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**DENSITY FUNCTIONAL THEORY BASED MODELING OF THE CORROSION ON IRON SURFACES****MODELOWANIE KOROZJI NA POWIERZCHNI ŻELAZA W OPARCIU O TEORIĘ FUNKCJONAŁU GĘSTOŚCI**

In order to understand the first steps of the aqueous corrosion of iron, we have performed density functional theory (DFT) based calculations for water molecules and pre-covered oxygen on iron surface. The surface structure is modeled by iron atomic layer and vacuum region, and then oxygen atom and water molecules are displaced on the surface. Self consistent DFT calculations were performed using a numerical atomic orbital basis set and a norm-conserve pseudopotential method. According to our calculations, with increasing surface oxygen coverage, the iron surface is found to be not activated, which leads to a feeble adsorption of water molecules on iron surface. Our results show that the surface covered oxygen exerts an influence on the adsorption of water molecules on iron surface.

*Keywords:* density functional theory, aqueous corrosion, iron surface, water molecules, oxygen

W celu zrozumienia początkowych etapów korozji żelaza w środowisku wodnym wykonaliśmy obliczenia dla cząsteczek wody i powierzchni żelaza pokrytej tlenem przy użyciu teorii funkcyjonału gęstości (DFT). Model struktury powierzchni zawiera warstwę atomów żelaza i obszar próżni, a następnie atomy tlenu i cząsteczki wody rozmieszczane na powierzchni. Obliczenia DFT wykonano w zastosowaniu bazy orbitali atomowych i metody pseudopotencjału zachowania normy (norm-conserve). Zgodnie z wynikami naszych obliczeń, ze wzrostem pokrycia powierzchni przez tlen, powierzchnia żelaza nie jest aktywowana, co prowadzi do słabej adsorpcji cząsteczek wody na powierzchni żelaza. Nasze wyniki wskazują, że powierzchnia pokryta tlenem wywiera wpływ na adsorpcję cząsteczek wody na powierzchni żelaza.

**1. Introduction**

It is widely known that iron is a relatively abundant and useful element. Numerous researchers have studied the characteristics. Most theoretical studies of iron surfaces have been focused on the magnetism, surface structure and model catalyst [1, 2]. Theoretical investigation of oxygen adsorption at iron surfaces has been reported by Błoński et al. [3]. Eder et al. have presented a first-principles analysis of initial stages of iron-oxidation caused by water on iron surfaces [4]. The adsorption of sulfur (S) [5] and hydrogen sulphide (H<sub>2</sub>S) [6] on iron surface have been studied using *ab initio* molecular dynamics (MD) simulations. However, the complicated aqueous corrosion mechanism of iron is not fully understood from microscopic levels. Participation of oxygen and water molecules plays a major role in the process of aqueous corrosion. The purpose of this theoretical study is to present a direction for an elucidation of iron aqueous-corrosion reactions from a microscopic point of view.

In the present study, as a first step of a microscopic approach for iron aqueous corrosions, we examined the microscopic effects of pre-covered oxygen for the water adsorption on Fe(100) surface using DFT-based computer simulations. In

conclusion, it was shown by microscopic theoretical calculations that an existent of the dissolved oxygen in an aqueous solution and lattice distortion have influence for corrosion.

**2. Computational approach**

*Ab initio* calculations within the spin-polarized density functional theory (DFT) [7] framework were performed using SIESTA software package [8]. The DFT calculations were carried out with the norm-conserving Troullier-Martins pseudopotentials [9]. Exchange and correlation effects were described using the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) [10]. The energy cutoff of 300 Ry for the grid computation of numerical integrals was used. Double-zeta with polarization functions (DZP) basis set was used as electronic wave functions. A Monkhorst-Pack mesh [11] with 7×7×1 k-point sampling was employed, whereas the Fermi surface was treated with a smearing technique, the electron temperature being set to 300 K.

The clean Fe(100) surface was modeled by a periodic array of symmetric seven layer iron slab in [2×2] unit cells. The dipole-dipole interaction was avoided by using the symmetric slab with no net dipole moment. The thickness of the vacu-

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um between adjacent slabs was set to 15 Å. It is known that four-fold hollow site is the most stable absorption location for the oxygen on Fe (100) surface [3,4], therefore oxygen atoms were located at four-fold hollow site of both sides of the slab. A single H<sub>2</sub>O molecule was adsorbed on both sides of the slab. During structure optimizations all atoms, except the central Fe layer, were allowed to relax until the forces on unconstrained atoms converged to less than 0.01 eV/Å. In order to examine the dynamical behavior at finite temperature, *ab initio* MD calculations were also performed using the Verlet algorithm with a time step of 1 fs at a temperature of 300 K within the canonical ensemble for at least 50 ps.

