

Hydrogen Bond Networks in the Electric Double Layer Dominate the Stability of Titanium Passivation Film

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Abstract This study explores how hydrogen bonding at electrochemical interfaces influences corrosion processes. While hydrogen bonds have recently been recognized for their role in electrocatalytic selectivity and hydrogen transfer, their impact on charge transfer at corrosion interfaces has not been thoroughly investigated. Our findings demonstrate that the hydrogen bonding network on metal surfaces significantly affects the corrosion process at atomic and electronic levels, highlighting how these bonds act as pathways for electron transfer. This insight offers a deeper understanding of the role of hydrogen bonding in corrosion electrochemistry. Building on this, our previous work provided detailed hydrogen bond characterization¹ and introduced quantitative indicators for assessing hydrogen bonds². Additionally, we examine the effects of key sulfides—hydrogen sulfide (H₂S), carbonyl sulfide (COS), and dimethyl sulfide (DMS)—on the stability of titanium oxide passive films in seawater. Through density functional theory (DFT) and ab initio molecular dynamics (AIMD), we analyze the adsorption and surface electronic properties of these sulfides on the anatase TiO₂(101) surface. The optimal adsorption configurations for H₂S, COS, and DMS on the anatase TiO₂(101) surface are 2O_b-vertical, O-down-vertical, and O_b-parallel, with adsorption energies of -1.32, -0.67, and -1.86 eV, respectively. Through comparative AIMD simulations of three different aqueous solutions on the TiO₂(101) surface, we have observed that COS exerts a more pronounced influence on the electrical double layer within 3.00 Å of the TiO₂(101) surface. Specifically, the hydrogen atoms of water tend to aggregate towards the O_b atoms, forming hydrogen bonds, which significantly impacts the corrosion resistance of the TiO₂ surface.

Keywords Titanium; DFT; AIMD; Charge Transfer; Hydrogen Bond

Reference

- (1) Meng, X.; Li, X.; Zhang, Q.; Zheng, R.; Wu, L.; Cao, F. Interfacial Adsorption and Electron Properties of Water Molecule/Cluster on Anatase TiO₂(101) Surface: Raman and DFT Investigation. *Langmuir* **2022**, *38* (3), 1057–1066.
- (2) Meng, X.-Z.; Li, X.-R.; Yan, H.-J.; Zhang, Q.-H.; Wu, L.-K.; Li, F.; Cao, F.-H. Spectroscopic and Simulation Insights into the Corrosion Mechanism of Sulfite on Titanium. *J. Phys. Chem. B* **2022**, *126* (44), 9016–9025.