

The Sensitivity of Metal Oxide Electrocatalysis to Bulk Hydrogen Intercalation: Hydrogen Evolution on Tungsten Oxide

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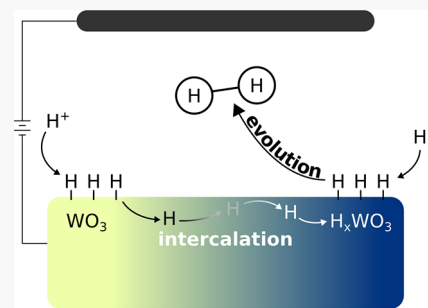


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ABSTRACT: Metal oxides are attracting increased attention as electrocatalysts owing to their affordability, tunability, and reactivity. However, these materials can undergo significant chemical changes under reaction conditions, presenting challenges for characterization and optimization. Herein, we combine experimental and computational methods to demonstrate that bulk hydrogen intercalation governs the activity of tungsten trioxide (WO_3) toward the hydrogen evolution reaction (HER). In contrast to the focus on surface processes in heterogeneous catalysis, we demonstrate that bulk oxide modification is responsible for experimental HER activity. Density functional theory (DFT) calculations reveal that intercalation enables the HER by altering the acid–base character of surface sites and preventing site blocking by hydration. First-principles microkinetic modeling supports that the experimental HER rates can only be explained by intercalated H_xWO_3 , whereas nonintercalated WO_3 does not catalyze the HER. Overall, this work underscores the critical influence of hydrogen intercalation on aqueous cathodic electrocatalysis at metal oxides.



INTRODUCTION

Metal oxides are tremendously important components of catalytic systems, being used both as supports for active materials and as catalysts themselves.^{1,2} Their widespread application is a result of their diverse chemical properties, offering tunable reactivity as a function of composition and structure. Historically, oxides have been used extensively in thermochemical environments and have seen only a few use cases in electrocatalysis. However, research in recent years has been reinvigorated and extended the application of oxide catalysts to a wider range of electrochemical reactions.^{3–7} With the potential for broad use in electrocatalysis, it is important to recognize that many metal oxides can undergo redox reactions themselves.^{8,9} In an electrochemical environment, this redox reactivity can be instigated by applied potential and interaction with the solvent environment, frequently manifesting in the transfer of ions to/from the oxide catalyst.

One redox reaction that occurs in aqueous environments is hydrogen intercalation, which is the insertion of protons and electrons into the full oxide lattice under sufficiently reducing conditions.¹⁰ Unlike surface processes, such as hydration and poisoning, intercalation is a bulk phenomenon: instead of being adsorbed only to the oxide surface, hydrogen also penetrates deep into the structure of the material. The reaction reduces the formal oxidation state of the metal in the oxide to generate a metal oxide hydrogen bronze.¹¹ This often results in electrochromism, where electrons populate the metal *d*-band and enhance photon absorption in the visible and near-infrared regions.¹² Filling the conduction band via bulk intercalation can also induce semiconductor-to-metal transitions in metal oxides.¹³ Moreover, empirically observed rates of hydrogen

intercalation occur on time scales similar to catalytic turnover.^{14,15} Therefore, the associated changes in electronic structure can also be expected to occur alongside electrocatalytic reactions on oxides.

Tungsten trioxide, WO_3 , is a redox-active metal oxide that undergoes bulk hydrogen intercalation to tungsten oxide hydrogen bronze, H_xWO_3 .¹⁶ It has also recently been used in a variety of technological applications, including in electronic devices and for enhancing fuel cell electrode stability.^{17,18} The ability of WO_3 to undergo H intercalation is understood to be critical for each of these applications. The changes in optical absorption and electrical conductivity accompanying WO_3 reduction to H_xWO_3 arise from a shift in electronic structure that is describable as a repositioning of the *d*-band. Considering the *d*-band model that describes trends in catalytic activity for metals, it is reasonable to expect that electronic changes resulting from bulk hydrogen intercalation will also affect the catalytic function of the bronze.¹⁹ In this direction, previous work has shown that premodified substoichiometric (high O vacancy) $\text{WO}_{3-\delta}$ electrodes exhibit greater HER rates than stoichiometric WO_3 .²⁰ Vacancy formation is understood to alter oxide electronic structure, which results in altered catalytic activity.^{21,22} However, when

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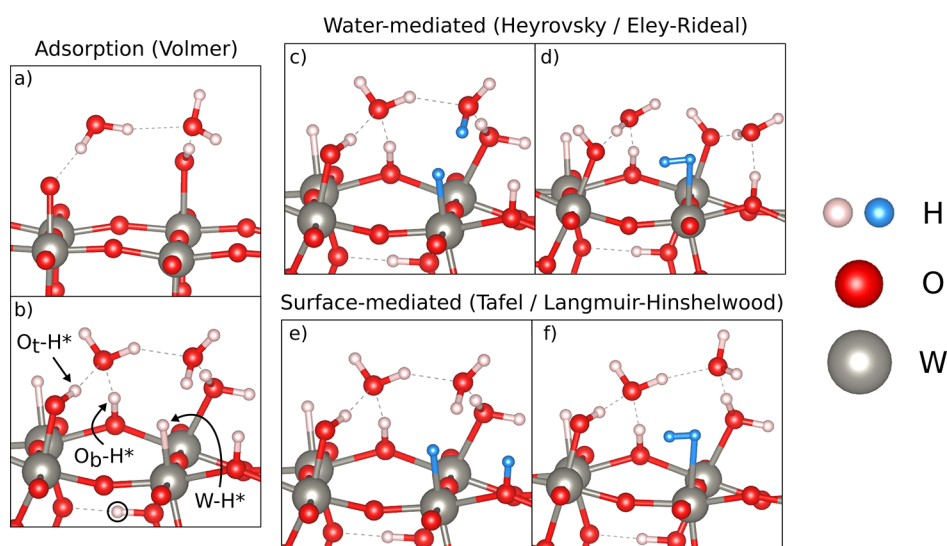


Figure 1. Major reaction steps to form H_2 on WO_3 . The blue atoms are hydrogens involved in the formation of molecular H_2 . Tungsten atoms are gray, oxygen atoms are red, and spectator hydrogen atoms are white. (a) A bare, non-hydrogenated surface with a near-surface explicit H_5O_2^+ cation. (b) An example of a $\text{H}_{0.625}\text{WO}_3$ surface demonstrating all possible hydrogen adsorption locations: terminal oxygen, O_t , bridge oxygen, O_b , and tungsten, W. Various combinations of site types are possible and will impact reaction energetics. The bulk intercalated hydrogen is also shown, marked by the circle. H_2 -coupling occurs after adsorption through two mechanisms. (c) Initial and (d) final states for the water-mediated (Heyrovsky, Eley–Rideal) mechanism. (e) Initial and (f) final states for the surface-mediated (Tafel, Langmuir–Hinshelwood) mechanism.

starting with stoichiometric WO_3 , it is unlikely that O vacancies form in significant concentrations in an electrochemical environment at potentials relevant to the HER.²³ Rather, WO_3 readily undergoes bulk hydrogen intercalation in a cathodic electrochemical environment.^{14,15,23,24} Since intercalation also alters oxide electronic structure and catalysis is dependent on band positioning, we can expect hydrogen intercalation to influence the catalytic activity of metal oxides like H_xWO_3 .

Combined computational and experimental studies of bulk hydrogen intercalation and its influence on cathodic reactions on metal oxides are yet to be performed.^{20,25–27} However, prior work has demonstrated that hydrogen intercalation has a significant impact on the activity of other catalysts.^{28,29} One example is a recent study on electrochemical hydrogen evolution catalyzed by MoS_2 .²⁸ The authors found that hydrogen intercalation directly impacts both the electrical conductivity and hydrogen adsorption behavior of MoS_2 , resulting in enhanced activity and increased robustness in neutral and alkaline pH environments. Another example is a study on Pd-catalyzed electrochemical hydrogen evolution, where the authors observed a steady increase in activity upon cycling applied potentials.²⁹ They concluded this performance increase was due to a change in H adsorption energetics induced by hydrogen intercalation. These reports further motivate an investigation into the influence of bulk hydrogen intercalation on metal oxides and their catalytic behavior.

In this work, we have combined theory and experiment to demonstrate that bulk hydrogen intercalation precedes hydrogen evolution on WO_3 in aqueous acidic electrolytes. H_2 generation does not occur on WO_3 , as might be expected. Instead, applying a potential forms a new catalyst, H_xWO_3 , which then allows the HER to occur. This process is reversible, and applying a sufficiently positive potential will eventually lead to removing H from H_xWO_3 to regenerate WO_3 .

Hydrogen intercalation fundamentally changes the reactivity of WO_3 . Specifically, intercalation drastically alters the

electronic structure of the oxide, essentially forming a new catalyst with markedly higher HER activity. With constant-charge (canonical) and constant-potential (grand canonical) DFT calculations, we show that these electronic changes activate surface metal sites for the HER. We further demonstrate that a constant-charge analysis, as is traditionally applied for gas-phase systems and in the computational hydrogen electrode (CHE) approach, does not fully describe the experimentally measured activities.³⁰ Rather, a constant-potential DFT (CP-DFT) approach accurately captures the experimentally observed hydrogen intercalation and evolution characteristics of H_xWO_3 . Using CP-DFT, we also observe that the elementary reaction energetics for the HER on H_xWO_3 are relatively insensitive to applied overpotential (i.e., individual steps exhibit small charge transfer coefficients). Instead, increasing the applied overpotential increases the equilibrium H content in the bronze, which indirectly increases the rate of HER turnover by altering the catalyst electronic structure and providing a surface that yields lower HER activation barriers. We further illustrate the effect of intercalation on HER catalysis by comparing experimentally measured rates of hydrogen evolution on H_xWO_3 to reaction rates derived from electrochemical microkinetic models of varying degrees of x in H_xWO_3 . Critically, the observed HER activity can only be rationalized by considering intercalated states with stoichiometries of $\text{H}_{0.500}\text{WO}_3$ or greater. Weak electrochemical activation is further evidenced via large apparent Tafel slopes (ranging from 120 to >400 mV/dec) that we observed experimentally and confirmed with first-principles electrochemical microkinetics. This work clearly demonstrates that bulk hydrogen intercalation is an important consideration in cathodic electrocatalysis on metal oxides.

