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pH effects on hydrogen evolution and oxidation over Pt(111): Insights from first principles

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Abstract

A long-standing question in electrocatalysis is how the electrolyte pH affects the catalytic activity of proton-electron transfer reactions. A prime example for this is the hydrogen evolution/oxidation reaction (**HER/HOR**) over metal catalysts. While it has long been established that alkaline conditions result in a more sluggish reaction kinetics than in acidic conditions, the underlying reason for this trend remains contentious. We apply density functional calculations to evaluate prevailing hypotheses for the origin of this effect: shifts in hydrogen binding, proton donor, and water reorganization energy. We present a microkinetic model, based on *ab initio* reaction energetics of all possible elementary steps. Our model shows a good agreement with experimental trends. We find that with increasing pH, the proton donor changes from hydronium to water. Our model suggests that the intrinsically larger barriers for the splitting of water with respect to hydronium are the cause of HER kinetics being slower in alkaline than in acidic media.

Keywords: Hydrogen evolution, electro-catalysis, DFT, micro-kinetic modelling, hydrogen oxidation, water splitting, kinetics

Introduction

The development of efficient electrocatalysts has the potential to play a critical role in the implementation of a sustainable energy cycle. Using electricity from intermittent renewable energy sources, electrocatalytic processes can produce sustainable fuels and fertilizers from H_2O , CO_2 and N_2 , respectively, though dramatic improvements in activity are needed.^{1,2,3} The hydrogen evolution (**HER**) and hydrogen oxidation reaction (**HOR**) have long served as model reactions to study electrochemical processes. Besides its use as a fuel, hydrogen gas also is essential for the synthesis of base and fine chemicals, fertilizers, and pharmaceuticals.⁴⁵

Despite its long history and relative simplicity, the hydrogen redox reaction remains a topic of active research. There is no consensus as to why HER proceeds orders of magnitude slower in alkaline as in acidic media, and this trend has been consistently observed on transition-metal based catalysts, including single crystals, poly-crystalline materials and carbon-supported metal nanoparticles.^{6,7,8} There are several prevailing hypotheses in the current literature:

1. The hydrogen binding energy (**HBE**), as estimated by peaks in the under potential deposition (**H_{upd}**) region of cyclic voltammograms, is pH-dependent.^{9,10,11}
2. The proton donor is pH dependent^{12,13,14,15}. This means that the proton donor can change from hydronium ions (H_3O^+) in acidic conditions to water (H_2O) in alkaline conditions, and buffer molecules may act either as proton donors or alleviate transport limitations of H_3O^+ to the interface. It has furthermore been suggested that changes in the configurational entropy of protons give rise to a pH dependence.¹⁶
3. There is a pH-dependent water reorganization energy at the electrode | electrolyte interface: Koper et al.¹⁷ suggested that, since interfacial fields are greater under alkaline conditions, the water-reorganization energy associated with proton electron transfer would also be greater.

Previous kinetic studies on HER and HOR have used a variety of approaches^{18,19}, such as cyclic voltammograms as functions of the H and OH adsorption energy^{14,15} or phenomenological rate models using effective rate constants^{13,20}. To the best of our knowledge, there are no microkinetic models based on *ab initio* derived reaction barriers

for every elementary step for HER over Pt(111), although single elementary reactions have been addressed.^{21,22,23} In this study, we investigate the pH-dependence of HER over Pt(111) using density functional theory (**DFT**) calculations of relevant electrochemical and chemical barriers with an explicit solvent model. To establish the prevalent reaction mechanism, we perform mean-field micro-kinetic modeling based on *ab initio* energetics of all possible elementary steps. We discuss and evaluate the three main hypotheses mentioned above and find that a change in proton donor to be responsible for the pH effect. Our simulated kinetics show consistent trends with experimental results.

