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Surface Orientation Dependent Water Dissociation on Rutile Ruthenium Dioxide

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ABSTRACT

Rutile RuO\textsubscript{2} is a highly active catalyst for a number of (electro)chemical reactions in aqueous solutions or in humid environments. However, the study of the interaction of RuO\textsubscript{2} surfaces with water has been confined largely to the ultra-high vacuum environment, and to the thermodynamically stable (110) surface. In this work, we combine ambient pressure X-ray photoelectron spectroscopy, \textit{in situ} surface diffraction and density functional theory calculations to investigate how four different facets of RuO\textsubscript{2} interact with water under humid and electrochemical environments. The vacant coordinatively unsaturated Ru site (CUS) allows for the adsorption and dissociation of water molecules. Different surfaces exhibit unique binding energetics for –H\textsubscript{2}O and –OH and can allow for different degrees of hydrogen bonding between the adsorbates. Consequently, the degree of water dissociation is found to be sensitive to the surface crystallographic orientation – being maximum for the (101) surface, followed by the (110), (001) and (100) surfaces. This study identifies crystallographic orientation as an important parameter to tune not only the density of active sites but also the energetics for water dissociation; this finding is of great significance for many catalytic reactions, where water is a key reactant, or product.
1. Introduction

Water is an important environmental molecule; it can serve either as a reactant, product, promoter or inhibitor for several different (electro)catalytic reactions on surfaces\(^1\text{-}\(^6\)). In particular, the interaction of water with rutile ruthenium dioxide surfaces is critical to understanding its unparalleled catalytic activity for a number of gas phase and (electro)catalytic reactions\(^7\). Under aqueous conditions, RuO\(_2\) exhibits state-of-the-art activity for the oxygen evolution reaction\(^8\text{-}\(^{13}\)), whose slow kinetics underpins the low efficiencies of renewable hydrogen production\(^14\text{-}\(^21\)). In addition, it serves as dimensionally stable anodes in chlor-alkali electrolysis, which is one of the largest industrial electrochemical processes\(^22\text{-}\(^{24}\)). It has also been used as a model system to study gas phase reactions, such as CO oxidation\(^{25\text{-}\(^{28}\)), NH\(_3\) oxidation\(^{29}\), CH\(_3\)OH oxidation\(^{30}\), HCl oxidation\(^{31\text{-}\(^{32}\)) and NO oxidation reactions\(^{33}\). Notably, RuO\(_2\) surfaces have shown high CO oxidation rates at low temperatures, in realistic humid atmospheres, where other metal oxides suffer from anodic corrosion\(^34\text{-}\(^{35}\)).

The unique interaction of water with RuO\(_2\) surfaces has been a subject of intense investigation, both theoretically\(^36\text{-}\(^{39}\)) and experimentally\(^40\text{-}\(^{41}\), with most studies being focused on the thermodynamically stable (110) facet. The (110) facet exposes two unique Ru sites, namely a coordinatively unsaturated site, CUS, bound to five oxygen atoms and a bridge site bound to six oxygen atoms\(^7\). Dosing gas molecules, such as O\(_2\)\(^{26\text{-}\(^{28}\),30\text{-}\(^{42\text{-}\(^{43}\), CO\(^{25\text{-}\(^{28}\) and NH\(_3\)\(^{29}\) resulted in their adsorption at the CUS site, which has been deemed as the active site for small molecule oxidation. Water on the other hand, has been shown to interact in different ways with rutile surfaces – it can adsorb directly as molecular water on
the CUS site, it can dissociate at the CUS site to form an -OH group, or it can dissociate on bridging oxygen vacancies, with the nature of the interaction being dependent on the defect density, water and oxygen chemical potential. Theoretical and experimental studies on RuO$_2$, and other oxides such as MgO, ZnO, and Fe$_3$O$_4$, suggest that lateral interactions between adsorbates (-H$_2$O, -OH) can stabilize structures where not every water molecule is dissociated, forming an ordered superstructure.

Previous studies have been limited to the ultra-high vacuum (UHV) environment and the (110) facet, with the applicability to high humidity environments, aqueous solutions and different crystallographic facets being unknown. While for the (110) surface, the CUS Ru atoms and the surface Ru atoms bonded to the bridging oxygen atoms are distinct, the CUS Ru atom on the (100), (001) and (101) surfaces are also coordinated to surface bridging oxygen atoms. In addition, for the (001) stoichiometric surface, the Ru surface atoms are only 4 fold coordinated, with the ability to form two additional bonds with reactant molecules. Pseudo-valence charge density contour plots of the (110) and (100) surface have revealed that the change of crystallographic orientation results in a change in hybridization of CUS Ru atoms, which can impact activity and selectivity for a number of different reactions. Previous DFT calculations on these two surfaces have suggested that this also leads to the difference in CO binding strength on the two surfaces, with the (110) surface binding CO more strongly (1.2 eV) as compared to the (100) surface (0.7 eV).

Furthermore, geometric arrangement of CUS sites and bridging oxygen sites that adsorb –OH and –H respectively in the water dissociation process also have had a considerable impact on water activation for isostructural TiO$_2$ surfaces, where the (100) surface was shown to be more active than the (110) termination. Thus, although crystallographic
orientation has shown to play an important role in the activation of small molecules on rutile oxide surfaces, the influence of surface structure on water dissociation ability on rutile RuO$_2$ remains unknown. The influence of the presence of bulk water on the energetics of water dissociation is also questionable. Recent studies on strained SrIrO$_3$ films suggest that while good correlation is observed between oxygen binding energetics and DFT in the gas phase environment (measured using APXPS), no influence on oxygen electrosorption was observed in aqueous solution (measured by shifts in redox peaks observed in cyclic voltammograms)$^{58}$.

