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Mechanism of Oxygen Reduction Reaction on Pt(111) in Alkaline Solution: Importance of Chemisorbed Water on Surface

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Abstract

We report a detailed mechanistic study of the oxygen reduction reaction (ORR) on Pt(111) in alkaline solution, combining density functional theory (DFT) and Kinetic Monte Carlo (KMC) simulations. A complex reaction network including four possible pathways via either $2e^-$ or $4e^-$ transfer is established, being able to reproduce the experimental measured polarization curve at both low and high potential regions. Our results show that it is essential to account for solvation by water and the dynamic coverage of $*OH$ to describe the reaction kinetics well. In addition, a chemisorbed water ($*H_2O$)-mediated mechanism including $4e^-$ transfers is identified, where the reduction steps via $*H_2O$ on the surface are potential-independent and only the final removal of $*OH$ from the surface in the form of OH^-_{aq} contributes to the current. For the ORR in alkaline solutions such a mechanism is more competitive than the associative and dissociative mechanisms typically used to describe the ORR in acid solution. Finally, $*OH$ and $**O_2$ intermediates are found critically important for tuning the ORR activity of Pt in alkaline solution. To enhance the activity, the binding of Pt should be tuned in such a way that $*OH$ binding is weak enough to release more surface sites under working conditions, while $**O_2$ binding is strong enough to enable the ORR via the $4e^-$ transfer mechanism.

1. Introduction

Recent studies have shown progress in anion-exchange membranes that can alleviate CO₂ poisoning,¹⁻³ which makes the alkaline fuel cell (AFC) an option as a power source. Similar to the fuel cell in acid solution, platinum (Pt) is the best metal catalyst for the oxygen reduction reaction (ORR) in the AFC.⁴ Extensive efforts in both experiment⁴⁻²⁰ and theory^{6, 21-38} have been made to study the underlying mechanism of the ORR on Pt in acid solution, while not as much attention has been paid to Pt-catalyzed ORR in alkaline solution.

The ORR on Pt in an alkaline environment generally operates in two different regions, the so-called inner- and outer-sphere.³⁹ The outer-sphere process exhibits near-independence on a large number of electrode materials and therefore is non-electrocatalytic, where in most cases adsorbed hydroxyl species (*OH with * referring a surface site) promote the partial reduction of solvated O₂ (O_{2aq}) to the hydroperoxyl (OOH⁻_{aq}) species via a 2e⁻ transfer mechanism.⁴⁰⁻⁴¹ The inner-sphere process is electrocatalytic in which chemisorbed O₂ (**O₂) at the Pt surface undergo a series of reductions to H₂O and OH⁻_{aq} via an efficient 4e⁻ transfer mechanism.³⁹⁻⁴⁰ In order to achieve high ORR activity in alkaline media, it is important to tune the performance of the cathode catalysts to facilitate the 4e⁻ transfer ORR at the inner-sphere, while limiting the 2e⁻ transfer reaction at the outer-sphere.

The electrocatalytic ORR in alkaline solution on Pt surfaces and/or particles have been proposed to operate via parallel mechanism as that in acid mainly based on rotating ring disk experiments.⁴²⁻⁴³ There is no agreement regarding pH dependence. Differences in electrolyte and charge carrier (H⁺ vs. H₂O/OH⁻) are likely to lead to different behavior, e.g. surface sensitivity of Pt toward the ORR.^{42, 44} Therefore the mechanism largely based on the ORR on Pt in acidic solution may not be adequate enough to describe. By identifying key reaction steps, such mechanistic study of the ORR can aid in the development of next generation catalysts, which are based on the non-precious metals and their oxides to greatly lower the cost and make the AFC more attractive.⁴⁵⁻⁴⁶

In the present study, we report a detailed mechanistic study of the electrocatalytic ORR at the inner-sphere in alkaline solution using theoretical calculations. The Pt(111) surface is chosen as a model system, since it has been found to be more active than Pt(100) and Pt(110) for the ORR in alkaline solution.⁴⁷⁻⁴⁸ In addition, the Pt nanoparticles are expected to be dominated by (111) facets.⁴⁹⁻⁵⁰ The combination of Density Functional Theory (DFT) and Kinetic Monte Carlo

(KMC) simulations allows us to pinpoint the complex reaction network and reproduce the polarization curve measured by rotating ring disk experiments.⁵¹ One of significant findings is that the presence of water on the surface is essential to describe the reaction kinetics realistically. More importantly, the contributions from parallel $4e^-$ transfer associative and dissociative mechanisms, typically considered for the ORR in acid solution,²¹ are unable to compete with a new mechanism discovered in this work involving $*H_2O$. In this newly identified pathway, O_2 reduction via surface bound $*H_2O$ leads to the formation of $*OH$, and the conversion of $*OH$ to OH^-_{aq} is the only potential-dependent step involved. Finally, a sensitivity analysis shows that to improve the ORR activity of Pt in alkaline solution, the $*OH$ binding with the Pt surface should be weakened to allow its facile removal and prevent $*OH$ -poisoning. At the same time, $**O_2$ binding should still be strong enough to promote the efficient $4e^-$ transfer mechanism at the inner-sphere. Our study highlights the importance of modeling a realistic environment including surface water and accounting for multiple mechanisms in parallel.