Methods

Computational Details

We performed density functional theory simulations using the using the QUANTUM ESPRESSO code²⁴ interfaced with the Atomistic Simulation Environment (ASE).²⁵ We used a plane-wave basis set with a kinetic energy cutoff of 500 eV and ultra-soft pseudopotentials. The Fermi-Dirac smearing scheme with a smearing of 0.1 eV was used. We applied the BEEF-vdW functional, which provides a reasonable description of van der Waals forces while maintaining an accurate prediction of chemisorption energies.²⁶ We used periodic slab models including four layers of Pt(111) in 3×3 supercells, of which the bottom three layers were fixed to the bulk atomic positions. For the Pt(533) surface, we used a (3×1) surface cell, shown in **Figure S7**. 4×4×1 Monkhorst-Pack *k*-point grids²⁷ were used. We tested the H adsorption energy for relaxing two or one top layer and found that the adsorption energy changes only by 0.06 eV. Structure optimizations were performed until forces on atoms were less than 0.05 eV/Å. Dipole corrections were applied perpendicular to the slab surface to avoid electrostatic interactions between the slab replica. To calculate reaction barriers, we made use of the climbing-image nudged elastic band (NEB) method.²⁸ The charge extrapolation method²⁹ was used to deduce the activation barriers at constant potential. All barriers are corrected for the zero-point energy. In order to reference the transition energy to the bulk proton energy, all proton (H₃O⁺) transition states were referenced to the initial state of aqueous protons and electrons in bulk solution, as determined using the computational hydrogen electrode, as illustrated in Figure S6.³⁰

We investigated the effect of an electric field perpendicular to the surface by applying different field strength values and calculating the adsorption energies. The field was applied to the OH/Pt joint system and the Pt reference. In ongoing work, we have tested the impact of countercharge on the energetics and find that, as a function of surface charge density, there is no difference amongst the various countercharge continuum models that have now been implemented³¹. These results will be published separately.

Explicit solvent was used to represent the electrode | electrolyte interface, as shown in Fig. 1. To simulate acidic conditions with H_3O^+ as the proton source, we applied a model with a monolayer of water in a hexagonal arrangement³², as shown in Fig. 1. (a-b). We assume sufficient solvation of the proton by its surrounding waters. We also investigated various different water configurations by investigating the dissociation of various water molecules and found the configuration shown in Fig. 1. (a-b) to give the lowest barrier. The relevant structures are shown in the Supporting Information and the coordinates are available at www.catalysis-hub.org/publications/Schlexer2019pH. The energetics of proton-electron (PE) transfers depend on the electrode potential and the electrolyte pH (in bulk and at the electrode). We made use of the charge extrapolation scheme to obtain reaction barriers at constant potential.²⁹ When a proton is transferred from the bulk electrolyte to the electrode surface, it loses configurational entropy³³ and possibly other energy contributions, like parts of its solvation energy. In order to obtain barriers in reference to the bulk protons based on the computational hydrogen electrode for the acidic barriers, we computed $E_a^{acidic} = E_a - \Delta E + E_{ads}(H/Pt)$, where ΔE is the reaction energy, E_a the activation energy and $E_{ads}(H/Pt)$ is our computed hydrogen binding energy on Pt(111), and has a value of -0.20 eV.

Fig. 1: Atomistic models employed to calculate the DFT-based electro-chemical barriers. (a-b) Model for H_3O^+ as proton source, (c-d) model for H_2O as proton source; the Na^+ ion is yellow.

To establish a realistic model for alkaline conditions, we used a bilayer of water including a Na^+ cation, representing NaOH alkaline solutions. Cations have been shown to significantly affect the activity of the hydrogen oxidation, oxygen reduction reactions, and CO_2 reduction in alkaline conditions.^{34,35} In our model, the distance between the Na^+ ion and the Pt(111) surface is more than 4.2 Å. It is not the intent of this study to determine whether the cation is specifically adsorbed or not. The distance should be large enough for the cation to not be considered “bonded” or “specifically adsorbed”. It is, however close enough to loose parts of its solvation shell and it may be considered to straddle the inner and outer Helmholtz layer.^{36,37,38,39} And while it is not the scope of this paper to investigate the exact position of cations at an electro-chemical interface, we consider its presence helpful in preventing OH from specific adsorption. Note that there is a large number of possible water splitting pathways, because the proton produced can be mediated via the “water-shuttle” or Grotthuss mechanism to the electrode surface. It is beyond the scope of this study to investigate all different possibilities. Our barriers therefore represent upper bounds to the minimum energy barriers. However, to investigate the proton transfer barrier, we considered various different water molecules as the proton source and compared proton transfers from water in systems with and without alkaline ions. Due to finite cell size

effects, the dipole created by the charge transfer from the metal surface to the OH radical to form OH⁻, forces the OH⁻ to be attracted to the surface, where it adsorbs. As this is not the final state expected under reducing conditions, we stabilize the OH⁻ by the presence of a cation in the water. For this reason, we report only barriers calculated in the presence of Na⁺ ion. The smallest barrier we found in the presence of Na⁺ is 1.20 eV.