RESULTS AND DISCUSSION

Influence of Bulk H Intercalation on H Adsorption and Electronic Structure. We first examined the possible reaction pathways to molecular H_2 on the metal oxide surface.

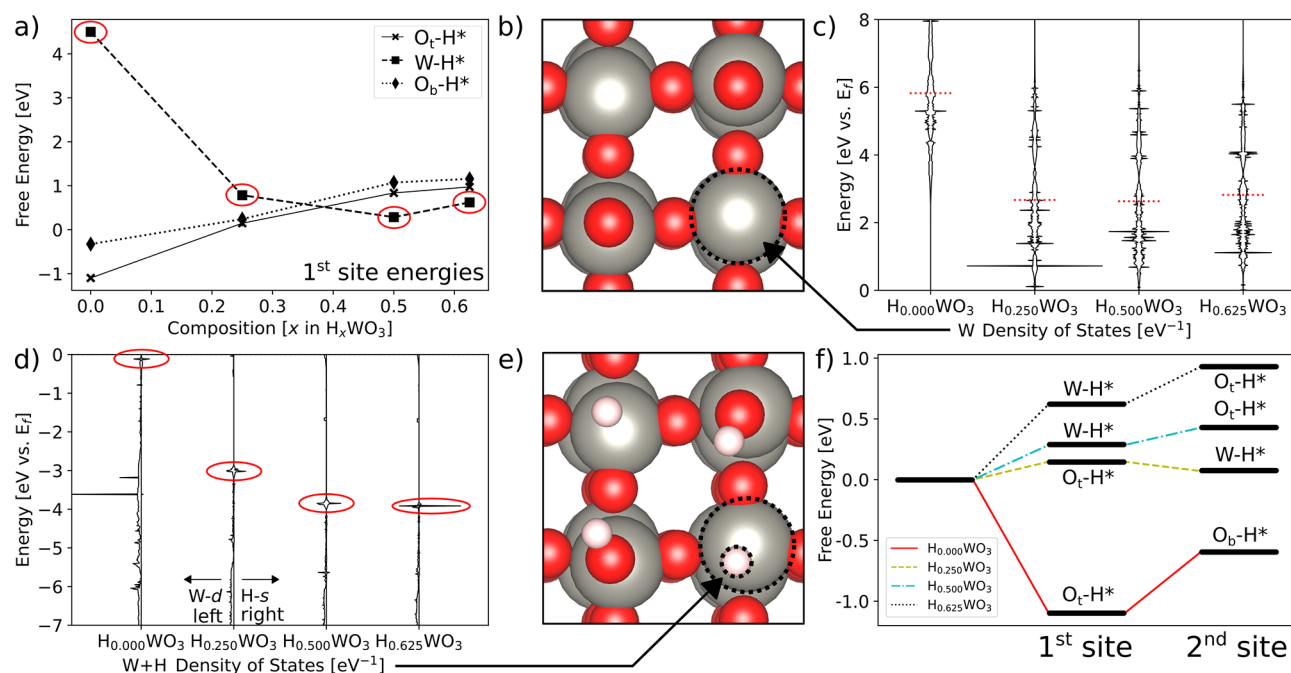


Figure 2. Effect of hydrogen intercalation on hydrogen adsorption free energies and electronic structure of H_xWO_3 . (a) Free energies of adsorption at the three unique site types on H_xWO_3 as a function of bulk H stoichiometry x . (b) Top view of bare oxide surface. (c) Unoccupied W d density of states associated with the W atom indicated in (b), where the red dashed lines indicate the location of the band centers. (d) Occupied local W d - and H s -projected density of states, with the W–H bonding states indicated by the red circles. The states in (d) are those corresponding to the atoms indicated in (e), which shows the oxide surface with H adsorbed at the W and O_t sites. (f) Minimum energy pathways for the consecutive adsorption of H atoms at different sites as a function of H stoichiometry x in H_xWO_3 .

We considered HER pathways through three elementary steps:^{31,32}

1. $* + H^+ + \lambda_n e^- \rightarrow H^*$ (Volmer)
2. $H^* + H^+ + \lambda_n e^- \rightarrow H_2$ (Heyrovsky, Eley–Rideal)
3. $H^* + H^* \rightarrow H_2$ (Tafel, Langmuir–Hinshelwood)

These are respectively referred to as adsorption, surface-mediated, and water-mediated steps, as shown in Figure 1. Each of these steps may be accompanied by the transfer of protons and/or electrons toward or away from the oxide/solution interface. Although proton transfer is restricted to integer amounts (e.g., 0 or 1), electron transfer can occur in fractional amounts, which we denote as λ_n .^{33–35} This partial electron transfer is tightly tied to electrochemical activation (vide infra).

Figure 1a shows a bare oxide surface consisting of only tungsten and oxygen atoms, plus a $H_3O_2^+$ cation composed of two water molecules and an extra proton. The first step in H_2 formation is the reductive adsorption of protons from the electrolyte. Figure 1b depicts an example $H_{0.625}WO_3$ surface with three distinct H-binding sites populated: terminal oxygens (O_t), bridging oxygens (O_b), and surface tungsten metal sites (W). Although O atoms behave as basic centers and metals as acidic centers, reduced protons can interact with both site types owing to the amphoteric nature of hydrogen.²⁴ We emphasize that catalytically relevant atomic configurations may include any combination of the site types illustrated in Figure 1b. A variety of surface configurations can be achieved with respect to the positioning of the adsorbed H units among the three different site types. Further, the stable arrangement of surface H atoms can change depending on the H_xWO_3 bulk hydrogen stoichiometry. Also shown in Figure 1b is a subsurface hydrogen representative of the bulk intercalated

hydrogen, indicated with a circle. The number of these particular hydrogen atoms was varied as required to achieve a certain value of x in H_xWO_3 (see computational methods).

Following the surface adsorption of hydrogen, H–H coupling must occur to form molecular H_2 . This can proceed through the water-mediated or surface-mediated routes. In the water-mediated mechanism, surface H atoms form H_2 by reacting with a proton from the electrolyte. This is demonstrated specifically in Figures 1c and 1d for the $H_{0.625}WO_3$ surface. In the surface-mediated mechanism, two surface H atoms react with one another to generate H_2 ; this is shown in Figures 1e and 1f for the $H_{0.625}WO_3$ surface.

When considering surface-mediated H_2 -coupling, it is important to note that metal oxides differ from metallic surfaces in that active sites of a single type are separated by relatively long distances. For example, the W sites on the WO_3 surface are separated by ~ 5.2 Å, which is too large for surface-mediated H–H coupling to occur. This contrasts with metallic catalysts like Pt, for example, where equivalent surface sites on the FCC (111) facet are separated by only ~ 2.8 Å. This distance can be feasibly traversed by neighboring adsorbed H's, allowing two congruent FCC top sites to support surface-mediated H_2 -coupling. Because of the large spacing between sites on the oxide, surface-mediated hydrogen evolution on H_xWO_3 must proceed through the contribution of multiple site types.

As an initial assessment of HER catalytic activity, we calculated hydrogen atom binding energies on (100) H_xWO_3 surfaces with varying levels of bulk hydrogen stoichiometry, x , as presented in Figure 2a. These energies were computed as binding energies referenced to H_2 and the relevant oxide surface. We observed a notable shift in the preferred site for H-adsorption as the value of x in H_xWO_3 was increased. At low H

stoichiometries, hydrogen tends to adsorb more strongly to the basic oxygen centers and interaction with W sites is modestly endergonic. The HER on tungsten oxide could therefore be expected to proceed at oxygen centers on the $\text{H}_{0.000}\text{WO}_3$ surface. However, as bulk H stoichiometry increases, H adsorption at oxygen sites becomes more endergonic and H adsorption at W sites becomes more exergonic. This is noted specifically for W–H* binding with the red circles in Figure 2a. In fact, the effects of hydrogen intercalation are pronounced enough to cause an inversion in site preference, where for $\text{H}_{0.500}\text{WO}_3$ and $\text{H}_{0.625}\text{WO}_3$ the W site is the most energetically feasible location for initial H adsorption. WO_3 and $\text{H}_{0.625}\text{WO}_3$ therefore interact with hydrogen intermediates in entirely distinct ways, with direct consequences for reaction mechanism and overall turnover.