Herein, we study the impact of surface structure on the dissociative tendency of water on oriented rutile surfaces of RuO$_2$. Four different orientations were studied – (110), (100), (101) and (001). First, ambient pressure X-ray photoelectron spectroscopy was used to study the chemical speciation on these oxide surfaces in water vapor atmospheres ranging from 0.01 mTorr to 1 Torr. The surface structural changes under electrochemical conditions and a well-defined oxygen chemical potential were studied using surface X-ray scattering, or crystal truncation rod analysis. Finally, density functional theory calculations were used to theoretically investigate the water dissociation tendency as a function of crystallographic orientation. Through the combination of these unique \textit{in situ} probes with \textit{ab initio} theory, our work provides the first molecular-level insight into orientation-dependent water dissociation on rutile RuO$_2$ surfaces. We find that the (101) orientation tends to adsorb water dissociatively, both under UHV and aqueous conditions, while other facets, such as the (100), result in molecular adsorption at higher water pressures. Their interaction with water is very different from the (110) surface where water only partially
dissociates. This study highlights the role of crystallographic termination as an additional lever to tune water dissociation ability on oxide surfaces.

2. Methods

2.1 Sample Preparation

Epitaxial thin films were grown using PLD. The (110), (100), (101) and (001) films were grown on (001)-oriented MgO, (001)-oriented SrTiO₃, (101)-oriented TiO₂ and (001)-oriented TiO₂ substrates (form CrysTec and MTI) respectively from a polycrystalline RuO₂ target. In order to obtain an atomically flat surface, the SrTiO₃ substrates were treated with NH₄F-buffered HF and annealed at 950°C in an oxygen atmosphere for 1 hour, while the MgO and TiO₂ substrates were not pre-treated but annealed at growth temperature for 30 minutes. PLD deposition was carried out using a KrF excimer laser (λ = 248 nm). Films of ~25 nm thickness were deposited at an oxygen pressure of 50 mTorr and cooled to room temperature under 200 Torr oxygen. X-ray diffraction measurements were performed using a four-circle diffractometer (X’Pert PRO, PANalytical) in normal and off-normal configurations and the morphology of the film surface was measured using atomic force microscopy (Bruker Dimension Icon).

Oriented single crystals of the (110), (100) and (101) orientation were obtained using an oxidative evaporation/redeposition method described elsewhere in references 59, 60. The (001) crystal was obtained by cutting and polishing a (110) crystal in the (001) normal direction. Electrical contacts were applied to the back of the crystals and the crystals were
mounted in a Teflon mould (FEP 100, DuPont, Wilmington, DE) with the desired orientation exposed to the electrolyte.

2.2 Electrochemistry

Electrochemical measurements were performed using a Biologic SP-300 potentiostat in a standard three-electrode setup. 120 mL of 0.1 M HClO₄ (70% Veritas® double distilled) was prepared using deionized water (Millipore, >18.2 MΩ cm). The reference electrode used was a 4 M saturated Ag/AgCl electrode (Pine), which was calibrated to the RHE scale. A large surface area Pt electrode was used as the counter electrode. For each measurement, fresh electrolyte was prepared and pre-saturated with Ar for 60 minutes, and Ar was also left bubbling while measuring to prevent oxygen reduction at low potentials. Cyclic voltammetry measurements were performed at 50 mV/s and electrical impedance spectroscopy measurements were conducted at open circuit potential with an amplitude of 10 mV. The potentials reported versus RHE are corrected for the electrolyte/cell resistance (~50 Ω) measured using the high frequency intercept of the real resistance obtained from the Nyquist plot as well as the pH of 0.1 M HClO₄ electrolyte measured using a pH meter. The electronic resistance between the single crystal surface and the wire is < 5 Ω.

2.3 Ambient Pressure XPS

APXPS measurements were collected at Beamline 11.0.2 at Lawrence Berkeley National Laboratory’s (LBNL) Advanced Light Source (ALS). The films were placed onto a ceramic heater and a thermocouple was mounted directly on the sample surface to probe the temperature. The O1s spectra at a given photon energy were calibrated by fixing the
Ru 3d$_{5/2}$ to a binding energy of 280.7 eV at the same photon energy. To ensure that the interaction with water is not affected by ionizing radiation, the O 1s spectra was measured at intervals of 1 hour at the same spot to ensure the spectra remain unchanged (Figure S11).

The samples were cleaned by heating to a temperature of 250 °C in an oxygen pressure of 100 mTorr, until the surface carbon species were removed. Following this, the sample was cooled down to room temperature and the chamber was evacuated to a pressure < $1.5 \times 10^{-7}$ Torr. Water was introduced into the chamber and measurements were made at $p$(H$_2$O) = 0.01 mTorr, 5 mTorr, 50 mTorr, 100 mTorr, 250 mTorr and 1000 mTorr (1 Torr = 133.32 Pa). The H$_2$O was prepared from deionized water (Millipore, >18.2 MΩ cm) and was subjected to several freeze-pump-thaw cycles to degass it. At defined experimental conditions, the O1s was measured 735 eV, 935 eV and 1135 eV incident photon energy, in order to distinguish the surface oxygen species from the bulk oxygen species (Figure S7). C1s/Ru3d measurements were made at photon energy of 490 eV and 735 eV. The valence band and survey spectra were also collected at 490 eV and 735 eV. For the (110) surface, an additional measurement was conducted wherein a clean sample was heated from room temperature to 200 °C in the presence of 100 mTorr water. The C1s/Ru3d and O1s spectra at a photon energy of 735 eV were measured every 25 °C, with the full set of scans measured every 100 °C.