Using the BEEF-ensemble²⁶ with a single point calculation of initial and transition state, we found that the standard deviations of the Tafel barriers are around 0.31 eV. The standard deviations for Volmer and Heyrovsky were 0.12 eV and 0.23 eV, respectively. As it has been shown that chemisorption errors are smaller than other errors, such as intra-molecular bond energetics²⁶, these values are upper estimates for the uncertainty. More information on the BEEF-vdW functional error estimation can be found in ref. [40]. As the Tafel barrier error is largest (0.3 eV), we tested how a change in the Tafel barrier changes the results, see discussion in the results and compare Fig. 3, **Figure S2-3**.

We computed the charge transfer coefficients by calculating the Bader charge in the solvent for the initial, transition and final states. For instance, the charge in the water layer in the initial state is 0 |e| and in the transition state, since an OH⁻ ion is formed, it is -0.7 |e|. Thus the charge transfer coefficient is $|q(\text{TS}) - q(\text{IS})| = 0.7$.

Mean-field micro-kinetic modelling was performed using the CatMAP package to compute the turn-over frequencies.⁴¹ We have considered the following possible elementary steps in our micro-kinetic model, including both electrochemical and chemical steps, as shown in Equations (1)-(7):

The net rate, r_i , for each elementary reaction described by Equations (1)-(7) is written below in Equations (8)-(14), where θ_i represents the surface coverage of adsorbate i , $k_{i+}/i-$ represent the rate constants of the forward and backward reactions, respectively, P_j represents the pressure of a gas phase species j , and C_k represents the concentration of solution phase species k ⁴². Rate constants are given by $k = Q \times e^{-G_a/(k_b T)}$, where Q represents the reaction pre-factor⁴² of $k_b T / \hbar$ ($\sim 1 \times 10^{13} \text{ s}^{-1}$), G_a represents the activation barrier, k_b represents the Boltzmann constant and T represents the reaction temperature. For electrochemical steps, G_a depends on the applied potential U in a linear fashion, and accordingly $k_{i+}/i-$ depend exponentially on U . Once the activation energy becomes zero, the reaction is considered barrierless. In this analysis, we have neglected the effect of adsorbate-adsorbate interactions through the coverage, θ , on the activation barrier, G_a . This is a reasonable approximation because we find that $*\text{H}$ is the most abundant adsorbate on our surface and our predicted OH^* coverage is negligible at 10^{-10} ML over the entire potential range considered for, as shown in **Figure S5** Furthermore, previous studies have shown that the binding energy of $*\text{H}$ exhibits a particularly weak coverage dependence up to a full monolayer.⁴³

$$r_1 = k_{1+} C_{\text{H}_3\text{O}^+} \theta_* - k_{1-} C_{\text{H}_2\text{O}} \theta_{\text{H}} \quad (8)$$

$$r_2 = k_{2+} C_{\text{H}_3\text{O}^+} \theta_{\text{H}} - k_{2-} C_{\text{H}_2\text{O}} P_{\text{H}_2} \theta_* \quad (9)$$

$$r_3 = k_{3+} C_{\text{H}_2\text{O}} \theta_* - k_{3-} C_{\text{OH}^-} \theta_{\text{H}} \quad (10)$$

$$r_4 = k_{4+} C_{\text{H}_2\text{O}} \theta_{\text{H}} - k_{4-} C_{\text{OH}^-} P_{\text{H}_2} \theta_* \quad (11)$$

$$r_5 = k_{5+} \theta_{\text{H}}^2 - k_{5-} P_{\text{H}_2} \theta_*^2 \quad (12)$$

$$r_6 = k_{6+} C_{\text{OH}^-} \theta_* - k_{6-} \theta_{\text{OH}} \quad (13)$$

$$r_7 = k_{7+} C_{\text{H}_2\text{O}} \theta_*^2 - k_{7-} \theta_{\text{OH}} \theta_{\text{H}} \quad (14)$$