We next considered the physical reasons for why bulk hydrogen intercalation changes the behavior of H adsorption on H_xWO_3 surfaces. Figure 2b shows a surface of tungsten oxide and Figure 2c depicts the local *d*-projected density of states for a bare surface W atom with no adsorbed H. We observed that increasing bulk H stoichiometry shifts unoccupied *d*-band centers (dashed red lines) closer to the Fermi level, indicating increased site acidity.³⁶ Comparing Figures 2a and 2c reveals that the stronger acid sites correspond to more favorable H adsorption energies. In a similar manner, Figure 2d shows the occupied W *d*- and H *s*-projected density of states for the surface atoms outlined in Figure 2e. The red circles in Figure 2d point out energy levels that show high densities of states for both the W *d* and H *s* electrons. These shared energy states imply W–H bonding, and we observed a stabilization of these bonding states as bulk H stoichiometry was increased. As with the increased W site acidities, the stabilized W–H bonding states correlate with more favorable H adsorption free energies.

While W sites are activated due to increased acidity, oxygen centers are deactivated due to decreased basicity. This is shown in Figure S1 of the Supporting Information. As electrons fill the electronic states of the oxide, the occupied O *p* band is shifted to lower energies and moves further from the Fermi level. This corresponds to less basic sites, which are less reactive toward amphoteric H. Notably, the relationship between reactant binding and acid–base character is well-characterized for oxides, and we have confirmed it for the interaction of hydrogen with the bulk lattice oxygens of WO_3 .³⁷

We further examined the energetics of multiple sequential H adsorption steps at different surface site types, as shown in Figure 2f. Multiple sites were considered because (1) they will together be important for evaluating surface-mediated mechanisms and (2) the water-mediated mechanism may be affected by H atoms that are not bound at the most energetically favorable site. Notably, only nonintercalated WO_3 yields exergonic H adsorption. However, under sufficiently negative applied potentials, it is possible that multiple sites are simultaneously populated. This is evidenced by the observation that for any nonzero level of hydrogen intercalation, the second H site adsorption is less energetically demanding than the first. Together, these results show that the oxide surface may indeed be populated with hydrogen at multiple types of sites. Therefore, the two site configurations shown in Figure 2f were used to evaluate H_2 formation via surface- or water-mediated mechanisms.

For this set of adsorption calculations, explicit waters were not included and solvation was accounted for with an implicit model. This simplification was made to facilitate the screening of all possible site configurations on both (100) and (001) surfaces, which are shown in their entirety in Figure S2 of the Supporting Information. For a given surface with constant bulk hydrogen stoichiometry, we do not expect the trend in adsorption energies to change in the presence of explicit waters.³⁸ Therefore, this approach is sufficient for screening and site selection purposes for the individual oxide surfaces as in Figure 2. Trends across different bronze stoichiometries, however, might be affected by the explicit waters owing to changes in surface electronic structure—specifically the semiconductor-to-metal transition and possible changes in surface polarizability. As a result, comparisons across stoichiometries were made with the inclusion of explicit water molecules. Combined implicit/explicit solvation was also employed for kinetic analysis, as detailed in the following sections.

Constant-Charge vs Constant-Potential Frameworks.

What we have shown so far underpins a complex reaction network for the HER on H_xWO_3 . Hydrogen intercalation significantly perturbs the acidity and basicity of the metal- and oxygen-based surface sites, leading to emergent reactivity. This highlights different H adsorption characteristics for different stoichiometries of H_xWO_3 , branching into distinct reaction pathways that may contribute to the observed HER activity over a range of applied overpotentials. While we have used constant-charge DFT to describe general trends in H adsorption energetics, we found it necessary to apply more realistic modeling techniques to arrive at quantitative reaction energies and barriers for each elementary step to producing molecular H_2 .

Since we are operating under electrochemical conditions, our quantum chemical approach must be carefully selected to produce accurate kinetic information. Canonical DFT methods (like those used in the CHE formalism) operate in the NVT ensemble, with the total number of electrons held constant.³⁰ For the adsorption of hydrogen to a surface site, we can consider the initial state as a proton in solution and the final state as a surface-bound H. Charge transfer between the surface and the proton occurs with adsorption, and this requires a change in the number of electrons in the simulated catalyst slab. This presents a problem for comparing canonical DFT calculations to electrochemical experiments, since the charge transfer yields a different apparent electrochemical potential for the initial and final reaction states.³⁹ Note also that this contrasts with thermochemical reactions, where canonical DFT is appropriate because the surface is not connected to an external circuit and the catalyst electrochemical potential can indeed change.⁴⁰ Using constant charge DFT for electrochemical reaction energies could therefore result in comparing experimental and theoretical data from different thermodynamic ensembles.

CP-DFT is more relevant to experimental electrochemical conditions, since electrochemical instruments are designed to manipulate the net charge in the working electrode (via transfer to or from the external circuit) to attain the desired electrochemical potential. CP-DFT methods replicate this behavior by shifting the thermodynamic ensemble from NVT to μVT : the number of electrons is treated as an additional variational parameter which drives the electrochemical potential to become a result of the calculation itself. Extensive

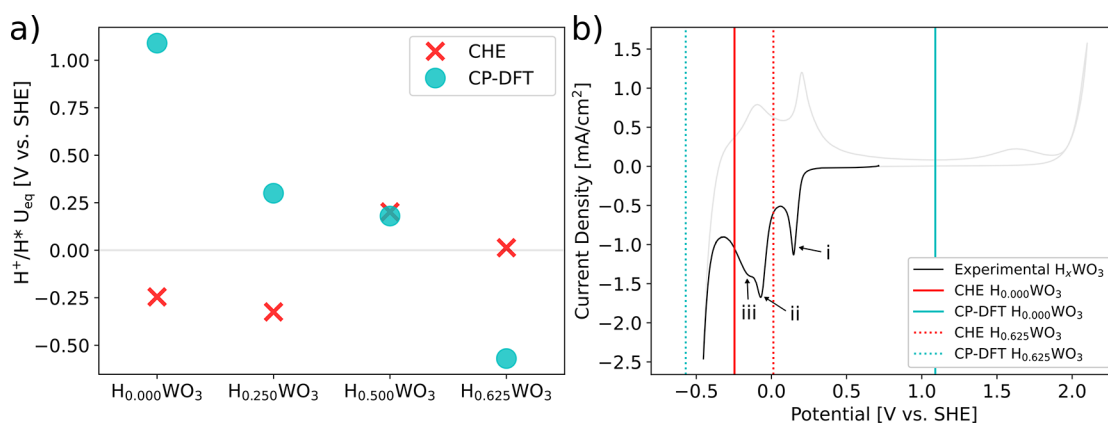


Figure 3. Comparison between constant-charge and constant-potential DFT approaches with experimental cyclic voltammetry. (a) Calculated equilibrium potentials for hydrogen adsorption at thermodynamically limiting steps of adsorption, identified in Figure 2f. Potentials determined via CHE and CP-DFT are shown. The CHE potentials here are different from those apparent from Figure 2f because the present calculations include explicit water solvent molecules. (b) A selection of equilibrium potentials from (a) overlaid with a representative cyclic voltammogram of WO_3 nanoparticles recorded in 0.5 M H_2SO_4 at a scan rate of 1 mV/s. The reference electrode was Ag/AgCl, the counter electrode was graphite, and an Ar purge was used. The cathodic peaks in the CV are attributable to bulk H intercalation and correspond to (i) $WO_3/H_{0.250}WO_3$, (ii) $H_{0.250}WO_3/H_{0.500}WO_3$, and (iii) $H_{0.500}WO_3/H_{0.625}WO_3$ redox couples. Intercalation is followed by the exponential onset of the HER at ~ -0.4 V vs SHE.

gains have been made over the past few years to enable constant-potential calculations, and we refer the reader to several prior reports for further explanation of constant-potential methods.^{41–45}

Figure 3 compares the CHE and CP-DFT approaches to assess which method is more viable for describing the HER on H_xWO_3 . Figure 3a compiles CHE and CP-DFT H adsorption equilibrium potentials on several bronze stoichiometries. The adsorption configurations we modeled correspond to the most endergonic H binding steps in Figure 2f. Notably, the equilibrium potentials returned via CHE and CP-DFT differed by as much as >1 eV, depending on bulk H content. At $H_{0.000}WO_3$ and $H_{0.250}WO_3$, the CHE returns more negative equilibrium adsorption potentials than CP-DFT. The CHE and CP-DFT approaches agree on the position of equilibrium for $H_{0.500}WO_3$, and CP-DFT predicts a more negative equilibrium potential than the CHE on $H_{0.625}WO_3$. Details on the calculation of equilibrium potentials using each method are given in Section S3 of the Supporting Information. This disagreement between the CHE and CP-DFT approaches is consistent with prior investigations into the differences in free energies of adsorption for intermediates relevant to CO_2 reduction.⁴⁵

Figure 3b overlays the equilibrium potentials for H adsorption on WO_3 and $H_{0.625}WO_3$ with an experimental cyclic voltammogram (CV) of WO_3 nanoparticles. The DFT-calculated H^+/H^* equilibrium potentials (vertical lines) are related to the interaction of solvated protons with the H_xWO_3 surface, whereas the peaks seen on the CV are related to bulk hydrogen intercalation.²⁴ From the experimental CV, it is clear that hydrogen intercalation occurs at potentials positive of the HER onset, and the HER does not achieve an appreciable rate until < -0.4 V vs SHE. This supports the conclusion that the HER occurs predominantly on the surface of the bronze (i.e., $x > 0$ in H_xWO_3) and not on WO_3 .