2.4 Crystal Truncation Rod Analysis

Surface diffraction measurements were carried out at Beamline 12 ID-D of the Advanced Photon Source. Specular and off-specular rods were collected using the reflection geometry for each surface at 0.5 $V_{RHE}$ and 1.0 $V_{RHE}$. An incident photon energy of 20 keV was used.
An X-ray transparent Kapton foil (100 µm) was used to seal the cell, and care was taken to trap only a thin layer of electrolyte between the single crystal surface and the membrane to avoid large background signals from the electrolyte. In order to do this effectively, air from the cell was sucked out using a syringe to create a vacuum in the cell. Following this, electrolyte was injected through another syringe to form a thin layer above the crystal surface, due to capillary forces. 0.1 M HClO₄ (70% Veritas® double distilled) solution was prepared using deionized water (Millipore, >18.2 MΩ cm). A saturated Ag/AgCl electrode was used as the reference (BAS, West Lafayette, IN) and a Pt counter electrode was used.

The assembled cell was mounted on a Huber five-circle (3S+2D) diffractometer. Initial sample alignment was performed using a laser beam to ensure that the sample surface normal was at a right angle to the main axis of the diffractometer. Specular rods were recorded using a configuration with the incidence angle = exit angle. For the off specular rods, the incidence angle was fixed at either 2° or 4°. An orientation matrix was calculated to relate the motor angles to the Miller indices (hkl) for the dry sample. The intensities were measured using a pixel photon-counting area detector (PILATUS 100K model). The measured intensities were extracted by integrating the photon counts of the pixels in the region of interest on the detector and were corrected for background noise, illuminated sample surface area, electrolyte thickness and a Lorentz factor that takes into consideration the experimental geometry.

For each surface, a model was created in GenX as shown in Figure S17, S18, S22, S23, S27, S28. At each potential, ~200-300 symmetrically independent data points were used for the fitting. Higher order reflections, such as (30L) and (50L) were not measured since the measured intensity at the anti-Bragg position was too weak to collect statistically
significant data. Details of the initial positions for each surface and the constraints are listed in Table S3-S17. The Figure of Merit to be minimized was:

\[ FOM_{logR1} = \frac{\sum_i |\log(\sqrt{Y_i}) - \log(\sqrt{S_i})|}{\sum_i |\log(\sqrt{Y_i})|} \]

where \( Y_i \) is the experimentally measured intensity for point \( i \) and \( S_i \) is the simulated intensity. All rods were fitted simultaneously, and a value <0.10 was obtained for all conditions, signifying a reasonably good fit. Uncertainties in the bond lengths were obtained by running the simulation ten different times with different initial conditions. The four best simulation results were used to compute the average atomic positions and their standard deviations, following the method described in reference 61. The reported error bars thus represent the robustness of the fitted structure, with the available data.

2.5 Computational Methods

The VASP package\textsuperscript{62-63} using the PBE functional\textsuperscript{64} and PAW projectors\textsuperscript{65,66} was used for the DFT calculations. The super cell used for each orientation was a 1x2 replication, with the replication being performed along the short axis of the cell. This allowed for symmetry breaking and adsorbate-adsorbate interactions. A cut-off energy of 500 eV was chosen and a 6x6x1 Monkhorst-Pack k-point sampling\textsuperscript{67} was used for the super cell. The Gibbs Free Energies were calculated by correcting the DFT obtained energies for the ZPE and vibrational entropy\textsuperscript{68}. The contributions of all atoms beyond the fully reduced surface were considered for the ZPE and vibrational entropy contributions. The adsorbed species were referenced to tabulated values\textsuperscript{69} of gas-phase hydrogen and water at the gas-liquid interface at 0.035 bar and 300 K respectively. The Computational Hydrogen Electrode, described by
Nørskov has been used to represent the data on the RHE scale\textsuperscript{70}. The gas-phase O\textsubscript{2} reference was calculated via the formation energy of water from experimental data to avoid the inaccuracy of DFT-GGA-level O\textsubscript{2} calculations\textsuperscript{71,72}:

\[ 0.5G_{\text{O}_2(\text{g})} = G_{\text{H}_2\text{O}(\text{g})} - G_{\text{H}_2(\text{g})} - \Delta G_{\text{H}_2\text{O} \text{form,exp}} \]

where $\Delta G_{\text{H}_2\text{O} \text{form,exp}} = -2.37$ eV at a pressure of 1 atm and a temperature of 298.15 K.

