Coupling of surface chemistry and electric double layer at TiO\textsubscript{2} electrochemical interfaces

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We used the latest development in density functional theory based finite-field molecular dynamics simulation to model protonic electric double layers at rutile TiO\textsubscript{2} (110)-NaCl electrolyte interfaces. It is found that, due to competing forces from surface adsorption and from the electric double layer, water molecules undergo rapid adsorption-desorption at the negatively charged interface and leads to a much larger Helmholtz capacitance. In addition, proton transfer at the positively charged interface because of the surface acidity contributes significantly to the capacitance value.

Since the discovery of the Honda-Fujishima effect in 1972 for TiO\textsubscript{2} [1], metal oxide photo-electrochemistry attracts the perennial interest in water splitting research using solar energy. One key aspects of water photo-electrolysis is the ability of metal oxides to absorb visible light and drive the hydrogen (oxygen) evolution reaction. This demands metal oxides to have the right band alignment with respect to the water redox potential, for example, the conduction band minimum should be higher than the H\textsuperscript{+}/H\textsubscript{2} reduction potential [2, 3]. In addition, metal oxide should be stable and resistant to photo-induced corrosion in aqueous solution [4].

Because of this interest, TiO\textsubscript{2} and water interactions in ultrahigh vacuum have been studied diligently using both experimental and computational techniques [5–7]. One particular question in attention is the percentage of dissociative absorption of water molecules at the rutile TiO\textsubscript{2} (110) surface [8–10], which serves as an appropriate model system for studying photocatalytic properties of metal oxides.

Comparing with solid-gas interfaces, solid-liquid interface is more relevant for metal oxide electrodes at working conditions. Recent advancements in surface x-ray diffraction and scanning tunneling microscopy provide information regarding the chemical state at the rutile TiO\textsubscript{2} (110) surface and reveal the existence of ordered hydroxyl groups coordinated by water molecules [11]. On the other hand, computer simulations highlight the dynamic nature of the rutile TiO\textsubscript{2} (110)-water interface [12].

The surface chemistry of metal oxides is more involved than that of metals because the surface charge depends on the pH of the environment [13, 14]. The condition in which the surface is charge neutral is called the point of zero net charge (PZC). However, working conditions for most earth-abundant metal oxide based photo-catalysts are not at PZC and the corresponding solid-liquid interface is highly electrified [15]. By attracting coutherions from the solution side, the electric double layer (EDL) is formed at the interface in which the electric field can be as high as 10\textsuperscript{9} V/m [16]. Therefore, including the coupling between surface chemistry and EDL at the rutile TiO\textsubscript{2} (110)-electrolyte interface is at the forefront of modeling its electrochemical reactivity.

Density functional theory based molecular dynamics (DFTMD) is a suitable technique for modeling the electrified rutile TiO\textsubscript{2} (110) interface at the atomic scale, which encompasses the electronic, structural and dynamical ingredients on an equal footing. DFTMD modeling of solid-liquid interface has has been applied to different areas, such as studying the structure of water (defects) at solid interfaces [12, 17–19], spectroscopic modeling of surface-sensitive vibrational signals [20–22], computing the surface acidity [23–26] and determining the redox potential [27–30].

In spite of these successes, electric properties, such as the dielectric constant and the interfacial capacitance which are at the heart of modeling the electrified solid-liquid interface, were usually thought to be beyond the reach of DFTMD. Thanks to the development of constant electric displacement $\bar{D}$ Hamiltonian for the modeling of ferroelectric nanocapacitors by Vanderbilt and co-workers [31], electric properties became more accessible to DFTMD simulations [32–37]. We are therefore in a position to apply the hybrid constant $\bar{D}$ simulation with PBE functional [38] to the charged rutile TiO\textsubscript{2} (110)-NaCl electrolyte interface as implemented in CP2K [39, 40].

The differential capacitance $C_{\text{EDL}}$ of the EDL at oxide materials-electrolyte interfaces has been long regarded as a key probe of its structure. For semiconducting oxides,
the capacitance can be resolved into three distinct components connected in series [2, 3]:

\[
1/C_{\text{EDL}} = 1/C_{\text{SC}} + 1/C_{\text{H}} + 1/C_{\text{GC}} \tag{1}
\]

The first component is the result of the depletion or accumulation of electrons in the space charge (SC) layer of the semiconductor electrode, which can be 10 to 100 nm thick. This is clearly beyond the typical dimension accessible to electronic structure calculation. The second component \(C_{\text{H}}\) is the Helmholtz capacitance due to specific adsorption of hydroxide groups or protons and corresponding counter ions. The last component \(C_{\text{GC}}\) called the Gouy-Chapman capacitance, stems from the diffusive electrolyte and depends on the ionic strength. \(C_{\text{SC}}\) is the smallest of three capacitances and will normally dominate in the inverse sum. However, its effect has been eliminated at the flatband potential [2]. At the high ionic strength which is relevant for photoelectrocatalysis, the diffuse ionic layer has the highest capacitance and the inverse \(C_{\text{GC}}\) term can therefore be ignored. Based on these considerations, modeling the Helmholtz capacitance \(C_{\text{H}}\) is what we focus on in this work.