Another key observation is that the CHE equilibrium potential for H adsorption on $H_{0.000}WO_3$ is negative of the $H_{0.000}WO_3/H_{0.250}WO_3$ reduction. This is inconsistent with the experimental observation of bulk hydrogen intercalation because H intercalation also requires the formation of surface bound H intermediates. Thus, the H^+/H^* equilibrium

potentials for a given H stoichiometry must be equal to or positive of the equilibrium potential for intercalation to a higher H stoichiometry, else intercalation would not be able to occur. In fact, the CHE-derived H^+/H^* equilibrium potential for $H_{0.000}WO_3$ is calculated to be at ~ -0.25 V vs SHE, which occurs negative of all intercalation features in the CV. If this equilibrium potential was valid for H adsorption, then H would not be able to interact with the WO_3 surface in any meaningful way and intercalation would not be observed until potentials negative of ~ -0.25 V vs SHE. Using CP-DFT, the apparent equilibrium potentials are in much better agreement with experimental observations. Specifically, hydrogen binding on WO_3 occurs at $\sim +1.1$ V vs SHE, meaning the surface can adsorb hydrogen before an intercalated bulk phase is formed. By contrast, the highly intercalated $H_{0.625}WO_3$ is seen to have an equilibrium potential for H adsorption that is negative of the observed $H_{0.500}WO_3/H_{0.625}WO_3$ intercalation feature in the CV. In fact, this is still consistent with experiments, since we do not see any experimental evidence of intercalation above the $H_{0.625}WO_3$ stoichiometry.

The results shown in Figure 3 suggest that the CP-DFT approach is an improvement over the CHE when describing the dynamics of H adsorption and intercalation on H_xWO_3 , and quite possibly other oxides. Indeed, although the CHE has seen widespread success in describing the thermodynamics of numerous electrochemical systems, it makes assumptions that may not accurately describe the kinetics of some electrocatalytic reactions. One important assumption of the CHE is that elementary steps require electrons to transfer in integer multiples. For elementary electrochemical reaction steps, the number of electrons transferred does not have to be an integer value.^{33,46} The possibility of partial electron transfer results from the ability of an electrode to redistribute charge in the near-neighborhood of the electrode surface; hence, forming or breaking a bond between a proton and the electrode surface does not always require the transfer of a full electron into or out of the electrode.³⁵ Since the number of electrons transferred prior to and during the rate-determining step of an electrocatalytic reaction governs the dependence of reaction barriers on applied potential, an accurate kinetic analysis would benefit from the relaxation of the unit electron transfer

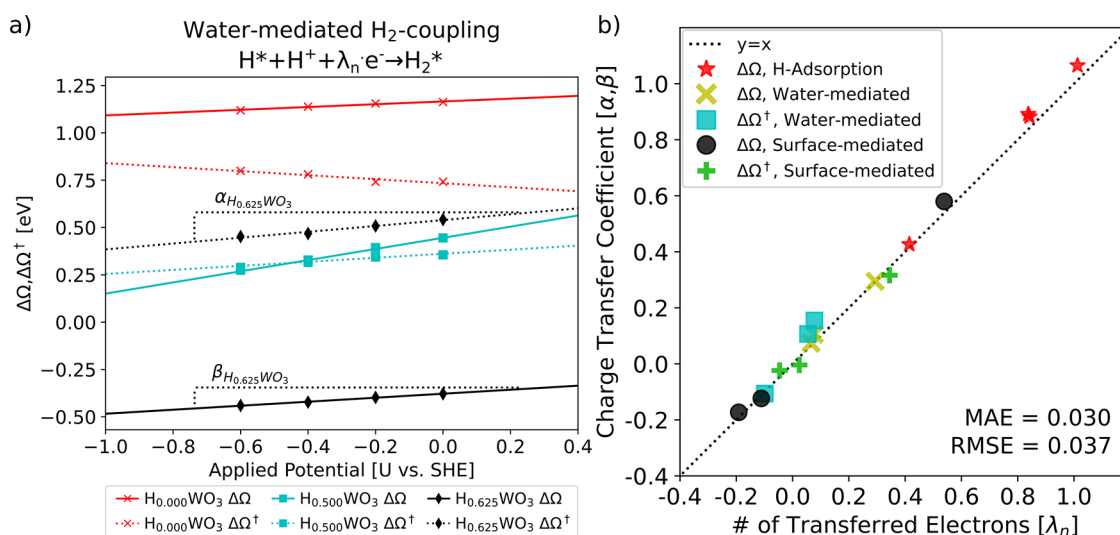


Figure 4. Energies and barriers for the water-mediated H_2 -coupling step on H_xWO_3 , which was found to be the most favorable pathway for hydrogen evolution. (a) Reaction energies and barriers determined at several potentials (markers), with lines of best fit showing the linear dependence on applied potential. Changes in stoichiometry result in larger energy shifts than changes in potential. (b) Parity plot demonstrating 1:1 correspondence between the number of electrons transferred and the apparent charge transfer coefficients.

assumption.⁴⁷ Still, the integer electron transfer assumption made by the CHE could be appropriate for fully thermodynamic investigations.

Overall, comparing the CHE equilibrium potentials with experiments suggests that the CP-DFT approach is better suited to describing the interaction of H_xWO_3 with hydrogen under electrochemical conditions. We note, however, that the $H_{0.000}WO_3$ CHE equilibrium potential for H adsorption does match well to the observed HER onset. Prior work has investigated WO_3 and its substoichiometric derivative, $WO_{2.9}$, for HER catalysis.²⁰ In that work, the limiting potential for hydrogen adsorption on WO_3 was found to occur at around -0.50 V vs SHE, in rough agreement with our value of -0.25 V vs SHE. The difference likely arises from our calculations including both explicit and implicit water solvation, whereas the prior results were computed in the gas phase. Notwithstanding that difference, either value is in reasonable agreement with the experimentally observed HER onset at -0.4 V vs SHE. However, we clearly observe the formation of $H_{0.250}WO_3$ at considerably more positive potentials, and so the H^+/H^* adsorption equilibrium on $H_{0.000}WO_3$ is likely irrelevant in the potential range where we experimentally observe hydrogen evolution. Accordingly, the H adsorption equilibria we calculated with CP-DFT are broadly consistent with the physical picture of H adsorption followed by H insertion, followed by further H adsorption and H_2 evolution on the oxide bronze. For these reasons, we applied CP-DFT to execute more detailed calculations of hydrogen evolution energetics on H_xWO_3 .

Partial Electron Transfer Governs the Potential-Dependence of Reaction Energies and Barriers. Using CP-DFT, we calculated from first-principles the dependence of reaction energies and barriers on applied potential. Figure 4a takes the water-mediated H_2 -coupling step as an example and shows the change in grand canonical free energy, $\Delta\Omega$, with potential. The surface-mediated energetics are shown in Figure S5, but we found that the water-mediated mechanism is always more feasible. For reduction reactions, we expect a positive slope for $d\Delta\Omega/dU$ and a negative slope for oxidation reactions.

Nonelectrochemical (thermal) reactions have slopes of zero. For reactions that obey classical mechanisms involving unit proton–electron transfer in each elementary step, we would further expect the magnitude of $d\Delta\Omega/dU$ to be near 0.5 for activation barriers and 1.0 for full elementary steps. Remarkably, we instead observe slopes <0.3 for the water-mediated energies and barriers; that is, each of the elementary steps we modeled depend only weakly on applied potential.

The weak potential dependence is especially clear on $H_{0.000}WO_3$, where the H_2 -coupling reaction energy changes by less than 0.25 eV over a span of at least 0.6 V. Interestingly, we observed a significantly larger change in the same reaction energy, greater than 1.5 eV, by changing from $H_{0.000}WO_3$ to $H_{0.625}WO_3$. This demonstrates that H-intercalation has a more substantial influence on reaction energetics than changes in applied potential for a hypothetically fixed H stoichiometry. Stated more simply, if we considered only the $H_{0.000}WO_3$ surface and were able to prevent bulk H intercalation, then we would expect to need massive overpotentials to achieve appreciable HER turnover. Instead, investigating multiple H_xWO_3 surfaces shows the HER only proceeds at a meaningful rate with $x > 0$. This observation suggests that applied potential only indirectly influences the rate of hydrogen evolution on H_xWO_3 —applying an electrochemical potential to the oxide primarily sets the bulk hydrogen stoichiometry, which in turn has a significant effect on reaction energies.

Although DFT calculations allow us to determine potential-dependent reaction energies at constant stoichiometries, the stoichiometry is also a function of applied potential. It is therefore challenging to experimentally measure the independent impacts of composition and overpotential on overall activity. Doing so would require that applied potential be modulated independently of bulk hydrogen stoichiometry. Since both hydrogen intercalation and hydrogen evolution are dependent on electrochemical potential, transient methods (e.g., electrochemical impedance spectroscopy or open-circuit potential/current decay⁴⁸) could perhaps be used in future studies to more fully map the composition-overpotential-activity space.

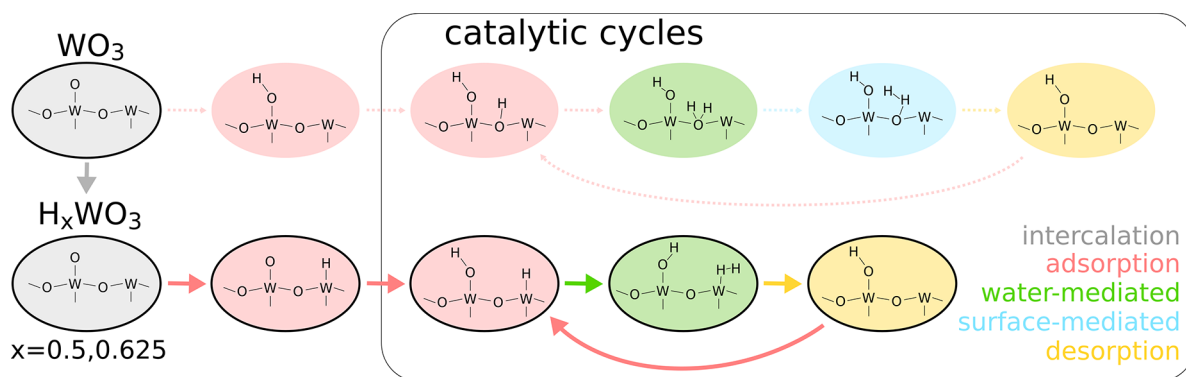


Figure 5. Reaction pathways from bare H_xWO_3 through H_2 formation and the relevant catalytic cycles. As bulk H stoichiometry increases, active sites for the HER shift from O centers to W centers. The bold arrows indicate the practical result of progressively decreasing applied potential, which first induces H-intercalation and then drives the HER.