2. Methods

2.1 DFT Calculation

DFT calculations were performed using Vienna Ab-initio Simulation Package (VASP)⁵²⁻⁵⁶ with projector augmented wave method, and the Perdew–Wang functional (GGA-PW91) within the generalized gradient approximation was used to describe exchange-correlation effects⁵⁷⁻⁵⁸. The cutoff energy was 500 eV and convergence of energy and forces were set to 1×10^{-5} eV and 0.01 eV/ Å. Pt(111) was modeled by 4-layer slab with 3×3 atomic arrangement in each layer, where the bottom two layers of every Pt atoms were fixed and the top 2 layers of Pt and adsorbates were fully relaxed with the adsorbates. All the slab models included a vacuum of 20 Å. A $3 \times 3 \times 1$ Monkhorst-Pack was used for k-point sampling to describe the unit cell⁵⁹. The transition states were searched by climbing image nudged elastic band method (NEB) method in VASP (VTST)⁶⁰.

Inspired by the method developed by Nørskov and coworkers,²¹ we assumed the equilibrium of the reaction

Assuming the coupling between an electron transfer to the electrode and the formation of OH^-_{aq} ($\text{OH}^-_{\text{aq}} - \text{e}^-$ in our notation), Eq.1 was also expressed as $(\text{H}^+_{\text{aq}} + \text{e}^-) + (\text{OH}^-_{\text{aq}} - \text{e}^-) \leftrightarrow \text{H}_2\text{O}_{\text{aq}}$. Using the standard hydrogen electrode (SHE) as the reference electrode, the free energy of $\text{OH}^- - \text{e}^-$, $G(\text{OH}^- - \text{e}^-)$, was then determined as

$$G(\text{OH}^-_{\text{aq}} - \text{e}^-) = G(\text{H}_2\text{O}_{\text{aq}}) - G(\text{H}^+_{\text{aq}} + \text{e}^-) = G(\text{H}_2\text{O}_{\text{aq}}) - 1/2G(\text{H}_2) \quad (2)$$

The corresponding free energy of reaction was calculated as

$$\Delta G = \Delta G_0 + \Delta G_{\text{solvation}} + \Delta \text{ZPE} + n\text{e}U \quad (3)$$

ΔG_0 was given by the standard definition as $\Delta G_0 = \Delta E + T\Delta S_0$, where ΔE was DFT-calculated reaction energy and $T\Delta S_0$ represented the entropic contributions. The contribution from solvation to the reactions involving aqueous species, $\text{H}_2\text{O}_{\text{aq}}$, OH^-_{aq} and OOH^-_{aq} and $\text{O}_{2\text{aq}}$, was accounted ($G_{\text{solvation}}$) by adding the difference in free energy between the gas-phase state and the aqueous-phase state.⁶¹ Zero-point energy (ZPE) corrections were also included based on the calculated vibrational frequencies. For the potential-dependent step involving n-electron transfer, ΔG at potential U were shifted by $n\text{e}U$ with respect to that at zero potential. Finally, in our modeling, the electrolyte was considered 0.1 M KOH (pH = 13) at room temperature and the free energy was corrected according to previous work.²¹ The binding of an adsorbate should also be affected by the external potential, but the correction was shown to be small according to the previous study.⁶² Therefore, we neglected adsorbate-electric field interactions.

2.2 Reaction network

To describe the reaction network for the ORR under alkaline conditions, eleven (11) elementary steps were taken into consideration. Firstly, an O_2 molecule is adsorbed on the Pt(111) surface from the electrolyte,

The DFT calculations show that O_2 prefers to adsorb at the bridge sites on the Pt(111) surface with and without presence of water. Both 2e^- and 4e^- mechanisms were included for the sequential reduction reactions of $**\text{O}_2$. Along the 4e^- pathway, $**\text{O}_2$ is dissociated into $*\text{O}$ at fcc hollow sites (Step 5), and then reduced by $\text{H}_2\text{O}_{\text{aq}}$ together with one electron transfer to form $*\text{OH}$ at top sites (Step 6) and a solvated OH^-_{aq} anion. The surface bound $*\text{OH}$ formed in Step 6 dissolves as OH^-_{aq} as result of a direct one electron reduction (Step 7), or by one electron

reduction with $\text{H}_2\text{O}_{\text{aq}}$ (Step 8). This series of reactions is via the so-called dissociative mechanism given below:

The second 4e^{-} sequence is via the associative mechanism.²¹ Similar to Step 6 above, the $^{**}\text{O}_2$ is reduced to form $^{**}\text{OOH}$ at bridge sites via $\text{H}_2\text{O}_{\text{aq}}$ and one electron transfer (Step 9). The $^{**}\text{OOH}$ product is the precursor for O-O bond cleavage, which is driven by a second electron transfer step (step 10).