Conventionally, the Helmholtz capacitance can be computed as \(C_{\text{H}} = q/\Delta \phi\) according to the textbook definition, where \(q\) is the surface charge and \(\Delta \phi\) is the potential drop crossing the Helmholtz layer [41, 42]. Instead, by exploring the modern theory of polarization and constant \(D\) method developed by Vanderbilt and co-worker for treating ferroelectric nanocapacitors [31], we reformulated this problem in terms of the macroscopic polarization \(P_z\) of the system [34]. In our setup, the two sides of the oxide material can be charged at fixed chemical composition (as in experiments) and the supercell cell contains a net polarization. This scheme leads to a succinct expression of the average Helmholtz capacitance \(C_{\text{H}}\) based on the supercell polarization \(P_z\) [34]:

\[
C_{\text{H}} = \left(\frac{\partial q}{2\pi L_z \partial (P_z)}\right)_D \tag{2}
\]

where \(L_z\) is the dimension of the model system perpendicular to the interface. The advantage of this formulation is three-fold. First, it does not require additional vacuum slab in the modeling as commonly used in surface science [43, 44] and the oxide is treated as one piece of material. Second, it removes the finite-size error which plagues the computation of the Helmholtz capacitance [34]. Third, by switching the electric boundary condition to constant \(D\), the relaxation of \(P_z\) is significantly accelerated as predicted by the Debye theory of dielectrics [32, 33].

When the oxide surface is charged by protonation or deprotonation, \(P_z\) deviates from zero in response. Therefore, \(P_z\) has to be zero at the PZC and this serves as a critical test for the convergence of DFTMD simulations [45]. As shown in Fig. 1, at the PZC, \(M_z\) relaxes to zero rapidly when switching the boundary condition from \(E = 0\) to \(D = 0\). Within 10 picoseconds, its time average is about 0.02 D. For the case of electrified interface with surface charge \(4e\), \(M_z\) turns out to be -4.76 D within a similar time-scale. In all cases, classical MD simulations were leveraged to pre-equilibrate the system before applying the hybrid constant \(D\) DFTMD simulations [36, 37].

Simulation results of the average Helmholtz capacitance \(C_{\text{H}}\) at the rutile TiO₂ (110)-NaCl interface is shown in Table I. Following Eq. 2, one obtains the average Helmholtz capacitance \(C_{\text{H}}\) which is about 76 \(\mu\)F/cm². Although starting from very different initial configurations, \(C_{\text{H}}\) at surface charge \(q = 2e\) and \(q = 4e\) are in excellent agreement with each other. In order to decompose the overall Helmholtz capacitance into protonic \(C_{\text{H}}^+\) and deprotonic \(C_{\text{H}}^-\), we resorted to the macroscopic averaging technique [40, 46] and monitored the shift of the macro-averaged electrostatic potential with respect to the PZC for the protonic side (Fig. 2 inset). From this decomposition, we found that \(C_{\text{H}}^-\) is about 50% higher than \(C_{\text{H}}^+\). At surface charge \(q = 2e\) (about 20 \(\mu\)C/cm² for the supercell used here [40]), the surface potential for the deprotonic side is about 200 mV and that for the protonic side is about 300 mV, which can be measured in principle.
TABLE I. The averaged Helmholtz capacitance $C_{H}$, protonic Helmholtz capacitances $C_{H}^{+}$ and deprotonic Helmholtz capacitance $C_{H}^{-}$ at different surface charge $q$.

| $q$  | $C_{H}$ (µF/cm$^2$) | $C_{H}^{+}$ (µF/cm$^2$) | $C_{H}^{-}$ (µF/cm$^2$) |
|------|---------------------|------------------------|------------------------|
| 2e   | 81                  | 67                     | 101                    |
| 4e   | 72                  | 59                     | 85                     |

