# Measurements of Oxygen Electroadsorption Energies and Oxygen Evolution Reaction on RuO<sub>2</sub>(110): A Discussion of the Sabatier Principle and its Role in Electrocatalysis

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# ABSTRACT

We report the hydroxide (OH<sub>ad</sub>) and oxide (O<sub>ad</sub>) experimental electroadsorption free energies, their dependences on pH, and their correlations to the oxygen evolution reaction (OER) electrocatalysis on RuO<sub>2</sub>(110) surface. The Sabatier principle predicts that catalyst is most active when the intermediate stabilization is moderate, not too strong such that the bound intermediate disrupts the subsequent catalytic cycle, nor too weak such that the surface is ineffective. For decades, researchers have used this concept to rationalize the activity trend of many OER electrocatalysts including RuO<sub>2</sub>, which is among the state-of-the-art OER catalysts. In this article, we report an experimental assessment of the Sabatier principle by comparing the oxygen electroadsorption energy to the OER electrocatalysis for the first time on RuO<sub>2</sub>. We find that the OH<sub>ad</sub> and O<sub>ad</sub> electroadsorption energies on RuO<sub>2</sub>(110) depend on pH and obey the scaling relation. However, we did not observe a direct correlation between the OHad and Oad electroadsorption energies and the OER activity in the comparative analysis that includes both  $RuO_2(110)$  and  $IrO_2(110)$ . Our result raises a question of whether the Sabatier principle can describe highly active electrocatalysts, where the kinetic aspects may influence the electrocatalysis more strongly than the electroadsorption energy, which captures only the thermodynamics of the intermediates and not yet kinetics.

## INTRODUCTION

An electrochemical oxygen production via the oxygen evolution reaction (OER) represents an important electrochemical process for a number of energy storage devices.<sup>1,2</sup> Unfortunately, the OER is a challenging reaction to catalyze; as a multi-electron reaction  $(2H_2O \rightarrow O_2 + 4H^+ + 4e^-)$  in acid,  $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$  in alkaline),<sup>3,4</sup> an OER electrocatalyst must support several intermediates with the exact intermediate details depending on the OER mechanism on the studied electrocatalyst.<sup>5-7</sup> To simplify the complexity, it is common to assume that (i) the proton and electron transfer simultaneously, (ii) the reaction rate of the elementary step obeys the Brønsted-Evans-Polanyi (BEP) relation<sup>8</sup> (*i.e.*, the driving force approximates the reaction rate), and (iii) the intermediates adsorption energies are linearly related (*i.e.*, the scaling relation).<sup>9-11</sup> The consequence of these assumptions is the Sabatier principle, which predicts the oxygen adsorption energy, typically  $\Delta G_0 - \Delta G_{OH}$ , should be at the optimum value, not be too strong nor too weak, for the electrocatalyst to facilitate the OER. This concept is also known as the volcano plot.<sup>12</sup>

While the volcano-plot approach have had successes in explaining the OER activity trend,<sup>10,13</sup> it is unclear what are the limits of the underlying assumptions. An important first step to unraveling this question is to compare the binding energies of the intermediates, a thermodynamic quantity, to the electrochemical kinetics. Unfortunately, the binding energies of the intermediates, *i.e.*, the electroadsorption energies, are difficult to measure. As a result, the community often uses first-principle calculations. As there is not yet a benchmarking experiment, this practice has resulted in a number of inconsistencies. For example, RuO<sub>2</sub> and IrO<sub>2</sub>, two of the most active OER electrocatalysts, have different calculated oxygen adsorption energies ( $\Delta G_0 - \Delta G_{OH}$ )<sup>14</sup> but comparable experimental OER kinetics.<sup>15,16</sup> Many researchers have suggested that this

discrepancy stems from the density functional theory (DFT)'s inability to capture the electronic structure of RuO<sub>2</sub> and IrO<sub>2</sub>, thus requiring a correction.<sup>14</sup> But this may not be the only explanation; the lack of information on the interfacial water structure and electric field could also play a role.<sup>17,18</sup> More importantly, it is not known whether the foundational assumption that the electroadsorption energies of the intermediates are directly correlated to the reaction barriers and kinetics, is necessarily valid. As part of an effort to resolve this puzzle, we report the measurement of the oxygen adsorption energies, specifically  $\Delta G_0 - \Delta G_{OH}$ , on well-defined RuO<sub>2</sub>(110) surfaces grown using molecular beam epitaxy (MBE) to assess the accuracy of the first-principle calculation and test the correlation between the oxygen adsorption energies and the OER electrocatalysis. We combine this measurement with our previously reported value on IrO<sub>2</sub>(110)<sup>19</sup> to provide insights into the origin of the OER electrocatalysis on RuO<sub>2</sub>(110).