Both the dissociative and associative mechanisms have been widely used to describe the ORR on Pt(111) in acid solution.^{21,43,44,56,59} Each reduction step is potential-dependent, and when mediated by $\text{H}_2\text{O}_{\text{aq}}$, the electron transfer step is coupled with the production of $\text{OH}^{-}_{\text{aq}}$. However, water is not only available as $\text{H}_2\text{O}_{\text{aq}}$ in the electrolyte, but also as adsorbed molecular $^{*}\text{H}_2\text{O}$ on the surface, which can also participate in the reduction process. This led us to consider a third pathway for the 4e^{-} mechanism, which we called the “ $^{*}\text{H}_2\text{O}$ -mediated mechanism.” Here, chemisorbed $^{*}\text{H}_2\text{O}$ rather than aqueous $\text{H}_2\text{O}_{\text{aq}}$ is the reagent for the reduction of $^{**}\text{O}_2$ (Step 11), $^{*}\text{O}$ (Step 12), and $^{**}\text{OOH}$ (Step 13) to $^{*}\text{OH}$, i.e.,

Steps (11) through (13) only involve the adsorbed species on the surface with no electron transfer, hence, they are potential-independent surface reactions. The only contribution to the current depends on the dissolution of the $^{*}\text{OH}$ produced via Step 7 or Step 8. In addition, the potential-independent dissociation of $^{**}\text{OOH}$ to $^{*}\text{O}$ and $^{*}\text{OH}$ (Step 13) was also included. The $^{*}\text{H}_2\text{O}$ -mediated mechanism was not considered in previous mechanistic studies for the ORR on Pt in acidic media, but as demonstrated below, it can be the dominant pathway in alkaline solution.

Although not likely,⁶³ the pathway via a $2e^-$ mechanism was also included as part of the reaction network. In this case, the $**OOH$ formed in Step 9 and Step 12 was dissolved directly into the electrolyte as OOH^-_{aq} (Step 14) by the reaction

2.3 KMC Simulation

To gain a better understanding of the complex reaction network for the ORR on Pt(111), we developed a KMC code to simulate a time series of the reaction. A Pt(111) surface model was constructed. For each adsorption site on the surface, the number of species occupied at neighboring sites was counted to account for the coverage and, therefore, coverage-dependent interactions. In the KMC simulation, all possible elementary steps i and the corresponding rates, r_i , were evaluated, and q was selected when it satisfied $\sum_{i=1}^q r_i \geq \rho \times R \geq \sum_{i=1}^{q-1} r_i$ according to Monte Carlo method.⁶⁴⁻⁶⁶ Here R is the sum of sequence for all reaction rates and ρ is generated by a random number generator. In order to improve the efficiency of simulation, a binary tree data structure was used.⁶⁷

In our KMC simulation, r_i was determined using the Arrhenius equation as $v_i \exp(E_{ai}/k_b T)$, where E_{ai} is the activation barrier for step i calculated from DFT (see Section 2.1). The pre-exponential factor, v , was set as 10^{13} which is typical surface reactions at room temperature and set to 10^9 for potential-dependent reactions involved in the ORR on Pt(111) according to previous studies.²⁴

The external potential range was varied from 0.2 V to 0.95 V. The corresponding change in current density at each potential was estimated by counting the electron-transfer steps as

$$j = \frac{e}{A} \sum TOF \quad (15)$$

where e is the electronic charge for an electron, A is surface area and the TOF is the turnover frequency of reactions involving electron-transfer. In this way, a polarization curve describing the variation of current density could then be calculated, which allowed direct comparison with experimental measurements.

3. Results and discussion

3.1 DFT calculations

3.1.1 Effect of water

Previous studies have shown that it is necessary to include water interactions in order to accurately simulate the mechanism of ORR on Pt(111) in acid solution.^{35, 68-72} In these studies, the interfacial water was described by several water molecules, a bilayer (BL) of water with an ice-like structure, or multiple layers of water saturated on the surface. It remains unclear which is the most appropriate way to describe solvation effects at the water-Pt(111) interface. In the present study, our interest is the double-layer region near Pt(111), which is essential for electrocatalytic ORR in alkaline solution. Based on a recent study using scanning tunneling microscopy (STM),⁷³ we chose the ice-like bilayer structure for the present study. It is constructed by a honeycomb ($\sqrt{3} \times \sqrt{3}$) R30 pattern with 2/3 monolayer (ML) of water coverage, where half of water molecules are $^*\text{H}_2\text{O}$ and the other half has an O–H bond pointing down (H-down),⁷⁴ which is slightly more stable than the H-up structure.