3. Results and discussion

3.1. Molecular versus dissociative adsorption of water vapor

We first examine the reactivity of gas phase water vapor with oriented RuO\textsubscript{2} thin films (Figure S1 and S2). The thin film surfaces were cleaned \textit{in situ} at 250 °C in an oxygen atmosphere (pO\textsubscript{2} = 100 mTorr) to remove any carbon contamination on the surface (Figure S3 and S4). Water isotherm measurements were performed at 25 °C from a relative humidity of 4.2$\times$10$^{-5}$ % (pH\textsubscript{2O} = 0.01 mTorr) to 4.2 % (pH\textsubscript{2O} = 1000 mTorr). With increasing water vapor pressure, different oxygen species form, distinguishable based on their binding energies in the Oxygen 1s (O1s) spectra\textsuperscript{73}. The lowest binding energy peak at $\sim$529.2 eV is characteristic of oxygen from the oxide lattice\textsuperscript{74,75}. Relative to the lattice oxygen peak, an additional peak at $\sim$1.5 eV higher binding energy grows with increasing water vapor pressure; this peak has been previously assigned to protonated bridging oxygen species\textsuperscript{73,76,77}. In concomitance with this feature, another peak appears at relatively higher binding energies, i.e. at $\sim$3.2 eV above the binding energy of lattice oxygen, which has been assigned previously to molecularly adsorbed water, or –OH adsorbed on the CUS site, with the distinction between the two adsorbates being within the energy resolution of the technique\textsuperscript{76,77}. We note that we find no evidence of the adsorption of carbon-related species.
Upon water dosing from the C1s spectra (Figure S8). This is in accordance with surface science studies probing the interaction of CO$_2$ with RuO$_2$ (110) surfaces, which suggest that carbonates are not stable at room temperature$^{78}$.

Figure 1: (A) Water isotherm at room temperature (~25°C) for the RuO$_2$(110) termination, probing the O1s core level at 735 eV incident energy. Spectra are offset for clarity. Spectra are deconvoluted into gas phase water (H$_2$O$_{\text{vap}}$) shaded in grey, H$_2$O and –OH adsorbed on the CUS site shaded in purple, protonated bridging oxygen in hatched purple and lattice oxygen outlined in black. (B) Intensity of the protonated species on the CUS, either –OH or –H$_2$O (filled) and bridge site (open) normalized to the lattice oxygen peak as a function of water pressure at room temperature. (C) Proposed surface structure at high water pressure showing every second water molecule on the CUS site being dissociated, with the hydrogen donated to the neighboring bridging oxygen (Top view shown in Figure S33).

Upon exposing a clean stoichiometric (110) surface to low partial pressures of water vapor (<100 mTorr), the peak intensities of the protonated species on the bridge and CUS sites normalized to the lattice oxygen peak are equal, indicative of dissociative adsorption of water. This behavior is contrary to that observed at high water partial pressures, wherein the intensity contribution from the protonated species on the CUS site (–OH or –H$_2$O)
grows more rapidly than that from the protonated bridging oxygen species, as seen in Figure 1A and 1B. This implies that with increasing coverage of water-related species on the surface, there is a tendency for water to both adsorb molecularly as well as dissociatively. Our recent work on RuO$_2$(110) surfaces under electrochemical conditions, revealed that at 1.0 V$_{RHE}$, the most stable interaction of water with the (110) surface involved the dissociation of every second water molecule to form –OH/H$_2$O on the CUS site and –OH/O on the bridge Ru site as shown in Figure 1C and Figure S33. Such findings are also consistent with high-resolution STM data and also corresponds to the two computationally energetically degenerate structures predicted by Reuter et al at high water pressure (H$_2$O$_{CUS}$/O$_{BRI}$ and OH$_{CUS}$/OH$_{BRI}$)\textsuperscript{36}.

Changing the surface orientation from the (110) to the (100), (101) and (001) increases the density of Ru$_{CUS}$-O bonds on the surface from 5/nm$^2$ to 7/nm$^2$, 8/nm$^2$ and 10/nm$^2$ respectively\textsuperscript{10,80,81}. However, the differences between the interaction of water with these surfaces cannot only be accounted for by changes in the density of the surface sites. Figure 2A (and Figure S9) compares the O1s spectra of the four different orientations at room temperature in a partial pressure of water vapor of 250 mTorr. It is evident that the (101) surface has the largest propensity to dissociatively adsorb water, with an equal contribution from bridging –OH groups and protonated species on the CUS site, suggesting that majority of the water dissociates to form –OH on the CUS site, with the hydrogen being transferred to the bridging oxygen. This deviates from the (100) surface, where at high pressure, the intensity of the peak corresponding to the protonated CUS oxygen species increases drastically, with minimal increase in protonated bridging species (Figure 2B). This suggests a largely molecular adsorption of water at high partial pressures. Shifts in
the gas phase peak relative to the lattice oxygen peak, used to probe changes in work function\textsuperscript{82} or formation of a surface dipole due to the formation of surface adsorbates, such as $-\text{OH}$\textsuperscript{83,84} (Figure S13, S14) also show that the offset is largest for the (101) facet, followed by the (110), (001) and (100) (Figure S14).

Figure 2: (A) Comparison of the O 1s spectra measured at a photon energy of 735 eV for the noted orientations. Spectra were measured at room temperature (~25°C) and a water vapor pressure of 250 mTorr. Spectra are offset for clarity and have been decomposed into the following components – gas phase water outlined in color, protonated species on the CUS site shaded in the corresponding color, protonated species on the BRI site hatched in the same color and lattice oxygen outlined in grey. (B) Intensity of the protonated species on the CUS (filled) and bridge site (open) normalized to the lattice oxygen peak as a function of water pressure at room temperature for the (101) surface (in red) and the (100) surface (in blue). At low partial pressures (<50 mTorr), both orientations adsorb water dissociatively, while at high partial pressures, the (101) surface preferentially adsors water dissociatively compared to the (100) surface. (C) Computationally calculated free energy for total (in solid lines) and partially dissociated water (in dashed line) configurations on the stoichiometric surface, for the four different surfaces. The free energy for the two conditions have been referenced to the corresponding stoichiometric surface with a full coverage of water adsorbed on the CUS site, which is shown as a solid grey line at a free energy of 0 eV.
In order to verify these experimental observations, DFT calculations were performed to study the energetic preference of the adsorbate configurations at high water partial pressures for the different oriented surfaces, as shown in Figure 2C. For each surface, a comparison was drawn between the energetics of a fully dissociated water configuration, where each water molecule dissociates to form –OH on the CUS and –OH on the bridge site and a partially dissociated water configuration where only every second water molecule was deprotonated to form –H₂O/OH on the CUS and –O/OH on the bridge site (Figure S32). The energetics of these structures was referenced to the configuration where water does not dissociate on the surface, but adsorbs molecularly (fixed at a Gibbs Free Energy of 0 eV). For both the (100) and (001) surfaces, the partial and total dissociation of water have positive free energies and are less stable than water adsorbing molecularly on the surface, in agreement with the experimental results. In contrast, the three configurations are almost isoenergetic for the (101) surface, with the total water dissociation case being the most favorable.

3.1. Interaction of water with RuO₂ under electrochemical conditions

While the interaction of water vapor with different facets of RuO₂ and the energetics of different surface sites for water dissociation can be probed using APXPS, the surface structure under electrochemical conditions remains unknown. We estimate that the O₂/H₂O equilibrium potential at room temperature for the pressure of water (and background oxygen) in the chamber during APXPS measurements corresponds to a potential of ~0.5-0.7 V_RHE⁸⁵ (calculation shown in Supplementary Information). In order to relate the
interaction of oriented RuO₂ surfaces with water vapor to their surface structure observed in an aqueous environment, we perform surface X-ray scattering measurements on single crystals of (110), (100), (101) and (001) surfaces at 0.5 V₉₉ and 1.0 V₉₉ in 0.1 M HClO₄. This allows us to capture the structural changes accompanying the redox transition at ~0.7 V₉₉, as shown in Figure S16. For further analysis and discussion, the surface normal is referred to as the (001) direction and the two in-plane directions as the (100) and (010) directions, irrespective of the surface orientations.

The measured intensity (in open circles) for the two potential conditions measured are shown in Figure 3 for the rods that change most drastically as a function of potential, with the remaining rods shown in Figure S21, S26 and S31. Surface structure models for each orientation were created in GenX86 (Figure S17, S18, S22, S23, S27, S28). The simulation model consists of distinct layers, and atoms in each layer are subject to fitting constraints. Detailed initial and final atomic positions and constraints are listed in Table S3-S17. In order to verify the experimental findings, DFT computed diagrams showing the most stable structure realized at a given potential were constructed. We note that based on experimental findings, energetics of several adsorption configurations were computed (Table S18-S20), with only the most stable configurations denoted in Figure 4.

Our previous work on the (110) surface79 assigned the surface structure at 0.5 V₉₉ to be one where the CUS site was filled with loosely bound water (RuCUS-O bond length (2.68
Å), owing to the fitted bond length being significantly larger than the equivalent $\text{Ru}_{\text{bulk}}$-O distance of 1.94 Å. It is deduced from Figure 3A, that at these low potentials, the bridging oxygen was protonated, with the fitted $\text{Ru}_{\text{BRI}}$-O bond length found to be 2.19 Å, significantly larger than previously observed $\text{Ru}_{\text{BRI}}$-O bond lengths (1.93 Å) on the stoichiometric surface from previous LEED measurements$^{25}$. A similar structure with water adsorbed on the CUS site with a protonated bridging oxygen was found to be stable at low potentials using DFT$^{39,79}$. At 1.0 $V_{\text{RHE}}$, the $\text{Ru}_{\text{CUS}}$-O bond distance was found to decrease significantly by ~0.5 Å to 2.19 Å and the $\text{Ru}_{\text{BRI}}$-O bond length was changed by ~0.24 Å to 1.95 Å. The $\text{Ru}_{\text{CUS}}$-O bond length is shorter than the computed $\text{Ru}_{\text{CUS}}$-O bond distance for adsorbed water (2.26 Å), but is still significantly longer than the $\text{Ru}_{\text{CUS}}$-O bond distance for an adsorbed oxygen on the CUS site (1.70 Å)$^{44}$ and the equivalent bulk Ru-O bond length (1.94 Å). This, along with our DFT results and previous experimental work suggested that the structure at 1.0 $V_{\text{RHE}}$ is a stoichiometric surface with every second water molecule on the CUS site dissociated to form –OH on the CUS site with the proton transferred to the neighboring bridging oxygen. As mentioned earlier, the structure realized at 1.0 $V_{\text{RHE}}$ under aqueous conditions is the same as the predicted “partially dissociated” water structure observed at high water pressure with APXPS.
Figure 3: (10L) rods measured at 0.5 $V_{RHE}$ (bottom) and 1.0 $V_{RHE}$ (top) for the (A) (110) (B) (101) (C) (100) surfaces and (D) the (00L) rod measured at 0.5 $V_{RHE}$ and 1.0 $V_{RHE}$ for the (001) surface in 0.1 M HClO$_4$. The experimentally measured intensities are shown in open points and the best-fit results from the fitting process are shown in solid lines of the corresponding color. Ball and stick models for the best-fit structures are shown adjacent to the fitted rods. Maximum experimental uncertainty in bond lengths is 0.06 Å, with detailed atomic positions found in Tables S3-S17. Pink and red spheres represent Ru and O atoms respectively. Bond lengths between surface Ru and adsorbed O species are labeled.

We next consider the (101) orientation, which, according to APXPS, was the surface upon which, water dissociation was most facile. The (10L) rod measured at the two potentials shows distinct changes in the anti-Bragg region at $L \sim 1.5$, in both the position of the minima and the degree of concavity, as seen in Figure 3B. These changes can be reproduced by a simple change in the RuCUS-O bond length (Figure S19 and S20). Performing a complete fitting of all rods, results in a surface structure with one loosely
bound water molecule on every alternate CUS Ru site with a RuCUS-O bond length of 2.79 Å, much larger than the Rubulk-O distance of 1.94 Å. The RuBRI-O bond length on the other hand, was found to be 2.06 Å, longer than the RuBRI-O bond distances observed by LEED for a stoichiometric surface (1.93 Å)\textsuperscript{25}, suggesting the presence of a protonated bridging oxygen species at low potentials. DFT results suggested that at low potentials, while the bridge Ru sites were hydroxylated, the CUS sites had an equal occupation of adsorbed -H\textsubscript{2}O and -OH groups. While the initial CTR fitting suggests that half the CUS sites were filled with water and the other half were vacant, filling 25% of the vacant sites with oxygen and a RuCUS-O bond length of 2.00 Å does not alter the figure of merit of the fit. Thus, we cannot completely exclude the presence of any –OH on alternate CUS sites. Increasing the potential to 1.0 V\textsubscript{RHE} results in a structure where the RuCUS-O bond length is dramatically decreased to 2.04 Å, while the RuBRI-O is largely unchanged from its value at 0.5 V\textsubscript{RHE}. While the RuCUS-O bond length is larger than the equivalent bulk Ru-O bond length of 1.94 Å, it is similar to a RuCUS-O bond length for an –OH group bound to the CUS site from DFT (2.07 Å) as well as previously computed RuBRI-O bond distance for a protonated bridging oxygen\textsuperscript{87}. This suggests that at 1.0 V\textsubscript{RHE}, water is completely dissociated to form –OH on the CUS site with the proton transferred to the adjacent bridging oxygen to form a completely hydroxylated surface.

Having considered the facet where water dissociation was most facile, we next consider the (100) facet, which favored molecular adsorption of water at high water pressures in APXPS. As is evident from Figure 3C, there is no significant difference in the intensity or shape of the anti-Bragg region of the (10L) rod, which is otherwise extremely sensitive to changes in RuCUS-O bond length, as can be seen in Figure S24. In order to validate that the
lack of changes observed (10L) rod (and hence the Ru\textsubscript{CUS}-O bond distance) is not an artifact of poor electrochemistry in the cell, we collect X-ray cyclic voltammograms at L = 1.65 and L = 2.50 positions. From Figure S24 and S25, it is evident that a decrease in the Ru\textsubscript{CUS} bond length increases the intensity at the reciprocal point L = 2.5 and decrease the intensity at the reciprocal point L = 1.65. However, we see that changes at these anti-Bragg conditions are detected only post 1.0 V\textsubscript{RHE}, confirming no structural changes associated with the atop oxygen prior to this potential. Fitting the rods collected at 0.5 V\textsubscript{RHE} and 1.0 V\textsubscript{RHE} results in a Ru\textsubscript{CUS}-O bond distance of 2.87 Å and 2.83 Å respectively and a Ru\textsubscript{BRI}-O bond distance of 2.04 Å and 2.01 Å respectively. The Ru\textsubscript{BRI}-O bond length is in good agreement with Ru\textsubscript{BRI}-O bond distances probed by LEED on a stoichiometric RuO\textsubscript{2} (100) surface, grown by oxidizing a Ru(10-10) surface, while the Ru\textsubscript{CUS}-O is significantly higher than the range of Ru-O bond distances for the (100) surface (1.90 Å to 2.05 Å)\textsuperscript{55}. This suggests the presence of a loosely bound water on the CUS site, of an otherwise stoichiometric surface. By probing the nature of the oxygenated adsorbates at the interface, we confirm that the (100) surface has a very low tendency to dissociate water even in an aqueous environment. The similarity of the structures obtained at the two potentials is confirmed by our DFT results, which suggest that at low potentials, the CUS site has an adsorbed water molecule and only every second bridging oxygen is protonated. Increasing the potential to 1.0 V\textsubscript{RHE} results in a structure where all bridging oxygen atoms are deprotonated, with water remaining adsorbed and undissociated on the CUS site.
Figure 4: DFT-generated diagram showing the relative Gibbs adsorption energies of the most stable adsorbate configurations as a function of electrochemical potential. The transition from one structure to another is representative of an experimentally observed redox transition at \( \sim 0.7 \text{ V}_{\text{RHE}} \) (Fig S16). The horizontal lines indicates the most stable water configuration on the surface. These configurations are similar to those shown in Figure 2C, wherein the (101) surface dissociatively adsorbs water, while the (100) and (001) surfaces molecularly adsorb water and the (110) surface partially dissociates water. For the (110), (101) and (100) surfaces, the stoichiometric surface is stable at higher potentials (\( \sim 1.0 \text{ V}_{\text{RHE}} \)) whereas a more reduced surface, with a water (and 50% coverage of –OH for the (101) surface) adsorbed on the CUS site and a (partially) protonated bridging site is observed at lower potentials. In contrast, for the more undercoordinated (001) surface, the stoichiometric surface is only stable at lower potentials, with one of the two adsorbed water molecules dissociating to form an –OH at high potentials. For the (110) surface, an intermediate state was obtained theoretically, shown in grey, where water was partially dissociated to form –OH on the CUS site, while the bridging oxygen is protonated. Pink, red and blue spheres represent Ru, O and H atoms respectively. Hydrogen bonds are drawn with blue dashed lines where applicable. The free energies have been referenced to the stoichiometric surface.