RuO<sub>2</sub> is known for its ability to stabilize the OER intermediates<sup>12,20</sup> via electroadsorption,<sup>18,21,22</sup> a process in which the chemical adsorption occurs simultaneously with the electron transfer. This electroadsorption feature gives rise to the pseudocapacitance behavior in RuO<sub>2</sub>, making it also an attractive charge-storage material.<sup>23–27</sup> It has, however, been difficult to assess the molecular details of the electroadsorption on RuO<sub>2</sub>. Specifically, well-defined experimental systems are necessary to deconvolute the observed redox feature(s) to specific electroadsorption(s). Recently, Rao and co-workers have reported the surface structure on RuO<sub>2</sub>(110) as a function of electrochemical potential using single crystals, where the transitions from H<sub>2</sub>O<sub>ad</sub> to OH<sub>ad</sub> to O<sub>ad</sub> were identified using X-ray scattering.<sup>28</sup> Inspired by this advance, we use the cyclic voltammetry (CV) features on RuO<sub>2</sub>(110) thin films grown on TiO<sub>2</sub>(110) to measure  $\Delta G_O - \Delta G_{OH}$  to establish the connection between the electroadsorption energy and the OER. We further measure the pH influence on the electroadsorption features and show that the pH dependence of the

electroadsorption<sup>29</sup> is not unique to platinum.<sup>30,31</sup> Finally, we use our experimental electroadsorption energies reported for the first time herein for RuO<sub>2</sub> and the values recently reported for IrO<sub>2</sub>(110)<sup>19</sup> to construct a relationship between the surface electroadsorption and the OER activity to experimentally address whether the  $\Delta G_O - \Delta G_{OH}$  descriptor can sufficiently describe the OER trend on RuO<sub>2</sub>(110) and IrO<sub>2</sub>(110), effectively putting an experimental test on the Sabatier principle.

# **EXPERIMENTAL METHODS**

*Molecular-beam epitaxy synthesis.* Inserted figure in **Figure 1A** shows a schematic of our MBEgrown RuO<sub>2</sub>(110) film: 40 formula-units thick RuO<sub>2</sub>(110) films (~16 nm) on single-crystal TiO<sub>2</sub>(110). RuO<sub>2</sub>(110) films were grown using a distilled ozone oxidant at a background pressure of  $10^{-6}$  Torr at 350 °C. The flux of ruthenium was initially calibrated using a quartz crystal microbalance. The epitaxial nature of the as-grown films was confirmed by *in situ* reflection high-energy electron diffraction (RHEED), low-energy electron diffraction (LEED), and X-ray diffraction (XRD, Rigaku SmartLab) (**Figure 1**).

*Preparation of electrolytes and pH titration.* 0.1 M perchloric acid (HClO<sub>4</sub>), 0.1 M potassium hydroxide (KOH), 0.1 M potassium phosphate monobasic (KH<sub>2</sub>PO<sub>4</sub>), and 0.1 M potassium phosphate dibasic (K<sub>2</sub>HPO<sub>4</sub>) were prepared by dissolving HClO<sub>4</sub> (with concentration 70%, EMD), KOH pellets (99.99% purity, Sigma Aldrich), KH<sub>2</sub>PO<sub>4</sub> (99.995% purity, Sigma Aldrich), K<sub>2</sub>HPO<sub>4</sub> (99.95% purity, Sigma Aldrich) in deionized water (18.2 M $\Omega$  cm). pH 2.8 phosphate buffer and pH 6.5 phosphate buffer were prepared by adding 0.1 M HClO<sub>4</sub> to 0.1 M KH<sub>2</sub>PO<sub>4</sub> and 0.1 M KH<sub>2</sub>PO<sub>4</sub> to 0.1 M K<sub>2</sub>HPO<sub>4</sub>.

The pH titration was conducted by adding 4 M HClO<sub>4</sub> into 0.1 M KOH.