The coverage of each surface species was determined using the steady-state approximation, requiring each θ_i to be time-invariant, as well as site conservation. These conditions are summarized in Equations (15)-(17) below. There are three equations and three unknowns (θ_H , θ_{OH} , and θ_*), and thus the net rates in Equations (8)-(14) can be computed numerically by CatMAP.

$$d\theta_H/dt = 0 = r_1 - r_2 + r_3 - r_4 - 2r_5 + r_7 \quad (15)$$

$$d\theta_{OH}/dt = 0 = r_6 + r_7 \quad (16)$$

$$\theta_* + \theta_H + \theta_{OH} = 1 \quad (17)$$

The effect of pH was included as a new feature of CATMAP as follows: the pH effect was treated explicitly in CatMAP by modifying the free energies of hydronium and hydroxide species to reflect the entropy changes arising from variations in proton activity. Since an increase in pH corresponds to a decrease in hydronium activity and an increase in hydroxide activity, the energy of H_3O^+ is shifted down by $2.3kT^*pH$ and the energy of OH^- is shifted up by $2.3kT^*pH$. Transition states, which by definition have a negligible surface coverage, are not affected by pH. In practice, this means that activation barriers for steps with H_3O^+ as a reactant increase with increasing pH, while activation barriers for steps with OH^- as a reactant decrease with increasing pH. We introduced a simplistic model for diffusion effects by limiting the concentration of protons at the reaction interface to the pH-dependent concentration in the bulk, corresponding to a boundary layer thickness of around 8 μm , see supporting information for more details.

3. Results

As outlined in the introduction, there are three main competing hypotheses that rationalize the differences in HER activity under alkaline and acidic conditions. In what follows, we evaluate and discuss all three.

3.2.1 H binding energy

It has been proposed that the hydrogen binding energy changes with pH and that this gives rise to the pH-effects.^{9,8,44} The pH-dependent peaks in the underpotential deposition (H_{upd}) region of cyclic voltammetry (cv) measurements on polycrystalline Pt were taken as a measure of the HBE to establish this hypothesis.^{9,10,11} In a recent study, the peak position was found to be linearly correlated with the HER and HOR activity of stepped and nano-structured metal catalysts.¹¹ A theoretical *ab initio* molecular dynamic study on Pt(100) has also suggested a change of the hydrogen adsorption energy of about 0.13 eV going from pH 0.2 to 12.8, because of water co-adsorption at lower pH.⁴⁴ We are unaware of experimental peak shifts on Pt(100), and will focus on the Pt(111) surface, and note that there is no shift in H_{upd} on Pt(111), but Pt(111) still shows a pH-dependence in HER activity.^{17,45}

An alternative explanation for the peak shifts in cyclic voltammetry measurements on *stepped* sites is the interaction of hydroxyl with pre-adsorbed hydrogen and replacement thereof.^{45,36,46} The peak shift of around 50 meV per pH unit was assigned to the interaction of OH^* with adsorbed hydrogen.⁴⁵ The non-Nernstian part of the peak shift was furthermore assigned to the effect of cation co-adsorption along with hydroxide on the steps in a combined experimental and theoretical study.³⁷

The effect of specifically adsorbed cations on the rate of catalytic reactions has been investigated with DFT simulations^{38,39}. However, there is no rigorous understanding of the effect of water solvation on the adsorption energy of cations. Experimental studies suggest that cations are solvated and interact with the electrode only via non-covalent interactions.^{47,48}

Alternatively, the shifts in CVs are consistent with a potential (or field) dependent OH adsorption energy⁴⁹. The hydroxide molecule has a dipole and therefore its interaction with the interfacial electric field would lead potential dependence of its adsorption energy as follows:

$$E = E_0 + \mu \vec{E} + \frac{\alpha \vec{E}^2}{2} \quad (18)$$

where E_0 is the adsorption energy in the absence of an electric field, μ the intrinsic dipole moment and α the polarizability of the adsorbate and $\vec{E}$ the electric field.