using the surface-sensitive vibrational spectroscopy [47] or the binding energy shift in X-ray photoelectron spectroscopy [48]. The range of experimental estimated capacitance for rutile TiO$_2$-NaCl electrolyte goes from 64 to 160 µF/cm$^2$ [49–51]. The scattered data reflect the nature of the observed capacitance which depends on ionic strength and surface roughness. In particular, the asymmetric pH-dependence (a higher Helmholtz capacitance at high pH) that we observed from DFTMD simulations is in accord with the experimental differential capacitance of rutile at high ionic strength [51] and has been also seen in other metal oxides, such as ZnO [52]. The Stern layer width (the charge separation distance) for the negatively charged TiO$_2$ surface is about 2Å in our simulations (Fig. 2b) and this leads to an estimation of the interfacial dielectric constant of about 23. This number can be compared with the commonly assumed value of 26 for rutile TiO$_2$ in geochemistry and colloid science [53]. On the other hand, we found the Stern layer width for the positively charged TiO$_2$ surface is about the same (~2Å, Fig. 2b), thus the smaller capacitance of the protonic side $C_{H}^{-}$ (Table I) suggests an interfacial dielectric constant of 15 instead. It is worth noting that the maxima in the radial distribution functions of Na$^+$–O$_w$ and Cl$^-$–H$_w$ in bulk salt solutions are 2.4Å and 2.9Å respectively with the PBE functional [54]. Therefore, the asymmetry of the interfacial capacitances found here should largely come from the difference in the dielectric screening at the interface.

At the PZC condition, water molecules are adsorbed to the rutile TiO$_2$ (110) surface as dimers [55]. This is evidenced by the angular distribution of water dipole moments with respect to the normal vector of the surface (Fig. 3a). Water dipole moment preferably points out towards the electrolyte solution with primary and secondary peaks at 48° and 75°. For the positively charged side, the electric field of EDL enhances this pattern by shifting primary peak and secondary peaks to 33° and 48° respectively. The splitting between the two peaks becomes narrower and the overall distribution is less broad in comparison with the neutral surface. The situation is reversed for the negatively charged side. The angular distribution spans almost the whole range of possible values with primary and secondary peaks around 89° and 130°. The much wider angular distribution of water molecules at the negatively charged side comes from two competing factors: chemisorption of water molecules at rutile (110) would orientate water dipole towards to the electrolyte while the electric field in EDL tends to flip it. Indeed, adsorption and desorption can happen dynamically at the negatively charged side in contrast to the positively charged side because of this competition, as seen in Fig. 3b. Since the extent of dielectric screening is proportional to the magnitude of dipole moment fluctuation as formulated in Kirkwood-Onsager theory [33, 56], it is not a surprise that we found the interfacial dielectric constant at the deprotonic side (therefore $C_{H}^{-}$) is much higher than that of protonic one. This dynamical adsorption-desorption process of water molecules observed at the negatively charged side may play a role for the alternative mechanism of O$_2$ production in alkaline solution (high pH) [57], since adsorbed water molecules at the TiO$_2$ surface not only provide the raw material for OH$^-$ production but also block surface sites [5].

The dissociative adsorption of water molecules at the bare rutile TiO$_2$ (110) surface was extensively discussed in literature [8–10]. Indeed, this is also observed for the neutral surface mediated by the neighboring water molecule (Ref. [12] and Fig. 4 a). One would expect the electric field due to the EDL will magnify this effect. However, instead of the dissociative adsorption, the hy-
FIG. 3. a) Probability distribution of the angle \( \theta \) between water dipole moment and surface normal for neutral, positively and negatively charged \((q = 2e)\) rutile TiO\(_2\) (110)-electrolyte interfaces; b) Dynamics of adsorbed water molecules at positively and negatively charged \((q = 2e)\) rutile TiO\(_2\) (110)-electrolyte interfaces.

Dissociation of adsorbed water molecules releases ions to the electrolyte solution. In our simulations, this dominantly happens for the positively charged rutile TiO\(_2\) (110) surface (Fig. 4 b), in accord with a much higher electric field generated in the protonic side.

The pKa of the protonic rutile TiO\(_2\) (110) is determined to be about -1.0 in DFTMD [23]. Therefore, the reaction free energy for the proton transfer between the charged surface groups Ti\(_2\)OH\(^+\) and solvating water molecules is comparable to thermal fluctuation energy at room temperature. Indeed, spontaneous proton exchange between them was observed for the protonic side of rutile TiO\(_2\) (110), as shown in Fig. 4 c. On the other hand, thermodynamics will prohibit the exchange of OH\(^-\) for the deprotonic side. Instead, the resonance of charged group TiOH\(^-\) and surface groups with adsorbed water molecules TiH\(_2\)O has been seen (Fig. 4 d).