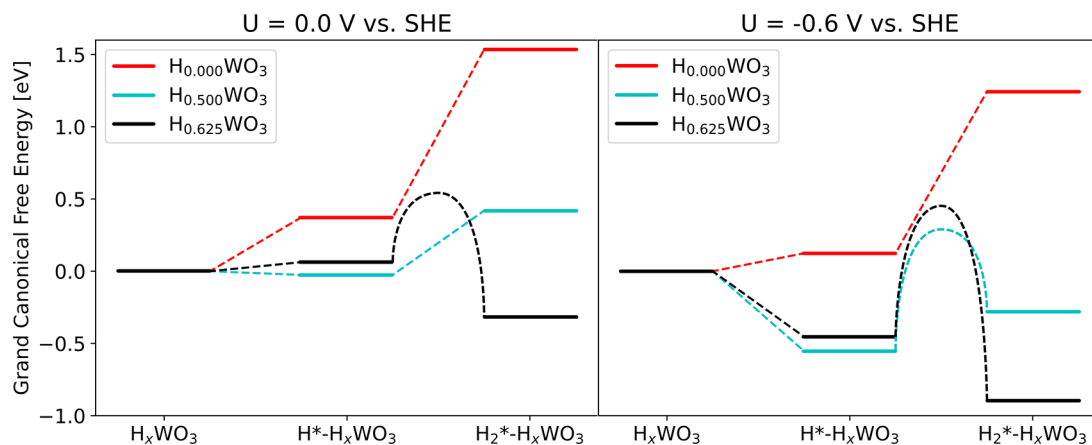


Figure 6. Reaction coordinate diagrams for three selected stoichiometries of tungsten oxide hydrogen bronze. The left panel shows reaction energies at an applied potential of 0.0 V vs. SHE, and the right at -0.6 V vs. SHE. Transition states are indicated via curved lines. Nonactivated steps are shown with straight lines. All energies are determined using the PBE-D3 functional in the grand canonical, constant-potential formalism.

We now examine why the energies shown in Figure 4a are such weak functions of applied potential. Figure 4b presents a comparison between two different types of charge transfer coefficients—defined as the slope of the relationship between reaction free energy or activation energy and applied potential—and the number of electrons transferred for each step, λ_n . The determination of these quantities is outlined in Section S4 of the Supporting Information. The charge transfer coefficients for transition states are labeled with α and the full elementary step reactions with β . We observed an excellent one-to-one agreement between charge transfer coefficients and λ_n , supporting the conclusion that partial electron transfer defines the potential dependence of the grand canonical free energies.^{34,46,47} This once again highlights the benefit of using CP-DFT vs the CHE model in our system. For these types of multisite, multistep catalytic reactions, charge transfer coefficients can deviate significantly from their expected values, and CP-DFT allows us to determine, from first-principles, these unexpected values.

The relationship between charge transfer coefficients and λ_n also offers a means to accelerate the determination of the potential dependence of electrochemical reaction energies and barriers. In Figure 4a, each data point comprises a separate pair of energy calculations (of the initial and transition state configurations or the initial and final state configurations). The charge transfer coefficients for a given step are extracted from

the resulting slope across multiple points, and therefore require many individual DFT calculations. We can instead perform a single pair of calculations at one potential and extract the number of electrons transferred between the states of interest. Because λ_n appears to remain virtually constant over modest overpotentials (see Figure S4 in the Supporting Information), Figure 4b suggests we can treat λ_n directly as the charge transfer coefficient. Doing so would avoid the execution of calculations at multiple potentials, reducing the total cost and increasing the speed of a CP-DFT analysis.

Effect of Bulk Hydrogen Intercalation on Preferred Reaction Pathways and HER Rates. Our computational and experimental data show that the energetics of hydrogen adsorption and of H_2 -coupling on H_xWO_3 are both strong functions of bulk hydrogen intercalation. In Figure 5, we summarize what we conclude are the minimum energy pathways for hydrogen evolution, starting from bare H_xWO_3 surfaces and considering both hydrogen intercalation and evolution. The most feasible pathway for the HER is highlighted with the bolded arrows and outlined ellipses. Beginning with a nonintercalated tungsten oxide electrode, applying an increasingly negative bias will first preferentially intercalate hydrogen and form the bronze instead of evolving H_2 . Once the bronze is formed, the reaction mechanism for the HER shifts from oxygen-centered surface coupling (top path) to metal-centered water-mediated coupling (bottom path).

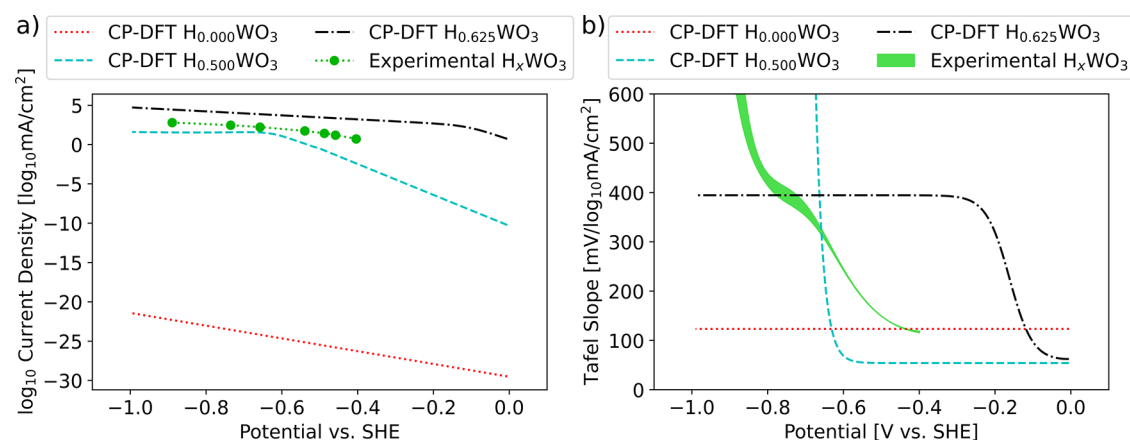


Figure 7. Comparison between microkinetic model rates and experimentally measured HER rates. (a) Kinetic current densities as a function of potential, with the experimental data as points. The line connecting experimental data points are meant to guide the eye. Kinetic currents were extracted from total measured currents with the Koutecký–Levich equation. (b) Tafel slopes computed from first-principles-based microkinetic rates and from the experimental data, with the green shaded area giving 99% confidence interval bounds for the experimental H_xWO_3 value.

The top path is the hypothetical minimum energy pathway to H_2 on nonintercalated $H_{0.000}WO_3$. In this path, hydrogen first populates the terminal oxygens and then the bridging oxygens. Next, a water-mediated H adsorption occurs at the bridge oxygen, forming a bridging $O-2H^*$ consisting of two individual H atoms bound to O. We consider this step to proceed prior to H–H bond formation because the second incoming proton prefers binding to the O center. These H atoms only subsequently combine to form H_2 , which then desorbs. Note, however, that the mechanism on $H_{0.000}WO_3$ should be considered as hypothetical, since it does not likely contribute meaningfully to hydrogen evolution. For the intercalated oxides, adsorption first occurs at the metal site, then at the terminal oxygen, but the latter H^* does not participate in catalytic turnover. Instead, a third H adsorption occurs to facilitate the water-mediated formation of H_2 at the metal site, which then desorbs. Although both paths lead to H_2 , the bold arrows in Figure 5 outline the practical consequence of applying a potential to WO_3 , which is to sequentially intercalate and then evolve hydrogen on an H_xWO_3 surface.

An important takeaway from Figure 5 is the configuration of the catalyst surface prior to initial H adsorption within the catalytic cycle; this configuration is indicated by the yellow ellipses at the end of each pathway. The site of initial hydrogen adsorption does not necessarily dictate this configuration because it may not be consistent with the surface composition resulting from catalytic turnover. For example, on $H_{0.625}WO_3$ the first H adsorbs to the metal site and the second adsorbs to a terminal O site. The desorption of molecular H_2 at the end of the cycle will expose only a metal site, leaving the terminal O-bound H as a spectator. Therefore, the start of the next catalytic cycle occurs as H adsorbs to an exposed metal site with the terminal oxygen site already populated. This elementary step is different from the initial adsorption of H to W, which occurs without a terminal O-bound H. Hence, the reaction coordinate diagrams shown in Figure 6 and the energies which informed the microkinetic models (vide infra) were referenced to the rightmost configurations shown in Figure 5 (i.e., desorbed states within the catalytic cycle).