According to our calculations, the effect of water on the binding energies of $^*\text{OH}$ and $^{**}\text{OOH}$ is more significant than that of $^{**}\text{O}_2$ and $^*\text{O}$ (see Supporting Information for details) in agreement with previous observations.^{21, 68, 72} This is due to the abilities of $^*\text{OH}$ and $^{**}\text{OOH}$ to form more hydrogen bonds compared to $^*\text{O}$ and $^{**}\text{O}_2$ (Figure 1). In consistent with previous study,⁷⁵ besides binding with a Pt atom on the surface each H_2O molecule also forms three hydrogen bonds with the surroundings in the water BL. To adsorb a reaction intermediate on the Pt(111) surface, one of $^*\text{H}_2\text{O}$ is removed, which results in the loss of three hydrogen bonds and disruption of the ice-like structure. The adsorption of $^*\text{OH}$ or $^{**}\text{OOH}$ not only restores the missing hydrogen bonds and the hexagonal ice-like conformation, but also stabilizes the water layer demonstrated by shorter hydrogen bonds than those in the water BL (Figure 1a, b and see SI). For $^{**}\text{O}_2$, two of the missing hydrogen bonds are recovered and one side of the hexagonal water ring is missing (Figure 1c). In the case of $^*\text{O}$, only one hydrogen bond is formed (Figure 1d). Moreover, $^*\text{O}$ adsorption destabilizes the hexagonal water BL structure by breaking one additional hydrogen bond between water molecules. When the water solvation shell was increased by adding the 2nd and the 3rd BL of water, much smaller effects on the binding geometries and energetics (Figure S1 and Table S1) were observed as compared to a single BL. Adsorbed intermediates only interact directly with water molecules in the 1st water bilayer via hydrogen bonds, while the contributions from the 2nd and 3rd water bilayers are indirect and much smaller.

Next we considered how variations in binding energies due to water solvation impact the potential energy diagram of the ORR. To check that, the variations in free energy along the ORRs via the three $4e^-$ mechanisms (Step 5-13) were plotted in Figure 2. Our results show that water solvation clearly affects the energetics of elementary steps involved in the ORR. Including the 1st BL of water is essential, which makes an obvious difference in the free energy profile for the ORR on Pt(111). Along the dissociative or associative pathways (Figure 2a, b), the presence of water stabilizes $**OOH$ and $*OH$, and facilitates the reduction of $**O_2$ (Step 9) and/or $*O$ (Step 6); while the removal of $*OH$ in the form of OH^-_{aq} (Step 7) is more difficult. Similarly for the ORR via the $*H_2O$ -mediated mechanism (Figure 2c), $*OH$ and $**OOH$ are stabilized and the reductions of $**O_2$ (step 11) and $*O$ (Step 12) are favored due to the interactions with water. The main difference among three mechanisms is observed when the external potential is applied. With potential increasing from 0V to 0.9V (vs. RHE), the potential-dependent steps involving electron transfers are less favorable in all three mechanisms. The associative mechanism is affected the most, where the $**OOH$ and $*OH$ formation and $*OH$ removal are hindered. The $*H_2O$ -mediated mechanism is least affected, with only the removal of $*OH$ becoming less favorable under applied potential compared to that under zero potential, while the energetics of the other potential-independent steps are essentially unchanged. By comparison, the effects of adding the 2nd and 3rd water BL's are much less (Figure 2). Accordingly, the results from the DFT calculations and KMC simulations presented below were performed using Pt(111) covered by one BL of water to describe the water-Pt(111) interface.

3.1.2 Effects of OH species

According to cyclic voltammetry studies in both acid and alkaline solutions, $*OH$ species are co-adsorbed on Pt together H_2O between 0.65 V and 0.85 V, which are interest for the ORR.^{39, 76} In addition, during the ORR, $*OH$ species are important reaction intermediates. Various ways have been proposed for the role of $*OH$ in the ORR in acid solution. Specifically, $*OH$ may act as a spectator to block active sites for catalytic reactions on the surface,^{7, 77-78} lead to surface oxidation,⁷ or help in stabilizing water molecules and the reaction intermediates via the formation of hydrogen bonds.^{27, 79-81} Previous theoretical studies^{27, 80-82} suggested the presence of a stable $*OH/H_2O$ network occurring at an $*OH$ coverage of 1/3 ML, due to the formation of an alternate arrangement of $*OH$ and H_2O in a hexagonal pattern. Other studies by

Nørskov, et al. also discussed the potential effects of $\ast\text{O}^{21, 83}$ and $\ast\text{OH}^{27, 82}$ coverage on the ORR in acid on Pt-based catalysts. For the AFC, the effect of $\ast\text{OH}$ can be an even more significant than that in acid solution, since $\ast\text{OH}$ can also be provided from the electrolyte. To account for the effect of $\ast\text{OH}$ coverage in our calculations, the variation in binding energies of reaction intermediates and E_a with the increasing $\ast\text{OH}$ on the surface was determined.

