The slow kinetics of the hydrogen oxidation and hydrogen evolution reactions (HER and HOR) in alkaline compared to acidic media are known to be several orders of magnitude slower in basic than acidic electrolytes, but the reasons behind such pH dependence are not yet understood. Identifying the root of this phenomenon is key to the rational design of catalysts for many applications, including CO2 reduction, oxygen evolution, and nitrogen electrochemistry. Beyond its practical importance, the pH dependence of HER/HOR kinetics is one of the long-standing fundamental conundrums in electrocatalysis.

There have been several proposed explanations for the effect of pH on hydrogen electrocatalysis. Traditionally, the hydrogen binding energy (HBE) alone has been used to describe HER/HOR kinetics.\(^1,2\) One hypothesis is that OH\(^{-}\) stabilizes the Pt-H bond,\(^3,4\) leading to stronger H binding and slower catalysis. This hypothesis is based on a measured shift with pH in peak potential for the hydrogen underpotential deposition (H-UPD) on Pt (110) and Pt (100) sites. However, a similar shift is not seen on Pt (111) sites, even though a drop in HER/HOR activity is still observed.\(^5,6\) Furthermore, weak-binding catalysts (such as gold-group metals) do not experience improved activity with higher pH,\(^5,6\) as the HBE mechanism predicts.

Another explanation for the pH dependence of HER/HOR kinetics considers OH adsorption more explicitly. Multiple groups have shown that the H-UPD peaks on Pt (110) and (100) are instead representative of hydrogen/hydroxide exchange (H/OH-X).\(^10,12\) The presence of alkali cations weakens the OH adsorption strength, and so the shift with pH in the H/OH/X peak is therefore instead caused by weaker competitive OH adsorption, allowing H to remain adsorbed up to higher potentials. The corresponding direct Volmer mechanism, in which H and OH compete for sites on Pt (111), and an OH-mediated mechanism, in which Pt (111) adsorbs H while transition metal clusters adsorb OH. Our experimental and computational results show that on a thermodynamic coverage basis, increasing OH adsorption strength cannot promote faster HER/HOR kinetics. Only changes to the kinetic rate constants can explain experimental observations. We speculate that adequate electrocatalyst design in alkaline media additionally requires manipulation of interfacial water structure to lower energetic barriers for HER and HOR.

The slow kinetics of the hydrogen oxidation and hydrogen evolution reactions (HER and HOR) in alkaline compared to acidic media remain a fundamental conundrum in modern electrocatalysis. Recent efforts have proposed that OH, as well as H, must bind optimally for improved kinetics. However, the exact role of adsorbed OH is not yet known. In this work, we combine steady-state single-crystal voltammetry and microkinetic modeling to determine the roles of adsorbed hydroxide and the so-called bifunctional mechanism in alkaline HER and HOR kinetics. We consider both a direct Volmer mechanism, in which H and OH compete for sites on Pt (110), and an OH-mediated mechanism, in which Pt (111) adsorbs H while transition metal clusters adsorb OH. Our experimental and computational results show that on a thermodynamic coverage basis, increasing OH adsorption strength cannot promote faster HER/HOR kinetics. Only changes to the kinetic rate constants can explain experimental observations. We speculate that adequate electrocatalyst design in alkaline media additionally requires manipulation of interfacial water structure to lower energetic barriers for HER and HOR.

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show that, unlike in base, H/OH-X and HER in acid occur close to the potential of zero charge (PZC).\textsuperscript{10,11} This observation implies that in alkaline media, water interacts strongly with the interfacial electric field and is therefore more difficult to reorganize and accommodate charge migration. The Koper group showed that Ni(OH)\textsubscript{2} clusters on Pt (111) shift the PZC in base by about \(-25\) mV\textsuperscript{3} closer to that in acid. It was suggested that at the PZC, a more dynamic water structure would allow rapid solvent reorganization and facilitate charge transfer processes.\textsuperscript{9,10}

While the beneficial effects of transition metal (TM) clusters are experimentally confirmed, the contrasting explanations for their fundamental effect, as well as the asymmetric effects on HER and HOR, shows that the role played by OH\textsubscript{A} is still unclear. Our previous work\textsuperscript{3} has shown that on a single-site catalyst such as Pt (110), an OH-mediated mechanism (analogous to Rxns. 5–8, but in a Fig. 1 setting) is energetically unrealistic and qualitatively inconsistent with experimental trends. However, neither the possibility of a two-site mechanism nor the effects on overall HER/HOR were considered.

