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Theoretical Insights into the Role of Water Molecule in The Aqueous/Cu(111) Interface during Corrosion Pathway

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Abstract: *The absorption and possible reaction paths during corrosion have been systematically identified at the molecular level by using density functional theory calculations. The results show that the co-adsorbed water molecule has a two-fold impact on the corrosive kinetics process. The one is the solvation effect, where water molecule affects the various reactions through ion dipole interaction, without bond fracture and formation. Another is the H-transfer mediator, where the bond of co-adsorbed water molecule breaks and regenerates in order to transfer hydrogen atoms.*

Keywords: Copper; Interfaces, Absorption, Kinetic parameters

1. INTRODUCTION

Cu and its alloys are among most widely used materials, especially in the chemical, naval construction and electronics industry[1,2]. However, the corrosion of Cu results into premature deterioration, threatening the integrity and safety of equipment and posing a serious economic loss, as well as potential danger to users[3,4]. Hence, it is vital to profoundly comprehend the mechanism of Cu corrosion in aqueous solution and find effective ways to protect Cu.

It is well-known that the double layered structure of the metal/solution interface is an important factor for influencing corrosion. In the double layer structure, it has been found that the adsorption of water molecules on the metal plane play an intrinsic role in the description of electrochemical interfaces and understanding the corrosion mechanism[5-8]. In our previous study, we found that the water monomers have a great impact on the structure and formation of copper surface[9,10].

Electronic structure calculations have been widely used to calculate the geometrical structure of water monomers, small clusters and extended hydrogen bonded networks, providing a powerful tool to compare with experimental measurements, particularly via Scanning Tunneling Microscope (STM) simulations[11,12].

As noted above, water molecule adsorption at metal planes is driven by density functional calculations within the generalised gradient approximation[13,14]. Some of these calculations have been successful. During the calculation, most users focus their attention on the monomer adsorption. For example, Michaelides et al. systematically studied the detailed interaction of the water monomer with close packed metal planes based on plane wave Density Functional Theory (DFT) calculations, using ultrasoft pseudopotentials and exchange correlations as described by the generalized gradient approximation (GGA)functional developed by Perdew and Wang (PW91). These calculations indicated that a near atop adsorption site is preferred, with the molecular plane orientated almost parallel to the plane, and the binding energy for Cu (111) is 0.24 eV. Tang and Chen reported the adsorption geometry of the monomer on the three lower indexes and stepped planes of Cu by using DFT calculations[15].

Since Mitsui et al. firstly observed the process of adsorption, diffusion and the clustering of single H_2O molecules on the Pd (111) plane by using STM[16], the co-adsorption, generally form dimers and larger structures, is being paid close attentions. The interaction of the adsorbed monomer with additional water molecule has also been examined using DFT calculations. The dimer

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adsorption on the metal results in both an enhanced bonding interaction between the lower water molecule and the metal and an enhanced hydrogen bond between the two water molecule types. The co-adsorption behavior between H_2O and some impurities has also been investigated. Xin Wei et al. studied the co-adsorption behavior of SO_2 and H_2O on face-centered cubic Cu (100) ideal plane. Ingrid Milosev[17,18] investigated the interaction between the five imidazole type molecules with various Cu planes and indicated that the bond between soluble complexes, such as $Cu(H_2O)_3$, $Cu(H_2O)_3.2H_2O$ and imidazole, have to be considered for the explanation of the trend of corrosion inhibition efficiency. For clustering adsorption, it generally considered that the distorted water bilayer is formed on the metal surface. Half of the water is bonded to the surface via electron donation from O to the metal, with alternate water molecules adsorbed between these, forming the upper half of a bilayer structure to complete the hydrogen-bonding network.

Furthermore, some researchers also examined the dissociation of H_2O molecules on the plane of metals by experimental and theoretical studies[19]. The results converge to the fact that H_2O molecules can be dissociated in most metals and that the process is irreversible.

Although the adsorption and co-adsorption behavior have been well described, an overall picture that describes the reaction process of corrosion from the atomic scale is still not fully understood by DFT calculations, despite of its practical importance.