The differential adsorption of $\ast\text{OH}$ at different coverages on Pt(111) was calculated, where $\ast\text{H}_2\text{O}$ in the water BL was sequentially replaced by $\ast\text{OH}$. The most stable structure at each OH coverage was used to calculate the adsorption energies of other reaction intermediates. When the $\ast\text{OH}$ coverage increased up to 1/3 ML, the number of hydrogen bonds remains the same as that in the 1st water BL, while the number of dangling O-H bonds in the water BL eventually decreases to zero (Figure 3 and Table S2). As a result, the $\ast\text{OH}/\text{H}_2\text{O}$ network is stabilized, which is demonstrated by the transition of the buckled water BL into a flat plane with hydrogen bond lengths shortened by ~ 0.1 Å. These results agree with previous studies,^{27, 81, 84-86} showing that the saturation coverage of $\ast\text{OH}$ at the water/Pt(111) interface is 1/3 ML (Figure 4a). At this coverage, stabilization in the water BL dominates the energetics. It corresponds to the so-called half-dissociated water network,²⁷ where each honeycomb is constructed by three $\ast\text{H}_2\text{O}$ and three $\ast\text{OH}$ in an alternating arrangement (Figure 3c). Replacing an additional $\ast\text{H}_2\text{O}$ by $\ast\text{OH}$ leads to a decrease in the number of hydrogen bonds and the differential binding energy of $\ast\text{OH}$ increases by 0.38 eV (Figure 4a).

Figure 4 shows that the binding energies of all the other adsorbates vary with the $\ast\text{OH}$ coverage with two distinct trends. For $\ast\text{OOH}$ (Figure 4b) and $\ast\text{O}$ (Figure 4c), the variation in binding energies follows similar upside-down volcano-like trends as that of $\ast\text{OH}$. At low $\ast\text{OH}$ coverage, the $\ast\text{OH}$ -induced stabilization by the formation of hydrogen bonds helps to hold the water/OH/adsorbate network on the surface. At high coverage, the bindings are weakened, which is determined by the increasing partial oxidation of surface Pt due to the direct interaction with $\ast\text{OH}$. These results clearly demonstrate that the variation in binding energy does not scale proportionally with increasing $\ast\text{OH}$ coverage. The exception is $\ast\text{O}_2$, where the binding energy decreases linearly with increasing $\ast\text{OH}$ coverage (Figure 4d). The presence of $\ast\text{OH}$ limits the mobility of $\ast\text{H}_2\text{O}$ via hydrogen bonds, which are not able to approach $\ast\text{O}_2$ (Figure S2); the resulting hydrogen bonds between $\ast\text{O}_2$ and $\ast\text{H}_2\text{O}$ are longer and weaker than that without $\ast\text{OH}$ present. Consequently, the stabilization due to formation hydrogen bonds has a minor effect,

while the increasing partial oxidation of surface Pt leads to the weakening of the Pt-O₂ interaction. Among the reaction intermediates, the binding of *OH and *O are more sensitive to *OH coverage (Figure 4), as their binding energies strongly depend on the stability of the *OH/H₂O network.

The variation in *OH coverage not only affects the binding energies of the reaction intermediates, but also the activation energies (E_a) of the ORR elementary steps which only involve adsorbed species (Step 5 and Steps 11-13). In general, the E_a are raised by increasing the coverage of *OH up to 1/3 ML (Figure S3a). That is, all the surface reactions become less favorable. In addition, the variations in E_a are strongly correlated with ΔG of the reaction (Figure S3b). Overall, the linear relationship via $E_a = a\Delta G + b$ (a and b are constants) or Brønsted–Evans–Polanyi (BEP) relationship between reaction energy and activation barrier is followed reasonably well, though a and b vary depending on the reaction species. For the steps involving species that are less sensitive to *OH coverage, e.g. $**O_2 + *H_2O \rightarrow **OOH$, the E_a vary less significantly than those involving the intermediates that are sensitive to *OH coverage, e.g. $**OOH \rightarrow *O + *OH$. For the other steps involving electron transfers, the E_a are not calculated due to limitations of standard DFT. Overall, the effect of *OH coverage on the ORR reactions is complicated; it affects the stability of the water BL, the binding energies of adsorbates, and E_a for the elementary steps. More importantly, the changes in both binding energies and E_a with *OH coverage depend on the species involved in the reaction. Embedding the dynamic effect of *OH coverage on the reaction energetics into our KMC program, as shown in Section 3.2, provides a better description of complex ORR than that assuming a fixed coverage of *OH or *O to adjust the binding for other reaction intermediates in the previous kinetic study for the ORR in acid.^{20-21, 24, 87-88} The effect of *O coverage was not considered here. Our interest in the ORR around working potential, when the amount of *O is still low.