We apply a simple model to relate the field at the electrode|electrolyte interface to the potential applied via the Helmholtz model: $\vec{E} = \frac{C_H}{\epsilon\epsilon_0} U$, where U is the potential relative to the potential of zero charge, and C_H is the Helmholtz capacitance. The latter can be assumed to be relatively constant at potentials far from the potential of zero charge⁵⁰, which has a value of around 0.26 V vs. SHE for Pt(111).⁵¹ We investigated the effect of the electric field on the OH binding energy on two prototypical Pt steps on Pt(533). We find that the OH adsorption energy is indeed field dependent, following the anticipated relation of more negative field weakening the OH adsorption. The computed relation is shown in Fig. 2.

In order to relate the adsorption energy to the potential, we assume a simple Helmholtz model with variable values of the ratio between Helmholtz capacitance C_H and dielectric constant of the at the interface ϵ . Experimentally determined values of ϵ and C_H generally cover a significant range of 2-10 and 10-60 μF , respectively.^{52,53} With a ratio of $\frac{C_H}{\epsilon}$ of roughly 10 we can reproduce the experimentally observed pH-dependent peak shift resulting in a dipole moment of around 0.16 |e|/Å on Pt(533).⁴⁵

We note that such a simple picture does not allow us to rationalize the cation-specificity that has been observed in Ref. ³⁷. The ions may modulate the local field at the reaction plane via a simple size effect⁵⁴ or they can specifically interact with the *OH which would mean that the electric field is not the sole descriptor for the pH-dependence of the peaks observed.

Fig. 2: Field-dependent adsorption energy of OH on Pt(533). The potential scale was deduced using different values for the ratio between Helmholtz capacitance and dielectric constant with $C_H/\epsilon = 0.89$ giving an effective double layer thickness of 3 Å.

3.2.2 Change in proton donor

Another hypothesis for pH-dependence is the change in proton donor between acidic and alkaline conditions, so that the proton source for hydrogen deposition and evolution comes from hydronium ion at low pH and from water at high pH. We investigate this possibility using explicit simulations of electrochemical barriers in conjunction with microkinetic modelling. Due to the difficulties in DFT descriptions of anions^{55,10}, we have considered only H_3O^+ and H_2O as the possible proton donors, although buffers for instance may also act as proton donors, or improve the transport of hydronium ions to the interface⁵⁶. We therefore limit our comparisons to experimental data taken under buffer-free conditions. We now solve the mean-field micro-kinetic model described in Equations (1)-(7) above, including all possible electrochemical and chemical steps.

Furthermore, hydronium and hydroxyl mass transport limitations were introduced by including diffusion through a boundary layer of thickness 8 μm (details in supporting information). This simplified approach assumes migration to be insignificant, i.e. it does not account for Ohmic losses in the solvent due to H^+ or OH^- concentration gradients. A

more detailed study on diffusion effects can be found in reference⁵⁷, which shows that mass transport effects are significant at pH 4-10. Mass transport effects based on the full Nernst-Planck equations will be investigated in future.

The computed proton transfer barriers from H_3O^+ and H_2O are reported at work functions of 4.4 and 3.6eV, respectively, are summarized in Table 1. Assuming a SHE reference of 4.4 eV, these potentials correspond to 0 V vs. RHE at pH of 0 and 14, respectively. We find that the alkaline barriers are systematically larger than the acidic barriers, which is in agreement with the experimental observations.⁵⁸ We find that, at low overpotential, the Heyrovsky barrier is always larger than the Volmer barrier and for the acidic case at 0 V vs. SHE, it is smaller than the Tafel barrier. Using the BEEF-ensemble we have obtained estimates of the uncertainties in the activation energies. Consistent with Ref. ⁵⁹ which found the Tafel barrier to be highly functional dependent, we found the Tafel barrier to have the largest uncertainty, see computational details. Note that the uncertainties are only uncertainties related to the BEEF ensemble and do not include uncertainties inherent to the sampling of possible water structures. Experimental activation energies have been reported in the literature for acidic (0.1 M HClO_4) and alkaline (0.1 M NaOH) conditions over Pt(111), see references [7,⁶⁰]. The experimentally determined activation energies are $\Delta H^{0\#}(\text{acidic}) = 0.19$ eV and $\Delta H^{0\#}(\text{alkaline}) = 0.48$ eV. This difference in activation energy translates to differences in turnover frequency of several orders of magnitude.

