

Effect of oxygen adsorption on the corrosion behavior of the Ti(0001)-surface: A DFT investigation

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■ SUPPORTING INFORMATION

Fig. S1. Adsorption structure of oxygen molecules dissociated on Ti(0001) surface.

Fig. S2. Side and Top view of the optimized 3×3 TiO₂(110) slab. The vacancy structures were achieved by removing the Ti atom circled by dotted lines.

Fig. S3. Vibrational and entropic contributions to the Gibbs surface free energy for the Ti(0001)/O structure due to the adsorbed O-atoms.

Fig. S4. Relationships between the $\Delta G_{Ti(0001)}$ and P_{O_2} at (a) $T = 300$ K, (b) $T = 500$ K, (c) $T = 700$ K, (d) $T = 900$ K.

Fig. S5. Side and Top view of the optimized 3×3 TiO₂(110) slab. The vacancy structures were achieved by removing the Ti atom circled by dotted lines.

Fig. S1. Adsorption structure of oxygen molecules dissociated on Ti(0001) surface.

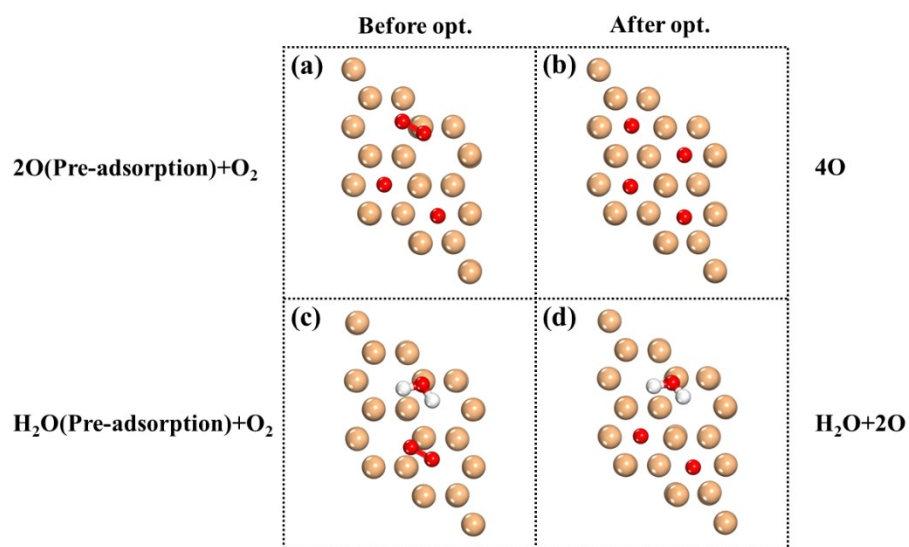


Fig. S2. Side and Top view of the optimized an oxygen atom stabilized at FCC and HCP sites on Ti(0001) surface, and the average length of the formed Ti-O bond is labeled.

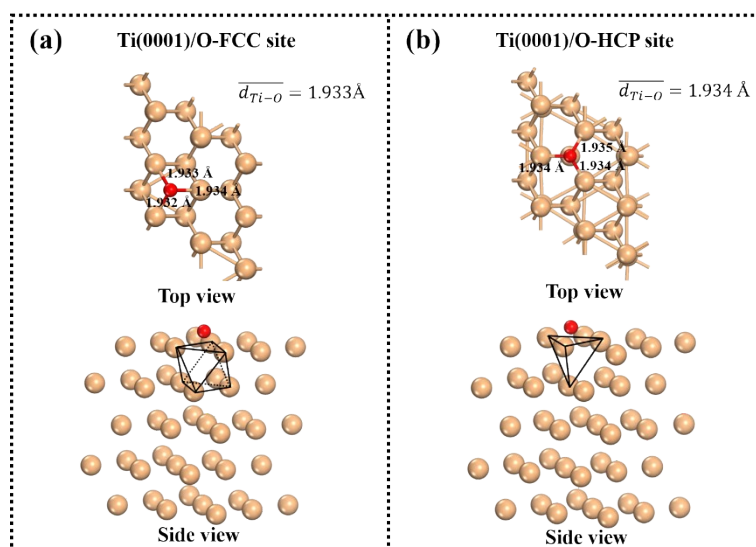
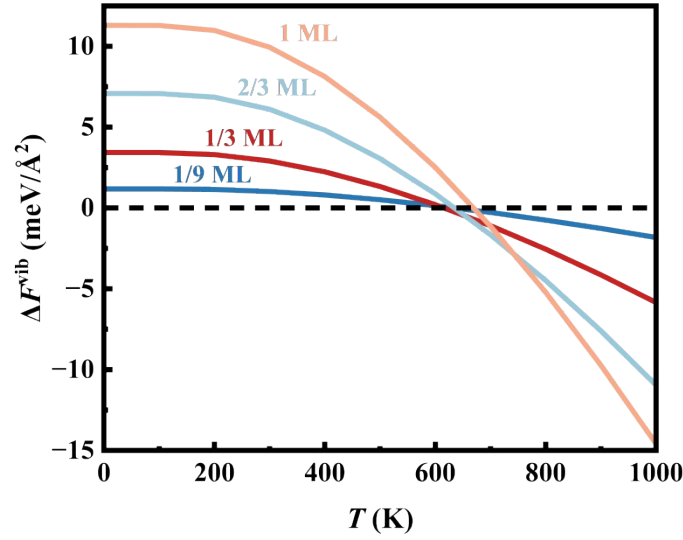


Fig. S3. Vibrational and entropic contributions to the Gibbs free energy for the Ti(0001)/O structure due to the adsorbed O-atoms.