### 3. Results and discussion

For calculations of the bcc iron bulk crystal, the obtained lattice parameter  $a = 2.882$  Å (2.867 Å) agrees well with the experimental data [12] (quoted in the bracket). The bulk modulus was calculated by fitting the energy curve to the Murnaghan equation of state [13]. The calculated value is 163.8 GPa (170 GPa [12]) in a good agreement with the experimental value. The obtained lattice parameter was used as an input parameter for the surface calculations.

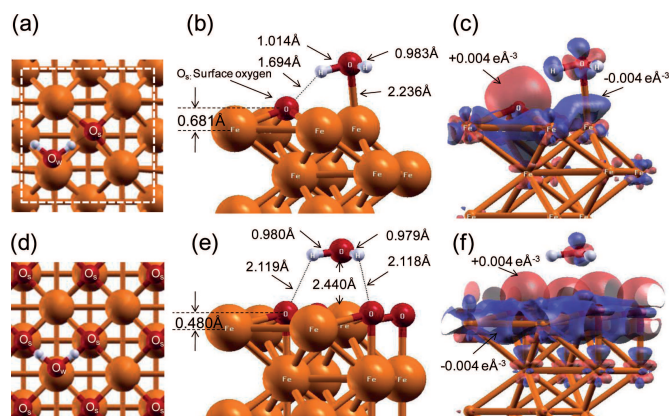


Fig. 1. Top and side views of the optimized structures of adsorbed H<sub>2</sub>O with pre-covered oxygen on the Fe(100) surface: (a),(b) for 0.25 ML and (d),(e) for 1 ML coverage of pre-covered oxygen. (c) and (f) stand for isosurface variations in the adsorption-induced electron density change for an adsorbed H<sub>2</sub>O on oxygen-covered Fe(100) of 0.25 and 1ML. Red (blue) region indicates a gain (loss) of electron density

Figure 1 shows the result of optimized adsorption structures and electron density difference for oxygen surface coverage at 0.25 and 1ML. In the case of surface oxygen (O<sub>s</sub>) coverage 0.25ML, the oxygen atom (O<sub>w</sub>) of H<sub>2</sub>O molecule adsorbs on the iron atom of the outermost surface layer, and the entire H<sub>2</sub>O molecule is slanted at the direction of a hollow site with surface oxygen, and a molecular plane slightly title to the surface. Furthermore, the formation of hydrogen bond (H-bond) is seen between the hydrogen atom of H<sub>2</sub>O and the surface oxygen. From this result, the reaction path to the dissociation via a transition state from a molecular adsorption is considered. At 1ML oxygen coverage, the interaction between the H<sub>2</sub>O molecule and the substrate is weak and the molecular planes of H<sub>2</sub>O remain parallel to the surface without H-bond. In order to examine the charge transfer between H<sub>2</sub>O

molecules and the surface, we have analyzed the H<sub>2</sub>O induced electron density difference on the substrate

$$\Delta\rho = \rho(\text{H}_2\text{O}/\text{sub}/\text{H}_2\text{O}) - \rho(\text{H}_2\text{O}) - \rho(\text{sub}), \quad (1)$$

which corresponds to the interaction-induced rearrangement of the electron density.

Figure 1 (c) and (f) illustrate the result of the induced electron density difference by H<sub>2</sub>O adsorption.

For iron atom, the topmost layer mainly is contributed. The electron density of oxygen atom increases and that of hydrogen and surface iron atom decreases. The result shows that the electron transfer occurs from hydrogen and surface iron atom to oxygen atom.

The binding energy ( $E_b$ ) per H<sub>2</sub>O molecule was calculated as

$$E_b = 1/2E(\text{H}_2\text{O}/\text{sub}/\text{H}_2\text{O}) - 1/2E_{\text{sub}} - E(\text{H}_2\text{O}), \quad (2)$$

where  $E_{\text{sub}}$ ,  $E(\text{H}_2\text{O})$  and  $E(\text{H}_2\text{O}/\text{sub}/\text{H}_2\text{O})$  are the total energies of the oxygen covered iron substrate, the isolated H<sub>2</sub>O molecule and the H<sub>2</sub>O-substrate adsorption system, respectively. Hence, a larger binding energy indicates a more stable structure. Figure 2 (a) shows the binding energy as a function of oxygen coverage. As we can see, the binding energy  $E_b$  decreases as surface oxygen coverage increases. The oxygen coverage versus atomic distance is shown in Figure 2 (b). We find that both  $d(\text{Fe}-\text{O}_w)$  and  $d(\text{H}_d-\text{O}_s)$  distances become longer with increasing the coverage of oxygen on the iron surface. These features are suggested to be due to surface oxygen coverage dependency. Note that the surface oxidation suppresses the adsorption of H<sub>2</sub>O molecules on iron surface. This finding is a step toward determining the mechanism of an iron aqueous-corrosion process.