Figure 6 shows reaction coordinate diagrams for the HER on $H_{0.000}WO_3$, $H_{0.500}WO_3$, and $H_{0.625}WO_3$. The different bronze compositions contrast starkly in apparent activity. $H_{0.000}WO_3$ gives rise to a highly unfavorable pathway to H_2 , further

supporting the notion that WO_3 cannot be responsible for HER activity. Furthermore, increased intercalation reduces the energy requirement for H_2 formation, thereby resulting in enhanced catalysis. Note that $H_{0.250}WO_3$ is not included in the remainder of this analysis since it is also unlikely to play a significant role at potentials relevant to HER on H_xWO_3 . This is apparent from Figure 3b, where significant HER is only seen at potentials negative of the equilibrium potentials for formation of H:W ratios ≥ 0.500 .

The reaction coordinate diagrams shown in Figure 6 further demonstrate the influence of applied potential on hydrogen evolution at H_xWO_3 . Each intermediate and transition state energy is evaluated as an independent function of potential, such that the potential dependence of each elementary step can be used as the basis of a full microkinetic model. Figure 6 also shows that composition not only has an outsized effect on the single elementary step shown in Figure 4a, but also for the full HER pathways on H_xWO_3 . We reiterate here that the initial states of the catalysts are the desorbed surfaces in Figure 5, with monatomic H adsorption occurring at full coverage of the respective adsorption sites. By constructing the reactions in this way, we can input all CP-DFT reaction energetics into a microkinetic model for the calculation of HER reaction rates and make direct comparisons to experimental HER measurements.

The experimental kinetic current density given by H_xWO_3 is shown in Figure 7a alongside the potential–current density relationships from first-principles-based microkinetic models for WO_3 , $H_{0.500}WO_3$, and $H_{0.625}WO_3$. Complete details on construction of the microkinetic models, including discussion of the underlying assumptions, are presented in Section S6 of the Supporting Information. Comparing experiments to theory clearly shows that only $H_{0.500}WO_3$ and $H_{0.625}WO_3$ replicate the steady state kinetic current densities observed in constant-current rotating disk electrode experiments. Indeed, the modeled HER rates on pure WO_3 were more than 20 orders of magnitude lower than the experimentally observed rates. In fact, as discussed in Section S6 of the Supporting Information, the calculated current densities specifically for WO_3 are an upper bound on the actual values. This motivates the conclusion that $H_{0.000}WO_3$ is irrelevant to the HER and should not be considered as an active catalyst. Instead, only the

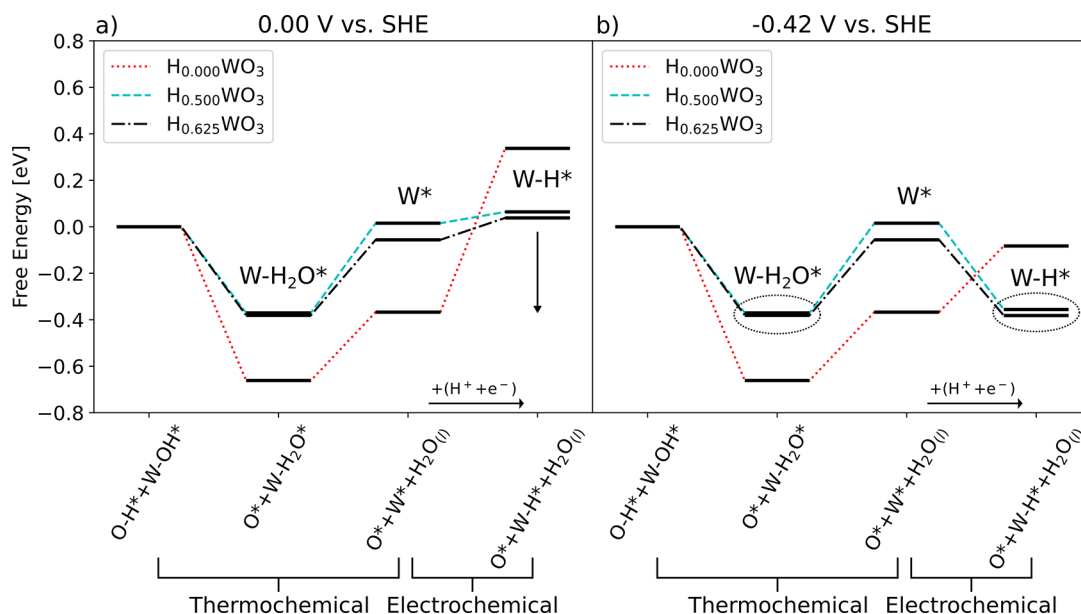


Figure 8. Reaction coordinate diagrams depicting dehydration of fully hydrated oxide surfaces, wherein each W atom is covered by a hydroxyl group and an adjacent bridge oxygen is protonated. (a) The pathway at 0.00 V vs SHE. (b) The pathway at -0.42 V vs SHE, which is near the experimental onset potential for the HER. Only the last step of the dehydration pathway is electrochemical, and therefore only the final configuration shifts in free energy between the two applied potentials. At the experimental HER onset potential, the relative energies of the water-blocked metal site and the adsorbed hydrogen states become equivalent, allowing the HER to proceed.

intercalated oxides provide sufficiently reactive sites for H_2 formation.

When first comparing the reaction coordinate diagrams in Figure 6 and the computed rates in Figure 7a, it seems unexpected that the $H_{0.500}WO_3$ gives lower activity than the $H_{0.625}WO_3$ surface. $H_{0.500}WO_3$ has a slightly lower barrier to H_2 than $H_{0.625}WO_3$ and would be expected to give faster turnover. However, the $H_{0.625}WO_3$ surface has a more favorable equilibrium balance between the H^* and H_2^* species, as can be seen by the relatively exergonic energy change in forming H_2^* . Because the $H_{0.500}WO_3$ surface results in an endergonic energy change for this step, the equilibrium position favors the H^* state, thereby inhibiting H_2 evolution.

As a further check on activity, we examined the Tafel slopes and their dependence on potential. We chose not to fit a single straight line through the data, as there is some evidence of curvature even after correcting for 100% of uncompensated resistance. Moreover, the nonclassical values of the charge transfer coefficients encountered through CP-DFT would be expected to cause Tafel slopes to deviate from cardinal values (e.g., 30, 40, 120), and we did not want to introduce modeling bias.^{32,49} However, with the experimental data points occurring at relatively large gaps in potential increments, using discrete differences as Tafel slopes is also not ideal. To address the uncertainty in fitting the data and associated inaccuracies, we opted to apply Gaussian process regression. This approach allowed us to fit and interpolate the experimental data, resulting in more accurate estimates of the (potential-dependent) Tafel slopes. Details on the regression methods are included in Section S7 of the Supporting Information.

Figure 7b compares potential-dependent Tafel slopes from the first-principles-based microkinetic models with the Tafel slope relationship derived from Gaussian process regression of the experimental measurements shown in Figure 7a. The experimental Tafel slope begins near a value of 120 mV/decade, but it exhibits a strong potential dependence,

increasing significantly at potentials negative of -0.5 V vs SHE. Note that we minimized the impact of transport limitations on the experimental current–potential measurements by using a rotating disk electrode with a rotation rate of 1600 rpm, and we further corrected for mass transfer limitations using the Koutecký–Levich equation as described in the experimental methods section.⁵⁰ We also accounted for uncompensated cell resistance, as detailed in the experimental methods section; thus we do not expect conductivity limitations. The steep Tafel slopes can therefore be interpreted as a manifestation of the small charge transfer coefficients shown in Figure 4, where applied potential has little effect on reducing activation barriers.

The large empirical Tafel slopes can also be rationalized from the microkinetic results. WO_3 shows a constant Tafel slope of ~ 123 mV/dec, suggesting consistent reaction dynamics across all applied potentials. On the other hand, $H_{0.500}WO_3$ and $H_{0.625}WO_3$ show increasing Tafel slopes as the applied potential becomes more negative, which generally agrees with the experimental result. The former starts at ~ 65 mV/dec, and negative of -0.6 V vs SHE the Tafel slope rapidly increases toward infinity. This is because the current density becomes independent of applied potential below -0.6 V vs SHE, as apparent from Figure 7a. The barriers for both H adsorption and H_2 -coupling become low enough at these potentials that the HER reaches a maximum rate that is no longer dictated by a potential-dependent activation energy, but instead by site density, surface coverage, and the magnitude of the Arrhenius prefactor. Nonetheless, the maximum rate predicted for $H_{0.500}WO_3$ is smaller than rates predicted for $H_{0.625}WO_3$ over the same range of overpotentials; this is because the H^*/H_2^* equilibrium on $H_{0.500}WO_3$ favors H^* , as discussed above. $H_{0.625}WO_3$ also exhibits a large increase in Tafel slope beginning at more modest potentials near -0.15 V vs SHE. This shift is due to the change in initial H adsorption from endergonic to exergonic. The H_2 formation barrier then

limits HER turnover on the $\text{H}_{0.625}\text{WO}_3$ surface, leading to a large ~ 400 mV/dec Tafel slope at potentials lower than ~ -0.3 V vs SHE.