3.2 KMC simulations

3.2.1 Estimation of ORR activity

The DFT calculations at the water/Pt(111) interface describe the binding structures of the reaction intermediates and thermodynamics of the elementary steps involved in the ORR in alkaline solution; However, the insight into the reaction kinetics is rather limited. To achieve kinetic understanding, the KMC simulations was carried out, where the three 4e⁻ mechanisms

(dissociative, associative, and $\ast\text{H}_2\text{O}$ -mediated) and 2e^- mechanism were all included (see Section 2.2). Besides, it also allows for a direct comparison between the calculated and the experimentally observed polarization curves. Thus, our theoretical model to describe the ORR in alkaline solution on Pt(111) can be validated. Finally, it also enables a better understanding of how the different mechanisms interplay under the ORR conditions.

The binding energies of adsorbates (Figure 4) and the E_a of the elementary steps (Figure S3a) employed in the KMC simulations were based on the DFT calculations and discussed in the preceding section. Both the forward and backward reactions were taken into considerations. For potential-dependent steps involving electron transfer, the E_a were estimated using the DFT-calculated and the BEP relationship based on previous studies for the ORR on Pt(111),²⁷ where $a = 0.5$ and $b = 0.26$ were reported for proton transfer on Pt(111) in acid solution. To account for the effect of $\ast\text{OH}$ coverage, a local $\ast\text{OH}$ coverage calculator was developed in the KMC code. It updated $\ast\text{OH}$ coverage on the surface at an applied potential, which allowed the E_a for each elementary step to be corrected accordingly.

In order to estimate the variation in current density with potential, the rate for O_2 adsorption from electrolyte to the Pt(111) electrode (Step 4) was determined by fitting the KMC simulated polarization curve to that previously measured for the ORR on Pt(111) in 0.1 M KOH (Figure 5).⁵¹ We note that the adsorption rate is only associated with the diffusion-limited current density at lower potential (< 0.4 V), rather the ORR working potential (~ 0.8 V). By fixing the maximum current density to be the experimental value,⁵¹ the TOF of O_2 adsorption was obtained. The BEP coefficients, a and b , are related to the kinetic current density at higher potential, which is the key to the performance of ORR catalysts.²⁴ According to our results, a controls the curvature of the polarization curve at the on-set potential, while b affects the half-wave potential. By using the values determined for the ORR in acid solution,²⁷ the estimated polarization curve reaches well agreement with the experimental observation. Only with a small tuning, $a = 0.42$ and $b = 0.24$, a finely match can be achieved (Figure 5). Our combined DFT and KMC simulations are able to describe well the measured polarization curve for the ORR on Pt(111), which capture not only the onset and half-wave potential at high potential region, but also the small variation in current density at low potential region.

3.2.2 Reaction intermediates

As shown in the simulation snapshots in Figure 6, the hexagonal ice-like network of water-Pt(111) interface determined by DFT is well reproduced by the KMC matrix. The adsorption sites for each reaction intermediate are located within the hexagonal lattice according to the DFT calculations. The KMC simulations also provided the coverage of the abundant reaction intermediates as a function of applied potential. Below 0.75 V, the surface is mostly covered by water in an ice-like structure (Figure 6). Adsorbed *OH emerges from 0.75 V (the green dash line, Figure 5), and accumulates with increasing potential and a rapid decrease in current density. At 0.83 V (Figure 6), the highly-stable, half-dissociated *OH/H₂O network starts to form locally. At 0.95 V, the accumulation of *OH slows down and reaches a coverage of about 0.23 ML. Starting from about 0.9 V, *O appear (yellow dash line, Figure 5) and replace *OH and *H₂O due to oxidation at higher potentials (Figure 6). As a result, the ORR comes to an end. The other reaction intermediates are either very small amount (e.g. **OOH) or barely seen (e.g. **O₂) over the entire potential range studied. Similar variations in the coverage of surface species during the ORR on Pt(111) were also observed in acid solution.^{7, 24, 79} In both cases, the ORR slows down at the potential when *OH start to build up on the surface and eventually stops when the potential is increased to allow the formation of *O.

3.2.3 Reaction mechanism

As evidenced by the present KMC results, there is not much difference between the polarization curves and abundant reaction intermediates for the ORR in alkaline and acid solution, in agreement with the experimental observations.⁸⁹ This raises the question as to whether the processes occurring during the ORR in acid solution are the same in alkaline solution. How do the multiple mechanisms interplay during the ORR? To address it, we made use of the ability within our KMC model to count the times that an elementary step occurs during a certain time interval at an applied potential, referred to as “reaction counts” in this paper. This procedure allows us to identify the main steps that occur during the ORR and, therefore, identify the dominant mechanism(s).

