that higher chloride ion adsorption on the passive oxide surface eventually causes higher corrosion of underlying Cu substrate. Our findings are in good agreement with the mechanism of pitting corrosion proposed earlier based on potentiostatic polarization and X-ray photoelectron spectroscopy, which suggested that dissolution of Cu atoms must occur via soluble complexes like CuCl_2^- [50].

Figure 4: Top view of the interface between the passive oxide layer and aqueous medium at selected times during our MD simulations of corrosion. For the sake of clarity, the adsorbed chloride ions are shown as big spheres (green), while the copper (tan), oxygen (red), and hydrogen (blue) atoms are shown as small spheres.

To further investigate the extent of dissolution of Cu atoms as well as adsorption of Cl ions, we computed the atomic number density distribution of Cl (ρ_{Cl}) and Cu (ρ_{Cu}) atoms along the surface normal direction (z -axis) as a function of the O-stoichiometry in the oxide film (Fig. 5). The density distributions were averaged over the configuration obtained in the last 0.5 ns of our aqueous corrosion MD simulations. As shown in Fig. 1, the interface between the passive oxide film and the aqueous media occurs at $z \sim 2.5$ nm. Proximal to this interface, we find an increase in the density of Cl atoms providing evidence for chloride ion adsorption. Consistent with the findings in Fig. 2(a), we find that Cl adsorption is the highest on the oxide films with very low oxygen content ($x_O = 0.2$) as indicated by highest intensity of the ρ_{Cl} peak at ~ 2.6 nm in Fig. 5(a). As the O-content increases, the amount of Cl adsorption drops significantly as illustrated by the drastic decrease in the intensity of ρ_{Cl} at the oxide-aqueous media interface. It is also important to note that there is considerable infiltration of chloride ions into the oxide layer, particularly at low values of x_O as shown by peaks of medium intensity; e.g., ρ_{Cl} increases to $\sim 1.5 \times 10^{-5} \text{ nm}^{-3}$ in the top layer of oxide film at $x_O = 0.2$.

Figure 5: Effect of oxygen stoichiometry on the atomic density profile ρ of (a) Cl, and (b) Cu in a direction normal to the oxide-aqueous media interface. For the sake

of clarity, only the spatial regions close to the oxide-aqueous media interface ($z \sim 2.5\text{--}2.6$ nm) are shown.

In terms of removal of Cu atoms from the oxide surface, most Cu dissolution takes place from oxide films of low O-content (e.g., see ρ_{Cu} peak at $z \sim 2.65$ nm at $x_O = 0.2$ in Fig. 5(b)). Furthermore, the smearing of the ρ_{Cu} peak at the oxide-aqueous media interface reveals that Cu atoms removed from O-deficient films dissolve further into the aqueous media, and results in significant thinning of the oxide film. To better understand the spatial arrangement of Cu atoms around the adsorbed chloride ions, we computed the PDFs of Cu-Cl pairs as a function of O-stoichiometry (Fig. 6). These PDFs show that the nearest neighbor spacing between Cu and Cl atoms is 0.22 nm – 0.235 nm; these values are in agreement with previous x-ray diffraction studies on aqueous $CuCl_2$, which report the Cu-Cl bond length to be $\sim 0.225 - 0.243$ nm [48, 51]. By analyzing the coordination of Cl around Cu atoms within the predicted nearest neighbor distance ($r \sim 0.22 - 0.235$ nm), we found that the Cu-Cl pairs can exist as $CuCl$, $CuCl_2$ or $CuCl_3$, especially at low values of $x_O = 0.2$. This is in good agreement with previous MD simulations of Cu corrosion [5] as well as x-ray photoelectron spectroscopy studies, which report the formation of $CuCl_2^-$ ions during the corrosion of Cu in chloride solutions [50]. In Fig. 6, it is also interesting to note that the intensity of the nearest-neighbor peak in the PDF of Cu-Cl decreases with increase in the O-content of the oxide films. This provides further evidence for higher chloride adsorption, and consequent higher thinning of the oxide films with low values of x_O .

Figure 6: Effect of oxygen stoichiometry on pair distribution function for Cu-Cl pairs averaged over the last 0.5 ns of MD simulations

3.4 Effect of surface oxide stoichiometry on solvation dynamics and molecular ordering of water

The above results clearly suggest that the oxide non-stoichiometry has a pronounced effect on the local density fluctuations and adsorption of the chloride ions. In this section, we further evaluate the impact of non-stoichiometry on the structure and dynamics of water layers in the vicinity of an oxide surface.