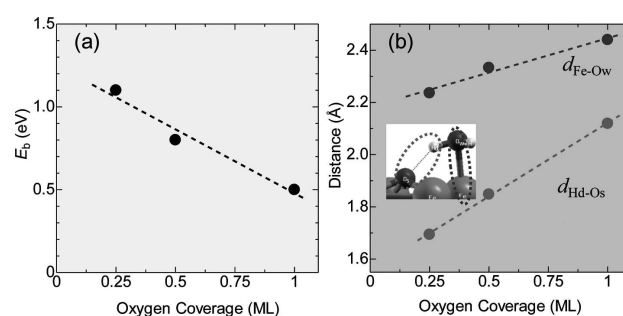


Fig. 2. (a) Calculated binding energies ( $E_b$ ) and (b) atomic distance as a function of oxygen coverage. The labels  $d_{\text{Fe}-\text{O}_w}$ , and  $d_{\text{H}_d-\text{O}_s}$  stand for iron-surface oxygen and hydrogen- surface oxygen, respectively

Figure 3 shows MD snapshots of the H<sub>2</sub>O/substrate system at a temperature of 300 K. The starting configuration of the system is shown as the optimized geometry in Fig. 1 (a) and (b). The hollow and bridge sites are the favorable sites for OH species. On the hollow site, OH group turn to upright standing. On the bridge site, it has lateral position. A surface-lattice distortion of iron is also observed following this behavior.

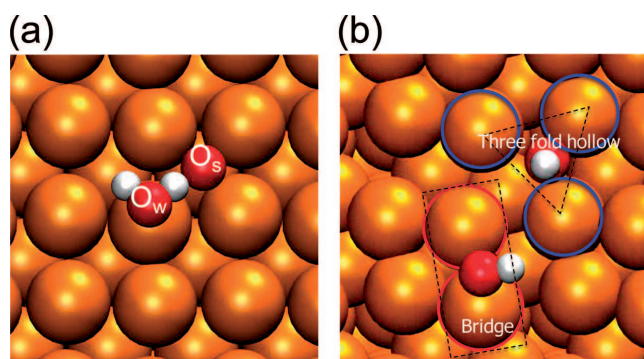


Fig. 3. MD snapshots of  $\text{H}_2\text{O}$  on the Fe(100) with pre-covered surface oxygen (coverage 0.25 ML) at 300 K. (a): initial structure; (b): after 50ps in the MD run

#### 4. Conclusions

DFT calculations were used to study the influence of oxygen pre-covered and the adsorption of water on the Fe(100) surface. In conclusion, as surface oxygen coverage increases, the surface is not activated, which makes the adsorption of water on the surface weak. In this adsorption system, a substantial amount of electronic charge flows from the Fe substrate, in particular, the Fe atoms in the top layer to the surface oxygen. Our MD simulations at 300 K show that the dissociative adsorption reaction of  $\text{H}_2\text{O}$  and oxygen-covered Fe(100) surface occurs with distortion of a surface lattice. The process of the hydroxylation on the surface of iron has been shown by MD simulations.

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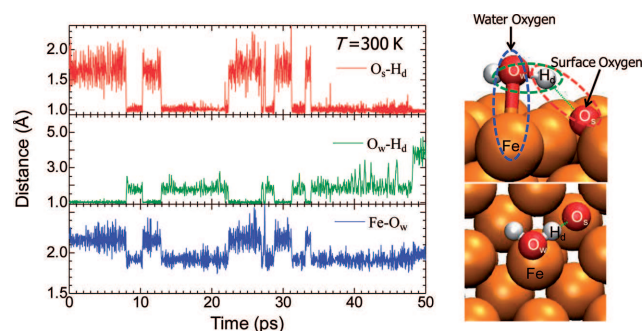


Fig. 4. Time dependence of the distance dissociative hydrogen atom  $\text{H}_d$ , and the surface oxygen atom  $\text{O}_s$  (the water oxygen atom  $\text{O}_w$ ) during MD simulations at 300 K

In Fig. 4, we find that the distance between the surface iron and the oxygen atom of  $\text{H}_2\text{O}$  molecule ( $\text{Fe}-\text{O}_w$ ) varies from 2.2 to 1.8 Å before and after dissociation of  $\text{H}_2\text{O}$  molecule, and the distance between the surface oxygen and the dissociated hydrogen atom ( $\text{O}_s-\text{H}_d$ ) leads to 1.0 Å. This result has suggested the process of the hydroxylation on the surface of iron.

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