At large negative potentials the experimental Tafel slope steadily increases at a rate that is between those computed for $\text{H}_{0.500}\text{WO}_3$ and $\text{H}_{0.625}\text{WO}_3$. We observed two contributions to shifting Tafel slopes in the microkinetic data, with the presence of nonzero barriers causing large, finite Tafel slopes, and low barriers for all elementary steps causing potential-independent behavior. Notably, there is a slight shoulder corresponding to a Tafel slope of ~ 400 mV/decade between -0.7 and -0.8 V vs SHE that agrees quite well with the microkinetic result for $\text{H}_{0.625}\text{WO}_3$. However, at still larger overpotentials the Tafel slope increases toward infinity, suggesting barrierless reactivity. At large overpotentials this behavior can be expected for reduction reactions, since the barriers will become small enough to cause potential independence. We also cannot rule out transport limitations at the largest overpotentials we measured, as the Tafel slope would be expected approach infinity as the reaction rate approaches an external mass transfer limit. Nevertheless, the potential-dependent behavior of the experimental Tafel slopes are generally consistent with the microkinetic data such that the intercalated $\text{H}_{0.500}\text{WO}_3$ and $\text{H}_{0.625}\text{WO}_3$ bronzes are likely responsible for the HER.

Prevalence of Exposed Metal Sites in an Electrochemical Environment. Metal oxides are known to interact strongly with water, resulting in adsorbed hydroxyls, protons, and associated water molecules that can block surface active sites.^{51,52} Thus, despite the agreement between experimental and computational results, we remained concerned that the aqueous electrochemical environment could facilitate strong surface hydration and limit H adsorption at active W sites. Since metal site blocking via hydration would inhibit the HER mechanism we proposed in Figure 5, we further examined the free energies of water interacting with various surface sites. The results are shown in Figure 8, and the specific configurations in Figure S12 of the Supporting Information.

Examination of the relative free energies compiled in Figure 8 show that only intercalated H_xWO_3 exhibits accessible and exposed metal sites. The first step depicted in these reaction coordinate diagrams is the association of a tungsten-bound hydroxyl and a bridging oxygen-bound hydrogen to form an adsorbed water at the tungsten atom. This is followed by the desorption of the formed water molecule and exposure of the metal site. A final step involves population of the bare W site with an H atom, and the thermodynamics of this reaction are potential-dependent—thus, applied potential can drive the equilibrium toward the dehydrated, H-adsorbed state. Comparing the second and fourth states shown in Figures 8a and 8b, H atoms at the exposed H_xWO_3 surface W sites are stabilized related to surface-bound water at potentials more negative than approximately -0.4 V vs SHE. Hence, applying a sufficiently negative bias to the intercalated bronzes brings the hydrogen- and water-terminated W sites to similar relative free energies, allowing the electrochemical HER to compete with surface hydration. At potentials lower than -0.4 V vs SHE—near the experimental onset potential for the HER—the W site will be preferentially populated with a hydrogen atom instead of a water molecule, allowing the HER to proceed unhindered by water molecules. Notably, this contrasts with non-intercalated WO_3 , where water remains strongly bound to surface W atoms even at potentials far negative of the onset of H intercalation. This agrees well with our previous observation

that the O sites are the ones that accommodate H binding on $\text{H}_{0.000}\text{WO}_3$ (Figure 2). Thus, it is plausible that bulk H intercalation proceeds primarily via H adsorbed to surface O atoms in WO_3 , whereas the HER proceeds primarily at W sites on the intercalated compound. We reiterate, however, that it remains unlikely that WO_3 is an effective catalyst for the HER, as the rates we have calculated and shown for $\text{H}_{0.000}\text{WO}_3$ in Figure 7 are much too slow to explain the experimentally measured HER currents. Overall, the results shown in Figure 8 further support the conclusion that bulk hydrogen intercalation enhances HER catalysis by activating surface W atoms that would otherwise be blocked by water and unreactive toward protons in solution.

CONCLUSIONS

In summary, this work presented DFT calculations, microkinetic modeling, and experimental electrochemical measurements directed at understanding the HER on WO_3 . The main finding of this work is that hydrogen intercalation changes the chemical identity of WO_3 , leading to enhanced catalytic activity for the HER. Under reducing conditions, WO_3 is converted into H_xWO_3 , which has a higher prevalence of active metal surface sites. These sites are virtually inaccessible on the initial WO_3 surface, and H_2 generation is only feasible on H_xWO_3 . This is important to recognize, because many catalytic modeling and experimental studies do not consider the possibility of bulk changes, and therefore may not be addressing the true active catalyst.

More specifically, the increase in HER activity with H-insertion occurs because of modulations in the oxide electronic structure, whereby electronic conductivity is enhanced, surface metal sites become more acidic, oxygen sites become less basic, and W–H bonds are stabilized. We also found that the HER rate on H_xWO_3 is not accelerated efficiently with increased overpotential for any single H stoichiometry. Instead, applying an electrochemical bias mainly serves to set the bulk hydrogen stoichiometry of the oxide, thereby enabling access to surfaces that are much more intrinsically HER active. Furthermore, the charge transfer coefficients for each elementary step on H_xWO_3 correlate tightly with the fractional number of electrons transferred for the respective steps. This observation gives avenues for simplifying CP-DFT analyses, whereby electron transfer numbers can be used as proxies for charge transfer coefficients in kinetic models involving modest changes (up to a few hundreds of mV) in applied potential.

More broadly, our findings highlight an underexplored complexity of metal oxide catalysts, wherein their bulk redox reactivity is at least as important as their surface reactivity in the context of cathodic (reductive) electrocatalysis. These results underscore the importance of considering how reaction conditions impact bulk catalyst composition and the associated surface reactivity. Owing to the fact that many redox-active metal oxides insert protons under aqueous electrochemical conditions, it is highly likely that hydrogen intercalation plays a critical role in the electrocatalytic activity of metal oxides toward numerous reactions involving hydrogen intermediates. Accordingly, it is important to consider the reducibility of a candidate metal oxide along with the relevant reaction conditions to determine whether bulk hydrogen intercalation will occur alongside the reaction of interest. Our results also suggest that the insertion of sodium, potassium, or other cations could influence catalytic activity in a similar way to proton insertion, thereby offering a potential route to

dynamically tune the catalytic activity of metal oxides. Even further, this phenomenon may not be restricted to the family of metal oxide bronzes, but could extend to any material which can accept a guest ion. Outside of electrochemical environments, the impact of hydrogen intercalation on catalysis may also be relevant in thermochemical reactions in which hydrogen spillover to oxide supports has been observed. In these situations, the associated changes in the electronic structure and surface chemistry of the oxide are not often interrogated in detail. Future materials screening efforts, kinetic analyses, and characterizations of metal oxides as catalysts and supports for, e.g., hydrogenation reactions would therefore benefit from careful consideration of their H insertion chemistry.

MATERIALS AND METHODS

Computational Methods. Spin-polarized DFT calculations were performed using VASP and the projector augmented wave (PAW) method.⁵³ Atomic visualizations were generated using VESTA.⁵⁴ For energy calculations and geometric relaxations, exchange-correlation was modeled using the PBE functional.⁵⁵ Dispersion corrections were included using the D3 method with Becke–Johnson damping.^{56,57} The PBE-D3 level of theory has previously been shown to give good energetic and structural results for the metal oxides and hydrogen bronzes explored in this work.^{58,59} Electronic density of states were determined using the hybrid HSE06 exchange-correlation functional in a single-point calculation at the optimized PBE-D3 geometry.⁶⁰ In all calculations, PAW pseudopotentials and a plane wave basis with a cutoff of 520 eV were used to model the electronic wave functions. Ground state geometries were optimized with an electronic convergence threshold of 1×10^{-6} eV. Electronic convergence was tightened to 1×10^{-7} eV for transition state optimizations. Transition states were located using the climbing image nudged elastic band (CI-NEB) method and further optimized using the improved dimer method (IDM).^{61,62} Both the ASE and VTST implementations of CI-NEB were used in initial transition state searches, while the IDM was executed as available in the standard VASP distribution.⁶³ For all states, geometries were relaxed until the largest observed force was less than 0.05 eV/Å. Intermediate ground states and transition states were confirmed via vibrational frequency analysis. Ground states that returned imaginary frequencies, or transition states that gave extra imaginary modes, were further optimized to a minimum with tighter force criteria. Reciprocal space was sampled using a k -point density of 0.3 Å and Gaussian smearing with a width of 0.02 eV was used to smooth the electronic occupancies.

H_xWO_3 surfaces were constructed as $1 \times 1 \times 2$ and $2 \times 1 \times 1$ supercells for the (001) and (100) facets.⁶⁴ The bulk geometries over a range of hydrogen stoichiometries, $x = 0.000, 0.250, 0.500$, and 0.625, were used as starting points. These values of x were chosen to match the compositions that form the discrete redox couples and staging levels observed in H_xWO_3 in prior experimental and computational studies.^{24,65} Moreover, while we cannot rule out the possibility that other H_xWO_3 phases form under HER conditions, the stoichiometries selected for this work give a progression of x values that allows us to probe the effect of increasing H content in WO_3 . Initially, the bulk unit cell for each stoichiometry was optimized with respect to lattice parameters and atomic positions. Volume- and position-optimized bulk cells were then used to create surface models. Including lattice parameters as additional degrees of freedom allowed us to track the effects of structural rearrangement on catalytic activity. The surface structures were further relaxed prior to any adsorbate calculations by including a 15 Å vacuum layer in the direction perpendicular to the surface.

All results shown in this work, unless otherwise mentioned, pertain to the (100) facet of H_xWO_3 . Although the most thermodynamically stable facet is (001), we find that adsorption energies of H are more favorable on (100). This is shown in Figure S2 of the Supporting Information. We also see from SEM images and XRD measurements

that there is a sufficient number of exposed (100) facets on the nanoparticles we used in experiments. This is discussed and illustrated in Section S8 of the Supporting Information.