3.4.1 Residence probability of interfacial layers as a function of passive oxide non-stoichiometry

We have calculated the residence time probability ($P_{res}(t)$) of interfacial water molecules as a function of the oxide stoichiometry. To facilitate comparisons between the various cases, the water molecules were divided into two different regions: (1) interfacial water molecules (water molecules located in the vicinity of the passive oxide layer i.e. within 1.5 nm) (2) bulk water (water molecules located beyond 1.5 nm from the oxide surface). $P_{res}(t)$ was defined in both the cases, as the probability of finding a water molecule in one of the above defined regions without departing from that region for the time interval t_0 and $t + t_0$ [52, 53]. $P_{res}(t)$ was averaged over several different simulation frames that were collected over the total time domain of 1 ns with intervals of 1 ps.

Figure 7 shows the $P_{res}(t)$ for interfacial water molecules as a function of the varying oxygen stoichiometry of the passive oxide surface. These calculations allowed us to quantify on an average, how long, a particular water molecule continuously resides in any given region, namely, either interfacial or bulk water. We find that $P_{res}(t)$ of interfacial water molecules decreases with increase in the extent of non-stoichiometry [Fig. 7]. Water molecules reside for longer time in the case of near-stoichiometric surface ($x_O > 0.7$) as compared to water molecules for non-stoichiometric oxides ($x_O < 0.5$). The slow dynamical behavior for interfacial water near stoichiometric oxides is suggestive of an ordered arrangement of water molecules, which is also an energetically stable configuration. The timescale for the residence time $P_{res}(t)$ to decay to $1/e$ is $\gg 1$ ns for interfacial water molecules corresponding to ($x_O > 0.5$) whereas $P_{res}(t)$ decays *ca.* 100-200 ps for $x_O < 0.5$. Note that the $P_{res}(t)$ for bulk water is ~ 8 ps which is similar to that obtained by Argyris *et al.* [54] As the extent of oxygen non-stoichiometry is increased, the dynamical properties of the interfacial water molecules begin to approach the properties shown by bulk water whereas in the near stoichiometric case ($x_O \sim 0.8$), the interfacial layers dynamically change and relax to energetically stable configurations of ordered water. It is worth noting that $P_{res}(t)$ obtained using the intermittent definition also showed a similar trend.

Figure 7: Effect of passive oxide non-stoichiometry on the residence probability of water molecules on Cu-oxide surface.

3.4.2 Hydrogen bond correlation function of interfacial layers as a function of passive oxide non-stoichiometry

To further explore ordering of water at the metal-oxide/aqueous medium interface, we performed HB analysis by employing a well-known configurational criterion [55]. In short, two water molecules are considered to be connected via HBs only if the oxygen atoms of the two water molecules are separated by a distance < 0.35 nm, as well as the O—H . . . O angle is less than 30° following our earlier works [31, 56]. To identify whether a pair of water molecules are hydrogen bonded, we use a binary function $h(t)$ following Ref. [55]. The value of h is unity when the tagged pair is hydrogen bonded, and is zero otherwise. In the dynamical equilibrium of liquid water, the fluctuations in h are characterized by the correlation function [55].

$$C_{HB}(t) = \frac{\langle h(0)h(t) \rangle}{\langle h^2 \rangle}$$

where $h(t)$ refers to the binary function for every pair of water molecules at time t , and the angle brackets denote average over all distinct pairs of water molecules and initial timeframes. Furthermore, HB lifetime τ_{HB} is defined such that $C_{HB}(\tau_{HB}) = e^{-1}$.

We calculate the HB correlation function and lifetimes for the interfacial water layers as a function of the passive oxide non-stoichiometry. We find that our calculated HB lifetimes comply with the diffusivity variation. In bulk water, it should be noted that the τ_{HB} are ~ 5 -6 ps which is reminiscent of the intermittent collective motion of water molecules as a result of extensive HB network rearrangement dynamics of liquid water [57]. In the case of interfacial water near a more stoichiometric oxide, HB correlation function decays much slower with lifetimes of ~ 250 ps, which implies characteristics of 2-D layered water (Fig. 8). A slow dynamical behavior indicates energetically stable configurations of interfacial water wherein significant extent of ordering is still preserved. This is consistent with previously reported simulations of Balasubramanian *et al.* [58] and our recent simulations on magnesium oxide-aqueous interfaces [18]. They observed that both the residence times and τ_{HB} among interfacial water molecules are much higher than bulk owing to the ordering.

As the extent of non-stoichiometry is increased from 0.79 to 0.2, we observe a significant lowering in the HB lifetimes; the corresponding HB correlation shows a much faster decay and approaches that of bulk water. This suggests that the interfacial water layers in the case of highly non-stoichiometric oxides are much more disordered than those that are nearly stoichiometric. The observed variation in the τ_{HB} can be explained by the fact that interfacial water molecules are strongly hydrogen-bonded to the passive oxide surface and hence have much higher τ_{HB} than pure bulk water. With an increase in oxygen non-stoichiometry, we find that the HB correlation function decays slightly faster, leading to reduced τ_{HB} . A strong decrease is seen when $x_O < 0.5$, which

coincides with the disruption of the ordered interfacial water. The τ_{HB} at these high levels of non-stoichiometry are ~ 180 - 1420 ps.