Table 1: Activation energies and Tafel slopes of HER over Pt(111) from different proton sources. Our Tafel barrier is 0.72 eV and the chemical water dissociation has a barrier of 1.02 eV.

	G_a Volmer (eV)	G_a Heyrovsky (eV)	β (e)	Tafel slope (meV/dec)
$\text{H}_3\text{O}^+/\text{Pt}(111)$	0.04	0.20	0.74	80
$\text{H}_2\text{O}/\text{Na}/\text{Pt}(111)$	0.42	1.20	0.59	100

Given the larger uncertainty in the Tafel barrier, we performed a sensitivity analysis of its effect on the resultant polarization curves. We find that a +0.05 eV increase to 0.77 eV of the barrier reproduces the qualitative features for HER from experiment¹³ (replotted in **SI-Fig. 1.**), and this result is shown in **Fig. 3**. The discrepancies of the diffusion-limited currents at pH 2-4 between experiments and theory are due to our simplistic diffusion model. The polarization curves without this increase is shown in **SI-Fig. 2**. Furthermore, **SI-Fig. 2** shows the polarization curves with a Tafel barrier 0.1 lower than our calculated DFT barrier, which shows a flat region at very low current density and low overpotentials, corresponding to the Volmer-Tafel mechanism. Since this feature is not seen experimentally, we rule out the Volmer-Tafel mechanism for HER at all pH values. As shown in Fig. 3, our polarization curves are in good agreement with those observed experimentally¹³.

We note that Ref. ¹³ has developed a phenomenological kinetic model that also reproduces the features of the experimental curves, but with fitted rate constants and a single effective rate equation for the redox reaction for each proton donor. In contrast our analysis is based on *ab initio* reaction energetics and full consideration of all elementary steps.

We find that at low pH, the reaction proceeds via the acidic Volmer-Heyrovsky mechanism, see Fig-S4. With increasing pH, hydronium ions are depleted from the reaction interface due to diffusion limitations, giving rise to the diffusion plateau at around pH 2-4. At a more negative potential of around -1.2 V, water splitting occurs via the alkaline Volmer-Heyrovsky mechanism. From a pH of around 4 and upwards, the HER proceeds solely via the alkaline Volmer-Heyrovsky reaction, as the interface is completely depleted of hydronium ions and direct water splitting becomes the only possibility for HER. As there is enough water at the reaction interface, the current density is independent of pH on a SHE scale for this pH-regime.

Fig. 3: Computed HER/HOR polarization curves using the DFT activation energies and mean-field micro-kinetic modelling. The DFT Tafel barrier applied here was 0.77 eV; sensitivity analysis for this barrier is shown in SI Fig 3.

We derived the Tafel slopes from the computed charge transfer coefficient of the rate determining step (Heyrovsky) using the charge transfer coefficient of the Heyrovsky reaction, see computational details. The alkaline Tafel slope of around 100 meV/dec is in good alignment with the experimental values summarized in Fig. 4. Rotating disk electrode measurements of the HER reaction kinetics under acidic conditions is convoluted with diffusion limitations⁶¹ and we therefore abstain from a comparison of the acidic Tafel slopes.

Fig. 4: Tafel plots of *experimental* HER data under alkaline conditions. Koper 2017¹⁷: pH 13 over Pt(111), Markovic 2013¹³: pH 7-14 over Pt(111), Markovic 2011⁶²: pH 13 over Pt(111).

It was proposed in Ref. ³³ that the pH effect arises from shifts in configurational entropy of protons. This effect is included in our kinetic model through the concentration, see computational details. Configurational entropy barriers alone, however, cannot rationalize the experimental observations, and result in about an order of magnitude shift per pH unit, while the exchange current densities differ by 2-3 order only between pH 0 and pH 14.⁶³ Therefore the experimental trends can only be rationalized where water is also a proton donor. The variation of the effect of potential and configurational entropy on Volmer barriers are shown schematically in Ref. ⁶⁴.