Based on previous electrochemical experiments, a plausible reaction pathway for the perfect Cu plane has been reported as the series of reactions (1)-(5), where the subscript of "ads" represents the adsorbed state and RDS represents the rate-determining step[20,21].

$$Cu + H_2O \rightarrow Cu(H_2O)_{ads} \quad (1)$$

$$Cu(H_2O)_{ads} \rightarrow Cu(OH^-)_{ads} + H^+ \quad (2)$$

$$Cu(OH^-)_{ads} \rightarrow (CuOH)_{ads} + e \quad (3)$$

$$(CuOH)_{ads} \rightarrow CuOH^+ + e[RDS] \quad (4)$$

$$CuOH^+ + H^+ \rightarrow Cu^{2+} + H_2O \quad (5)$$

Although corrosion of Cu in aqueous solutions has been experimentally proved as an impeccable process, the micro-mechanisms behind it, especially for the role of water molecule during corrosion, are still obscure. Up to date, owing to the complexity of the structure and the properties of the interface, an intact graph that would synthetically convey the effect of water molecule on the corrosion process is still missing from the literature. In this paper, a comprehensive theoretical analysis of the effect of water molecule is presented in the entire corrosive process, from the perspective of the adsorption and reaction pathways. This study helps clarifying that water molecule affects the adsorption of the reaction species, as well as the elementary steps of the corrosion kinetics.

2. COMPUTATIONAL ANALYSIS

Quantum chemical calculations can provide insights into the design of inhibitor systems with superior properties and elucidate the adsorption process at a molecular level[22]. The Dmol^{3+} module of the Materials Studio software (Accelrys Inc.) was employed for the quantum chemistry calculations. During the calculations, Cu (111) plane has been widely chosen as an ideal model system to investigate the structure, stability and adsorption properties, since it is the most stable surface under the realistic conditions[23]. The Cu (111) lattice structure was divided into 4 layers and the bottom two layers were constrained. A supercell (4×4) was built with size of 10.22×10.22×7.43 Å^3, as shown in Fig. 1. Furthermore, a top site (above the Cu atom of the central plane), a bridge site (between the two Cu atoms, above contact location) and a hollow site (above a triangle of the Cu atoms of the plane or directly above a Cu atom in the following layer, below the plane) were considered during adsorption and the most stable adsorption site was characterized according to the minimum energy of the system. Only one co-adsorbed water molecule was considered as there is not significant difference in the electronic character between the water molecule contained in isolated or condensed phase[24].

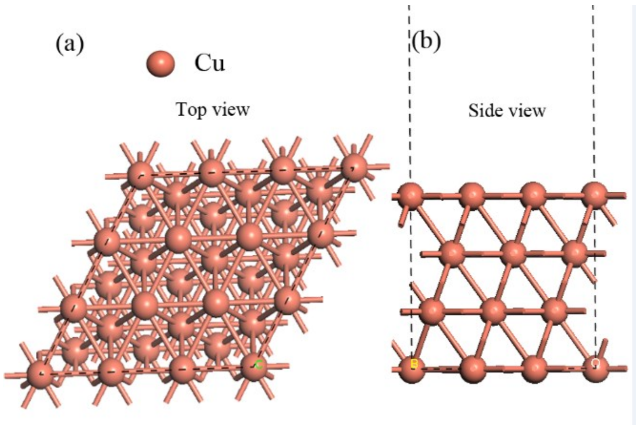

Figure 1. (a) Top view of the Cu (111) plane and (b) side view of a four-layer slab. The dash line defines the lattice of the slab model.

During the calculations, self-consistent periodic DFT calculations were used to study the relative stabilities and reactivities of surface species on Cu (111) surface. The GGA, in the form of the Perdew-Burke-Ernzerhof (PBE) approximation to the exchange-correlation energy, and the double-numerical quality basis, which was set with Double Numerical plus Polarization functions (DNP), were employed. The Effective Core Potential (ECP) was used to handle the core electrons of the metallic atoms. A thermal smearing was adopted at 0.002 hartree and a real-space cutoff at 4.5 Å. The k-point separation is 0.04 Å.

