Effects of Oxygen Coverage and Hydrated Proton Model on the DFT Calculation of Oxygen Reduction Pathways on the Pt(111) Surface

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Abstract: DFT calculation is used to study various possible steps in the oxygen reduction reaction (ORR), including the adsorption and dissociation process of O2 and the serial protonation process of dissociated products to form H2O on the Pt(111) surface. By using slabs of different sizes, and different numbers of pre-adsorbed oxygen atoms, the coverage effects on the pathways are investigated. The calculated results using different hydrated proton models are also compared. It is shown that the initial step of the ORR is the formation of a protonated end-on chemisorbed state of OOH*, which can transform to an unprotonated top-bridge-top state of O2* or dissociate into adsorbed O* species with similar activation barrier. The calculated activation barriers for various possible steps at different oxygen coverages suggest that the protonation of O* to form OH* species is the rate-determining step in the ORR. With the increased oxygen coverage, the activation energy of this step decreases. It is found that the use of hydrated proton models more complicated than H2O+, does not change the calculated pathways.

Key words: minimum energy path; ORR mechanism; oxygen coverage; hydrated proton model

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The oxygen reduction reaction (ORR) has long been a model reaction in electrocatalysis. In the mean time, as the cathode reaction in the fuel cells, its sluggish kinetics has become one of the major bottlenecks for improving the efficiency of fuel cells. Pt is so far the best ORR catalyst among various metals. Understanding the ORR mechanism and kinetics on the Pt electrode surfaces is of great significance in designing efficient cathode catalysts for fuel cells. Therefore, the ORR on the Pt surfaces has been a research focus of recent experimental and theoretical studies.

Despite of extensive studies during the last a few decades, the atomic level mechanism of the ORR on Pt is still unclear in several aspects. Earlier experimental studies of the ORR on Pt electrodes in acid solutions exhibited a reaction order of ca. 1.0 with respect to O2 and a Tafel slope of ca. 120 mV · decade−1 in the potential range where the Pt surface is practically free of chemisorbed oxygen. Accordingly, the first proton-coupled charge transfer and proton transfer reaction, namely, O2 + H+ + e → OOH‡, was proposed as the rate-determining step (rds)31. However, the measurement by Neyerlin et al.41,41,42 using Pt/C catalyst in the cathode of a fuel cell showed that the full description of ORR kinetics in the potential range relevant to fuel cell operation should be based on a
constant Tafel slope of 60 mV·decade⁻¹ and a reaction order of 0.5 with respect to oxygen molecule. They therefore conjectured that the rds in the ORR may be the electron and proton transfers to the adsorbed hydroxyl (OH_ads) or oxygen atom (O_ads), namely, \( O_{ad} + H^+ + e^- \rightarrow OH_{ad} \) or \( OH_{ad} + H^+ + e^- \rightarrow H_2O \). Lately, Wang and her colleague[16] analyzed the 4-electron ORR on the Pt(111) surface in an acid medium with an intrinsic kinetic equation using free energies of activation and adsorption as the kinetic parameters. The model fitting to experimental data suggested that the 4-electron ORR on Pt is desorption-limited because the dissociative adsorption is facile, while O and OH are strongly trapped on the surface. Above the reversible potential for the O and OH transition, the O coverage is high, causing severe inhibition of the ORR activity. As O coverage falls with decreasing potential, the kinetic current increases with the lowering the reductive desorption activation barrier and increasing OH coverage. Thus, ORR mechanism is strongly coverage-dependent.

In recent years, the ab initio calculations become a necessary and valuable alternative for unveiling the molecular mechanism of the ORR due to the essential inaccessibility of electrode/electrolyte interface to low temperature and ultrahigh vacuum conditions using various surface science techniques. Based on density functional theory (DFT) calculations, the ORR pathways including the adsorption and dissociation of \( O_2 \) were first investigated by Anderson and his colleagues[5] with a dual-Pt-atom cluster representing the electrode and a hydrated hydronium cluster of \( H_2O_3^+ \) to model the acidic solution, and by Hyman and Medlin[6] who used a Pt(111) periodical slab to model the electrode and a \( H_2O_2^+ \) cluster to model the acid solution. These two studies both showed that top-bridge-top adsorption between two Pt atoms is the most favored adsorption state for \( O_2 \) in the presence of hydrated hydron ion, which seemed to support Yeager’s proposition[12] that bridge molecular adsorption is necessary for the direct 4-electron reduction of \( O_2 \). These theoretical calculations suggested different rds for the ORR, namely, the formation of OOH[5] and the dissociation of OOH*[6]. The ab initio molecular dynamic (MD) simulations using a \( H_2O_3^+ \) hydronium cluster as the proton model by Wang and Balbuena[7] showed that the proton transfer occurs accompanying the adsorption of \( O_2 \) molecule, forming an end-on OOH* intermediate which can dissociate with negligible activation barrier. However, the research results have shown that the Pt-based alloy catalysts binding atomic oxygen more weakly have better ORR activity, which seemingly can not be well accounted for the views that the rds of ORR is the formation of OOH* or its dissociation.

Recent DFT calculation studies on the ORR have been focused on treatments of the potential and solvent. By incorporating more complicated solvent model, the DFT calculations by Yao et al.[13] showed that the OH formation is the rds in Pt-catalyzed ORR, whereas the results by Nørskov et al. suggested that the process of OH reduction to \( H_2O \) molecule is the potential determining step for ORR using DFT calculations[10]. In the meantime, the DFT-calculated results by Yao et al. also showed that the barrier of rds is oxygen-coverage dependent, and the barrier decreases as oxygen increases[10]. Recent ab initio calculations studies of ORR by Neurock et al.[14] and by Liu et al.[15] are also worthwhile to mention. In these two studies, the authors have attempted to incorporate the influence of electrode potential in DFT calculations on the activation barriers of possible steps in ORR by adding charge to reaction systems. The optimal electrochemical reaction paths were determined kinetically under the specific electrode potential, in which the proton-coupled \( O—O \) bond breaking, i.e. \( \frac{1}{2}H^+ + e^- + O_{2ad} \rightarrow O_{ad} + OH_{ad} \) channel, is identified as the major mechanism for ORR on Pt catalyst.

Despite numerous theoretical studies, the detailed electrocatalytic mechanisms for ORR on the Pt(111) surface remains unclear and various conclusions have been drawn in different studies. It remains a great challenge so far for electrochemists to formulate the entire steps for Pt-catalyzed ORR due to a number of key questions that remain. In the existing theoretical
Calculation studies on ORR mechanisms, different solvation and hydrated proton models have been used to mimic an acid medium, which may affect the calculated results. Additionally, the coverage effect of the oxygenated species has not been adequately considered. In present paper, we would like to highlight the effects of oxygen coverage and hydrated proton model on DFT calculations of ORR pathways through performing detailed calculations on the geometric structural optimization and the minimum energy path analysis, including the adsorption and dissociation process of \( \text{O}_2 \) and the serial protonation process of dissociated products to form \( \text{H}_2\text{O} \) on the Pt(111) surface. In addition, the effect of solvation is also considered by adding explicit water molecules on hydrated hydronium ion model.

1 Models and Methods

Calculations were performed in the framework of DFT on periodic super-cells, using the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) functional\(^{[20]} \) for exchange-correlation and ultrasoft pseudopotentials\(^{[21]} \) for Nuclei and core electrons. The Kohn-Sham orbitals were expanded in a plane-wave basis set with a kinetic energy cutoff of 30 Ry and the charge-density cutoff of 300 Ry. The Fermi-surface effects have been treated by the smearing technique of Methfessel and Paxton, using a smearing parameter of 0.02 Ry\(^{[22]} \). The PWSCF codes contained in the Quantum ESPRESSO distribution were used to implement all calculations\(^{[23]} \), while figures of the chemical structures were produced with the XCRYSDEN graphical package\(^{[24-26]} \).

In all calculations, we used (2×2) three-layer and (3×3) four-layer fcc(111) slabs with theoretical equilibrium lattice constant of 0.399 nm (Pt) to model the Pt(111) surface, which is well consistent with experimental equilibrium lattice constant of 0.3923 nm (Pt). Brillouin-zone (BZ) integrations were performed with the special-point technique, using (4×4) and (3×3) uniformly shifted k-meshes for (2×2) and (3×3) slabs, respectively. Vacuum layers of 1.6 nm in thickness were added above the top layer of slabs in all cases. The Pt atoms in the bottom two layers were fixed at the theoretical bulk positions, whereas the top layer on (2×2) three-layer slabs and top two layers on (3×3) four-layer slabs were allowed to relax and all the other structural parameters had been optimized so as to minimize the total energy of the system. Structural optimization was performed until the Cartesian force components acting on each atom were brought below \( 10^{-3} \) Ry \( \cdot \) Bohr\(^{-1} \) and the total energy converged to within \( 10^{-5} \) Ry with respect to structural optimization.

The climbing image nudged elastic band method (CI-NEB) was employed to locate the saddle points and minimum energy paths (MEPs)\(^{[27-29]} \). The transition state images from the NEB calculations were optimized using the quasi-Newton method, which minimizes the forces to find the saddle point. Geometry optimization was performed for each intermediate point in MEPs, in which the bottom two layers of metal atoms were fixed while the top layer of metal atoms and all other nonmetal atoms were allowed to relax.

2 Results and Discussion

2.1 Adsorption and Dissociation of \( \text{O}_2 \) in the Presence of Hydrated Proton

1) Effects of O Coverage

The adsorption and dissociation of \( \text{O}_2 \) on the (2×2)-Pt(111) surface have been investigated by \textit{ab initio} DFT calculations in our previous work using hydronium ion \( \text{H}_2\text{O}^+ \) as a model of solvated proton in acid solution\(^{[28-30]} \). The results indicated that \( \text{O}_2 \) first forms a metastable end-on chemisorption state OOH in the presence of hydrated hydronium, which can transform to a stable unprotonated top-bridge-top (t-b-t) molecular chemisorption state or dissociate directly into O and OH species in nearly nonactivated processes. To evaluate the effects of oxygen coverage and hydrated proton model on the DFT calculations of ORR pathways, we investigated first the adsorption and dissociation process of \( \text{O}_2 \) molecule on the (3×3)-Pt (111) surface in the presence of hydrated hydronium ion \( \text{H}_n\text{O}_y^+ \). Similar to the (2×2)-Pt(111) /\( \text{O}_2/\text{H}_n\text{O}_y^- \) system, physisorption and two molecular chemisorption (one having a tilted end-on configura-
tion and the other one having a top-bridge-top bridge configuration) states, respectively, were also identified for (3×3)-Pt(111)/O₂/H₂O₄ system through geometry optimizations (Fig. 1A-C). However, it was found that the dissociation of O₂ formed two adsorbed O atoms at fcc hollow site of Pt surface, rather than an O and an OH as did in (2×2)-Pt(111)/O₂/H₂O₃ system. This indicated that the oxygen coverage and the model of hydrated hydronium impact the dissociation.

Tab. 1 gives the geometric and energetic parameters for various adsorption states of (3×3)-Pt(111)/O₂/H₂O₄ system. The corresponding value of (2×2)-Pt(111)/O₂/H₂O₃ system is also given for comparison. The physisorption state had negligible change in O-O bond length compared with the isolated O₂ molecule, and that the O-O bond length and the distance between Pt and O₂ of two chemisorption states on the (3×3)-Pt (111) surface are consistent with that on the (2×2)-Pt(111) surface. According to the values of the adsorption energy $E_{ad}$,[28-30] the top-bridge-top chemisorption state represents the most stable molecular adsorption state. The energy difference between end-on chemisorption state and the physisorption state is $-0.31$ eV, and it is $-0.57$ eV between top-bridge-top chemisorption state and the physisorption state in (2×2)-Pt(111)/O₂/H₂O₃ system, whereas corresponding energy differences in present system are $-0.64$ eV and $-0.92$ eV, respectively. The results showed that the reaction energy between the chemisorption state and the physisorption state is more negative under low oxygen coverage. Based on

![Various geometric configurations of (3×3)-Pt(111)/O₂/H₂O₄ system: A. the optimized physisorption state; B. the optimized end-on chemisorption state; C. the optimized top-bridge-top chemisorption state; D. the dissociative atomic chemisorption state.](image)

Tab. 1. The geometric and energetic parameters for various adsorption states of (2×2)-Pt(111)/O₂/H₂O₃ and (3×3)-Pt(111)/O₂/H₂O₄ systems

<table>
<thead>
<tr>
<th>System</th>
<th>Adsorption state</th>
<th>$R_{P/O}/\text{nm}$</th>
<th>$R_{OC/\text{nm}}$</th>
<th>$R_{O/O}/\text{nm}$</th>
<th>$E_{ad}/\text{eV}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2×2)-Pt(111)/O₂/H₂O₃</td>
<td>Physisorption</td>
<td>0.348</td>
<td>0.124</td>
<td>0.210</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>End-on chemisorption</td>
<td>0.204</td>
<td>0.134</td>
<td>0.131</td>
<td>-0.31</td>
</tr>
<tr>
<td></td>
<td>Top-bridge-top chemisorption</td>
<td>0.194</td>
<td>0.144(0.141)$^*$</td>
<td>0.179</td>
<td>-0.57</td>
</tr>
<tr>
<td>(3×3)-Pt(111)/O₂/H₂O₄</td>
<td>Physisorption</td>
<td>0.392</td>
<td>0.126</td>
<td>0.150</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>End-on chemisorption</td>
<td>0.204</td>
<td>0.134</td>
<td>0.134</td>
<td>-0.64</td>
</tr>
<tr>
<td></td>
<td>Top-bridge-top chemisorption</td>
<td>0.195</td>
<td>0.142(0.142)$^*$</td>
<td>0.164</td>
<td>-0.92</td>
</tr>
</tbody>
</table>

$^*$ The values in parenthesis are O-O bond length of top-bridge-top state considering solvent effect, which is consistent in the presence or absence of bilayer structure of H₂O molecule, indicating little solvent effect on geometry structure of chemisorption state.
the Brønsted-Evans-Polanyi (BEP) relationship\(^{[31]}\), the reaction energy becomes more negative, the activation energy will be predicted to be smaller, which will be validated by a subsequent MEP analysis.

Fig. 2 shows the MEPs for the formation of the most stable top-bridge-top molecular chemisorption state and its dissociation in the (3\times3)-Pt(111)/O\(_2\)/H\(_2\)O\(_4^+\) system. It can be seen that the physisorption state is separated from the top-bridge-top chemisorption state by an activation barrier of ca. 0.02 eV, and the subsequent dissociation of the top-bridge-top adsorbed O\(_2\) requires an activation energy of ca. 0.15 eV, both of which are smaller than the value of corresponding process in the (2\times2)-Pt(111)/O\(_2\)/H\(_2\)O\(_4^+\) system\(^{[31]}\). These results indicated that the adsorption and dissociation may be more easily to occur under low oxygen coverage.

![Image](https://via.placeholder.com/150)

**Fig. 2** The minimum energy paths for the transformations from physisorbed O\(_2\) to the chemisorbed molecular O\(_2\) of top-bridge-top configuration and the subsequent dissociation of the top-bridge-top adsorbed O\(_2\) in the presence of hydrated proton H\(_2\)O\(_4^+\).

It can be found in Fig. 2 that there is an end-on adsorbed state in the process of forming top-bridge-top chemisorption state in the (3\times3)-Pt(111)/O\(_2\)/H\(_2\)O\(_4^+\) system. Fig. 3 gives more meticulous MEPs for the formation of the most stable top-bridge-top molecular chemisorption state from physisorption state via end-on intermediate. It can be seen that a relatively level region is formed in the middle of the energy path, which is both preceded and followed by a continuous energy falling section, as observed in the (2\times2)-Pt(111)/O\(_2\)/H\(_2\)O\(_4^+\) system. The occurrence of such an energy plateau in MEP infers that a relatively stable intermediate state is involved in course of the formation of top-bridge-top chemisorption state on the (3\times3)-Pt(111) surface. As indicated by the given geometric configurations for the intermediate points along MEP in Fig. 3, the states associated with the energy plateau are very similar to the end-on chemisorption state obtained in geometry optimization of (3\times3)-Pt (111)/O\(_2\)/H\(_2\)O\(_4^+\) system (Fig. 1B). The activation barrier for the transformation of end-on state to top-bridge-top state is ca. 0.05 eV.

![Image](https://via.placeholder.com/150)

**Fig. 3** The minimum energy paths for the transformations from physisorbed O\(_2\) to the top-bridge-top adsorbed O\(_2\) via the chemisorbed molecular O\(_2\) of end-on configuration in the presence of hydrated proton H\(_2\)O\(_4^+\).

We also performed MEP analysis for direct dissociation of the end-on chemisorption state. As shown in Fig. 4, the activation barrier for this transformation is ca. 0.20 eV, which is very close to that for the dissociation of the top-bridge-top state. Thus, it is possible that the end-on chemisorption state may undergo a direct dissociation pathway.

In order to further examine the effect of oxygen coverage on ORR pathways, taking adsorption process of O\(_2\) molecule as an example, the MEP analysis was performed for the transformation from physisorption state to top-bridge-top chemisorption
state on the (3×3)-Pt(111) surface with different numbers of pre-adsorbed oxygen atoms (O) in the presence of hydrated hydronium ion $\text{H}_3\text{O}^+$, as shown in Fig. 5. It can be seen that the reaction energy and activation barrier for this transformation change little when O coverage is 1/3 ML as compared with that on the (3×3)-Pt(111) surface without adding pre-adsorbed oxygen atoms. The activation barrier and the reaction energy show obvious changes only when oxygen coverage is increased to 5/9 ML. The values of -0.61 eV and 0.085 eV at this coverage are very close to that obtained on the (2×2)-Pt(111) surface (-0.61 eV and 0.13 eV respectively). This suggests that the change of slab size somewhat can mimic the effect of changing pre-adsorbed O in the calculation when investigating the oxygen coverage effect.

It should be pointed out that the electrode potential and proton concentration will be changed by using a different slab size. Moreover, along the reaction coordinate in Figs. 2-5, the electrode potential and proton concentration are not constant. So far, it remains a great challenge to perform MEP under constant potential control. Recently, Neurock et al.\textsuperscript{[16]} and Liu et al.\textsuperscript{[17]} have treated the effect of electrode potential in DFT calculations of electrochemical reaction paths by changing charge of reaction systems. The activation barriers in each reaction step were calculated under different charges and the optimal electrochemical reaction paths were determined under the charges which give same work function. This represents a significant advancement in modeling surface electrochemical processes. However, the results from this work function method remain of semi-quantitative significance when they are related to the experiments. First, the work function calculation of solvated surfaces in DFT frame is largely affected by the solvation conditions. In addition, it has considerable uncertainty when transferring the calculated work function to potential of hydrogen electrode scale since the exact work function of the latter is differently reported in the literature, from 4.4 eV to 4.8 eV. Therefore, attempt is not made to correct the varied potential effect in the present calculation. This makes the calculated activation barriers and reaction energies not quantitatively significant. However, they should still give the useful information on the sites and configuration for $\text{O}_2$ adsorption at the Pt/electrolyte interface, and the possible pathways of ORR and the effect of oxygen coverage. In addition, the similar adsorption intermediates obtained on slabs of different sizes suggest that the intermediate structures in ORR are not affected significantly by the proton concentration in acid media.

2) On the Use of Different Hydrated Proton Models
Ab initio molecular dynamics simulations indicate that two limiting proton structures exist: the Zundel structure \( (\text{H}_3\text{O}_2^-) \)\(^{32}\) and the Eigen structure \( (\text{H}_9\text{O}_4^+) \)\(^{33}\), and numerous other proton structures exist between these two limits\(^{34}\). The rationality of using \( \text{H}_2\text{O}^+ \cdots (\text{H}_2\text{O})_n \) cluster \( \text{H}_2\text{O}^+ \) to represent the solvation of proton in solution had been verified by the equilibrious structures of super-cell systems of Pt(111) /\( \text{H}_2\text{O}^+ \cdots (\text{H}_2\text{O})_n \) and Pt(111)/\( \text{O}_2\text{H}_2\text{O}^+ \cdots (\text{H}_2\text{O})_n \), with \( n \) varying from 0 to 3 in our recent report\(^{29}\), in which the proton can be reduced or specifically adsorbed on an uncharged Pt surface at Pt(111)/\( \text{H}_2\text{O}^+ \) interface, and the spontaneous proton transfer from the hydronium ion to Pt(111) surface can be prevented by replacing \( \text{H}_2\text{O}^+ \) with the Zundel cluster \( \text{H}_2\text{O}^+ \cdots \text{H}_2\text{O} \), \( \text{H}_2\text{O}^+ \cdots (\text{H}_2\text{O})_n \), and Eigen cluster \( \text{H}_2\text{O}^+ \cdots (\text{H}_2\text{O})_n \), implying that these hydrated hydronium ion can stabilize the proton at Pt/solution interface, whereas in geometry optimizations of Pt(111)/\( \text{O}_2\text{H}_2\text{O}^+ \cdots (\text{H}_2\text{O})_n \) systems, for \( \text{H}_2\text{O}^+ \cdots \text{H}_2\text{O} \), the optimization leads to a proton transfer from core hydronium ion to the chemisorbed oxygen molecule, forming a stable chemisorption state of bridge OOH\(^*\). This means that the Zundel cluster alone cannot stabilize the hydronium ion at \( \text{O}_2\text{H} \)-adsorbed Pt/solution interface. To perform DFT calculations on these systems, a positive charge is introduced to the super-cells to form a hydrated proton. In the mean time, a homogeneous negative background charge of the same amount will be imposed automatically into the super-cells so that the entire periodic super-cell remains neutral to avoid the divergence of Coulomb energy. It is known that the background charge will distort the distribution of electrostatic potential in the system and makes contribution to the DFT total energy. However, the geometric structures of the adsorbates at/near slab surface would not be substantially affected since the background charge mainly affects the potential distribution in the vacuum region\(^{35}\).

A question may be asked whether the positive charge is added to the hydrated proton or it is distributed uniformaly in the super-cell. We have performed the Löwdin charge analysis on an isolated \( \text{H}_2\text{O}^+ \) and the Pt(111)/\( \text{H}_2\text{O}^+ \) system. It was found that the Löwdin charge of \( \text{H}_2\text{O}^+ \) in Pt(111)/\( \text{H}_2\text{O}^+ \) system is ca. 23.7733 electrons, which is very close to the calculated Löwdin charge for the isolated \( \text{H}_2\text{O}^+ \) (23.7667 electrons). This makes us believe that the charge will be added to the hydrated proton, which will be energetically more favored than uniformly distributing the charge in entire super-cell system.

The adsorption property of the surface species forming hydrogen bond with \( \text{H}_2\text{O} \) molecules can be affected by solvent environment\(^{36-37}\). Thus, in present study, we consider the solvent effect on hydrated proton model. The most accurate way of including the effect of water is to explicitly add water molecules with sufficient quantity into the simulations. At temperatures and pressures relevant for an electrochemical experiment, the water-containing electrolyte will be liquid. However, since in this context we are mainly interested in the effect of different hydrated ion models on DFT calculation of ORR pathways and not so much the actual structural of liquid water itself, we can probably simplify the problem by additionally adding a water bilayer around the hydrated proton. The water bilayer on Pt(111) has been used extensively in DFT calculation study of surface electrochemical processes\(^{37-38}\). The advantage of using the bilayer structure of \( \text{H}_2\text{O} \) molecules to model solvent effect lies in that the model only requires limited amounts and well-defined structure of \( \text{H}_2\text{O} \) molecules. However, it should be pointed out that it is still not clear whether the water bilayer structure is thermodynamically stable or not at temperatures and pressures relevant for an electrochemical experiment\(^{39}\).

In order to further confirm the stability of bare \( \text{H}_2\text{O}^+ \), we added additional bilayer structure of \( \text{H}_2\text{O} \) molecules in Pt(111)/\( \text{H}_2\text{O}^+ \) system in present study. As shown in Fig. 6A, the geometry optimization of “Pt/\( \text{H}_2\text{O}^+ \)” system produces similarly an adsorbed hy
drogen and a water molecule on the Pt(111) surface, such an instability of the bare H$_2$O$^+$ at Pt(111)/H$_2$O$^-$ interface was also shown by Hyman and Medlin\cite{[8]}. This seems to imply that the bare H$_2$O$^+$ is instable even if the presence of bilayer structure of H$_2$O molecules, namely, using the bare H$_2$O$^+$ to simulate hydrated hydronium ion is inappropriate. A top-bridge-top configured chemisorption state of O—O$^*$ is obtained without obvious proton transfer occurring via the geometry structure optimization of Pt (111)/O$_2$/H$_2$O···(H$_2$O)$_n$ with $n$ varying from 1 to 3 in the presence of bilayer structure of H$_2$O structure (as shown in Fig. 6B-D), indicating that H$_2$O$_2^+$, H$_3$O$^+$, and H$_5$O$_4^+$ all can stabilize the proton therein.

However, the dissociation adsorbed state obtained from H$_5$O$_4^+$ is inconsistent with that obtained from H$_2$O$_3^+$ and H$_3$O$^+$. Adsorbed O atom at fcc hollow site and adsorbed OH species at top site are formed on the Pt(111) surface when using H$_5$O$_2^+$ model (as shown in Fig. 7A), whereas two adsorbed O atoms are obtained at fcc hollow sites when using H$_2$O$_3^+$ or H$_3$O$^+$ (as shown in Fig. 7B-C). Therefore, proton cannot be stabilized by H$_5$O$_2^+$ model even if considering additional solvent effect. These results provide further support for the rationality to use H$_2$O$_3^+$ and H$_5$O$_4^+$ to represent the hydration interaction of proton in acid solution for DFT calculation of ORR pathways.

The effect of hydrated proton model on DFT calculations of ORR pathways on the Pt(111) surface was further validated. Similarly, taking adsorption process of O$_2$ molecule as an example, the MEP analysis was performed for the transformation from physisorption state to the chemisorbed molecular O$_2$ of top-bridge-top configuration on the (2×2)-Pt(111) surface in the presence of hydrated proton H$_n$O$_4^+$, which has been studied using hydrated proton model H$_n$O$_4^+$ in our previous paper\cite{[28,30]}. As shown in Fig. 8, the reaction energy and activation barrier when using hydrated proton H$_n$O$_4^+$ are ca. -0.68 and 0.084 eV, respectively, which are very close to the value of corresponding process when using hydrated proton H$_n$O$_4^+$.

Thus, the results provide further support for the rationality to use H$_n$O$_4^+$ and H$_n$O$_4^+$ to represent the hydrated proton model in acid solution for studying the ORR pathways based on DFT calculation, and the effect of both these hydrated proton models on DFT calculations of ORR pathways is not significant. In the mean time, we scrutinize carefully the MEP, and an intermediate of end-on chemisorption state was found. Thus, the result also supports the conclusion of the above analysis that a relatively stable end-on adsorbed intermediate is formed in course of the formation of top-bridge-top chemisorption state. Additionally, the reaction energy and activation barrier on the (2×2)-Pt(111) surface when using hydrated proton H$_n$O$_4^+$ are also very close to that of corresponding process on the (3×3)-Pt(111) surface with oxygen.

![Fig. 6 The optimized structures of chemisorption state of Pt(111)/H$_2$O$^+$ and Pt(111)/O$_2$/H$_2$O···(H$_2$O)$_n$ super-cell systems in the presence of the H$_2$O bilayer: A. H$_2$O$^+$; B. H$_2$O$_2^-$; C. H$_3$O$^+$; D. H$_5$O$_4^+$-O$_2$](image-url)
Based on above analysis and our previous report, the results may be able to give two possible four-electron ORR pathways on the (2×2) and on the (3×3)-Pt(111) surfaces, respectively, see Tab. 2. However, these ORR pathways may be not accurate completely due to the drawbacks of computational methods. In these both ORR pathways under different oxygen coverages, the chemisorbed state dissociated to form O and OH species under high oxygen coverage, whereas two dissociative adsorbed O atoms were formed under low oxygen coverage. The reason for the difference may lie in that high oxygen coverage makes O atoms more attractive to hydrated hydronium ion, thus leading to the formation of OH species.

The activation barriers of each step in both ORR pathways are also summarized in Tab. 2. It can be seen that the O atoms protonation formed OH species on the Pt(111) surfaces under different oxygen coverage and hydrated proton model, which can explain well why Pt-based alloy catalysts of weak adsorbed oxygen species were excellent ORR catalysts. Recently, Nørskov et al. [41] theoretically and experimentally investigated metallic ORR catalysts made from alloys. The results demonstrated that new and excellent ORR electrocatalytic materials such as Pt5Sc and Pt3Y alloys can be found, and that theoretical work can effectively support the search for improved catalytic materials, in which the oxygen species are more weakly adsorbed onto Pt5Sc and Pt3Y alloys than on pure Pt surface. Regarding other Pt-based alloy catalysts binding atomic oxygen more weakly, calculations have also predicted that PtM (M = Fe, Co, Ni, etc.) alloys should have higher catalytic activity than pure Pt, which has also been experimentally proven [40, 42-46].

Comparison in the activation barriers of the ORR pathways showed that the adsorption and dissociation process of O2 molecule may easily occur by the thermo-active process regardless of being high or low oxygen coverage although the activation barriers for O2 adsorption and dissociation on the (2×2)-Pt(111) surface are slightly higher than those on the (3×3)-Pt(111) surface. For the serial protonation process of the dis

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**2.2 Serial Protonation of Dissociative Products**

The abovementioned results indicate that the adsorption and dissociation process is almost non-activated on the (3×3)-Pt(111) surface. In order to validate the degree of difficulty in dissociative products further reduction, we performed MEP analysis for the protonation of O and OH species using Cl-NEB method, respectively. As shown in Fig. 9, the activation barriers need to be overcome by O protonation to form OH and by OH protonation to form H2O are 0.85 and 0.07 eV, respectively. This finding indicated that the activation barriers of these two protonation processes are higher than those of adsorption and dissociation process as previously mentioned.

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**Fig. 7** The optimized structures of dissociation adsorbed state of Pt(111)/O2/H2O⋯(H2O)n super-cell systems: A. H4O4-O2; B. H4O4-O2; C. H4O4-O2

**Fig. 8** The minimum energy paths for the transformations from physisorbed O2 to the chemisorbed molecular O2 surface in the presence of hydrated proton H2O4.
Tab. 2 Two possible four-electron ORR pathways on the (2×2) and (3×3)-Pt(111) surfaces

<table>
<thead>
<tr>
<th>Surface</th>
<th>The possible dissociation pathway of $O_2$ Molecule</th>
<th>The possible dissociation pathway of OOH species</th>
<th>Activation barrier/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2×2)-Pt(111)/O$_2$H$_2$O$_3^-$</td>
<td>$O_2 \rightarrow O_{ad}$</td>
<td>$O_2 + H^+ + e \rightarrow O_{ad}$</td>
<td>-0.13</td>
</tr>
<tr>
<td></td>
<td>$O_{ad} + H^+ + e \rightarrow O_{ad} + OH_{ad}$</td>
<td>$OOH_{ad} \rightarrow O_{ad} + OH_{ad}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$2OH_{ad} + 2H^+ + 2e \rightarrow 2H_2O_{ad}$</td>
<td>$O_{ad} + H^+ + e \rightarrow OH_{ad}$</td>
<td>0.56</td>
</tr>
<tr>
<td>(3×3)-Pt(111)/O$_2$H$_2$O$_3^-$</td>
<td>$O_2 \rightarrow O_{ad}$</td>
<td>$O_2 + H^+ + e \rightarrow OOH_{ad}$</td>
<td>-0.02</td>
</tr>
<tr>
<td></td>
<td>$O_{ad} \rightarrow O_{ad} + O_{ad}$</td>
<td>$OOH_{ad} \rightarrow O_{ad} + OH_{ad} + e$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$2O_{ad} + 2H^+ + 2e \rightarrow 2OH_{ad}$</td>
<td>$2O_{ad} + 2H^+ + 2e \rightarrow 2OH_{ad}$</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>$2OH_{ad} + 2H^+ + 2e \rightarrow 2H_2O_{ad}$</td>
<td>$2OH_{ad} + 2H^+ + 2e \rightarrow 2H_2O_{ad}$</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Associative products to form H$_2$O molecule, the activation barriers needed to be overcome by O protonation to form OH and by OH protonation to form H$_2$O are 0.56 and 0.29 eV on the (2×2)-Pt(111) surface, respectively. By contrast, the activation barriers of the same processes are 0.85 and 0.07 eV on the (3×3)-Pt(111) surface, respectively, indicating that the protonation process of OH species to form H$_2$O molecule may more easily occur on the Pt(111) surface with low oxygen coverage. However, the activation barriers for the process of O atom protonation to form OH species become larger on the (3×3)-Pt(111) surface. Larger activation energy for this process explains why the chemisorbed state dissociated to form O and OH species on the Pt(111) surface with high oxygen coverage, whereas two adsorbed O atoms are formed on the Pt (111) surface with low oxygen coverage during geometry optimization. Simultaneously, The reason for larger activation energy may be that weaker repulsive interaction among adsorbed O atoms on the Pt(111) surface with low oxygen coverage leads to stronger adsorption of O atoms, thus, it is more difficult for further O protonation to form OH species on the Pt(111) surface with low oxygen coverage compared with that under high oxygen coverage. Additionally, the reaction energy is 0.72 eV for the process of O atom protonation to form OH species on the (3×3)-Pt(111) surface, it is more positive than that of the corresponding process (0.50 eV) on the (2×2)-Pt(111) surface. Based on the BEP relationship, the larger activation energy for this process on the Pt(111) surface with low oxygen coverage could be also explained.
The findings will lead to a deeper understanding of ORR and can provide a theoretical basis for designing Pt-based alloy catalysts of ORR in fuel cells. As reported in our previous work\cite{30}, the effect of zero point energies is insignificant and does not alter the trends of reaction path regardless of being in the gas phase or in the presence of hydrated hydronium ion. Thus, the effect of zero point energies on reaction paths has not been considered in present work.

3 Conclusions

The effects of oxygen coverage and hydrated proton model on the DFT calculations of ORR pathways on the Pt(111) surface have been studied. It is shown that the use of different hydrated proton models does not change the calculated pathways. The formation of aprotinated end-on chemisorbed state of OOH* is likely the first step of ORR on the Pt(111) surface regardless of the oxygen coverage. The MEP calculations on various possible steps suggest that the protonation of O* to form OH* species may be the rds in the ORR regardless of the O* coverage, which may explain why catalysts that bind atomic oxygen more weakly have better ORR activity. With increased oxygen coverage, the activation energy of the rds decreases. Thus, the ORR activity should be strongly coverage-dependent.

References:


基于 DFT 计算的 Pt(111)表面氧覆盖度和水合质子模型对氧还原反应路径的影响

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摘要：利用基于平面波的密度泛函理论(DFT)计算研究了氧气分子在 Pt(111)表面的吸附和解离, 以及解离产物进一步质子化形成H2O的过程。通过使用不同尺寸的平板模型和在表面预吸附不同数量的氧原子, 研究了氧覆盖度对氧还原反应(ORR)路径的影响, 并对使用不同水合质子模型的计算结果进行了比较。研究结果表明：质子化的 end-on 化学吸附态 OOH* 的形成是 ORR 的初步步骤; OOH* 能够转化形成非质子化的 top-bridge-top 化学吸附态 O2*, 或者解离形成吸附的 O* 物种。对于不同氧覆盖度下各种可能步骤的活化能计算结果表明, O* 的质子化形成 OH* 物种是 ORR 的决速步骤。增加氧覆盖度时, 该步骤的活化能减少。此外, 还发现使用比 H2O2更复杂的水合质子模型不会改变计算所得的反应路径。

关键词：最低能量路径; ORR 机理; 氧覆盖度; 水合质子模型