Vibrational contributions to differences in the Gibbs free energies of extended systems often exhibit some cancellation. However, when there are additional atomic or molecular species which are not present in the clean Ti(0001) surface, the situation may be different as there will be no cancellation possible. For the Ti(0001)/O structure, we investigate the contribution due to the adsorbed O atoms. To do this, we calculate the zone-center (Γ -point) normal vibrational modes by diagonalizing the dynamical matrix. We then use the obtained oxygen modes ω_i to evaluate the vibrational and entropic contributions to the Gibbs free energy $\Delta F^{vib} = E^{vib} - TS^{vib}$ as

$$\Delta F^{vib}(T) = \sum_i \left[\hbar\omega_i \left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega_i} - 1} \right) - k_B T \left(\frac{\beta\hbar\omega_i}{e^{\beta\hbar\omega_i} - 1} - \ln(1 - e^{-\beta\hbar\omega_i}) \right) \right],$$

Where $\beta = \frac{1}{k_B T}$.¹ We have altogether 3, 9, 18 and 27 frequencies for $\theta = 1/9, 1/3, 2/3$ and 1 ML, respectively, since there are 1, 3, 6 and 9 O atoms per cell and each with x, y, z modes. **Fig. S3** shows the resulting curve for $\Delta F^{vib}(T)$, showing that the vibrational and entropic contributions to the Gibbs free energy increases with the increase of θ . We take the example of $\theta = 1$ ML. It can be seen that for a temperature of ~ 700 K, the contribution is negligible. At 900 K, it gives rise to a stabilization of the surface structure by about 10 meV, and for a temperature of 300 K, a destabilization by about the same amount is found. Overall, these contributions do not change our qualitative conclusions.

¹ K. Reuter, M.V. Ganduglia-Pirovano, C. Stampfl, M. Scheffler, Metastable precursors during the oxidation of the Ru(0001) surface, *Phys. Rev. B.*, 2002, **65**. <https://doi.org/10.1103/Physrevb.65.165403>.

Fig. S4. Relationships between the $\Delta G_{Ti(0001)}$ and P_{O_2} at (a) $T = 300$ K, (b) $T = 500$ K, (c) $T = 700$ K, (d) $T = 900$ K.

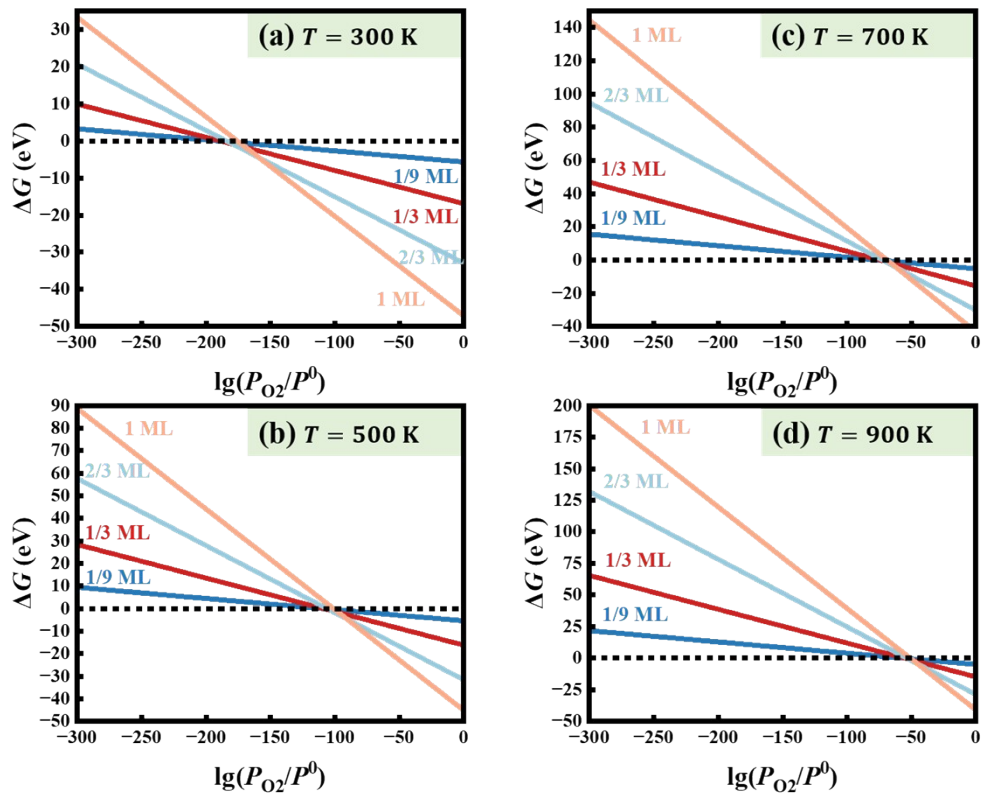


Fig. S5. Side and Top view of the optimized 3×3 $TiO_2(110)$ slab. The vacancy structures were achieved by removing the Ti atom circled by dotted lines.