The pH values of the electrolytes were calculated from  $H_2/H^+$  equilibrium potential (vs. Ag/AgCl) experimentally measured using a platinum electrode. At the zero-current potential, the pH values satisfy the Nernst equation:

$$E_{H_2/H^+}(vs. Ag/AgCl) = -E_{Ag/AgCl} - \frac{2.303RT}{F}pH$$

*Electrochemical characterization.* Electrical contacts were made by following the same protocol as reported previously.<sup>32</sup> Titanium wires were attached to RuO<sub>2</sub> films using silver paint (Ted Pella, Leitsilber 200). The edges and backside of samples were covered with epoxy (Omegabond 101) except for the RuO<sub>2</sub> films. All electrochemical characterization was conducted in a standard three-electrode glass cell (Pine) with a potentiostat (Bio-Logic). A Pt wire was used as a counter electrode. The reference electrode was an Ag/AgCl electrode (Pine), calibrated to the H<sub>2</sub> redox. All the potentials in this study were resistance-corrected potentials. The electrolyte/cell resistance was obtained from an impedance measurement by using the high frequency intercept of the real resistance. We conducted CV in Ar-saturated electrolytes with a 200 mV/s scan rate to observe surface adsorption. The OER measurements were conducted in O<sub>2</sub>-saturated electrolytes with a 10 mV/s scan rate to avoid large capacitance current. Capacitance-free CV curves were obtained by averaging the forward and backward scans.

*DFT calculations*. All DFT computations were performed using the FHI-aims<sup>33</sup> code using the Van-der-Waals corrected<sup>34</sup> RPBE functional<sup>35</sup> with default tight basis settings. Our slab model consists of a four trilayer hydrogen terminated slab and has two coordinatively unsaturated sites ('cus'). The two bottom layers are fixed to bulk position while the two top layers including adsorbs are allowed to fully relax. This choice of functional and slab configuration is consistent with previous work.<sup>10,12,36</sup> The criteria for a converged geometry was set to achieve all forces

below 0.01 eV/Å and we use a 8x4x1 Gamma-centered *k*-point grid for slab computations. We use zero point energies (ZPEs) for adsorbates computed for similar adsorbate structures on IrO<sub>2</sub>.<sup>19</sup> It is generally assumed these ZPEs do not change much with the nature of the slab.

A surface diagram can be computed using a grand canonical approach with respect to hydrogen adsorption. Slabs with different amount of hydrogen (e.g., H<sub>2</sub>O, OH or O) are computed and their thermodynamic potential  $\gamma$  defined as surface area normalized (G – n<sub>H</sub> ·  $\mu$ <sub>H</sub>) where G is the free energy, n<sub>H</sub> is the amount of hydrogen in the slab and  $\mu$ <sub>H</sub> is the chemical potential of hydrogen. The amount of ruthenium, and oxygen are fixed.  $\mu$ <sub>H</sub> is linked to the potential applied to the computational hydrogen electrode (CHE) which uses the computed H<sub>2</sub> molecule as well as the experimental entropy of H<sub>2</sub> at room temperature.<sup>37</sup> The entropy term is considered neglectable except for the gaseous species (e.g., H<sub>2</sub>). Structures with different adsorb configurations are labeled in **Figure 2** and referenced by their number throughout the text. For each surface one obtains a  $\gamma$  and then we plot the difference to the water saturated reference slab (phase 1). (See Supporting Information for more details.)

## **RESULTS AND DISCUSSION**

Sample Characterization. The XRD verifies the epitaxial nature of the RuO<sub>2</sub> films (**Figure 1A**). The reflective fringes indicate the smoothness of surface during the layer-by-layer growth. Lowenergy electron diffraction (LEED, **Figure 1B**) and reflection high-energy electron diffraction (RHEED, **Figure 1C**) show that the grown RuO<sub>2</sub> film contains a (110) termination, consistent with an expectation of an epitaxial RuO<sub>2</sub> film adopting the symmetry of the underlying TiO<sub>2</sub>(110) substrate. These characterizations support the formation of a well-defined RuO<sub>2</sub>(110) surface, a structure we will use in the DFT calculation.