The interaction energy is the key parameter to evaluate the inhibition performance. The interaction energy $E_{\text{interaction}}$ between a Cu plane and water molecules was computed as follows:

$$E_{\text{int}eraction} = E_{total} - (E_{water} + E_{surface}) \quad (6)$$

where E_{total} is the total energy of the system, including the water molecules and the metal plane; E_{water} is the water molecules energy; E_{plane} is the energy of metal planes. In the definitions, the higher negative value of E_{ads} indicates a more stable adsorption on the plane. The total computed energy values have displayed that this location does not contain ZPE correction.

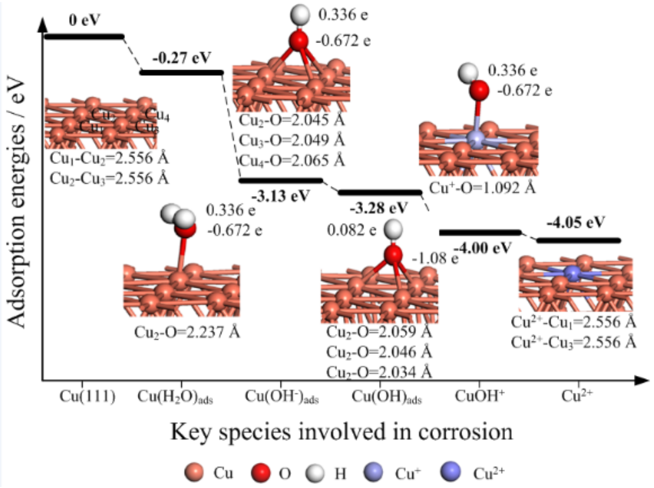

Figure 2. Adsorption sites, adsorption energies and structural constants of pivotal kinds related to corrosion on the Cu (111) plane.

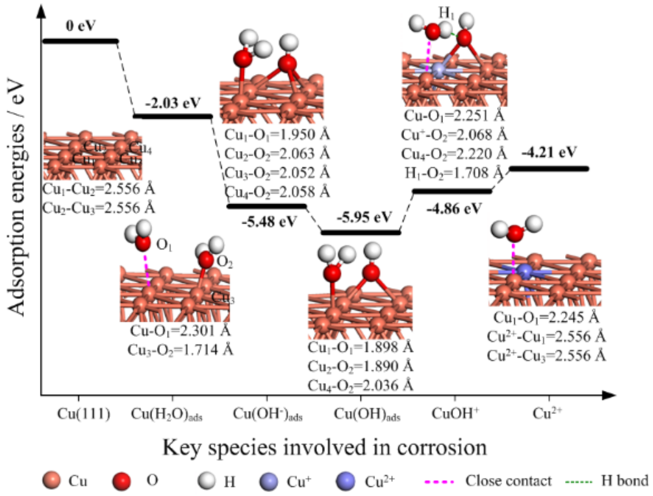

Figure 3. Adsorption sites, co-adsorption energies, and geometric constructions of some pivotal species with a water molecule involved in corrosion on the Cu (111) plane.

Following optimization, the lattice parameters of Cu were obtained as shown in Table 1.

Table 1 indicates that the maximum deviation for optimized lattice constants is 0.011 Å, the ratio is 0.30%, with respect of the experimental value of 3.604 Å, which is less than the acknowledged tolerance of 0.50%, and hence the calculation method and model are acceptable.

3. RESULTS AND DISCUSSION

3.1. Adsorption of single species on Cu (111) plane

Based on the above mentioned reactions, it can be observed that adsorption is the first step of chemical reactions. So, the adsorption of the species on Cu (111) plane was firstly examined. Fig. 2 demonstrates the adsorption sites, adsorption energies and structural constants of some pivotal types related to corrosion, without the involvement of water molecule on the Cu (111) plane. The sum of energy in the gas phase and on the clean Cu (111) plane is precisely equivalent to the zero energy reference.

Fig. 2 indicates all the potential adsorbed sites of Cu atoms through O, for various species. The feasible reason is that atomic O, having many electrons, prefers the acidic Cu sites. $Cu(H_2O)_{ads}$ is easy to adsorb on the top sites of Cu atoms, while $Cu(OH^-)_{ads}$ and $Cu(OH)_{ads}$ favor the hollow sites. This is consistent with previous findings, where the saturated species are easy to adsorb on the top sites, while the unsaturated species prefer the bridge or hollow sites[26]. This conclusion is also consistent with the experimental results from STM, which indicate a top adsorption site[27]. The calculation results also manifest that the Cu-O and O-H bond length of $Cu(H_2O)_{ads}$ are 2.237 Å and 0.983 Å, respectively, and the absorption energy is -0.27 eV, which is consistent with the calculation results obtained by using the ultrasoft pseudopotentials and exchange-correlation, as described by the PW91 generalised gradient approximation[28]. Furthermore, the Cu-O bond length of Cu(OH) is 2.046 Å, which is also consistent with the DFT theoretical results of 2.05±0.05 Å[29]. The bond lengths of Cu-O follow the decreasing order of $Cu(H_2O)_{ads}$, $Cu(OH^-)_{ads}$, $Cu(OH)_{ads}$, $CuOH^+$. This trend indicated that the interaction of the species can enhance the strength of Cu-O bond along with the reactions processes, which is attributed to the charge separation and redistribution between the atoms. In addition, the adsorption energies for $Cu(H_2O)_{ads}$, $Cu(OH^-)_{ads}$, $Cu(OH)_{ads}$, $CuOH^+$ and Cu^{2+} are -0.27 eV, -3.13 eV, -3.28 eV, -4.00 eV and -4.05 eV, respectively. The adsorption energies decrease gradually, along with the reactions. It is suggested that Cu^{2+} is more stable than others on the Cu (111) plane, which is supported by the fact that Cu can be easily oxidized. Based on the above analysis, it can be concluded that the plausible reaction pathway mentioned above is more rational from a thermodynamics point of view, when single species is absorbed on the Cu (111) plane.

3.2. Co-adsorption between species and a water molecule on the Cu (111) plane

Fig. 3 demonstrates the adsorption contents of several pivotal species on the Cu (111) plane in the presence of co-adsorbed water molecule.

Fig. 3 shows the majority of the species and water molecules that could co-adsorb at the adjacent sites of the Cu (111) plane. It indicates that the OH/H_2O compositions are more stable, which has been verified by several previous studies[30-32]. Furthermore, this

Table 1: The lattice constants of Cu, experimental results from reference[25].

Source	a	b	c	α	β	γ
Our calculation	3.614 Å	3.615 Å	3.614 Å	89.87 °	89.87 °	89.87 °
Experimental	3.604 Å	3.604 Å	3.604 Å	90.00 °	90.00 °	90.00 °
Relative error	0.28 %	0.30%	0.28%	0.144%	0.144%	0.144%

is also consistent with the reaction (4), which is the control step in previous reaction pathway, obtained by electrochemical experiments[33]. Compared with the cases of the absence of one co-adsorbed water molecule on the neighbor, the adsorbed sites have not been significantly changed in most cases expect for $Cu(OH)_{ads}$ and $CuOH^-$. For $Cu(OH)_{ads}$, the adsorbed sites change from hollow to bridge site, while for $CuOH^-$ from top to bridge site. The details can be obtained by comparing the bond lengths. It can be seen that the bond length of co-adsorbed water molecule has been significantly changed during the reaction pathway. There is only close contact (where the scaled sum of van der wales radii is 0.891 Å) between the Cu (111) and the co-adsorbed water molecule for $Cu(H_2O)_{ads}$, $CuOH^-$ and Cu^{2+}, respectively. The bond between Cu (111) and co-adsorbed water molecule will generate into $Cu(OH^-)_{ads}$ and $Cu(OH)_{ads}$. The shortest bond length is 1.918 Å, exited in $Cu(OH)_{ads}$. In general, the bond length values between Cu (111) and co-adsorbed water molecule are decreased and then gradually increased along with the reactions processes. Furthermore, the bonds between species and Cu (111) are also changed after inducing the co-adsorbed water molecule. When the adsorption energy values for single species and co-adsorption with a water molecule were compared, it is interesting to note that the co-adsorption energies of H_2O-H_2O, $Cu(OH^-)_{ads}$-H_2O, $Cu(OH)_{ads}$-H_2O and $CuOH^+$-H_2O on the Cu (111) plane are 1.49 eV, 2.08 eV, 3.40 eV and 0.59 eV, respectively, higher than the sum of those of the individual (where the adsorption energy values of H+ on the Cu (111) plane is 2.64 eV). This indicates that co-adsorption of species and water molecule can substantially enhance the bond strength of Cu-O.