In this work, we specifically investigate the effect of OH adsorption strength on HER and HOR kinetics. We develop a microkinetic model of the alkaline hydrogen reaction and relate the OH coverage to reaction kinetics via its adsorption strength, \(\Delta G\text{OH}\). We focus our study on two different reaction schemes: (1) a single-site model proceeding through the direct Volmer step (Fig. 1) and (2) a bifunctional model proceeding through an OH-mediated water recombination/dissociation step (Fig. 2). The models are compared to the experimental systems of bare Pt (110) and a Pt (111) surface doped with oxophilic TM clusters, respectively. The single-site model is analogous to a bare Pt (110) facet because the overlapping H and OH adsorption energies result in competition for adsorption sites. In contrast, the benchmark for the bifunctional model is a Pt (111) surface because the H and OH adsorption energies are so different that competition for Pt surface sites does not occur on Pt (111). A direct Volmer step on a bifunctional catalyst is not considered as it provides no opportunity for adsorbed H and OH species to interact. Further, our previous work has shown that the bifunctional mechanism where adsorbed OH is an active participant is not energetically viable on a single-site catalyst.\textsuperscript{9} Therefore, the microkinetic analysis was limited to the two reaction schemes described above. The predicted effect of stronger OH binding is compared with experiment to determine the role of adsorbed OH on reaction kinetics.

**Experimental**

**Cell and electrolyte preparation.**—Electrolyte solutions were prepared using KOH pellets (99.99\% [metal basis], Sigma) or high purity HClO\textsubscript{4} (70 wt\%, Suprapur). All electrochemical experiments were carried out in a FEP cell. Prior to its use, the FEP cell was soaked in 50\% HNO\textsubscript{3}/50\% H\textsubscript{2}SO\textsubscript{4} for 2 hours followed by repeated boiling and rinsing in Millipore water. A Pt wire was used as the counter electrode and a Ag/AgCl reference electrode (BASI) was used for the experiments. All potentials reported in this work are calibrated against the reversible hydrogen electrode (RHE) scale.

**Electrode preparation and TM decoration.**—Pt (111) and (110) disks were annealed at 1100°C in 3\% H\textsubscript{2}/Ar flow for 10 minutes followed by cooling for 5 minutes in the same gas. Each disk was then protected with a drop of Millipore water before being mounted in the RDE holder. A drop of 0.05 M solution of perchloric salt of Ni, Mn or Co was drop-casted onto the disk for 5 minutes after which it was rinsed with Millipore water. The disk then transferred to the cell under potential control at 0.08 V.

**Electrochemical measurements.**—The electrochemical measurements were made with an Autolab PGSTAT302N potentiostat in a rotating disk electrode (RDE) setup. The electrolyte in the cell was purged with Ar (Research grade, Airgas) and the potential was cycled between 0.08–0.9 V to obtain the cyclic voltammetry (CV) profiles. HER and HOR polarization curves were obtained through potential cycling between \(-0.3 – 0.9\) V in H\textsubscript{2}-purged electrolyte at a rotation rate of 1600 rpm. The CV profile and HER-HOR polarization curves were obtained in 0.1 M KOH. The coverage of the TM clusters on the Pt (111) surface was obtained by the difference in H-UPD between the bare Pt (111) and the disk decorated with the clusters (approx. 30–40\% coverage). After the measurements, the Pt (111) disk was cycled between 0.1–1.1 V in 0.1 M HClO\textsubscript{4} to dissolve the TM clusters and clean the disk.

**Microkinetic Model Development**

Previous alkaline hydrogen reaction models have neglected the competition between H and OH,\textsuperscript{20–22} or used only thermodynamic descriptors without considering kinetics.\textsuperscript{12,24} Here, following our previous methodology,\textsuperscript{19} we relate the equilibrium potential of elementary steps to the free energy of adsorption, while considering possible reaction mechanisms on single-site and bifunctional catalysts. For each of the reaction schemes, the hydrogen reaction may progress via either a Tafel-Volmer or Heyrovsky-Volmer mechanism. Assuming quasi-equilibrium for non-rate-determining steps (RDS) then yields eight possible mechanisms. The resulting rate laws are summarized in Tables I and II. For illustration, one mechanism is derived below.

Considering a bifunctional catalyst where water recombination is relatively fast and Heyrovsky is the RDS, the corresponding Butler-Volmer\textsuperscript{25} rate expression is:

\[
r_{\text{Hey}} = r_{\text{OH}} e^{\theta \Delta G_{\text{R}}/(RT)} e^{-(\alpha V - \beta)}
\]

Because there are two possible binding sites with exclusive adsorption, there is no site competition between H and OH and the fraction of empty sites is represented as \(1-\theta\text{H}\) instead of \(1-\theta\text{OH}\). The activities of hydroxide, water, and hydrogen are assumed to be unity in this work. Following the previous model development,\textsuperscript{19} the rate expression can be ultimately written as:

\[
r_{\text{Hey}} = A_{\text{f}} Q_{\text{H}_2} e^{\Delta G_{\text{H}_2}^*/F} \left[ e^{\theta \Delta G_{\text{R}}/(RT)} e^{-(\alpha V - \beta)} \right] \left[ e^{\theta \Delta G_{\text{H}_2}^*/F} \left(1 - \theta_{\text{H}_2} \theta_{\text{OH}} \right) \right] \left[ e^{\theta \Delta G_{\text{H}_2}^*/F} \left(1 - \theta_{\text{H}} \right) \right] \left[ e^{\theta \Delta G_{\text{H}_2}^*/F} \left(1 - \theta_{\text{OH}} \right) \right]
\]

The equations above represent the rate expression intrinsic to this reaction mechanism (Heyrovsky RDS). Here, \(A_{\text{f}}\) is a rate constant with units of s\textsuperscript{−1} that includes an exponential activation energy dependence as well as a frequency factor with contributions from interfacial water structure and the time constant for solvent reorganization.\textsuperscript{26–29} Adsorption energies are taken from literature while \(A_{\text{f}}\) is used to fit simulations to experimental current densities measured at ±0.1 V. The transfer coefficient \(\beta\) relates to the symmetry of the charge-transfer reaction barrier, and is assumed to be equal to 0.5 for all elementary steps. The theoretical maximum surface charge, \(Q_{\text{max}}\), is 240 \m C/cm\textsuperscript{2} for Pt (111),\textsuperscript{26} and is assumed to be independent of catalyst loading, although increasing the density of TM clusters will decrease \(Q_{\text{max}}\). Assuming all other reactions involved are fast and in equilibrium (i.e. \(r_{\text{OHads}} = r_{\text{R}} = 0\)), the H and OH coverages can be expressed in terms of potential and binding energies using a similar Butler-Volmer approach.\textsuperscript{25} Adsorption of OH is always assumed to be fast, due to the high concentration of OH\textsuperscript{−} ions in solution. Thus:

\[
U_{\text{OH}} = V = \frac{\Delta G_{\text{OH}}^*}{F} + \frac{RT}{F} \ln \left( \frac{\theta_{\text{OH}}}{1 - \theta_{\text{OH}}} \right)
\]

The overall change in free energy of OH adsorption is affected by the enthalpy and entropy of adsorption, changes in zero-point energy, and the configurational entropy.\textsuperscript{24,25} The enthalpy of adsorption, zero-point energy, and entropy of adsorption can be calculated via DFT simulations, while the configurational entropy is given by the logarithmic term in Eq. 4. Again, competition is eliminated by representing the
fraction of empty sites as $1 - \theta_{OH}$. Solving for OH coverage thus gives:

$$\theta_{OH} = \frac{e^{\frac{V_F - AG_H^R}{RT}}}{1 + e^{\frac{V_F - AG_H^R}{RT}}}$$

Substituting in $\theta_{OH}$ and the equilibrium constant, and simplifying:

$$\theta_H = \frac{e^{\frac{G_{H,tot} - AG_{OH,tot}}{RT}}}{e^{\frac{V_F - AG_H^R}{RT}} + e^{\frac{G_{H,tot} - AG_{OH,tot}}{RT}}}$$

Eq. 8 shows that, after simplification, $\theta_H$ is independent of $\Delta G_{OH}$, but is still a function of $\Delta G_{H}$ and potential. The obtained $\theta_H$ is used to calculate the rate of reaction for this mechanism.

The derivation outlined above is applicable to all reaction mechanisms in this study. All relevant equations are summarized in Tables I and II. For a single-site reaction (Pt (110)), the maximum surface charge is 147 μC/cm². Moreover, site competition between H and OH must be considered, and so the site balance used is $\theta_H + \theta_{OH} + \theta_e = 1$. This interdependence can have significant effects on the predicted current density, to be later discussed.
**Table II. Microkinetic Model of Possible Dual-Site Reaction Mechanisms.**

| Mechanism | Relevant Expressions | Eq. # |
|-----------|----------------------|-------|
| Water Recombination RDS, Heyrovsky fast | \( r_R = A_f \frac{q_{F_R}}{n_R} \left[ (1 - \theta_H)(1 - \theta_{OH}) - \alpha \frac{\Delta G_{R}^0 + \Delta G_{OH}^0 - \alpha e}{RT} \right] \) | (26) |
| \( \theta_{OH} = \frac{\Delta G_{R}^0 + \Delta G_{OH}^0}{RT} \) | (5) |
| \( \theta_H = \frac{\Delta G_{R}^0 + \Delta G_{OH}^0 - \alpha e}{RT} \) | (27) |
| \( i_R = \frac{-eF}{RT} \) | (28) |
| Water Recombination fast, Heyrovsky RDS | \( r_{HE} = A_f \frac{q_{F_R}}{n_R} \left[ (1 - \theta_H)(1 - \theta_{OH}) - \alpha \frac{\Delta G_{R}^0 + \Delta G_{OH}^0 - \alpha e}{RT} \right] \) | (2) |
| \( U_{HE} = \frac{\Delta G_{R}^0 + \Delta G_{OH}^0}{RT} + \frac{RT}{i_R} \ln \left( \frac{1 - 0.09}{1 - \theta_H} \right) \) | (3) |
| \( \theta_{OH} = \frac{\Delta G_{R}^0 + \Delta G_{OH}^0}{RT} \) | (5) |
| \( \theta_H = \frac{\Delta G_{R}^0 + \Delta G_{OH}^0 - \alpha e}{RT} \) | (8) |
| \( i_R = \frac{-eF}{RT} \) | (19) |
| Water Recombination RDS, Tafel fast | \( r_R = A_f \frac{q_{F_R}}{n_R} \left[ (1 - \theta_H)(1 - \theta_{OH}) - \alpha \frac{\Delta G_{R}^0 + \Delta G_{OH}^0 - \alpha e}{RT} \right] \) | (26) |
| \( \theta_{OH} = \frac{\Delta G_{R}^0 + \Delta G_{OH}^0}{RT} \) | (5) |
| \( \theta_H = \frac{\Delta G_{R}^0 + \Delta G_{OH}^0 - \alpha e}{RT} \) | (29) |
| \( i_R = \frac{-eF}{RT} \) | (28) |
| Water Recombination fast, Tafel RDS | \( r_T = A_f \frac{q_{F_R}}{n_R} \left[ \theta_H^2 - (1 - \theta_H)^3 e \frac{\Delta G_{R}^0}{RT} \right] \) | (30) |
| \( \theta_{OH} = \frac{\Delta G_{R}^0 + \Delta G_{OH}^0}{RT} \) | (5) |
| \( \theta_H = \frac{\Delta G_{R}^0 + \Delta G_{OH}^0 - \alpha e}{RT} \) | (8) |
| \( i_R = \frac{-eF}{RT} \) | (25) |

**Simulated polarization curves calibration.**—Experimental HER and HOR data for bare Pt (110) and Pt (111) in KOH was used to calibrate the simulated single-site and bifunctional polarization curves, respectively. The kinetic current from HOR data was extracted using Koutecky-Levich to adjust for hydrogen mass transport limitations:

\[ i_k = \frac{i_{lim} - i_R}{i_{lim} - i_n} \]  

[9]

The experimental current densities measured at ±0.1 V were then used as reference points to fit all simulated HER and HOR polarization curves. The rate constants used for these calibrations are displayed in Table III. As reported by other works,\(^6,12,26\) the equilibrium adsorption potentials of adsorbing species depend significantly on the catalyst surface structure. Here, H and OH adsorption strengths of \( \Delta G_{H} = -0.37 \text{ eV} \) and \( \Delta G_{OH} = 0.18 \text{ eV} \) (for Pt (110)) or \( \Delta G_{H} = -0.2 \text{ eV} \) and \( \Delta G_{OH} = 0.80 \text{ eV} \) (for Pt (111)) were used as the benchmark for all simulated polarization curves\(^6,12\) and are assumed to be independent of coverage. Equilibrium adsorption potentials can depend significantly on coverage due to interactions between adsorbates. On a Pt (111) facet, strong H-H and H-OH repulsions lead to significant peak broadening.\(^{15}\) If adsorbates interact, the enthalpy of adsorption could be expressed as \( \Delta H = a + b\theta \), where \( b > 0 \) corresponds to...

**Table III. Rate constants used to fit simulated polarization curves to experimental current densities at ±0.1 V. HER values for mechanisms in which Volmer is assumed to be fast were not possible to fit due to the shift in OCP.**

| RDS | Fast Step | Rate constant (s\(^{-1}\)) | \( \frac{\text{HER}}{\text{HOR}} \) | RDS | Fast Step | Rate constant (s\(^{-1}\)) | \( \frac{\text{HER}}{\text{HOR}} \) |
|-----|----------|---------------------------|-------|-----|----------|---------------------------|-------|
| Volmer | Heyrovsky | 1.54 E8 | 3.58 E9 | WR | Heyrovsky | 3.90 E4 | 3.80 E4 |
| Volmer | Tafel | 7.70 E9 | 3.64 E9 | WR | Tafel | 1.93 E6 | 3.90 E4 |
| Heyrovsky | Volmer | - | 2.57 E-2 | Heyrovsky | WR | 2.20 E2 | 4.60 E0 |
| Tafel | Volmer | - | 1.18 E-6 | Tafel | WR | 7.80 E2 | 3.35 E-1 |
repulsive interactions. However, coverage dependence is much less pronounced on stepped surfaces such as Pt(110), so it is appropriate to neglect enthalpic interactions between adsorbates. More importantly, including the coverage dependence of adsorption strength would not alter the qualitative trends of HER/HOR activity with OH adsorption strength, which is the focus of this study.

**Results and Discussion**

**Effect of $\Delta G_{OH}$ on single-site reaction.**—Experimental HER and HOR on bare Pt(110).—Several studies have shown that the OH binding strength can be tuned experimentally via the choice of electrolyte cation. Figure 3 shows HER/HOR polarization curves on Pt(110) in either LiOH or KOH. While the difference between the curves is small, it is highly reproducible on Pt(110), and is also observed on polycrystalline Pt. Because adsorbed Li has weaker effects on OH adsorption strength than adsorbed K, $\Delta G_{OH}$ is stronger in LiOH than KOH. The difference in the curves thus reveals that stronger OH binding improves HER and HOR kinetics. The improved HER/HOR kinetics in the presence of LiOH differs from our previous findings in which the Volmer step was found to proceed more rapidly in KOH than LiOH. However, such trends can be rationalized if the Volmer step of HER/HOR is not the RDS.

To determine if the experimental effects of LiOH/KOH can be described by OH binding strength alone, the various models of Figure 1 were applied to the experimental data. This approach yields four possible reaction mechanisms for the single-site reaction scheme, where HER and HOR are considered separately as they may follow different mechanisms. Figure 4 compares the experimental and simulated HER and HOR polarization curves for all mechanisms. The simulated polarization curves that best fit experimental data correspond to the mechanism where Volmer is the RDS and Tafel is fast. However, experimental evidence on H/OH-X in LiOH and KOH indicates that Volmer cannot be the RDS, as explained above. In addition, Shinagawa et al. demonstrated that a Tafel slope of 120 mV dec$^{-1}$, often considered a Volmer RDS reaction, can also be observed for other mechanisms such as Heyrovsky RDS, suggesting that Tafel slopes can be inaccurate descriptors of surface electrochemistry. Therefore, Tafel plot analyses might not be adequate indicators of the reaction pathway. Importantly, the curves of Figure 4 are generated assuming that all steps other than the RDS are in complete equilibrium, and that only Tafel or Heyrovsky contributes to current. Better fits between the simulated and experimental HER/HOR curves for other mechanisms may be possible by relaxing these assumptions. Regardless, the aim of this work is not to quantitatively match experimental polarization curves nor to identify a precise mechanism, but rather to qualitatively shed light onto the effect of OH adsorption strength on kinetics. We
therefore examine the effect of OH adsorption strength on each mechanism individually.

**Simulated HER and HOR on single-site catalyst.**—In the first case, the direct Volmer step is the RDS, and Heyrovsky and OH adsorption are fast. Tafel plots of the simulated baseline HER/HOR, as well as the effect of $\Delta G_{\text{OH}}$, are shown in Figure 5. The H and OH coverages at different potentials with varying $\Delta G_{\text{OH}}$ are also shown. Experimentally, H is known to desorb at higher potentials in Ar-purged electrolyte. In this case, however, the assumption that the Heyrovsky step is fast implies that H binds more strongly at higher potentials instead of desorbing from the surface (Rxns. 4, 8). Therefore, both H and OH coverages increase at higher potentials. Due to the strength of H adsorption ($\Delta G_{\text{H}} = -0.37$ eV) and site competition, the catalyst surface is predominantly occupied by H for potentials above $-0.37$ V. It is only for very strong OH adsorption (e.g. $\Delta G_{\text{OH}} < -0.2$ eV) that OH can begin to adsorb onto the surface to a noticeable degree. However, the Volmer step requires only H$_{\text{ad}}$ for oxidation or empty sites for reduction. Therefore, increasing OH adsorption strength results in surface poisoning and slows the kinetics of both HER and HOR.

Similar trends are observed for the case in which Volmer is the RDS and Tafel is fast (Fig. 6). Because Tafel is a chemical, rather than an electrochemical step, for it to be in equilibrium implies that the driving force for H adsorption is independent of potential. However, H coverage is still affected by competitive OH adsorption. If there were no competition for sites, the strength of H adsorption would result in the surface being almost entirely covered by H for all potentials (i.e. $\theta_{\text{H}} \approx 1$). With site competition, H begins to desorb at higher potentials as it is displaced by OH. For stronger OH binding strengths, this H/OH exchange occurs at lower potentials. Because the Volmer step requires only H$_{\text{ad}}$ for oxidation or empty sites for reduction, increasing OH adsorption strength once again results in surface poisoning and downgrades the kinetics of both HER and HOR for this mechanism as well.

If the Volmer step is instead in equilibrium and Heyrovsky is the RDS, the results are quite different from the previous mechanisms, as shown in Figure 7. The most immediate feature is the shift in OCP as a function of $\Delta G_{\text{OH}}$, as also seen in Figure 4. Because both Volmer and OH adsorption are in equilibrium, the contributions from site competition and configurational entropies lead to an added sensitivity to potential and adsorption strengths, manifested in the denominator of Eqs. 17, 18, 23, and 24. The OCP therefore shifts toward lower potentials as OH binding becomes stronger. In this mechanism, H desorbs from the surface at high potentials since the Volmer step is fast. Due to the convoluted H and OH adsorption behavior arising from competition, stronger OH binding also shifts the potential at which H spontaneously adsorbs or desorbs from the surface. As OH binding strength increases, H is desorbed from the surface at lower potentials. The Heyrovsky reaction requires H$_{\text{ad}}$ as well as empty sites to progress. Hence, stronger OH binding results in slower HER kinetics and faster HOR kinetics. An identical trend in which stronger OH adsorption shifts the OCP to improve HOR only is observed for the mechanism where Volmer is fast and Tafel is the RDS.
The overpotential needed to reach a given current is a common metric of comparing electrocatalysts. To summarize the trends observed for the single-site reactions, the overpotential needed to reach ±10 mA cm$^{-2}$ as a function of OH binding strength for each mechanism is shown in Figure 8. An overpotential of smaller magnitude corresponds to higher catalyst activity and faster kinetics. When Volmer is the RDS, as $\Delta G_{OH}$ decreases and the catalyst binds OH more strongly the required overpotentials are seen to increase, in contrast to what is observed experimentally (Fig. 3). Faster HOR kinetics can only be achieved via stronger OH binding strength if the Volmer step is fast, a case which agrees with our previous experimental results. However, our simulations, which use only thermodynamic descriptors and surface coverages to calculate current, predict that this increase in HOR kinetics should be accompanied by a corresponding decrease in HER kinetics. From the trends shown in Fig. 8, however, stronger OH adsorption cannot improve HER kinetics, regardless of the reaction mechanism. Thus, based solely on the relationships between thermodynamic adsorption strength and surface coverage, OH binding strength proves itself to be an insufficient descriptor for predicting HER and HOR kinetics on a single-site catalyst surface.

**Effect of $\Delta G_{OH}$ on bifunctional reaction.**—Experimental HER and HOR on Pt (111) with oxophilic sites—Similar to OH binding onto a bare Pt (110) surface, the strength of OH adsorption onto an oxophilic site on a Pt (111) surface can be influenced experimentally via the choice of TM. As shown in Figure 9, HER is seen to improve considerably with the introduction of TM clusters with varying oxophilicity, usually attributed to the presence of OH$_{ad}$ on the surface. Conversely, HOR is seen to decrease slightly, but this effect results from the decrease in available Pt (111) surface sites needed for H$_2$ formation. Below a coverage of 40%, HOR current was identical to bare Pt (111). Thus, introducing oxophilic sites has little or no effect on HOR.

Due to the improved activity in the presence of oxophilic sites, some studies have concluded that OH$_{ad}$ must be an active participant in the hydrogen reactions through the bifunctional mechanism (Fig. 2). If so, then there should exist an OH adsorption strength that optimizes HER/HOR kinetics. To determine if the experimental effects from Figure 9 can be described by OH binding strength alone, the Figure 2 models were applied to the experimental data. Here, H and OH adsorption strengths of $\Delta G_H = -0.20$ eV and $\Delta G_{OH} = 0.80$ eV (for Pt (111)) were used as the benchmark for the simulated polarization curves, and the rate constant $A_f$ was again adjusted to match experiment. Assuming that H and OH bind exclusively onto their respective sites eliminates effects of site competition. Because H and OH have widely different adsorption strengths on Pt (111), it is appropriate to assume that only H binds to the bare Pt (111) surface. Meanwhile, the non-noble TMs are more likely to be hydroxylated than hydrogenated at HER/HOR potentials, so it is assumed that only OH binds to the oxophilic sites. However, the model makes no assumptions on the oxidation state of the oxophilic clusters. The TM clusters only provide an adsorption site other than bare Pt (111) onto which OH can adsorb non-competitively. Figure 10 compares experimental and simulated HER and HOR polarization curves for all four of these reaction.
Figure 7. Effect of $\Delta G_{OH}$ on HER (a) and HOR (b) polarization curves for the mechanism where Volmer is fast and Heyrovsky is the RDS. The corresponding H (solid) and OH (dashed) surface coverages are also shown (c). The assumption that the Volmer step is in equilibrium leads to a shift in OCP with increasing OH adsorption strength.

Figure 8. Trends in overpotential for the simulated HER (negative overpotentials) and HOR (positive overpotentials) single-site mechanisms as a function of $\Delta G_{OH}$ for the studied mechanisms: Volmer RDS, Heyrovsky fast (red squares), Volmer fast, Heyrovsky RDS (blue triangles), Volmer RDS, Tafel fast (green diamonds), and Volmer fast, Tafel RDS (black circles) (HER data out of scale). An overpotential lower in magnitude indicates faster kinetics.

Simulated HER and HOR on bifunctional catalyst.—For the case in which water recombination is the RDS and Heyrovsky is fast, Tafel plots of the simulated HER and HOR, along with the effect of $\Delta G_{OH}$, are shown in Figure 11. The trends in H and OH coverages with $\Delta G_{OH}$ are also shown. Because there is no site competition between H and OH, the potential at which each species can adsorb onto their corresponding surfaces is simply dictated by their individual adsorption strengths (Fig. 11c). The Heyrovsky step is fast for this mechanism, so once again H adsorption becomes favorable at higher potentials. Therefore, due to the strength of H adsorption ($\Delta G_H = -0.37$ eV), the H coverage is essentially unity for potentials above $-0.2$ V. Importantly, water recombination is a chemical, rather than an electrochemical step. Thus, for this potential window, the HOR reaction kinetics is mainly dictated by the OH coverage. Once both the H and OH coverages reach unity at high potentials, current becomes independent of potential, as seen in Figure 11b. For this mechanism, stronger OH binding (decreasing $\Delta G_{OH}$) depletes HOR reaction kinetics because it shifts the equilibrium constant to favor the reactants of H$_{ad}$ and OH$_{ad}$. Increasing the OH binding strength reaches the limiting current faster, but decreases the limiting current value significantly due to the shift in the equilibrium constant.

For moderate OH adsorption strengths ($\Delta G_{OH} > 0$ eV), OH coverage is essentially zero for negative potentials, and the HER current density is dictated by the desorption of H. To observe the effect of OH adsorption strength, $\Delta G_{OH}$ must be close to $\Delta G_H$, below which it becomes increasingly difficult to remove OH from the surface, thereby deteriorating HER kinetics. Hence, for this mechanism, stronger OH binding only worsens the hydrogen reaction kinetics, which disagrees...
with what is observed experimentally. An identical effect is observed for the mechanism where water recombination is the RDS and Tafel is in equilibrium (Fig. 12). Because Tafel is a chemical step, it being in equilibrium implies that H coverage is independent of potential. Further, as there is no site competition in a bifunctional mechanism, H coverage will be essentially unity for all potentials due to the equilibrium constant, itself dictated by the strength of H adsorption (Fig. 12c). Therefore, only OH coverage has an impact on the simulated current. The observed effect of ΔGad is identical to the one discussed above (Fig. 11), where stronger OH binding depletes both HOR and HER kinetics.

If the water recombination step is in equilibrium and either Heyrovsky or Tafel is the RDS, varying the OH adsorption strength has no effect on the simulated current density, as shown in Figure 13. The lack of dependence on OH adsorption occurs because the reaction kinetics for Heyrovsky or Tafel depend only on the H coverage. As there is no site competition on a bifunctional catalyst, altering the OH coverage by varying its adsorption strength has no effect on the simulated current density. This agrees with experimental observations for HOR (Fig. 9).

To summarize the trends observed for the bifunctional reactions, the overpotential needed to reach ±10 mA cm⁻² as a function of OH binding strength for each mechanism is shown in Figure 14. For a bifunctional reaction, decreasing ΔGad either leads to an increase in overpotential or has no effect. Our simulations therefore predict that stronger OH binding cannot improve HER/HOR kinetics, regardless of the reaction mechanism. The Figure 2 mechanisms all assume that the hydrogen reaction requires OH ad to proceed, an assumption which ultimately fails to match what is observed experimentally (Fig. 9). These results strongly suggest that, for a bifunctional catalyst containing oxophilic sites, OH ad cannot be an active participant in the alkaline hydrogen reaction.

The purpose of this work is to qualitatively investigate the effect of OH adsorption strength on hydrogen reaction kinetics, which
Figure 11. Effect of $\Delta G_{\text{OH}}$ on HER (a) and HOR (b) polarization curves for the mechanism where water recombination is the RDS and Heyrovsky is fast. The corresponding H (solid) and OH (dashed) surface coverages are also shown (c). The H coverage curves collapse for all $\Delta G_{\text{OH}}$ due to no site competition.

was modeled on two different surfaces (Figs. 1, 2). All mechanisms studied herein therefore include OH\text{aq} as an active adsorbate, and the effect of stronger OH binding is integrated using only thermodynamic adsorption energies. Table IV summarizes the comparison of experimental and simulated kinetic trends with varying OH adsorption strength. In the single-site model, simulations predict that stronger OH binding can only lead to faster HOR kinetics if the Volmer step is assumed to be fast, and that such change should be accompanied by a decrease in HER kinetics. Stronger OH binding, however, never improves both HER and HOR simultaneously, as opposed to what is observed experimentally (Fig. 3). Thus, based only on thermodynamic adsorption strength and surface coverages,
OH binding strength proves itself to be an insufficient descriptor for predicting HER and HOR kinetics on a single-site catalyst surface. For the bifunctional model, simulations match experimental HOR observations for the trivial case where water recombination is assumed to be fast and OH adsorption strength has no effect. However, none of the mechanisms predict that stronger OH adsorption leads to faster HER kinetics, which is experimentally the far more significant observation.

While it is tempting to deduce that these results disprove the bifunctional mechanism, they rather re-define its meaning. Clearly, the presence of oxophilic sites on the surface is beneficial, and so the bifunctional mechanism here forth implies that OH\textsuperscript{−} must improve reaction kinetics indirectly. In this regard, the results here are consistent with the Koper group’s evidence that Ni(OH)\textsubscript{2} clusters on Pt (111) shift the PZC in base closer to that in acid.\textsuperscript{5} Unlike in acid, the PZC of bare Pt (111) in alkaline media is far from the reversible hydrogen potential, which is hypothesized to lead to a more rigid water orientation and a larger barrier for solvent reorganization required for charge transfer through the double layer. It may be that the high activity of Pt (111) with oxophilic sites stems not from facile water dissociation, but from a more dynamic interfacial water structure.

In the model presented here, the dynamics of solvent reorganization are reflected in the rate constant $A_f$. However, solvent reorganization is not the only phenomenon affecting $A_f$. For example, Chen et al recently showed that the solvation geometry of hydronium results in more frequent and concerted rearrangement of hydrogen bond networks than that of hydroxide.\textsuperscript{35} Regardless of the reason for lower or higher values of $A_f$, the results of this study indicate clearly that this kinetic parameter, rather than the thermodynamic quantities of adsorption strength, is critical to explaining the trends between catalysts and electrolytes.

**Conclusions**

We have explicitly modeled the effect of OH adsorption strength on both single-site and bifunctional alkaline HER/HOR catalysts in order to interpret experimental voltammograms on single-crystal Pt (110) and TM-doped Pt (111). After considering all possible combinations of Tafel, Volmer, Heyrovsky, and water recombination as rate-limiting steps, we conclude that the thermodynamic effects of stronger OH binding do not lead to improved HER nor HOR kinetics in alkaline media. For the single-site case, experimental voltammetry
Figure 13. Effect of $\Delta G_{\text{OH}}$ on HER (a) and HOR (b) polarization curves for the mechanisms where water recombination is fast and either Heyrovsky is the RDS (blue) or Tafel is the RDS (red). The corresponding H (solid) and OH (dashed) surface coverages are also shown (c). When either Heyrovsky or Tafel is the RDS, $\Delta G_{\text{OH}}$ has no effect on current, so all polarization curves collapse for all $\Delta G_{\text{OH}}$. The H coverage curves also collapse for all $\Delta G_{\text{OH}}$ due to no site competition.

Figure 14. Trends in overpotential for the simulated HER (negative overpotentials) and HOR (positive overpotentials) bifunctional mechanisms as a function of $\Delta G_{\text{OH}}$ for the studied mechanisms: water recombination RDS, Heyrovsky fast (red squares), water recombination fast, Heyrovsky RDS (blue triangles), water recombination RDS, Tafel fast (green diamonds), and water recombination fast, Tafel RDS (black circles).

of Pt (110) in electrolytes with different cations shows faster kinetics for both HER and HOR when OH binding is stronger. However, microkinetic models predict that increasing OH binding strength cannot achieve faster HER kinetics, and can only lead to improved HOR kinetics by shifting the OCP. In general, stronger OH binding leads to surface poisoning rather than increased reaction kinetics due to site competition.

For the bifunctional case, experimental voltammograms of Pt (111) with TM surface clusters varying in OH affinity shows that stronger OH binding is associated with faster HER kinetics only. However, the simulations predict that HER activity is always either deteriorated or unchanged by increasing OH adsorption strength. Stronger OH binding shifts equilibrium away from products during HOR and poisons the surface during HER. Comparing theory and experiment therefore concludes that $\text{OH}_{\text{ad}}$ cannot be an active participant in the hydrogen reactions in alkaline media, regardless of the catalyst structure or kinetic pathway. This work therefore emphasizes that thermodynamic adsorption energies are insufficient for describing hydrogen reaction kinetics. Instead, adsorbed OH must affect the intrinsic rate constants indirectly, either through stabilizing a transition state, by modifying the interfacial electronic structure, or perhaps by affecting the orientation and dynamics of water molecules near the catalyst surface. These phenomena, which must also be responsible for the kinetic effects of pH on HER and HOR in acid and alkaline media, must be considered when designing electrocatalysts to be used in alkaline environments.
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List of Symbols

\( A_f \) Rate constant, \( s^{-1} \)
\( F \) Faraday’s constant, \( \text{C mol}^{-1} \)
\( i_k \) Kinetic current density, \( \text{mA cm}^{-2} \)
\( i_r \) Current density, \( \text{mA cm}^{-2} \)
\( Q_{\text{tot}} \) Total surface charge, \( \text{C cm}^{-2} \)
\( r \) Reaction rate, \( \text{mol cm}^{-2} \)
\( T \) Temperature, \( \text{K} \)
\( U \) Equilibrium potential, \( \text{V} \)
\( V \) Potential, \( \text{V} \)

Greek

\( \Delta G \) Change in free energy of adsorption, \( \text{eV} \)
\( \theta \) Surface coverage

ORCID

Luis Rebollar 🐛 https://orcid.org/0000-0002-6010-6793
Joshua D. Snyder 🐛 https://orcid.org/0000-0003-3162-4126
Maureen H Tang 🐛 https://orcid.org/0000-0003-0037-4814

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