Figure 8: Hydrogen bond correlation function for the interfacial water layers as a function of the passive oxide non-stoichiometry.

3.4.3 Diffusivity of water molecules and chloride ions

We then consider the relationship between the molecular order and transport characteristics of water and halide ions. We show in Fig. 9(a) and (b) the calculated dependence of the diffusion coefficient D of chloride ions and water molecules, respectively as a function of the non-stoichiometry of the passive oxide. Our reactive MD simulations suggest atomic diffusivity of interfacial water depends strongly on the extent of non-stoichiometry. In particular, we find that diffusion coefficients of water near a more stoichiometric oxide are fairly small ($D \sim 2 \times 10^{-5} \text{ cm}^2/\text{s}$ for $x_O \sim 0.8$), comparable to those in a copper oxide without any Cl⁻ ions. As the extent of non-stoichiometry increases, however, we observe that the diffusion of water becomes significant ($D \sim 16 \times 10^{-5} \text{ cm}^2/\text{s}$ for $x_O \sim 0.2$). There is a facile rearrangement of atoms in the layered structure at such higher non-stoichiometry levels. Closer analysis of the MD trajectories suggests significant disruption of the quasi-two dimensional interfacial water

structure. It should be noted that there is a significant loss of molecular order as a result of rapid diffusion of the chloride ions; their diffusivity increases from $0.2 \times 10^{-5} \text{ cm}^2/\text{s}$ to $1.4 \times 10^{-5} \text{ cm}^2/\text{s}$ as oxygen stoichiometry changes from $x_O \sim 0.80$ to $x_O \sim 0.20$. This, in turn, suggests that rapid adsorption of chloride ions to the passive oxide should be possible for high levels of oxide non-stoichiometry. Indeed, this behavior is corroborated by the atomic density profile of Cl ions shown in Fig. 5(a).

Figure 9: Diffusion coefficients of (a) chloride ions and (b) water molecules at room temperature as a function of the passive oxide stoichiometry.

The observed effect of oxide non-stoichiometry on the molecular order, structure and dynamics of aqueous interfaces is rather interesting. In a typical ordered aqueous interface such ice-water system, there is a tendency for chloride ion rejection from the ordered ice phase into water (phenomenon is termed brine rejection). The increased propensity of water to solvate chloride ions leads to their expulsion from an

ordered ice structure into liquid water as demonstrated in the MD simulations by Jungwirth and co-workers [59]. The ordered quasi-two dimensional structure near the passive oxide is therefore expected to suppress corrosion by having a similar tendency to expel chloride ions and maintain its ordered structure as in the ice-water case.

We, however, observe that the extent of interfacial ordering is a strong function of the oxide stoichiometry. We note that the extent of non-stoichiometry can lead to an imbalance in the distribution of the charges; the average surface charges are higher when the extent of non-stoichiometry is higher. For higher levels of oxide non-stoichiometry, the surface preference of the chloride ions due to long-range Coulombic interactions seems to overcome the tendency to expel these ions into the bulk of the liquid.

4. Conclusions

MD simulations indicate that breakdown of the passive Cu-oxide films proceeds by adsorption of Cl^- ions onto the film (from the aqueous medium), which preferentially bind to Cu atoms in the oxide and form soluble Cu-Cl complexes. These complexes dissolve in the aqueous medium resulting in Cu dissolution and chemical thinning of the film. We explored the role of interfacial solvation dynamics in influencing the dissolution of Cu. In the close proximity of the O-rich oxide films, we found that water molecules arrange in well-ordered quasi-2D layers as indicated by high residence probabilities and hydrogen bond lifetimes. These layers are energetically favorable, as evidenced by the slow diffusion characteristics of the water molecules belonging to these layers. For a near stoichiometric oxide, the two-dimensional ordered layers of water (reminiscent of ice-like) tend to expel the chloride ions back into the disordered regions far away from the oxide/aqueous medium interface. At higher oxygen non-stoichiometry, we observe

chloride ion induced disruption of these ordered layers, which facilitates aggressive dissolution and breakdown of passive oxide film. Our study indicates that reduced Cl^- ion adsorption occurs not only due to impaired Coulomb interactions owing to the presence of low surface charges in O-rich films, but also due to interesting solvation effects at the metal-oxide/aqueous medium interface.

Acknowledgements

Use of the Center for Nanoscale Materials was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. This research used resources of the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. An award of computer time was provided by the Innovative and Novel Computational Impact on Theory and Experiment (INCITE) program. This research used resources of the Argonne Leadership Computing Facility, which is a DOE Office of Science User Facility supported under Contract DE-AC02-06CH11357.

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