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How the hydroxylation state of the (110)-rutile TiO₂ surface governs its electric double layer properties[†]

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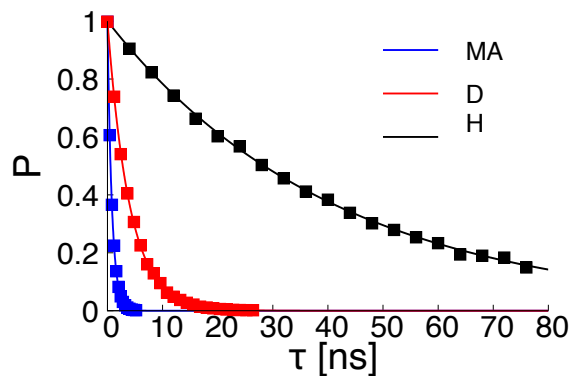


Fig. S1 Survival time correlation function for Na^+ -ions adsorbed between the first and the second hydration layers obtained for the MA, D, and H-type of hydroxylation states.

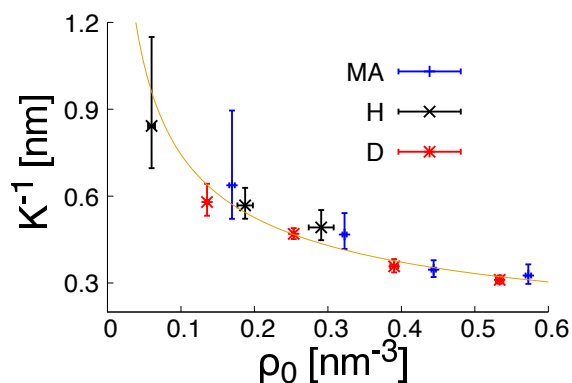
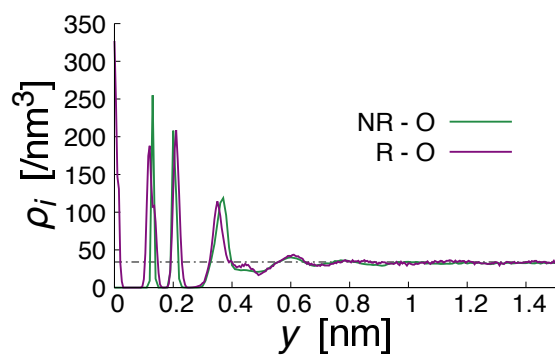


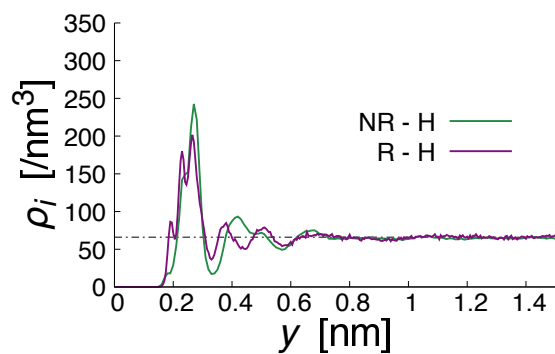
Fig. S2 Variation of the screening length, κ^{-1} , as a function of the salt concentration, ρ_0 , obtained for the MA, D, and H-type of hydroxylation states.

mechanism	ReaxFF	DFT
pristine		
$\text{Ti}_{5c} + \text{H}_2\text{O}_w \rightarrow \text{Ti}_{5c}\text{O}_w\text{H}_2$	-0.82	-0.83 ¹ ; -0.98 ²
$\text{Ti}_{5c} + \text{O}_{br} + \text{H}_2\text{O}_w \rightarrow \text{Ti}_{5c}\text{O}_w\text{H} + \text{O}_{br}\text{H}$	-0.76	-0.63 ¹ ; -0.82 ²
defective surface		
$\text{O}_{vac} + \text{H}_2\text{O}_w \rightarrow \text{O}_{br}\text{H}_2$	-0.98	-0.67 ³ ; -0.92 ⁴
$\text{O}_{vac} + \text{O}_{br} + \text{H}_2\text{O}_w \rightarrow 2\text{O}_{br}\text{H}$	-1.7	-1.1 ³

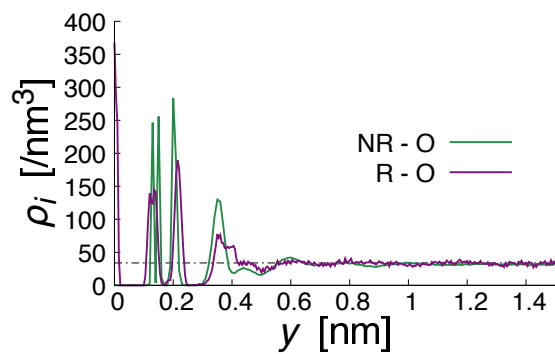
Table S1 Adsorption energies per molecule (in eV) predicted with ReaxFF and compared with DFT values.



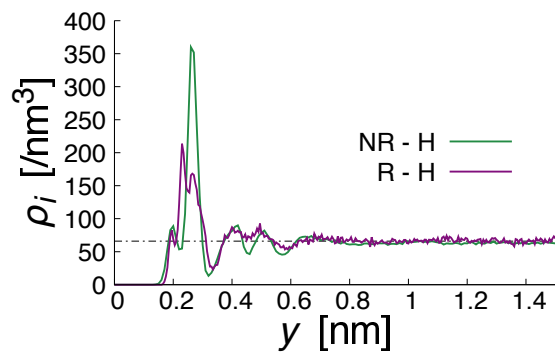
(a)



(b)



(c)



(d)

Fig. S3 Density profile of oxygen and hydrogen atoms along the y -direction normal to the interface modelled in the ReaxFF and Non-Reactive frameworks when considering a pristine surface (a and b), and a surface containing initially 25% of vacancies (c and d) interacting with bulk water.

References

- 1 P. Kowalski, B. Meyer and D. Marx, *Phys. Rev. B*, 2009, **79**, 115410.
- 2 M. Patel, G. Malia, L. Liborio and N. Harrison, *Phys. Rev. B*, 2012, **86**, 045302–1–045302–15.
- 3 S. Wendt, R. Schaub, J. Matthiesen, E. Vestergaard, E. Wahlstrom, M. Rasmussen, P. Thstrup, L. Molina, E. Laegsgaard, I. Stensgaard, H. B. and F. Besenbacher, *Surface Science*, 2005, **598**, 226–245.
- 4 B. Hammer, S. Wendt, and F. Besenbacher, *Topics in Catalysis*, 2010, **53**, 423–430.