Finally, we consider the highly undercoordinated (001) surface where each surface Ru site is only four fold coordinated and can form two “CUS-like” Ru-O bonds on the surface. The intensity at the midzone of the anti-Bragg region could not be measured due to larger
crystal roughness compared to the other facets. Nevertheless, for this orientation, like the (100) facet, only symmetry changes about the Bragg peak are expected with changing RuCUS-O bond distances (Figure S29). The fitted structure at 0.5 VRHE corresponds to the Ru being 5-fold coordinated, by filling one out of the possible two binding sites with an oxygen atom. The fitted bond distance is 3.05 Å, signifying that this species is probably a loosely bound water molecule. The fitted RuBRI-O bond distance is 2.02 Å, which is slightly larger than the RuBRI-O bond lengths measured on the (110) surface (1.93 Å)\(^2\). Interestingly, unlike the other facets, for the (001) surface, the stoichiometric surface with additional loosely bound water molecule on the CUS site was realized at low potentials (0.5 VRHE). The highly undercoordinated nature of the surface could explain the higher tendency of surface Ru to be oxidized upon contact with an aqueous solution. Increasing the potential to 1.0 VRHE results in a small change in the (00L) rod corresponding to the presence of two oxygen atoms with relatively large RuCUS-O bond distances of 2.93 Å and 2.51 Å respectively. The bridging oxygen bond distances from Ru remain largely unchanged at \(\approx 1.98\) Å. DFT results suggest that while the structure at low potentials corresponds to a stoichiometric surface with loosely adsorbed water on the surface Ru sites, the increase in potential results in the dissociation of one of the water molecules to form -OH. While the CTR results do not show an extreme decrease in the surface Ru-O bond distance to justify the presence of only an –OH species on one of the two sites (change in bond length from 3.00 Å to 2.52 Å), the decrease in bond distance suggests the possibility of some water dissociation.

This study demonstrates the effect of surface crystallographic orientation on the dissociation of water, in the gas-phase environment, as well as in aqueous solutions. These
observations on well-defined oriented systems can also be extended to nanoparticles, where depending on the oxygen partial pressure and temperature, different particle shapes, exposing unique facets are realized\textsuperscript{88,89}, which can interface differently with water. Different facets can stabilize protonated species to a different extent due to the different binding energetics of these species, as well as different degrees of hydrogen bonding. Interestingly, surfaces that are more facile towards water dissociation in the gas phase environment are also capable of dissociating water more easily in the aqueous environment. This trend is in contrast to a recent study on the rutile TiO\textsubscript{2} (110) surface that suggested that while in the UHV-like environment, bridging oxygen vacancies reacted with H\textsubscript{2}O to form –OH species on the bridge Ti sites, the interaction with liquid water was different\textsuperscript{46}. In an aerobic aqueous environment, -OH species on the CUS site were stabilized. Similarly, recent studies on strained SrIrO\textsubscript{3} films showed good correlation between gas-phase oxygen adsorption and density functional theory calculations, but these trends did not translate to the more complex aqueous electrochemical environment\textsuperscript{59}. Our results on the other hand, demonstrate that in spite of the presence of a complex solid-liquid interface, the tendency for water dissociation remains the same in humid atmospheres and in the presence of bulk solution. Furthermore, the lack of any surface reconstruction upon the interaction with water validates its applicability as a model system to study different catalytic processes. This observation also validates the use of gas-phase DFT on these oriented surfaces to model the electrochemical interface. The implications of the differences of water interaction with oriented RuO\textsubscript{2} surfaces are far-reaching. Water dissociation is the first step in the oxygen evolution reaction, for which RuO\textsubscript{2} is considered to be a highly active. Differences in water dissociation tendency on these surfaces suggest that the difference in
activities of these surfaces for OER can originate from the different binding energetics for oxygenated intermediates, in addition to differences in active site density. On the other hand, for reactions such as methanol oxidation and hydrochloric acid oxidation, water is the reaction product, and the modification of stability of protonated species at the surface can dramatically influence reaction energetics.

4. Conclusions

In this study, we combine different in situ synchrotron techniques as well as theoretical calculations to understand the interaction of oriented RuO$_2$ surfaces with water. By studying four distinct surface terminations, namely the (110), (100), (101) and (001) surfaces, we highlight the role of surface coordination in the water dissociation ability of these surfaces. The combined use of experimental and theoretical techniques provides unprecedented atomic level insights into the differences in the interaction of water with rutile RuO$_2$ surfaces as a function of crystallographic orientation. Using ambient pressure XPS, the speciation of water under a wide range of relative humidity conditions, from $4.2 \times 10^{-5}$ % ($p_{\text{H}_2O} = 0.01$ mTorr) to 4.2 % ($p_{\text{H}_2O} = 1000$ mTorr) was studied. Stark contrasts were observed in the tendency for water dissociation at high relative humidities, with the highest water dissociation for the (101) surface, and lowest for the (100) surface. These studies were complemented by in situ surface diffraction performed on single crystal surfaces as a function of potential. Interestingly, the water dissociation ability under high relative humidity gas-phase conditions is in good agreement with the interaction of liquid water at an electrochemical interface, validating the use of gas-phase DFT to understand the electrochemical interface. This study also confirms the unique role of the two distinct
sites on the surface, the CUS and bridge sites, in the water activation process. Under the range of experimental conditions studied here (pH2O = 0.01 mTorr – 1000 mTorr and 0.5 VRHE – 1.0 VRHE), the bridge site is always filled, with the bridging oxygen providing the site for hydrogen adsorption upon water dissociation on the CUS site. Lowering the potential results in the removal of adsorbed –OH groups from the CUS site, while the bridging oxygen site is always present and (partially) protonated under these conditions.

The importance of the CUS site for water activation as well as the effect of local coordination on the water dissociation ability for these surfaces provides an additional lever to tune both the density of active sites and the adsorption energetics of key intermediates.

This finding can have important ramifications for different (electro)catalytic reactions where water is a reactant (oxygen evolution), product (methanol oxidation, hydrochloric acid oxidation) or a spectator (catalytic reactions in a humid atmosphere). Probing water dissociation at an atomic level provides the first step towards understanding complex processes occurring at the electrochemical interface during water splitting, where questions about the active sites, reaction mechanisms and surface structure remain unknown. The differences in water dissociation tendency observed on different facets opens new avenues to use crystallographic orientation as an additional lever to tune the binding energetics of key intermediates such as –OH, -O, and –OOH.

FIGURE CAPTIONS

Figure 1: (A) Water isotherm at room temperature (~25°C) for the RuO2(110) termination, probing the O1s core level at 735 eV incident energy. Spectra are offset for clarity. Spectra are deconvoluted into gas phase water (H2O vap) shaded in grey, H2O and –OH adsorbed on the CUS site shaded in purple, protonated bridging oxygen in hatched purple and lattice oxygen outlined in black. (B) Intensity of the protonated species on the CUS, either –OH or –H2O (filled) and bridge site (open) normalized to the lattice oxygen peak as a function of water pressure at room temperature. (C) Proposed surface structure at high water pressure showing every second water molecule on the
CUS site being dissociated, with the hydrogen donated to the neighboring bridging oxygen (Top view shown in Figure S33).

Figure 2: (A) Comparison of the O 1s spectra measured at a photon energy of 735 eV for the noted orientations. Spectra were measured at room temperature (~25°C) and a water vapor pressure of 250 mTorr. Spectra are offset for clarity and have been decomposed into the following components – gas phase water outlined in color, protonated species on the CUS site shaded in the corresponding color, protonated species on the BRI site hatched in the same color and lattice oxygen outlined in grey. (B) Intensity of the protonated species on the CUS (filled) and bridge site (open) normalized to the lattice oxygen peak as a function of water pressure at room temperature for the (101) surface (in red) and the (100) surface (in blue). At low partial pressures (<50 mTorr), both orientations adsorb water dissociatively, while at high partial pressures, the (101) surface preferentially adsorbs water dissociatively compared to the (100) surface. (C) Computationally calculated free energy for total (in solid lines) and partially dissociated water (in dashed line) configurations on the stoichiometric surface, for the four different surfaces. The free energy for the two conditions have been referenced to the corresponding stoichiometric surface with a full coverage of water adsorbed on the CUS site, which is shown as a solid grey line at a free energy of 0 eV.

Figure 3: (10L) rods measured at 0.5 VRHE (bottom) and 1.0 VRHE (top) for the (A) (110) (B) (101) (C) (100) surfaces and (D) the (00L) rod measured at 0.5 VRHE and 1.0 VRHE for the (001) surface in 0.1 M HClO₄. The experimentally measured intensities are shown in open points and the best-fit models from the fitting process are shown in solid lines of the corresponding color. Ball and stick models for the best-fit structures are shown adjacent to the fitted rods. Maximum experimental uncertainty in bond lengths is 0.06 Å, with detailed atomic positions found in Tables S3-S17. Pink and red spheres represent Ru and O atoms respectively. Bond lengths between surface Ru and adsorbed O species are labeled.

Figure 4: DFT-generated diagram showing the relative Gibbs adsorption energies of the most stable adsorbate configurations as a function of electrochemical potential. The transition from one structure to another is representative of an experimentally observed redox transition at ~0.7 VRHE (Fig S16). The horizontal lines indicates the most stable water configuration on the surface. These configurations are similar to those shown in Figure 2C, wherein the (101) surface dissociatively adsorbs water, while the (100) and (001) surfaces molecularly adsorb water and the (110) surface partially dissociates water. For the (110), (101) and (100) surfaces, the stoichiometric surface is stable at higher potentials (~1.0 VRHE) whereas a more reduced surface, with a water (and 50% coverage of –OH for the (101) surface) adsorbed on the CUS site and a (partially) protonated bridging site is observed at lower potentials. In contrast, for the more undercoordinated (001) surface, the stoichiometric surface is only stable at lower potentials, with one of the two adsorbed water molecules dissociating to form an –OH at high potentials. For the (110) surface, an intermediate state was obtained theoretically, shown in grey, where water was partially dissociated to form –OH on the CUS site, while the bridging oxygen is protonated. Pink, red and blue spheres represent Ru, O and H atoms respectively. Hydrogen bonds are drawn with blue dashed lines where applicable. The free energies have been referenced to the stoichiometric surface.

ASSOCIATED CONTENT

Supporting Information Available:
Thin film characterization, ambient pressure XPS experimental protocol, Ru3d and O1s fitting parameters and comparison of spectra of different surfaces as a function of water vapor pressure. Electrochemical measurement results of single crystal surfaces in the potential range of 0.4 V_{RHE} tp 1.2 V_{RHE}. Crystal truncation rod analysis fitting model, sensitivity of fit tests and best-fit results for 0.5 V_{RHE} and 1.0 V_{RHE} measurements. Energetics for different structures considered using density functional theory. This material is available free of charge via the Internet at http://pubs.acs.org.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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