The reaction counts for both the potential-dependent (solid lines) and potential-independent surface reactions (dash lines) are shown in Figure 7. The elementary step with the largest number of reaction counts over the entire potential range studied is *OH removal as OH_{aq}⁻, which is representative of electron transfer during the ORR. Since this step is involved in

all reaction mechanisms, we cannot specify the preference of each mechanism accordingly. However, different contributions for the other steps are clearly observed. For $^{**}\text{O}_2$ reduction to $^{**}\text{OOH}$, the potential-independent surface reaction conducted via $^*\text{H}_2\text{O}$ (Step 11, blue dash line) is more populated than the potential-dependent step (Step 9, blue solid line), which has a reaction count close to zero. Similarly, the $^*\text{H}_2\text{O}$ -mediated surface reaction involving the reduction of $^*\text{O}$ to $^*\text{OH}$ (Step 13, green dash line) is dominant with no contribution from the corresponding potential-dependent step (step 6, green solid line). For $^{**}\text{OOH}$ dissociation, both the potential-independent (Step 12, yellow dash line) and the potential-dependent steps (Step 10, yellow solid line) help, though the former is more intensive than the latter. The reaction count results clearly show that the ORR on Pt(111) in alkaline solution mainly follows a $4e^-$ transfer mechanism, with the $^*\text{H}_2\text{O}$ -mediated mechanism dominated. The reduction of $^{**}\text{O}_2$ via $^*\text{H}_2\text{O}$ rather than $\text{H}_2\text{O}_{\text{aq}}$ leads to the formation of $^{**}\text{OOH}$, $^*\text{O}$ and $^*\text{OH}$. During the reduction reactions, there is no electron transfer until the final removal of $^*\text{OH}$ from the surface in the form of OH^-_{aq} . In contrast, the contributions from both the associative and dissociative mechanisms, which are proposed for the ORR in acid solution, are much less.

The ORR via the partial $2e^-$ mechanism represented by formation of OOH^-_{aq} only occurs at low potentials (< 0.4 V, Figure 7). When the potential increases, the ΔG for $^{**}\text{OOH}$ removal as OOH^-_{aq} (step 14, red solid line) is positively shifted by eU (Eq.3) and the E_a increases accordingly. As a result, the corresponding reaction counts decrease to zero when the potential increases over 0.4 V (Figure 7). The ORR via $2e^-$ mechanism at low potential agrees very well with the experimental observation (Figure 5). Of course, our model is only able to describe the ORR at the potential which $^*\text{H}_2\text{O}$ is still present on the surface. Specifically, $^*\text{H}_2\text{O}$ can be fully oxidized to $^*\text{O}$ at higher potential, yet it is beyond the interest of the ORR.

3.2.4 Activity-controlling factors

On the basis of the results presented above, we now consider which parameters are most important in determining ORR activity of Pt(111) in alkaline solution. This topic has been extensively studied in acid solutions, where either the $^*\text{O}^{21, 83, 88, 90-92}$ or $^*\text{OH}$ binding energy^{24, 87-88, 93} are selected as a descriptor to capture the difference in the ORR activity of one catalyst to the next. The strong O/OH-Pt(111) interaction can make proton and electron transfer to $^*\text{O}$ or $^*\text{OH}$ very difficult, which is the major cause for the high overpotential” of the ORR in acid

solution. Slightly weaker binding, ~ 0.2 eV for $\ast\text{O}$ or ~ 0.1 eV for $\ast\text{OH}$, is predicted to promote the ORR activity of Pt, though over-weakening should also be avoided to allow the facile formation of $\ast\text{OOH}$.^{21, 87, 93}

In the present study, sensitivity analyses were carried out, where each parameter in the KMC model was shifted by a small amount from its original value and the other parameters were kept constant.⁹⁴⁻⁹⁶ Such analyses enable the identification of the key steps that control the activity. Here, we shifted the binding energy of each reaction intermediate by less than 0.2 eV, which in turn varied ΔG . For the steps involving electron transfers, the E_a was estimated according to the BEP relationship as indicated Section 3.2.1. For the potential-independent surface reactions, E_a was determined based on the established relationship between ΔG and E_a for each step (Figure S3b). Two intermediates, $\ast\ast\text{O}_2$ and $\ast\text{OH}$, were found to change the profile of the polarization curve significantly with small shifts (< 0.2 eV) in binding energy. Variations in the binding of $\ast\ast\text{O}_2$ affect the initial current density, rather than the onset potential. When the Pt- O_2 interaction is decreased by 0.2 eV, a reduction in the current density (~ 4 mA/cm², Figure 8a) is observed. Such weakening limits the sticking of O_2 on the surface and therefore the ORR activity. When decreasing the $\ast\ast\text{O}_2$ binding energy by less than 0.2 eV or increasing the binding up to 0.2 eV, the O_2 adsorption is no longer the activity-controlling step and no obvious change in polarization curve is observed. By comparison, the effect of $\ast\text{OH}$ binding on the shift of polarization curve is much more significant, which in particular affects the onset potential. If the $\ast\text{OH}$ binding is weakened by only 0.1 eV, the onset is shifted to higher potential by 0.1 V, while the strengthened $\ast\text{OH}$ binding by 0.1 eV leads to a decreased onset by 0.1V (Figure 8b). Such a small variation in $\ast\text{OH}$ binding energy (0.1 eV) affects only the current-contributing step, $\ast\text{OH}$ removal, along the dominant $\ast\text{H}_2\text{O}$ -mediated mechanism. Consequently, the polarization curve responds the most sensitively to the $\ast\text{OH}$ binding energy. Overall, the sensitivity analysis indicates that to facilitate the ORR activity of Pt(111) in alkaline solution, a good promoter should be able to weaken Pt-OH binding and accelerate $\ast\text{OH}$ removal, while still allowing the stabilization and reaction of $\ast\ast\text{O}_2$. Ideally, the binding of $\ast\text{OH}$ and $\ast\ast\text{O}_2$ should be tuned differently; weakening OH binding should be accompanied with a small weakening or a strengthening in $\ast\ast\text{O}_2$ binding. For catalysts which only have one kind of active sites on the surface, $\ast\text{OH}$ and $\ast\ast\text{O}_2$ binding always vary together, e.g., comparing one metal surface to the