*Redox Assignment.* Using CV, we measure the oxygen electroadsorption energies on  $RuO_2(110)$ . Figure 2A shows the CV of RuO<sub>2</sub>(110) in Ar-saturated 0.1 M KOH. We observe two striking sets of reversible peaks in the CV: ~1 V vs reversible hydrogen electrode (RHE) and ~1.3 V vs RHE. We compare the redox positions to the calculated free energies of  $RuO_2(110)$  surfaces terminated with different amounts of hydrogen (H<sub>2</sub>O, OH, O) as a function of electrochemical potential using the CHE reference approach (Figure 2B & 2C). Based on this comparison, we assign the first peak as the  $OH_{ad}$  electroadsorption ( $H_2O_{ad} \rightarrow OH_{ad} + H^+ + e^-$ ) and the second peak as the  $OH_{ad}$  deprotonation ( $OH_{ad} \rightarrow O_{ad} + H^+ + e^-$ ), *i.e.*, the  $O_{ad}$  electroadsorption, in agreement with previous work.<sup>19,28</sup> We use these assignments for analysis for the rest of this work. Before moving on to the next section, we point out that our DFT predicts that H<sub>2</sub>O<sub>ad</sub> can adopt different structural configurations; many forms of H2Oad have similar energies, for example,  $H_2O_{ad}$  on the 5-fold coordinately unsaturated sites (*cus* sites) can transfer its hydrogen to the 6-fold bridging oxygen (*i.e.*,  $(H_2O_{ad})_{5f} + (O)_b \rightarrow (OH_{ad})_{5f} + (OH)_b$ ) with very little energy difference (see Supporting Information). This surface configuration flexibility suggests that H<sub>2</sub>O<sub>ad</sub>/OH<sub>ad</sub> likely has a mixture of competing microstates, which may explain why the width of the first peak  $(H_2O_{ad} \rightarrow OH_{ad})$  is wider than the second peak  $(OH_{ad} \rightarrow O_{ad})$ .



**Figure 1.** (A) X-ray diffraction  $\theta$ -2 $\theta$  scan of a RuO<sub>2</sub>(110) film (40 formula units thick) grown on a TiO<sub>2</sub>(110) substrate. The labeled (\*) sharp peaks indicate diffraction from the substrate. (B) The low energy electron diffraction (LEED) pattern obtained during the growth of the RuO<sub>2</sub>(110). (C) The reflection high-energy electron diffraction (RHEED) pattern obtained during the growth of the RuO<sub>2</sub>(110).



**Figure 2.** (A) Cyclic voltammogram (CV) of RuO<sub>2</sub>(110) in Ar-saturated 0.1 M KOH at a scan rate of 200 mVs<sup>-1</sup>. (B) Thermodynamic potential ( $\gamma$ ) vs electrochemical potential (V) for different hydrogen coverage using the computational hydrogen reference electrode. A surface phase diagram is built by identifying the coverage of lowest thermodynamic potential. Computations are performed within DFT-GGA-RPBE with Van der Waals correction. (C) Slabs

with different hydrogen coverage used in our computations. White, red, and turquoise spheres represent hydrogen, oxygen, ruthenium atoms.

pH influence on the oxygen electroadsorption. Figure 3A shows the pH influence on the CVs of RuO<sub>2</sub>(110). We find the electroadsorption peaks shift to more positive potential at lower pH (more acidic environment) on the RHE scale. To quantify this shift, we used the potential at the adsorption peak (V<sub>peak</sub>) and the potential window at 90% peak current as an error bar (Figure 3B) to demonstrate the peak widths of the OH<sub>ad</sub> and O<sub>ad</sub> electroadsorption. The slopes of peak shifts are 7.4 and 11.5 mV/pH on the RHE scale. To estimate the free energy of formation of OH<sub>ad</sub> and  $O_{ad}$  on RuO<sub>2</sub>, we examine the potentials of  $OH_{ad}$  (acidic:  $H_2O_{ad} \rightarrow OH_{ad} + H^+ + e^-$ ; alkaline:  $H_2O_{ad} + OH^- \rightarrow OH_{ad} + H_2O + e^-$ ) and  $O_{ad}$  (acidic:  $OH_{ad} \rightarrow O_{ad} + H^+ + e^-$ ; alkaline:  $OH_{ad} + OH^ \rightarrow$  O<sub>ad</sub> + H<sub>2</sub>O + e<sup>-</sup>). We use the water-covered surface as the reference state because our DFT calculation shows that water adsorbs on the RuO<sub>2</sub> surface. The electrochemical potentials of  $OH_{ad}$  ( $\Delta G_{OH} = V_{peak 1}$ ) and  $O_{ad}$  ( $\Delta G_O = V_{peak 1} + V_{peak 2}$ ) correspond to the free energies of H<sub>2</sub>O<sub>ad</sub>  $\rightarrow$  OH<sub>ad</sub> + 1 /2H<sub>2</sub> and H<sub>2</sub>O<sub>ad</sub>  $\rightarrow$  O<sub>ad</sub> + H<sub>2</sub>, respectively. Ideally, these adsorption energies should be pH-independent. We attribute the observed pH dependence of the OH<sub>ad</sub> and O<sub>ad</sub> electroadsorption energies to the electrified interfacial water and/or the change of surface work function at different pH.<sup>18</sup> Besides the interfacial water structure, the cation in the electrolytes could also have influence on the adsorption energy.<sup>38</sup> The pH dependence of the OH<sub>ad</sub> and O<sub>ad</sub> electroadsorption energies had been observed on IrO<sub>2</sub>(110) in our previous work.<sup>19</sup>

