Electronic Supplementary Information

First-principles Study on Atomistic Corrosion Processes of Iron

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The First Stage: An O_2 Molecule Adsorption on the Fe(100) Surface near the Fe Dimer

We performed the simulation on the O_2 dissociative adsorption on the Fe(100) surface. We also calculated the adsorption energy of O_2 around the dimer on the Fe(100) surface, not on the top of the Fe dimer. The result is as follows: The absorption energy of O_2 around the Fe dimer on the Fe(100) surface is 6.244 eV (Fig. S1),

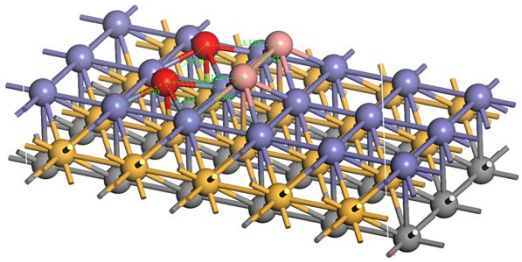

Fig. S1. O_2 adsorbed around the Fe dimer on the Fe(100) surface.

which is larger than the absorption energy of O_2 on the Fe dimer: The absorption energy of O_2 on-top of the Fe dimer (chemisorption) is 4.237 eV (Fig. S2),

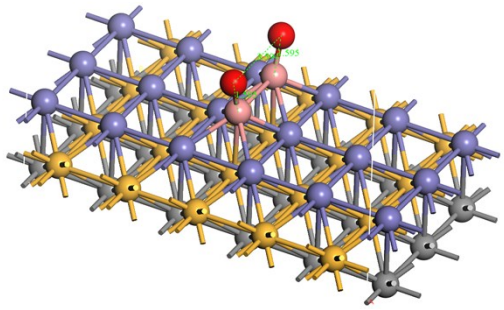

Fig. S2. O_2 chemisorption on the Fe dimer on the Fe(100) surface.

and the absorption energy of O_2 on-top of the Fe dimer (physisorption) is 2.841 eV (Fig. S3):

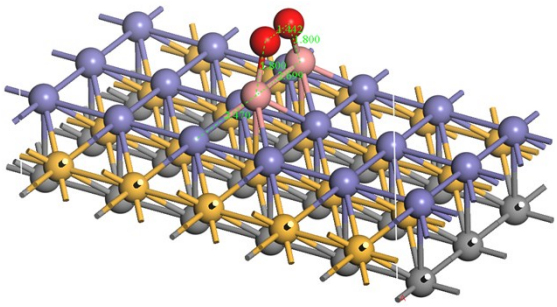

Fig. S3. O_2 physisorption on the Fe dimer on the Fe(100) surface.

However, the O_2 adsorption on the flat Fe surface just facilitates passivation to cover the Fe surface with O, which will protect the Fe surface from further corrosion. On the other hand, the O_2 molecule adsorbed on top of the Fe dimer is locally stable, and it facilitates a catalytic reaction for water splitting. It is well known that the first stage of the iron corrosion process is the hydroxylation of the Fe surface in aqueous solution with oxygen component. Therefore, in nature, it is natural to consider a situation such that the oxide passivation film is at least partially removed by e.g. the Cl^- ion attack. We confirmed also that such a behaviour to facilitate hydroxylation never happens on the flat Fe surfaces.

The Second Stage: Reaction of H_2O and O_2 with $Fe_2(OH)_4$ Molecules

The second stage of iron corrosion process involves the reaction of H_2O and O_2 molecules with $Fe_2(OH)_4$ complexes. The $Fe_2(OH)_4$ molecules are assumed to detach from the Fe(100) surface. The structural properties of the optimized $Fe_2(OH)_4$ molecules such as bond lengths and angles, corresponding to FIG. 9(a) are listed in Table S1.

In the absences of H_2O molecules, the O_2 molecule dissociates into two oxygen atoms to form $Fe_2O(OH)_4$ complexes, as shown in Fig. 9(b). The reaction

$$2Fe_2(OH)_4 + O_2 \rightarrow 2Fe_2O(OH)_4\,, \qquad \text{(S1)}$$

occurs spontaneously without an activation barrier. The bond lengths and angles of the $Fe_2O(OH)_4$ molecule are listed in Table S1.

TABLE S1: Bond lengths and angles of $Fe_2(OH)_4$ and $Fe_2O(OH)_4$ molecules.

molecule	bond	bond length (Å)	bond	bond angle (°)
$Fe_2(OH)_4$	Fe^1-Fe^2	2.448	Fe^1-O^1-H^1	128.320
	O^1-Fe^1	1.782	Fe^1-O^2-H^2	118.635
	O^2-Fe^1	1.810	O^1-Fe^1-O^2	165.781
	O^1-H^1	0.968		
	O^2-H^2	0.979		
$Fe_2O(OH)_4$	Fe^1-Fe^2	2.738	Fe^1-O^1-H^1	120.737
	O^1-Fe^1	1.775	Fe^1-O^2-H^2	118.797
	O^2-Fe^1	1.791	O^1-Fe^1-O^2	142.606
	O^1-H^1	0.975	O^1-Fe^1-O^3	111.580
	O^2-H^2	0.973	O^2-Fe^1-O^3	105.743
	Fe^1-O^3	1.773	Fe^2-Fe^1-O^3	39.411

If H_2O molecules exist around the $Fe_2O(OH)_4$ molecule, the following reaction takes place

$$Fe_2O(OH)_4 + H_2O \rightarrow Fe_2(OH)_6 \quad \text{(S2)}$$

by getting over an activation barrier. By conducting a TS search, the reactant R_3^2, intermediate structure IM_3^2, transition state TS_3^2 and product P_3^2 of this reaction are obtained, as depicted in Fig. 10. The bond lengths and angles of the structures are summarized in Table S2.

TABLE S2: Bond lengths and bond angles of reactant, transition state and product that form during the reaction between two $Fe(OH)_3$ molecules.

molecule	bond	bond length (Å)	bond	bond angle (°)
reactant	Fe^1-O^1	1.841	Fe^1-O^2-Fe^2	126.934
	O^1-H^2	2.909		
	Fe^1-O^2	2.026		
	O^2-H^2	0.975		
	Fe^2-O^2	1.909		
transition state	Fe^1-O^1	2.018	Fe^1-O^2-Fe^2	140.621
	O^1-H^2	1.313		
	Fe^1-O^2	1.986		
	O^2-H^2	1.168		
	Fe^2-O^2	1.830		
product	Fe^1-O^1	2.144	Fe^1-O^2-Fe^2	133.973
	O^1-H^2	1.021		
	Fe^1-O^2	1.802		
	O^2-H^2	2.870		
	Fe^2-O^2	1.775		