It has been suggested that *OH binding can be an important descriptor for alkaline HER, due to the effect of oxide clusters on alkaline HER activity. Here we find that the *OH coverages on Pt(111) are essentially zero under HER conditions, **Figure S5**. While we do not exclude the possibility that, in the presence of oxides, *OH may play a role, our current analysis does not suggest that *OH takes part in the HER mechanism on Pt. This conclusion is consistent with a recent work, where, using kinetic modelling of stepped Pt(110) CV's, it was suggested that adsorbed OH does not actively take part in the HER/HOR reaction mechanism, but behaves as a rapidly equilibrated spectator species that decreases available surface sites and slows hydrogen kinetics¹⁴.

Let us now consider in more detail the HOR part of the polarization curves in Fig. 4. At low pH, our micro-kinetic model suggests that the HOR proceeds via the reverse Tafel – reverse acidic Volmer reaction mechanism. This is why the HOR polarization curves shift with pH over the entire pH range, Fig. 5 (a). At higher pH, the mechanism proceeds via Tafel – reverse alkaline Volmer. With decreasing pH, this pathway becomes more and more limited by OH⁻ mass transport, so that the low-pH reaction pathway is fully recovered already at already at pH 11. Our results are in line with experimental polarization curves from Sheng et al.⁹, who find a slightly flattened low-potential onset at around pH 11, indicating the onset of diffusion limitations. At very positive potentials, the surface becomes covered by OH*, consistent with the experimental observations of Ref. ¹⁷, which leads to a depletion in HOR current density, see Fig. 3.

3.2.2 Water reorganization

Independent of the two prevalent hypotheses described above, the charging behavior of the metal has been hypothesized to affect the pH dependence of hydrogen redox reactions. Koper et al.¹⁷ have suggested that since HER operates under alkaline conditions at potentials farther from the potential of zero free charge (pzfc), the water mobility would be lower and therefore results in higher proton-electron transfer barriers. They further suggest that the experimentally determined 25meV shift in the pzfc upon the modification of Pt(111) with Ni(OH)₂ leads to a decrease in interfacial field and improved water mobility, which results in improved kinetics. We established a rough estimate of the order of magnitude of the effect of such a change in potential of zero charge on the stability of water configurations with different dipoles via $\Delta E = \mu \Delta \vec{E}$ where $\Delta \vec{E} = \frac{C_H}{\epsilon \epsilon_0} \Delta U_{pze}$ and $\Delta U_{pze} = 0.025$ V, and a $\frac{C_H}{\epsilon \epsilon_0}$ ratio of about 10. The dipole moment was derived from the work-function change $\Delta \phi$ via $\mu = \epsilon_0 A \Delta \phi$, where A is the unit cell area induced by positioning a water bilayer above the Pt(111) surface, shown in the supporting information **Figure S6**, which gave a H-down water dipole moment of $\mu = 0.4$ eÅ. We find that the change in stability, ΔE , is 0.009 eV, which translates into a slight but significant an increased turn

over frequency by roughly a factor of 1.4. The effect of Ni(OH)₂ nano-islands in experiments also give an increased turn over frequency in that order of magnitude.⁶⁵

We note also that, if there are significant differences in water reorganization energies as a function of pH, then such an effect would be present in other electrochemical processes. We consider the universality of the presence of such a shift as inconclusive: For instance, OXR both the absence⁶¹ as well as the presence⁶⁶ of such a shift has been observed. This hypothesis would also suggest the pzfc of a given material to be an important descriptor for activity, but HER/HOR do follow trends in H* binding quite well, under both acidic and alkaline conditions.^{12,9,10}

Conclusions

We developed a microkinetic model for hydrogen evolution and oxidation with simple diffusion limitations based on first-principles DFT kinetic barriers. The resultant theoretical activities were qualitatively consistent with experimental polarization curves and Tafel slopes (in the case of the alkaline pathway) for both HER and HOR and suggest that differences in the HER/HOR activity with pH arises from a shift from hydronium to water as proton sources. Our model suggests that at low pH, HER proceeds via the acidic Volmer-acidic Heyrovsky mechanism. Here, the proton donor is the hydronium ion (H₃O⁺). The alkaline pathway proceeds via the alkaline Volmer-alkaline Heyrovsky mechanism with water as the proton donor. Our model also finds that the hydrogen oxidation reaction proceeds via the reverse Tafel-reverse Volmer mechanism, whereby the second step forms hydronium ions under acidic conditions and water under alkaline conditions.

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Graphical TOC: