Equilibrium geometric structure and electronic properties of Cl and H₂O co-adsorption on Fe (100) surface

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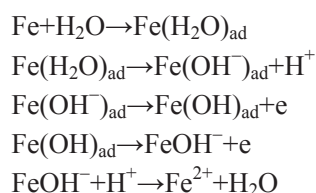
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Based on the first principles density functional theory, the equilibrium geometric structure and surface electronic properties of Cl and H₂O co-adsorption on the Fe (100) surface are investigated. The results indicate that the optimal adsorption site for Cl and H₂O co-adsorption on the Fe (100) surface is the location of Cl at the bridge site and H₂O at the top site. Compared with the Fe (100)/H₂O adsorption system, remarkable changes in geometric structure and electronic properties occur, owing to the presence of Cl in the Fe (100)/(H₂O+Cl) adsorption system. The analysis of equilibrium geometric structure and surface electronic properties shows that the presence of Cl in the Fe (100)/(H₂O+Cl) adsorption system unstablizes the Fe surface, making it easy to lose electrons.

The annual economic loss caused by corrosion is valued at 3 percent of the world's GDP. Thus, corrosion is an important issue and has been studied for a century. However, researches on the mechanism of electrochemical corrosion mostly focused on the effects from the material structure or properties, such as crystal defects, material stress concentration[1,2]. There are few reports concerning the interfacial structure, relationship between the metal and surrounding solution as well as the initial mechanism of electrochemical corrosion. Since the electrical double layer structure at the interface of metal/solution is a significant factor in corrosion[3,4], research on the interfacial structure during electrochemical corrosion at the atomic level is of practical importance.

The reaction process of Fe anode dissolution is as follows:

$$Fe+H_2O \rightarrow Fe(H_2O)_{ad}$$
$$Fe(H_2O)_{ad} \rightarrow Fe(OH^-)_{ad}+H^+$$
$$Fe(OH^-)_{ad} \rightarrow Fe(OH)_{ad}+e$$
$$Fe(OH)_{ad} \rightarrow FeOH^-+e$$
$$FeOH^-+H^+ \rightarrow Fe^{2+}+H_2O$$

The reaction process of anode dissolution shows that the adsorption of H₂O molecules on the iron surface is the first step of anode dissolution reaction. Besides, the electrochemical corrosion will be intensified after adding chlorine ions into the system. Many researchers[5–10] reported that the changes of chlorine ion concentration significantly affect the thermodynamics and dynamics of electrochemical corrosion, although the chlorine ion itself does not participate in the reaction. The effect of chlorine on electrochemical corrosion is directly related to its higher adsorption activity, which affects the electrical double layer structure at the metal/solution interface.

Recently, the adsorption and dissociation of H₂O monomers on metal surfaces were presented by scanning tunneling spectroscopy (STM) and theory calculation methods[11–19]. Some other studies focused on the properties of the metal/solution interface with an H₂O mole-

cules and chlorine atom co-adsorbed on the metal surface by experimental techniques, such as HREELS, ESDIAD and LEED. These papers mainly concern inert noble metals, such as Au, Pt, Ru, Rh, Pd, Cu and Ag. However, there are few reports about H_2O molecule and chlorine atom co-adsorption on the active Fe metal surface. In addition, because of the detection and resolution limits of experimental instruments, it is difficult to accurately clarify the geometric structure and electronic properties at the metal/solution interface. With the rapid improvement of computer power, the simulation by theoretical calculations may compensate for the limits of experimental studies. Actually, the theoretical studies of NH_3, O_2, CO and O adsorption on Ir, Al, Rh, Cu metal surfaces and non-metallic diamond surface have been extensively carried out[20–25]. The simulation method of theoretical calculations also becomes an indispensable method for studying the metal/solution interfacial structure[26,27].

In this work, in order to determine the effect of Cl on the Fe/(H_2O+Cl) interfacial structure and elucidate the relationship between the Fe/solution interfacial electric double layer structure and corrosion mechanism, the equilibrium geometric structure and surface electronic properties of Cl and H_2O co-adsorption on Fe (100) surface are studied based on the first principles density functional theory.

1 Computational methods and models

Density functional theory (DFT), performed with the CASTEP code, has been employed to calculate the geometry optimizations and total energies[28]. Ultrasoft pseudopotentials are expanded within a plane wave basis set with a cutoff energy of 340 eV. The generalized gradient approximation (GGA) for the exchange and correlation effects by the Perdew-Wang 1991[29] is used. The Brillouin zone is sampled using a grid of 3×3×1 Monkhorst-Pack special k points for the adsorption system. Electronic self-consistent field (SCF) cycles are converged to $2.0×10^{-6}$ eV. Based on these calculation parameters, some structure parameters of H_2O molecules and substrate Fe atoms have been calculated: the bond length of O—H and the bond angle of H—O—H are 0.972 nm and 104.8°, respectively, which are in good agreement with the experimental values of 0.971 nm and 104.5°. The calculated lattice constant of Fe is 0.287 nm, which is consistent with the experimental value of 0.289

nm.

Metal surfaces have been modeled by a periodic slab model[15,18,26], which has been extensively used in surface calculations. The crystal structure of Fe is body-centered cubic (bcc). Based on a compromise between the calculation accuracy and efficiency, Fe (100) surfaces are modeled by a periodic array of three layer slabs, separated by a vacuum region equivalent to 15 Å. A p (2×2) unit cell is employed with a single H_2O molecule and a Cl atom on one side of the slab. The experimental structure parameters of H_2O molecules are adopted, and an H_2O molecule is placed parallel to the Fe (100) surface. The surface coverage of an H_2O molecule and a Cl atom is 0.25 molecule layers. In this model, there are nine possible highly symmetric adsorption positions for H_2O molecules and Cl atoms on the Fe (100) surface: H_2O atop site-Cl atop site, H_2O atop site-Cl bridge site, H_2O atop site-Cl hollow site, H_2O bridge site-Cl atop site, H_2O bridge site-Cl bridge site, H_2O bridge site-Cl hollow site, H_2O hollow site-Cl atop site, H_2O hollow site-Cl bridge site and H_2O hollow site-Cl hollow site.

2 Results and discussion

2.1 Geometric structure

(i) Stable geometric structure of the adsorption system The adsorption energies of the nine possible adsorption sites for H_2O molecules and Cl atoms on the Fe (100) surface are listed in Table 1. The adsorption energy is calculated as follows:

$$E_{ad} = E_{slab/H_2O+Cl} - E_{clean} - E_{H_2O} - E_{Cl},$$

where E_{slab/H_2O+Cl} is the total energy, E_{clean} is the energy of the clean Fe (100) surface, E_{H_2O} is the energy of the gas H_2O molecule, and E_{Cl} is the energy of the

Table 1 Nine possible adsorption sites for H_2O molecules and Cl atoms on the Fe (100) surface

The sites for H_2O molecules and Cl atoms	E_{ad} (eV)
H_2O atop site-Cl atop site	−6.13
H_2O atop site-Cl bridge site	−6.47
H_2O atop site-Cl hollow site	−6.44
H_2O bridge site-Cl atop site	−6.22
H_2O bridge site-Cl bridge site	−5.32
H_2O bridge site-Cl hollow site	−6.45
H_2O hollow site-Cl atop site	−6.45
H_2O hollow site-Cl bridge site	−6.31
H_2O hollow site-Cl hollow site	−5.17

gas Cl atom.

According to Table 1, when the initial sites for H_2O molecules and Cl atoms are H_2O atop site and Cl bridge site, the adsorption energy is the largest, with a value of 6.47 eV. It is only 0.02, 0.03 and 0.16 eV lower than those at the site of H_2O bridge site-Cl hollow site, H_2O hollow site-Cl atop site, H_2O atop site-Cl hollow site and H_2O hollow site-Cl bridge site, respectively. Therefore, from the viewpoint of energy, the stable structure of H_2O molecules and Cl atoms co-adsorbed on the Fe (100) surface would be the co-existence of the above five geometry structures. However, the final equilibrium geometric structure figure does not support this proposal.

The above five possible stable geometric structures for H_2O molecules and Cl atoms co-adsorbed on the Fe (100) surface are illustrated in Figure 1. These are the initial sites for H_2O molecules and Cl atoms on the Fe (100) surface: H_2O atop site-Cl bridge site, H_2O bridge site-Cl hollow site, H_2O hollow site-Cl atop site, H_2O atop site-Cl hollow site, and H_2O hollow site-Cl bridge site. In Figure 1, the big white balls and grey balls represent the Fe atoms in the first layer and the second layer, respectively; the small grey balls, white balls and black balls represent Cl, H and O atoms, respectively. Figure 1 reveals that no matter where the H_2O molecule and Cl

atom are in the beginning, the H_2O molecule tends to be located at the top site of the neighboring Fe atom and the Cl atom tends to be located at the bridge site of the two neighboring Fe atoms after geometric optimization. Therefore, it could be deduced that the most stable geometrical structure of H_2O molecules and Cl atoms co-adsorbed on the Fe (100) surface is that the H_2O molecule is located at the atop site and the Cl atom is located at the bridge site. Previous studies[14–19] about the H_2O monomer adsorbed on Au, Pt, Ru, Rh, Pd, Cu, Ag, etc. surfaces indicated that the most optimized site for H_2O adsorbed on the metal surfaces is the atop site and the H_2O molecule tends to align parallel to the substrates. Our earlier research on H_2O monomer adsorbed on single crystal Fe surfaces also obtained the similar results. Consequently, it may be inferred from the calculation results that Cl slightly affects the equilibrium geometric structure of H_2O molecule adsorbed on Fe surfaces.

(ii) Optimized geometric structure of H_2O molecule and substrate Fe atoms

The adsorption energies of the Fe (100)/(H_2O+Cl) co-adsorption system, the Fe (100)/H_2O system and the optimized geometric structure parameters of an H_2O molecule are listed in Table 2, where d_{O-H} is the bond length of the H_2O molecule; $\angle$(HOH) is the bond angle
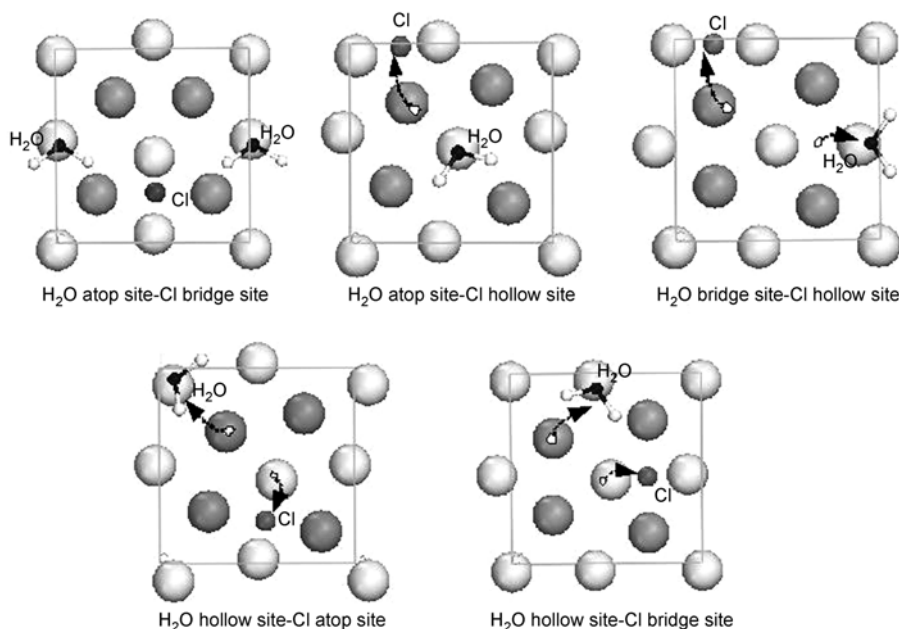

Figure 1 The equilibrium geometric structure for the Fe (100)/(H_2O+Cl) co-adsorption system. The big white balls and grey balls represent Fe atoms in the first and the second layer, respectively. The small white balls and black balls represent H atoms and O atoms, respectively, which comprise the H_2O molecule. The small grey balls represent the Cl atom.

Table 2 Adsorption energies and geometric structure parameters of the adsorption systems

System	E_{ad} (eV)	d_{O-H} (Å)	$\angle$(HOH) (°)	α (°)	d_{12} (Å)	d_{23} (Å)
Clean Fe (100)	–	0.97	104.5	–	1.31	1.31
Fe (100)/H_2O	−1.68	0.98	106.9	19.4	1.05, 1.21	1.05, 1.21
Fe (100)/(H_2O+Cl)	−6.47	0.99	109.2	26.4	1.01, 1.45	0.90, 1.29

of the H_2O molecule; α is the title angle between the H_2O molecule and the substrate; d_{12} is the distance between the first and the second layer of Fe atoms; d_{23} is the distance between the second and the third layer of Fe atoms.

Compared with the Fe (100)/H_2O system, the adsorption energy of Fe (100)/(H_2O+Cl) co-adsorption system is much larger, which indicates that the existence of Cl in the system hastens the interaction of the solid/solution interface. The geometric structure parameters of the H_2O molecule on the Fe (100)/(H_2O+Cl) co-adsorption system and on the Fe (100)/H_2O adsorption system are also quite different: the H_2O molecule in the Fe(100)/(H_2O + Cl) co-adsorption system has a bond length of 0.99 Å, 0.01 Å longer than that in the Fe (100)/H_2O adsorption system. Concerning the $\angle$(HOH) and α, they are 109.2° and 26.4° for the H_2O molecule on the Fe(100)/(H_2O + Cl) system, 2.3° and 7° larger than that for the H_2O molecule on the Fe (100)/H_2O system. These results imply that the existence of Cl significantly affects the geometric structure of H_2O molecule, especially the tilt angle α between the H_2O molecule and substrate. This change in orientation of the H_2O molecule relative to the Fe surface may alter the dipole effect of the H_2O molecule on the substrate and then alter the charge distribution on the Fe substrate.

The layer distance in the Fe (100)/H_2O adsorption system decreases, compared with that in the clean Fe (100) substrate, which indicates that the relaxation of the Fe atoms in the second layer and the third layer occurs. Additionally, d_{12} and d_{23} both have two values, 1.05 Å and 1.21 Å respectively, which shows that the displacement of the atoms in the same layer varies greatly in the vertical direction. Thus, the calculation results demonstrate that the surface Fe atoms relax and are reconstructed due to the adsorption of an H_2O molecule on the substrate. In fact, the atoms in the second layer are displaced much more in the X, Y, and Z directions. For the Fe (100)/(H_2O+Cl) co-adsorption system, compared with the clean Fe (100) surface, d_{12} and d_{23} both decrease. Besides, compared with the Fe (100)/H_2O adsorption system, d_{12} is also different while d_{23} does not

change. The difference between d_{12} and d_{23} demonstrates the effects of the Cl on the Fe(100)/(H_2O+Cl) co-adsorption system. Furthermore, both d_{12} and d_{23} have two different values, indicating the distance variations among atoms of the same layer in the vertical direction. Thus, the surface Fe atoms relax and are reconstructed because of the co-adsorption of H_2O molecule and Cl atom.

2.2 Electronic structure

(i) Work function analysis

The surface work function reflects the stability of the surface electrons. The larger the value of the work function is, the more stable the surface electrons are. The formula for the work function is as follows:

$$\Phi = E_{vacuum} - E_{Fermi},$$

where E_{vacuum} is the vacuum energy and E_{Fermi} is the Fermi energy.

Table 3 The work function of the Fe (100)/(H_2O+Cl) co-adsorption system and Fe (100)/H_2O adsorption system

System	Φ (eV)
Clean Fe (100)	6.20
Fe (100)/H_2O	5.50
Fe (100)/(H_2O+Cl)	4.91

The work functions of the Fe (100)/(H_2O+Cl) co-adsorption system and the Fe (100)/H_2O adsorption system are listed in Table 3. The results indicate that the surface work function decreases by 0.7 eV when an H_2O molecule is adsorbed onto the Fe (100) surface. By contrast, the surface work function decreases by 1.29 eV when an H_2O molecule and Cl are co-adsorbed onto the Fe (100) surface. This implies that the adsorption of the H_2O molecule on the clean Fe (100) surface makes the surface electrons unstable, and the addition of Cl into the system strengthens this instability. Therefore, it may be inferred that although Cl does not directly participate in the electrochemical corrosion reaction, it promotes the activity of the electrons on the Fe surface. This work function analysis is consistent with the results of co-adsorption of an H_2O molecule and Cl on the Pd (111) surface[30].

(ii) Mülliken population analysis

Mülliken charges population of the Fe (100)/(H$_2$O+Cl) co-adsorption system and Fe (100)/H$_2$O adsorption system is listed in Table 4. It can be seen that (1) the positive charge of an H$_2$O molecule increases by 0.04 eV when it is adsorbed on the Fe (100) surface. However, when Cl is added into the adsorption system, the surface positive charge of the H$_2$O molecule decreases from 0.03 to 0.01 eV; (2) for substrate Fe atoms, the total negative charge of the surface Fe atoms increases by 0.04 eV with an H$_2$O molecule adsorbed on the Fe (100) surface. However, when Cl is added into the adsorption system, the total negative charge of the surface Fe atoms decreases and the total positive charge increases to 0.28 eV; (3) for the Fe (100)/(H$_2$O+Cl) co-adsorption system, the negative charge of Cl increases to −0.29 eV; (4) for the Fe (100)/H$_2$O adsorption system, the charge population of the surface atoms shows that the charge of second-layer atoms changes greatly, while that of the first and third layer atoms does not change. For the Fe (100)/(H$_2$O+Cl) co-adsorption system, the charge of the first- and second-layer atoms all changes obviously, but that of the third-layer atoms does not change.

The above results show that the interaction between an H$_2$O molecule and the substrate Fe atoms induces the surface Fe atoms to obtain more electrons and become negatively charged. On the contrary, it induces the H$_2$O molecule to lose more electrons and become positively charged. The sp^3 hybrid orbital of the H$_2$O molecule may exchange electrons with the 3d orbital of a surface Fe atom. The addition of Cl into the system further changes the charge population of the Fe (100)/H$_2$O interface. It makes Fe surface atoms lose more electrons and become more positive, while causing the H$_2$O molecule to obtain more electrons and become positively charged. Therefore, owing to the extremely strong electronegativity of the Cl atom, its existence in the Fe (100)/(H$_2$O+Cl) co-adsorption system significantly changes both the charge population on the metal side of the Fe (100)/(H$_2$O+Cl) interface and the orientation of the H$_2$O molecule in the interface. These two changes both affect the surface dipole effect, decrease the surface potential and lower the Fe surface work function so that Fe surface atoms are more likely to lose electrons and cause electrochemical corrosion. These analyses are in agreement with the geometric structure analysis of H$_2$O molecule after and before adsorption on the Fe surface.

Table 4 Mülliken charges population of the Fe (100)/(H$_2$O+Cl) co-adsorption system and Fe (100)/H$_2$O adsorption system

Atom layers	Before H$_2$O adsorption on the Fe (100) surface and clean Fe (100) surface	Fe (100)/ H$_2$O	Fe (100)/ (H$_2$O+Cl)
H$_1$	0.53	0.43	0.40
H$_2$	0.53	0.43	0.42
O	−1.06	−0.82	−0.81
H$_2$O	0	0.04	0.01
Cl	0	−	−0.29
The first Fe atom layer	0.56	0.56	0.72
The second Fe atom layer	−1.12	−1.16	−1.00
The third Fe atom layer	0.56	0.56	0.56
The total Fe atoms	0	−0.04	0.28

(iii) Density of electronic state analysis

The PDOSs of H, O, Cl and Fe atoms for Fe (100)/H$_2$O and Fe (100)/(H$_2$O+Cl) adsorption systems are shown in Figure 2. Compared with the gas H$_2$O molecule, the H 1s, O 2s and O 2p orbitals of H$_2$O all shift towards deep energy when H$_2$O is adsorbed on the Fe (100) crystal surface. This demonstrates that the substrate Fe atom has some effects on the H$_2$O molecule in the Fe (100)/H$_2$O system. However for the Fe (100)/(H$_2$O+Cl) co-adsorption system, although the addition of Cl does not change the H 1s, O 2s or O 2p orbital energies of the H$_2$O molecule, it creates an obvious shoulder apex near −5 eV of the O 2p orbital. The analysis of electron density difference shows that the electron density near −5 eV energy is all contributed by the Cl atom and O atom (Figure 3(a)), which indicates the significant effects of the Cl on the electron distribution in the system. Figure 2 also clearly shows that such influence mainly comes from the Cl 3p orbital. However, for the substrate Fe atoms, the DOSs of 3p, 4s and 3d outmost orbitals of Fe atoms are obviously intensified when the H$_2$O molecule is adsorbed on the Fe surface. It indicates that the existence of an H$_2$O molecule in the Fe (100)/H$_2$O system greatly affects the electrons density distribution of the substrate Fe atoms. This result is consistent with the analysis of optimized geometric structure. Furthermore, although the existence of Cl in the system does not intensify the electron density of 3p, 4s and 3d outmost orbitals of Fe atoms, the shape of the DOS apex changes greatly near the Fermi level and −2.5 eV energy for the 3d orbital of the Fe atom. Besides, the analysis of electron density difference shows that the electron densities all come from the contribution of surface Fe atoms (Figure 3 (b)), which demonstrates that neither O atoms of H$_2$O molecules nor Cl contribute to
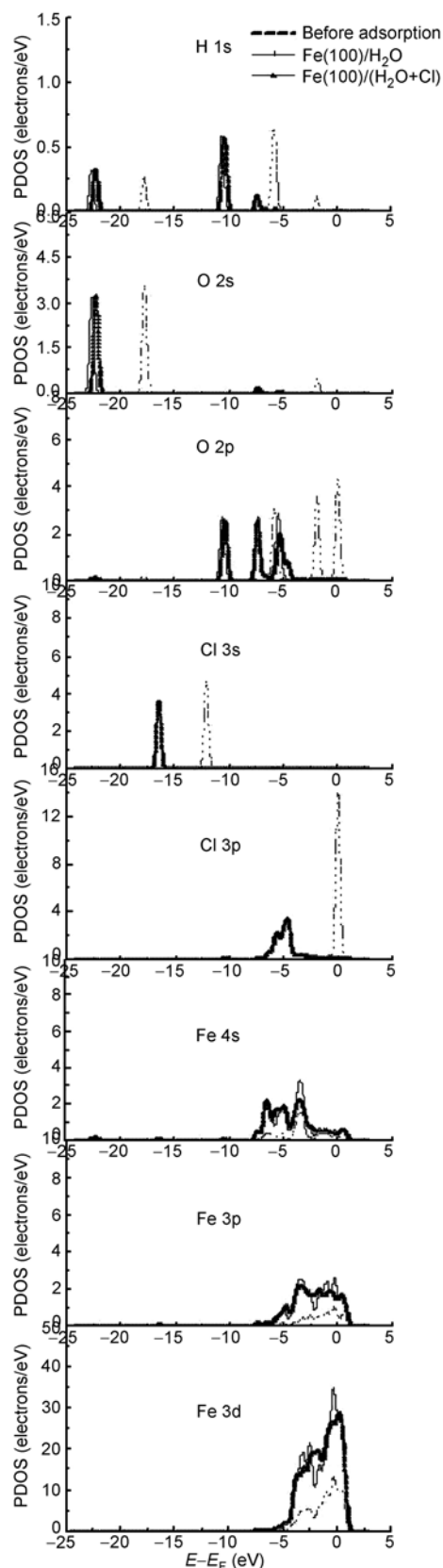
Figure 2 PDOS of the Fe (100)/H_2O and Fe (100)/(H_2O+Cl) adsorption system.
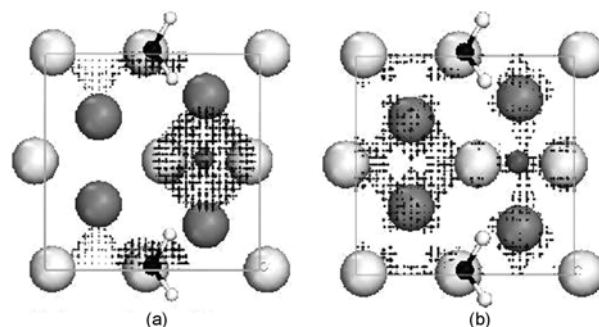

Figure 3 Electrons density difference of the Fe (100)/(H_2O+Cl) adsorption system. (a) Electrons density difference near 5 eV energy; (b) electrons density difference near Fermi energy. The big white balls and grey balls represent Fe atoms in the first and the second layer; the small grey balls represent Cl atoms; the small white balls and black balls represent H atoms and O atoms, respectively, which comprise the H_2O molecule.

the DOS of the Fe atom near the Fermi level. Shape changes of the DOS apex near the Fermi level emerge in the Fe (100)/(H_2O+Cl) co-adsorption system. Because the interaction of Cl with the surface promotes the reconstruction of the substrate Fe atoms, DOS of substrate Fe atoms would alter significantly. Therefore, the existence of Cl in the Fe (100)/(H_2O+Cl) co-adsorption system not only changes the structure of the electronic double layer on the solution side of the Fe (100)/(H_2O+Cl) co-adsorption system, but also obviously changes the equilibrium geometric structure and electronic structure of the substrate atoms. This analysis yields the results identical to the results of the geometric structure and Mülliken population analysis. The discussion above implies that Cl intensifies the interaction of H_2O molecules with substrate Fe atoms. Such results are similar to the results of Cl and Br co-adsorbed with H_2O molecules on Ag (110) surfaces[31–36].

3 Conclusions

(1) The most stable geometric structure for H_2O molecule and Cl co-adsorbed on the Fe (100) crystal surface is the H_2O atop site-Cl bridge site with the H_2O molecule parallel to the substrate.

(2) Compared with the Fe (100)/H_2O adsorption system, the existence of Cl in the Fe (100)/(H_2O+Cl) co-adsorption system increases the adsorption energy and the tilt angle between H_2O molecule and substrate. Additionally, the orientation of the H_2O molecule on the Fe (100) surface changes significantly, and obvious relaxation and reconstruction occur among the substrate Fe atoms. This demonstrates that the co-adsorbed effect

of H_2O molecule and Cl on the Fe (100) surface caused stronger interactions with the substrate Fe.

(3) The existence of Cl in the Fe (100)/(H_2O+Cl) co-adsorption system decreases the surface work function and causes obvious changes in the charge population of the Fe surface. This unstablizes the surface Fe atom and makes electrochemical corrosion reactions occur easier. Furthermore, Cl alters the DOS of the electronic orbital of H_2O molecule and substrate Fe atoms. It also makes the electronic cloud of the Fe (100)/(H_2O+Cl) interface different, and therefore changes the electronic structure of the Fe (100)/(H_2O + Cl) interface.

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