There are two reasons that explain the increasing of the co-adsorption energy values. One reason is that the adsorption energy between Cu (111) and H_2O increased when the close contact changes into bond contact; the adsorption energy between co-adsorbed water molecule and Cu (111) plane will increase during the changing process. Another reason is that the electrons of the species easily reunite with the dynamic fluctuation of dipolar water molecules. This interaction can strengthen the binding of the species with the metal plane, which can also be verified by the bond length of Cu-O with the species. Hence, it can be concluded that co-adsorbed water molecule is able to strengthen the adsorption of pivotal species on the Cu (111) plane. The relatively low increased adsorption energy value of $CuOH^+$-H_2O is attributed to hydrogen bonding interactions between the crucial species and co-adsorbed water molecules. Fig. 2 expresses that the lengths of the hydrogen bonds that exist in the water molecule and pivotal species are calculated at 1.708 Å and belong within the typical region for a hydrogen bonding interaction, which is between 1.5-1.8 Å. The hydrogen bonds will weaken the adsorption of pivotal species on Cu (111).

Furthermore, the co-adsorption energies of Cu^{2+}-H_2O are 0.11 eV lower than the sum of those of the individual. Another reason is the hydrogen bonding interactions between the crucial species and co-adsorbed water molecules. This indicates that co-adsorption of water molecule will weaken the adsorption strength between Cu and Cu^{2+}.

3.3. Kinetics reactions of corrosion with or without co-adsorbed water molecule on the Cu (111) plane

In the corrosion process, it is not only desirable to characterize the corrosion tendency, but also analyze the corrosion kinetics process. As previously mentioned, the whole corrosive process was made up of six preliminary stages, referring two chemical reaction processes (reaction (2) and (5)). In the following, the kinetics of corrosion in chemical reactions process will be discussed in details.

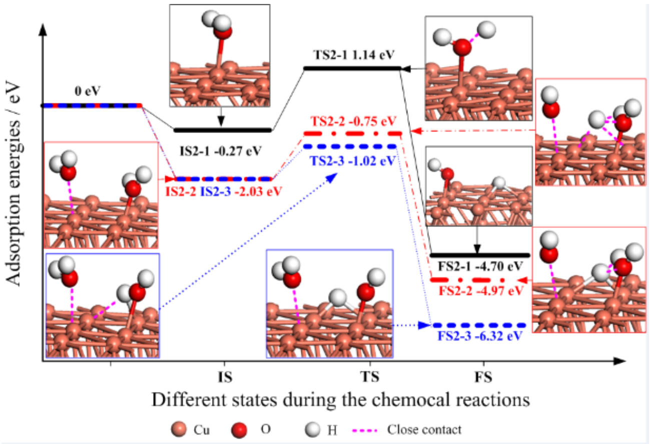

Figure 4. Potential energy plane for reaction (2) with (red and blue curves) or without (black curve) co-adsorbed water molecule on Cu (111) plane and the optimized structures of initial states (IS), transition states (TS) and final states (FS).

3.3.1. $Cu(H_2O)_{ads} \rightarrow Cu(OH^-)_{ads}+H^+$

Fig. 4 manifests the transition search results for the above reactions with or without co-adsorbed water molecule on Cu (111) plane.

Fig. 4 manifested that the disintegratation of single water molecular begins from an initial state (IS2-1), with H_2O_{ads} being placed on the Cu top site, to the final state (FS2-1), with OH_{ads} and H_{ads} anchored to the hollow sites. The activation barrier and reaction energy were calculated at approximately 1.41 eV and 4.43 eV, respectively.

In the presence of co-adsorbed water molecule, disintegratation of water molecule has two optional approaches. One approach is the IS2-2→TS2-2→FS2-2, claims that the dissociation process merely happens in close contacted water molecules, while bond contacted water molecule merely serves as a bystander without participating in the dissociation. The activation barrier and the reaction energy are 1.28 eV and 2.94 eV, respectively. The dissociation barrier of water dimer was reduced by 0.13 eV, compared to that of single-water dissociation. The other approach, IS2-3→TS2-3→FS2-3, claims that the dissociation process only occurs in bond contacted water molecule, while close contacted water molecule only serves as a bystander without participating in the dissociation. The activation barrier and reaction energy were calculated up to 1.01 eV and 4.29 eV, respectively. The dissociation barrier of water dimer was decreased by 0.40 eV, compared to that of single-water dissociation. Thermodynamically, water molecule prefers to follow this step by decreasing the reaction energy, rather than the path without co-adsorbed water molecule, demonstrating that water molecule itself acts as an increasingly part in its disintegration procedure. As water molecule is incapable of forming hydrogen bonds with hydrogen atoms from O-H bonds, the part of water molecule enacting as a mediator of H-transfer is unprocurable here. One reasonable explanation is that the electrons of adsorbed water molecule immediately reorganize the dynamic fluctuation of the dipolar water molecules through close contact, which is named as solvation effect. This interaction is of similar strength to the binding of water molecules with the metal and depending on its strength may cause the dissociation of water molecule[34]. During this process, water molecule only acts as a by-stander to influence the reactions without participating in the bond fracture and formation. Furthermore, the pathway of 2-3 has lower activation barrier and higher reaction energy, indicating the bond contacted water molecule is much easier to dissociate than the close contacted water molecule.

3.3.2. $CuOH^{+}+H^{+} \rightarrow Cu^{2+}+H_2O$

Fig. 5 demonstrates the transition search results for the above reaction with or without co-adsorbed water molecule on Cu (111).

As shown in Fig. 5, $CuOH^{+}$ and H^{+} can strongly adsorb on the Cu (111) plane with an adsorption energy value of -6.22 eV. The high activation barrier (3.15 eV), as well as reaction energy (2.01 eV), indicate that the reaction is difficult to occur. There are two alternative pathways with the help of co-adsorbed water molecule. One is the IS5-2→TS5-2→FS5-2, where the H in generated H_2O was from the adsorbed H^{+} on the Cu (111) plane. The high activation barrier and reaction energy are 3.28 eV and 1.94 eV, respectively, which has no significant difference with the pathway of 5-1. During this process, water molecule only acts as a by-stander to influence the reactions without participating in the bond fracture and formation.

The other is IS5-3→TS5-3→FS5-3, where the H in generated H_2O came from the co-adsorbed water molecule on the Cu (111) plane. Under these circumstances, co-adsorbed water molecule participates in the reaction process with the following mechanism: while a hydrogen of co-adsorbed water molecule is transferred to $CuOH^{+}$, the hydrogen of adsorbed H^{+} is simultaneously transferred to co-adsorbed water molecule, resulting in the final species of Cu^{2+}, H_2O and H_2O. Although the co-adsorbed water molecule is not consumed in the whole reaction, the bond of the co-adsorbed water molecule will break and regenerate in order to transfer hydrogen atoms. Hence, the co-adsorbed water molecule acts as an H-transfer media. The activation energy (2.24 eV) was significantly decreased compared to that of the above two pathways, which indicate that this is the most likely pathway during the corrosion process.

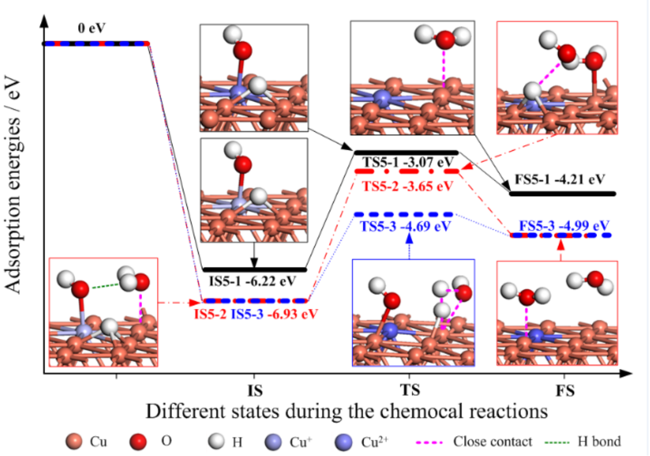

Figure 5. Potential energy plane for reaction (5) with (red and blue curves) or without (black curve) co-adsorbed water molecule on Cu (111) and the optimized structures of initial states (IS), transition states (TS) and final states (FS).

3.3.3. Overview of the effects of co-adsorbed water molecule during the kinetics of corrosion

Based on the above analysis, it can be concluded that the co-adsorbed water molecule, favoring the chemical reactions by decreased reaction energy, plays a promotional role during the corrosion process. In general, co-adsorbed water molecule has two functions to accelerate corrosion. The first one is the solvation effect, where water molecule only acts as a by-stander to influence the reactions through ion dipole interaction, without involving in the bond fracture and formation. This type occurs in the pathways of 2-2, 2-3 and 5-2. During this process, water molecule prefers to merely accelerate the reactions through the solvation effect rather than play the role of the media for H-transfer and the reason is primarily that water molecule is very difficult to form a hydrogen bond with a weakly polarized O-H bond. The second one is the H-transfer mediator, where the bond of co-adsorbed water molecule will break and regenerate in order to transfer hydrogen atoms. This type occurs in the pathways of 5-3. During this process, hydrogen bonding interactions plays an important role. As an overall conclusion, water molecule can accelerate the corrosion of Cu regardless of the solvation effect or the H-transfer mediator mechanism.

4. CONCLUSIONS

The effects of water molecule in the overall corrosion process of Cu were systematically analyzed by using first-principles calculations. The results identify herein that co-adsorbed water molecule has a momentous impact on the thermodynamics and kinetics behavior on the interface. Firstly, water molecule is put forward to play a reinforcing role in the adsorption of pivotal species that are involved in the corrosion process. The co-adsorption energies of H_2O-H_2O, $Cu(OH^{-})_{ads}$-H_2O, and $Cu(OH)_{ads}$-H_2O are 1.49 eV, 2.08 eV, 3.40 eV, respectively, higher than the sum of those of the individual, due to the dynamic fluctuation of the dipolar water molecules. Secondly, co-adsorbed water molecule also favors the fundamental steps of corrosion kinetics. It can significantly decrease activation energy and endothermic reaction energy. Co-adsorbed water molecule uses two mechanisms to accelerate the corrosion. The one is the solvation effect, where water molecule merely acts as a by-stander to influence the reactions through ion dipole interactions, without involving in the bond fracture and formation. The other is the H-transfer mediator, where the bond of co-adsorbed water molecule will break and regenerate in order to transfer hydrogen atoms. The interpretation of the roles of water molecule in Cu corrosion process would provide deeper insights into the reaction mechanisms. During these calculations, the only the co-absorption of water monomers was considered. Many attempts have been made to calculate the co-absorption of small clusters and extended hydrogen bonded networks. Furthermore, co-adsorption of impurities can have a profound effect on the structures formed, particularly in systems where dissociation can be induced by impurities. All of them should be considered for future studies and investigation.

5. ACKNOWLEDGMENTS

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