It is important to point out that the  $O_{ad}$  peak area decreases in the phosphate-containing electrolytes in comparison to the phosphate-free ones (**Figure 3A**). We highlight this salient observation by color-coding the CVs in phosphate-containing electrolytes in gray (pH 2.8) and light gray (pH 6.5) to differentiate the phosphate CVs from the phosphate-free ones. Based on

the observed suppression of the  $O_{ad}$  electroadsorption feature, we suspect that the phosphate ions adsorb on RuO<sub>2</sub>(110) by interacting with and stabilizing the OH<sub>ad</sub> group, effectively suppressing the O<sub>ad</sub> formation. To verify this hypothesis, we compare the CV of RuO<sub>2</sub>(110) at a similar pH with and without phosphate (pH 2.8 with phosphate and pH 2.7 without phosphate, **Figure 3C**). We find that the presence of phosphate affects the electroadsorption and suppresses the O<sub>ad</sub> peak area, consistent with our hypothesis that the phosphate anions adsorb on RuO<sub>2</sub>(110) by interacting with the OH<sub>ad</sub> group. This observation suggests that it is best to test RuO<sub>2</sub> in nonphosphate-containing electrolytes to avoid a possible surface poisoning. We note that the phosphate poisoning effect was not observed on IrO<sub>2</sub>(110) in our prior study.



**Figure 3.** (A) CVs of RuO<sub>2</sub>(110) in Ar-saturated 0.1 M buffer solutions with different pH at a scan rate of 200 mVs<sup>-1</sup>. Blue: pH 1.0; gray: pH 2.8 (with phosphate); light gray: pH 6.5 (with phosphate); red: pH 12.0; green: pH 12.9. (B) The shift of the adsorption peak potentials with pH obtained from Figure 3A. (C) The influence of phosphate on CV of RuO<sub>2</sub>(110) in Ar-saturated electrolytes at a scan rate of 200 mVs<sup>-1</sup>. Yellow: pH 2.7 (without phosphate); gray: pH 2.8 (with phosphate).

To isolate the influence of pH on the electroadsorption without using buffer, we use titrations to control the electrolyte pH. **Figure 4A** shows the CVs of  $RuO_2(110)$  in HClO<sub>4</sub>-KOH electrolytes at different pH. The surface charge densities extracted from the area underneath the O<sub>ad</sub> peak

(Figure 4B) show similar values independent of pH, suggesting no surface poisoning with perchloric anions (in comparison, the  $O_{ad}$  peak area decreases by ~70% in the phosphate's presence.) Interestingly, we observe a similar pH dependence of the oxygen electroadsorption on RuO<sub>2</sub>(110) as the one measured using phosphate buffers. Figure 4C shows that the potential at the  $O_{ad}$  peak increases with decreasing pH (more acidic environment) in the same manner as the data collected in phosphate buffers. This finding indicates that the phosphate anions poison the RuO<sub>2</sub> surface but does not interfere with the electrified interfacial water that causes the electroadsorption to be pH-dependent.

Interestingly, the electrolyte pH plays an important role on the adsorbate-adsorbate interaction. To investigate the influence of pH on this adsorption behavior, we compare the full width half maximum (FWHM) of the electroadsorption peak which contains information on the adsorbate-adsorbate interaction in electrolytes with different pH. The FWHM of a non-interacting adsorption isotherm (Langmuir) is 90 mV.<sup>39</sup> In comparison, the FWHM of our O<sub>ad</sub> peak is 53 mV (suggesting an attraction between adsorbate-adsorbate interaction depends on pH—from attractive interaction in alkaline to repulsive interaction in acid—implies that the water likely mediates the adsorbate-adsorbate interaction. As the structure of the interfacial water depends on pH, the extent of the adsorbate-adsorbate interaction varies accordingly. Thus, pH can impact the interaction between adsorbates in addition to the electroadsorption energetics.