Electrolyte and solvent effects were included using the VASPsol extension.⁴¹ This approach leverages the linear GLSSA-13 implicit model to describe the solvent, which is water in this case.⁶⁶ As such, all calculations were run using a relative permittivity of 78.4. The cavitation energy was not included in the determination of total energy, since this effect is small and its inclusion can cause oscillations and inefficiencies in optimizations.^{38,67} The electrolyte was modeled using a linearized Poisson–Boltzmann equation with a Debye length of 4.3 Å, which corresponds to the 0.5 M H_2SO_4 electrolyte used in the experiments included in this work. In addition to the implicit solvent and electrolyte models, explicit waters were included to better approximate the Helmholtz layer and to provide a hydrogen source in our calculations. Two water molecules and an extra hydrogen atom forming the H_3O_2^+ Zundel cation were used per surface unit cell (Figure 1), as including more water molecules did not significantly alter energies.

For DFT calculations at constant charge (i.e., no excess electrons), the free energy of a given state was calculated as follows:

$$F = E_{\text{elec}} + E_{\text{ZPE}} + T \cdot S \quad (1)$$

In eq 1, F is the total canonical free energy of the system, E_{elec} is the electronic DFT energy, E_{ZPE} is the zero point energy, and $T \cdot S$ is the entropic contribution. The zero point energies and entropies were determined from vibrational modes calculated using the harmonic oscillator approximation. All free energies were computed at 298.15 K, to compare calculated results to room-temperature experimental data.

Constant-potential DFT (CP-DFT) calculations were performed by varying the number of excess electrons included in the cell until a desired electrochemical potential was achieved. Our approach and analysis follows that given by the authors of the VASPsol package and is described in detail here.⁴¹ The electrochemical potential on the SHE scale was calculated as

$$U = -(\epsilon_{\text{fermi}} - \phi_{\text{solvent}}) - \phi_{\text{SHE}} \quad (2)$$

In eq 2, ϕ_{SHE} is the value of the SHE redox couple which was taken to be 4.44 eV, ϵ_{fermi} is the Fermi level of the electrode, and ϕ_{solvent} is the electrostatic potential deep in the solvent region.⁶⁸ Rather than manually changing the number of excess electrons after individual DFT calculations, an automated script was used to search for a desired potential via a gradient descent algorithm:

$$N_e[i + 1] = N_e[i] - a \cdot (U_{\text{target}}[i] - U[i]) \quad (3)$$

Here, N_e is the number of excess electrons at a given image i , U_{target} is the desired electrochemical potential, $U[i]$ is the electrochemical potential of the current configuration, and a is a scaling factor used to control the size of the correction applied to N_e for the next guess. Previous work found an a value of 1.0 V^{-1} to be sufficient, but this caused oscillations around the target potential in our calculations.⁴² Reducing a to a value of 0.5 eliminated these oscillations. A tolerance of 0.020 V was used as a convergence criterion for terminating the optimization of electron numbers.

To account for the excess electrons in the systems held at constant potentials, the grand canonical free energy, Ω , was considered instead of the typical canonical free energies.^{41,43,44} This was achieved through a modification of eq 1:

$$\Omega = E_{\text{elec}} + E_{\text{ZPE}} + T \cdot S - N_e \cdot \phi_{\text{solvent}} - N_e \cdot (-\phi_{\text{SHE}} - U) \quad (4)$$

By combining eqs 1 and 4, we considered the grand canonical free energy as the canonical free energy with two additional corrections:

$$\Omega = F - N_e \cdot \phi_{\text{solvent}} - N_e \cdot (-\phi_{\text{SHE}} - U) \quad (5)$$

The second term on the right-hand side of eq 5 is required to account for the excess electrons in the system. The third term on the right-hand side of eq 5 arises from the Legendre transform that connects the canonical ensemble to the grand canonical ensemble.⁴¹

Combining these two corrections and considering eq 2 results in the following, simplified total grand canonical energy expression:

$$\Omega = F - N_e \cdot \epsilon_{\text{fermi}} \quad (6)$$

Eq 6 clearly shows how excess electrons influence the total grand canonical energy, where each electron (or fractional electron) makes an energy contribution to the system's Fermi level on an absolute energy scale. Grand canonical free energy differences were then computed by considering eq 6 for two unique states at a common electrochemical potential, U . Again, this potential was achieved for each state by varying the excess electrons according to eq 3. Details concerning the implementation of the electrochemical microkinetic model are included in Section S7 of the Supporting Information. The software is available on an open-source basis for use according to the MIT license on GitHub.

Experimental Methods. Electrochemical measurements were collected using a Gamry Interface 1000 potentiostat in a three electrode setup. Considering the relatively low HER activity of H_2WO_3 , contamination of the working electrode or electrolyte by adventitious transition metals would result in false activity measurements. Thus, we did not use any electrode materials containing transition metals with comparatively higher HER activity, such as Pt. The counter electrode in all measurements was a graphite rod (Electron Microscopy Sciences 0.25 in. diameter, Spectro-Grade). The reference electrode for all experiments was Ag/AgCl (CH Instruments CHI111P), and was experimentally calibrated to the RHE scale by measuring the open circuit potential of a platinum electrode (0.5 mm Pt wire, 99.997% metals basis, Alfa Aesar) submerged in fresh H_2 (99.999%, Matheson) saturated 0.5 M H_2SO_4 electrolyte. Applied potentials were further converted to the SHE scale using a small adjustment for solution pH—this facilitates direct comparisons to computational results. Reference electrode calibration was always performed after HER activity measurements of H_xWO_3 in a separate electrochemical cell (using electrolyte transferred from the testing cell), again to minimize the possibility of Pt contamination. Only the graphite counter electrode and the Ag/AgCl reference electrode were used between activity measurements and calibrations. The electrolyte was discarded after the RHE–SHE calibrations so as not to introduce Pt to the testing cell. As further evidence of sample cleanliness, we observed none of the characteristic features of Pt contamination, such as erratic changes in HER activity or steadily increasing activity with time.

Films of WO_3 nanoparticles were deposited by drop casting catalyst ink onto glassy carbon disk electrodes (CH Instruments CHI 104, 3 mm diameter for nonhydrodynamic experiments, or SPI 4181GC-AB, 5 mm diameter for rotating disk electrode experiments). A representative catalyst ink contained 0.05 g of WO_3 nanoparticles, 0.05 g of Nafion dispersion (Ion Power, 1100 EW @ 20 wt % in IPA), and 250 μL of >18.2 M Ω -cm water. The ink was dried using an infrared heat lamp. The WO_3 nanoparticles were synthesized using a modified literature procedure.⁶⁹ Our modifications and the effect on particle morphology has been reported previously.¹⁴ Section S8 of the Supporting Information provides confirmation of the identity and morphology of the synthesized WO_3 .

Cyclic voltammetry measurements were performed in a static cell setup, which consisted of a glass beaker with an in-house machined polytetrafluoroethylene (PTFE) cap. All cyclic voltammograms were collected at a scan rate of 1 mV/s. The working electrode for this setup was glassy carbon (CH Instruments CHI 104, 3 mm diameter) on which 1 μL of catalyst ink was deposited. Chronopotentiometry measurements were performed using a rotating disk setup (Pine Research MSR). The working electrode consisted of a glassy carbon disk (SPI 4181GC-AB, 5 mm diameter) polished to a mirror finish. Two μL of catalyst ink were deposited onto this larger disk. The glassy carbon disk with WO_3 film was inset into a PTFE shroud (Pine Research E4TQ ChangeDisk) and was rotated at 1600 rpm. An argon purge was used to remove dissolved oxygen and other atmospheric contaminants. Voltage responses during the constant-current chronopotentiometry experiments were converted to steady-state potentials by averaging the final two seconds of data after the

potential reached a constant value. Constant-current measurements were run between 5 and 60 s, depending on the applied potential and the approach to steady state.

Kinetic currents were extracted from the rotating disk measurements by applying the Koutecký–Levich equation:⁵⁰

$$\frac{1}{i_m} = \frac{1}{i_k} + \frac{1}{0.62nFAD_0^{2/3}\omega^{1/2}\nu^{-1/6}C_0^*}$$

where i_m is the measured current, i_k is the kinetic current (free of mass transfer), n is the number of electrons involved in the reaction, F is Faraday's constant, D_0 is the Grotthuss diffusion coefficient of protons, ω is the disk rotation rate, ν is the kinematic viscosity of the electrolyte, and C_0^* is the concentration of protons in the electrolyte. This equation was solved for i_k , which was then converted to the reported current densities by considering the area of the disk electrode.

Solution resistance was measured using electrochemical impedance spectroscopy, wherein a 10 mV AC waveform was applied over a DC potential. The solution resistance ranged from 5 to 6 Ω , which is within the expected range for the cell geometry used in experimental data collection.⁷⁰ EIS was performed at both open circuit potential (approximately +0.3 V vs SHE) and at potentials where significant hydrogen evolution occurred (approximately −0.5 V vs SHE), and no systematic differences were observed exceeding sample-to-sample variation. The resulting data were then adjusted to account for 100% of the iR drop associated with this solution resistance after experiments were complete.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.2c00825>.

Effect of bulk intercalation on surface oxygen basicity, active surface facets of H_xWO_3 , equilibrium potentials as determined via CHE and CP-DFT, determining α , β , and λ_m , energetics of surface-mediated H_2 -coupling, microkinetic model construction and execution, Gaussian process regression for calculation of Tafel slopes, nanoparticle characterization, hydrated and dehydrated surface configurations (PDF)

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Notes

The authors declare no competing financial interest.

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