next.²¹ As an alternative, multifunctional catalysts might be able to provide various active sites that allow heterogeneous tuning of *OH and **O₂ binding.

4. Conclusion

Combined DFT calculations and KMC simulations were performed to understand the mechanism of the ORR on Pt(111) in alkaline solution. Our KMC simulations based on extensive DFT calculations allowed well description of the experimentally measured polarization curve from 0.20 V to 0.95V with basically only one fitting parameter associated with the performance at low potential (< 0.4 V). At the mechanistic level, the calculations also revealed several aspects of the surface chemistry which strongly impact the ORR kinetics on Pt in alkaline solutions. Firstly, our results show that the inclusion of water is necessary for predictive modeling. The intermediates involved in the ORR are stabilized to different extents by interacting with environmental water molecules via hydrogen bonds. One bilayer of water is found to be a good compromise; specifically, one bilayer is able to provide sufficient water molecules to describe solvation effects close to the surface with reasonable computational cost. Secondly, we find that the *OH coverage, the most abundant intermediate on the surface, strongly impacts the binding of other intermediates and therefore, the ORR rate. Thirdly, chemisorbed *H₂O on the surface is essential as it acts as the reducing agent for **O₂ and *O. The *H₂O-mediated 4e⁻ transfer mechanism, which dominates the overall ORR, involves mostly potential-independent surface reactions with only the final removal of *OH from the surface as OH_{aq}⁻ contributing to the current. By comparison, the contributions from other 4e⁻ transfer mechanisms (associative and dissociative), which are typically used to describe the ORR in acid solution, as well as the 2e⁻ transfer mechanism only at low potential (< 0.4 V) are much less. Finally, sensitivity analyses show that the binding of *OH and **O₂ are the key factors to tune the ORR activity on Pt(111). A good promoter should be able to weaken the Pt-OH bond and prevent the buildup of *OH, while still interacting with O₂ well enough to enable the ORR. The results of this study not only provide a mechanistic foundation for understanding experimental observations of ORR on Pt in alkaline solution, but also offer specific guidance for future optimization of ORR catalysts.

Supporting Information. Details of binding geometries and binding energies of reaction intermediates as well as reaction free energies and activation barriers of elementary steps involved in the ORR at water/Pt(111) interface. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Figure and Caption

Figure 1. Optimized structures for the adsorption of reaction intermediates, (a) $\ast\text{OH}$; (b) $\ast\ast\text{OOH}$; (c) $\ast\ast\text{O}_2$; (d) $\ast\text{O}$ on Pt(111) covered by 1BL of water (Blue: Pt; red: O; white: H; dashed blue lines: hydrogen bond).

Figure 2. Free energy diagram of the ORR on Pt(111) surface via associative (a), dissociative (b) and $^*\text{H}_2\text{O}$ -mediated (c) mechanisms. The free energy are from DFT calculation under 0V vs. RHE. The black line shows the reaction pathway on bare surface while red, blue and green lines represent the ORR with 1, 2 and 3 bilayers of water, respectively.

Figure 3. Optimized structures for OH adsorption on OH/H₂O-covered Pt(111), where the coverage of OH varied from 1/9 ML (a), 2/9 ML (b) to 1/3 ML (c) (Blue: Pt; red: O; white: O; dashed blue lines: hydrogen bond).

Figure 4. Differential binding energies of *OH (a), **OOH (b), *O (c) and **O_2 (d) as a function of *OH coverage.

Figure 5. KMC-simulated polarization curve and surface coverage for the ORR on Pt(111) in 0.1 M KOH at room temperature. The experimental results were cited from Ref. ⁵¹.

Figure 6. Snapshots of Pt(111) under the ORR in 0.1 M KOH at room temperature on the basis of KMC simulations.

Figure 7. Reaction counts with respect to potential from KMC simulation of the ORR on Pt(111) in 0.1 M KOH at room temperature.

Figure 8. Sensitivity of polarization curve for the ORR on Pt(111) in 0.1 M KOH at room temperature in response to the variation in binding energy of reaction intermediates: $**O_2$ decreased by 0.2 eV (a); $*OH$ increased by 0.1 eV and reduced by 0.1 eV (b).

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