**Figure 4.** (A) CVs of RuO<sub>2</sub>(110) at a scan rate of 50 mVs<sup>-1</sup> in Ar-saturated electrolytes with different pH controlled by titration (without phosphate ion). (B) The surface charge density of the O adsorption peak in electrolytes with different pH. (C) The shift of the O adsorption peak potentials with pH obtained from Figure 4A. The labeled (\*) symbols indicate the electrolytes with phosphate ion obtained from Figure 3.

*pH influence on the OER electrocatalysis.* An OER measurement can drastically change local pH if buffer is not used. Therefore, we only present the OER activity in buffered solution as a function of pH. Figure 5 shows the OER activity on RuO<sub>2</sub>(110) at different pH. We observe the pH-dependent OER activity follows the rank: pH 1.0 (most acidic) > pH 12.9 (most basic) > pH 12.0 > pH 2.8 > pH 6.5 (most neutral). Quantitatively, the OER activity of RuO<sub>2</sub> is 3x higher in 0.1 M HClO<sub>4</sub> than 0.1 M KOH at 400 mV overpotential, a similar trend observed for  $RuO_2$ nanoparticles.<sup>15</sup> The pH trend with the OER activity of  $RuO_2(110)$  is similar to  $IrO_2(110)$ , displaying V-shaped relationship between the OER activity vs. the oxygen electroadsorption descriptor that is commonly used in literature,  $\Delta G_O - \Delta G_{OH}$ . We have previously attributed this observation to (1) the OOH<sub>ad</sub> formation energy is pH-dependent and (2) the dual pathway of the OOH<sub>ad</sub> formation (acid:  $O_{ad} + H_2O \rightarrow OOH_{ad} + H^+ + e^-$ ; alkaline:  $O_{ad} + OH^- \rightarrow OOH_{ad} + e^-$ ) on IrO<sub>2</sub>.<sup>19</sup> If the OOH<sub>ad</sub> formation is also the rate-limiting step for the OER on RuO<sub>2</sub>, it is more energetically favorable in acid which results in higher OER activity in more acidic environment. In comparison, increasing pH makes the OOH<sub>ad</sub> formation less energetically favorable, as manifested by the decreasing difference between the Oad and OHad electroadsorption energies; however, increasing pH simultaneously increases OH<sup>-</sup> concentration driving the OOH<sub>ad</sub> formation kinetics via the reaction order effect (from  $O_{ad} + OH^- \rightarrow OOH_{ad} + e^-$ ). The consequence is the lower OER activity on  $RuO_2(110)$  at neutral pH. We note that we cannot rule out the possibility that the OER performance at neutral pH may be lowered by the surface poisoning effect. However, we suspect that this scenario is unlikely since IrO<sub>2</sub> also shows the same v-trend despite having no anion poisoning. We also caution that this trend of adsorption energy might change due to different surface state at the potential where OER occurs. Future

studies using in situ characterization to reveal the surface state are crucial to unlock the OER mechanism.



**Figure 5.** (A) Tafel plot for the OER kinetics of RuO<sub>2</sub>(110) in O<sub>2</sub>-saturated buffer solutions with different pH. Blue: pH 1.0; gray: pH 2.8 (with phosphate); light gray: pH 6.5 (with phosphate); red: pH 12.0; green: pH 12.9. (B) Overpotentials for the OER at 10  $\mu$ A/cm<sup>2</sup><sub>geo</sub> at different pH. (C) Current density of the OER at  $\eta = 400$  mV at different pH. (D) Tafel slope of the OER on RuO<sub>2</sub>(110) at different pH.

Measurement of the scaling relation. One of the most powerful approximations in electrocatalysis is the scaling relation, an idea that the intermediates energies (*i.e.*,  $\Delta G_{O}$ ,  $\Delta G_{OH}$ , and  $\Delta G_{OOH}$ ) form a linear relationship with one another.<sup>10</sup> This assumption is one of the foundational postulates underlying the Sabatier principle; on  $RuO_2(110)$ , where the rate-limiting step has been suggested to be the OOH<sub>ad</sub> formation,<sup>20,40</sup> the scaling relation connects the OOH<sub>ad</sub> formation energy back to the oxygen binding strength, *i.e.*, O<sub>ad</sub> formation. The scaling relation has been consistently validated with many first-principle calculations; however, the experimental comparison is still elusive. We use the electroadsorption peaks, which correspond to the coverage at 50% saturation from the mean-field approximation, to estimate  $\Delta G_0$  and  $\Delta G_{OH}$ . Thus, the  $\Delta G_0$  and  $\Delta G_{OH}$  values reported here refer the adsorption (or chemical potential) at approximately 50% saturation. We convert the electrochemical potential to the reaction's free energy using the RHE reference, *i.e.*, for the OH<sub>ad</sub> formation, the electrochemical potential of  $H_2O_{ad} \rightarrow OH_{ad} + H^+ + e^-$  becomes the free energy of  $H_2O_{ad} \rightarrow OH_{ad} + \frac{1}{2}H_2$ . We have previously used this conversion to estimate the OH<sub>ad</sub> and O<sub>ad</sub> electroadsorption energies on IrO<sub>2</sub> at different pH. We now use the  $\Delta G_0$  and  $\Delta G_{OH}$  measurements to experimentally test this scaling relation for RuO<sub>2</sub> and compare the results to IrO<sub>2</sub>. We find a linear relationship between the OH<sub>ad</sub> and O<sub>ad</sub> on  $RuO_2(110)$  and  $IrO_2(110)$ , supporting the validity of the scaling relation (Figure 6A). The OH<sub>ad</sub> and O<sub>ad</sub> electroadsorption energies obtained in the electrolytes containing phosphate fit in the linear relation, verifying that the primary role of the phosphate ions is surface poisoning with minimal influence on the adsorption energies.

*Discussion of the measured electroadsorption energies vs. DFT.* We find that DFT reproduces the electroadsorption energy well despite the inherent errors with the used functional and the solvation and electric-field effects being neglected. The CV second peak sits around 1.1 V in our

surface phase diagram in comparison to 1.3 - 1.45 V (experiment, depending on the electrolyte pH). Likewise, the middle broader first peak is around 1 - 1.1 V in experiment and compares fairly with the first transitions around 0.8 V within DFT. We emphasize that the error of a few hundred meV is not surprising in view of the typical error of DFT in reproducing the energetics of redox processes for instance when computing lithium ion battery voltages.<sup>41</sup> The systematic underestimation of the computed voltage is also not surprising and often seen for semi-local functionals such as GGA.<sup>41</sup> The relatively small magnitude of the underestimation is however remarkable in view of our use of the standard GGA-RPBE approach without any +U or exact exchange. We attribute this to the *4d* nature of Ru, which could be reasonably modeled by a semi-local functional in comparison to the more localized *3d* systems. This has been observed in voltage of lithium ion battery as well for instance in Li<sub>2</sub>RuO<sub>3</sub>.<sup>42</sup> We cannot, however, entirely rule out a possibility of a cancelation between the DFT errors and the neglected effects such as water and interfacial electric field, which would require a more in-depth theory work to assess. We also note that a comparison with the 5*d* IrO<sub>2</sub> shows errors on similar magnitude.<sup>19</sup>

*The volcano plot assessment*. We now test the hypothesis of the Sabatier principle by comparing  $\Delta G_0 - \Delta G_{OH}$ , a widely used OER descriptor,<sup>10,13,43</sup> to the OER activity of RuO<sub>2</sub>(110) and IrO<sub>2</sub>(110). We note that the OER activity trend of MBE-grown RuO<sub>2</sub>(110) and IrO<sub>2</sub>(110) are comparable to the nanoparticle results, and thus the same conclusion can be reached with the literature nanoparticles data in the activity axis.<sup>15</sup> As shown in **Figure 6B**, we do not observe the volcano relationship between the OER activity *vs*. the oxygen electroadsorption energy. Notably, while the electroadsorption energies are different, RuO<sub>2</sub>(110) and IrO<sub>2</sub>(110) are similarly active for the OER (**Figure 6B**). The lack of a trend between the  $\Delta G_0 - \Delta G_{OH}$  descriptor and the OER

on  $RuO_2(110)$  and  $IrO_2(110)$  beckons the question of what could be missing in the Sabatier analysis used in the OER.

We begin this discussion by doing a comparative analysis between theory and experiment, starting with the electro-adsorption energy comparison between RuO<sub>2</sub> and IrO<sub>2</sub>. We first emphasize that the use of DFT to assess the electro-adsorption energy does not necessarily have to obtain the absolutely correct electro-adsorption energies as long as the trends and relative values are conserved. Comparing the computed results on RuO<sub>2</sub> and our previous result on IrO<sub>2</sub>, we observe that the  $\Delta G_O - \Delta G_{OH}$  value is lower for RuO<sub>2</sub> than IrO<sub>2</sub> (1.1 eV vs. 1.3 eV). This observed trend is in qualitative agreement with the experiment as both experiment and theory indicate a lower binding energy for RuO<sub>2</sub> vs. IrO<sub>2</sub>. We therefore suspect that the shortcoming in the volcano-plot analysis is not due to the DFT problem.

Based on the volcano-plot trend analysis,<sup>10</sup> the reduced  $\Delta G_0 - \Delta G_{OH}$  value should make RuO<sub>2</sub> less active than IrO<sub>2</sub>; our and many previous experimental data however show that the OER on RuO<sub>2</sub> and IrO<sub>2</sub> are comparable.<sup>15,16</sup> Given that our experimental data support the existence of the scaling relation (**Figure 6A**), it is likely that  $\Delta G_0 - \Delta G_{OH}$  can be used to estimate  $\Delta G_{OOH} - \Delta G_O$ which describes the energy barrier of OOH<sub>ad</sub> formation. These analyses lead us to suggest that the failure of the volcano trend when both RuO<sub>2</sub>(110) and IrO<sub>2</sub>(110) are compared is likely due to other factors. One possible explanation is to recognize that the volcano plot assumption does not capture the micro-kinetic details and thus is valid only when the catalysts have vastly different adsorption energies. In other words, the volcano relationship crudely approximates between the difference between a highly active catalyst and an inactive one; however, when for the comparison of similarly active catalysts in a narrow energy range, it lacks the necessary micro-kinetic details that make up the pre-factor in the rate expression (e.g., mechanism of the proton and electron transfers as well as whether the energy barrier linearly related to driving force or not).



**Figure 6.** (A) Experimentally measured adsorption energies of  $O_{ad}$  and  $OH_{ad}$  on  $RuO_2(110)$  (blue: without phosphate; gray and light gray: with phosphate) and  $IrO_2(110)$  (red) at different pHs. (B) Comparison of the OER current density at 1.63 V vs. RHE of  $RuO_2(110)$  and  $IrO_2(110)$  at different pHs. The labeled (\*) symbols indicate the electrolytes with phosphate ion. The adsorption energies and OER activity on  $IrO_2(110)$  extracted at different pHs are reproduced from Ref.19.

#### CONCLUSIONS

In summary, we report the O<sub>ad</sub> and OH<sub>ad</sub> electroadsorption energies on MBE grown RuO<sub>2</sub>(110) on TiO<sub>2</sub>(110) substrate. Our results show that the electroadsorption energies of O<sub>ad</sub> and OH<sub>ad</sub> are pH-dependent and obey the scaling relation. The pH dependence is observed whether the CVs of RuO<sub>2</sub>(110) were measured in phosphate-containing electrolytes, where surface poisoning can occur, or in buffer-free electrolytes. The FWHM of the Oad adsorption isotherm varies with pHthe adsorbate-adsorbate interaction is attractive in alkaline but repulsive in acid. We attribute this observation to the changing interfacial water structure, which causes pH-dependent electroadsorption energies and adsorbate-adsorbate interaction. The pH influence on the OER activity of  $RuO_2(110)$  is similar to that on  $IrO_2(110)$ , where the lowest activity has been observed at near neutral pH. To investigate the relation between electroadsorption energy and the OER activity, we combine the measurements on  $RuO_2(110)$  with our previously reported values on  $IrO_2(110)$ . Our results support the existence of the scaling relation between  $OH_{ad}$  and  $O_{ad}$ electroadsorption energy of  $RuO_2(110)$  and  $IrO_2(110)$  and that DFT can reproduce the electroadsorption trend well within the known computation errors. However, we did not observe a volcano trend in the OER activity of RuO<sub>2</sub> and IrO<sub>2</sub> as a function of the adsorption energy. Our finding suggests the possible shortcoming of the volcano relation for similarly active catalysts with small adsorption energy differences. In this regime, which is near the tip of the volcano plot, the micro-kinetic details of the OER may play a more important role on the OER than the electro-adsorption energetics.

#### SUPPORTING INFORMATION

Lattice constant measurement, rocking curve, surface phase structures, free energies of adsorbed water configurations on  $RuO_2(110)$  from our DFT calculation. This material is available free of charge via the Internet at http://pubs.acs.org.

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# **TOC GRAPHICS**