To quantify the effect of surface acid-base chemistry on the Helmholtz capacitance, we also carried out additional simulations by constraining adsorbed water molecules and charged surface groups Ti\(_2\)OH\(^+\) to not undergo reaction. When only constraining adsorbed water molecules, the average Helmholtz capacitance \(C_H\) at \(q = 4e\) turns out to be about 80\(\mu\)F/cm\(^2\). This value is very similar to the one about 72\(\mu\)F/cm\(^2\) in Table I without constraints. However, when both adsorbed water molecules and charged surface groups are constrained, \(C_H\) becomes about 44\(\mu\)F/cm\(^2\) which is close to results obtained previously [42]. This significant reduction of capacitance can be understood, because the proton exchange between Ti\(_2\)OH\(^+\) and solvating water molecules will shorten the charge separation distance in the EDL. Therefore, the surface acidity of the oxide is another determining factor for the Helmholtz capacitance.

In summary, the finding of pH-dependent Helmholtz capacitance as an outcome of surface chemistry and EDL coupling highlights the importance of understanding at the atomistic scale. This paves the way to investigate electrochemical reactivity at electrified metal oxide interfaces in solution, e.g. the effect of the capacitance on the Pourbaix diagram and the hole trapping in alkaline solutions.

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Coupling of surface chemistry and electric double layer at TiO$_2$ electrochemical interfaces

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Supplemental Material

THE HYBRID CONSTANT $\bar{D}$ HAMILTONIAN

In this study, we used the hybrid SSV constant $\bar{D}$ Hamiltonian which can be derived either from the thermodynamics argument originally [1] or from a current dependent Lagrangian as shown recently [2]:

$$H_D(v, \varphi, \bar{D}) = H_{PBC}(v, \varphi) + \frac{\Omega}{8\pi} (\bar{D} - 4\pi P_z(v, \varphi))^2$$  \hspace{1cm} (1)

where $P_z$ is the itinerant polarization in the direction of $\bar{D}$ (See Secs. IV B and IV C in Ref. [3] for the elaboration), which is formally defined as a time integral of the volume integral of current [4–9]. $\Omega$ is the supercell volume and $v = (r^N, p^N)$ are the classical degrees of freedom of a $N$-particle system. The electronic degrees of freedom $\varphi_\alpha$, $\alpha = 1 \ldots M$ determining the induced dipoles are collectively represented by $\varphi$. The bar over $D$ emphasizes that it is a control variable instead of an observable. “Hybrid” means the field is only applied in the direction perpendicular to the surface.

In CP2K, one can switch on the hybrid constant $\bar{D} = 0$ scheme by using the following keyword block:

&PERIODIC_EFIELD
  INTENSITY 0.00
  DISPLACEMENT_FIELD T
  POLARISATION 0.0 0.0 1.0
  D_FILTER 0.0 0.0 1.0
&END PERIODIC_EFIELD

CP2K SIMULATIONS OF ELECTRIFIED RUTILE TiO$_2$(110)-NaCl ELECTROLYTE INTERFACES

The electronic structure of rutile TiO$_2$ (110)-NaCl electrolyte systems was solved applying DFT in the Perdew-Burke-Ernzerhof (PBE) approximation [10] using CP2K suit of programs [11, 12]. Basis sets optimized for molecular systems (MOLOPT) [13] with double-\(\zeta\) basis sets with one additional polarization functions (DZVP) and a charge density cutoff of 320 Ry were used. Core electrons were taken into account using the dual-space Goedecker-Teter-Hutter (GTH) pseudopotentials [14].

The model system consisted of a symmetric periodic slab of five layer O-Ti-O trilayer with (4x2) surface cell, 110 water molecules, 5 Na$^+$ and 5 Cl$^-$ ions in a periodic cell of 11.90 Å x 13.20 Å x 38.28 Å. To keep the composition fixed in all setups, the negatively charged side of TiO$_2$ slab is formed by removing H$^+$ from absorbed water molecules and the positively charged side is formed by adding removed H$^+$ to oxygen sites of the other side of TiO$_2$ slab. The integration time-step is 0.5 fs and MD trajectories were collected for about 15ps for each step-up at $\bar{D} = 0$ condition after initial equilibration at $\bar{E} = 0$ condition. The initial configuration for different charge densities were obtained from our previous work of charged insulator-electrolyte systems using a classical point-charge like model [3]. Bussi-Donadio-Parrinello thermostat [15] was used to keep the temperature at 330K throughout all simulations.

The macroscopic polarization is computed using both Resta formula [16] and maximally-localized Wannier functions (MLWFs) [17], as implemented in CP2K. This is an important technical check to ensure the branch consistency because of the multi-valued nature of the macroscopic polarization, as discussed in details in Sec. VI B in Ref. [18]. Electrostatic potential cube files were saved from CP2K every 50 fs and macro-averaging of the averaged electrostatic potential cube file was carried out using MACROAVE code [19].

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