

What Is the Rate-Limiting Step of Oxygen Reduction Reaction on Fe–N–C Catalysts?

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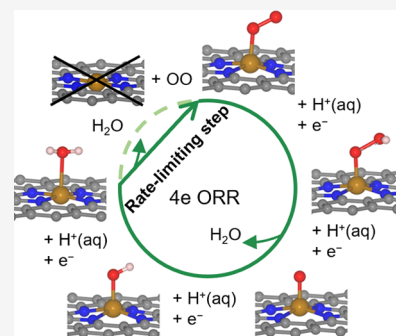


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ABSTRACT: Oxygen reduction reaction (ORR) is essential to various renewable energy technologies. An important catalyst for ORR is single iron atoms embedded in nitrogen-doped graphene (Fe–N–C). However, the rate-limiting step of the ORR on Fe–N–C is unknown, significantly impeding understanding and improvement. Here, we report the activation energies of all of the steps, calculated by ab initio molecular dynamics simulations under constant electrode potential. In contrast to the common belief that a hydrogenation step limits the reaction rate, we find that the rate-limiting step is oxygen molecule replacing adsorbed water on Fe. This occurs through concerted motion of H₂O desorption and O₂ adsorption, without leaving the site bare. Interestingly, despite being an apparent “thermal” process that is often considered to be potential-independent, the barrier reduces with the electrode potential. This can be explained by stronger Fe–O₂ binding and weaker Fe–H₂O binding at a lower potential, due to O₂ gaining electrons and H₂O donating electrons to the catalyst. Our study offers new insights into the ORR on Fe–N–C and highlights the importance of kinetic studies in heterogeneous electrochemistry.



INTRODUCTION

Oxygen reduction reaction (ORR) is essential to a variety of renewable energy technologies such as fuel cells and metal–air batteries. Platinum is the best-performing catalyst for ORR. However, it suffers from high cost, which impedes its commercial use.^{1–4} To overcome this obstacle, tremendous research efforts have been dedicated to finding cost-effective alternative catalysts to Pt.^{5–10} One of the most promising candidates is single iron atoms embedded in nitrogen-doped graphene (Fe–N–C), which is often used in acidic conditions.^{11–18} Despite extensive studies on this catalyst, it is still unknown what step limits the ORR rate on Fe–N–C. The lack of this critical information significantly limits catalyst development.

A commonly suggested pathway for ORR on Fe–N–C has the following steps (Figure 1a): $* + \text{O}_2 \rightarrow *\text{OO}$, $*\text{OO} + \text{H}^+ + \text{e}^- \rightarrow *\text{OOH}$, $*\text{OOH} + \text{H}^+ + \text{e}^- \rightarrow *\text{O} + \text{H}_2\text{O}$, $*\text{O} + \text{H}^+ + \text{e}^- \rightarrow *\text{OH}$, $*\text{OH} + \text{H}^+ + \text{e}^- \rightarrow * + \text{H}_2\text{O}$. Experimental determination of the rate-limiting step is challenging. On the other hand, density functional theory (DFT) offers a means to calculate the reaction energetics, including activation energies, and thus in principle can answer the question about the rate-limiting step. However, directly calculating activation energies of heterogeneous electrochemistry is difficult due to the complexity of the system, which requires careful treatments of the effects of solvation and electrode potential.^{19–29} Therefore, most computational studies calculate the thermodynamics of each step and use it to infer the kinetics, based on the assumption that the most thermodynamically uphill (or the least downhill) step has the highest activation energy. Those

papers typically show that either the $*\text{OO} + \text{H}^+ + \text{e}^- \rightarrow *\text{OOH}$ or the $*\text{OH} + \text{H}^+ + \text{e}^- \rightarrow * + \text{H}_2\text{O}$ step is the thermodynamically limiting step.^{29–36} Both steps involve hydrogenation of the adsorbate. However, thermodynamics does not necessarily correlate with kinetics. Hence, the information on activation energies is indispensable to identify the rate-limiting step.

To address this critical need, here we calculate the activation energies of ORR steps on Fe–N–C, using a recently developed model: “constant-potential hybrid solvation-dynamic model” (CP-HS-DM).²⁰ This model enables effective simulation of electrochemical kinetics at the solid–water interface, by directly including the explicit solvation and electrode potential into the model. The results reveal a different reaction mechanism from the commonly believed one: instead of the hydrogenation step, the rate-limiting step is the replacement of the preadsorbed H₂O molecule by the O₂ molecule on the Fe atom; despite being an apparent “thermal” process, the activation energy of this step decreases with decreasing electrode potential, due to the enhanced Fe–O₂ binding while weakened Fe–OH₂ binding at a lower potential. Our work provides new insights into the ORR and Fe–N–C

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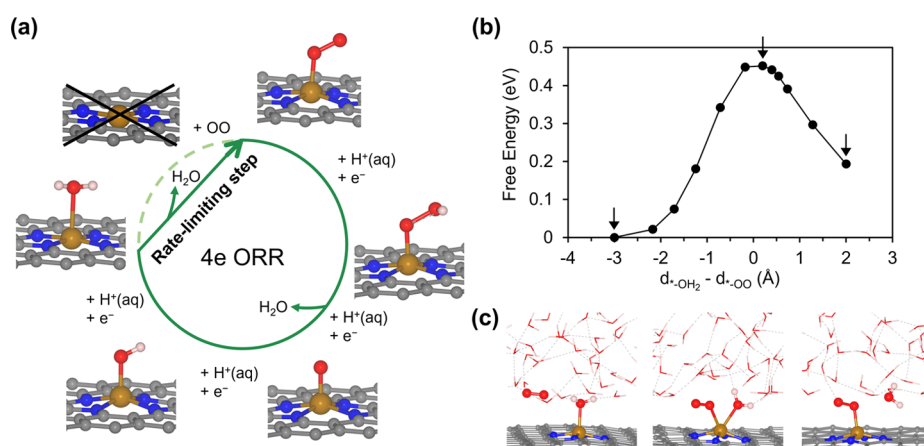


Figure 1. (a) Schematic illustration of the ORR mechanism. (b) Free energy profile of $^*\text{H}_2\text{O} + \text{O}_2 \rightarrow ^*\text{O}_2 + \text{H}_2\text{O}$ at 0.5 V vs SHE. (c) Representative structures chosen from the reaction coordinate values marked by arrows. Brown, blue, gray, red, and white spheres represent iron, nitrogen, carbon, oxygen, and hydrogen atoms, respectively.

catalytic mechanisms and highlights the significance of kinetic information that is generally lacking in the current study of heterogeneous electrocatalysis.

METHODS

The CP-HS-DM²⁰ is one realization of the constant-potential ab initio molecular dynamics (cp-AIMD) with explicit water. The supercell contains a thin film of explicit water molecules on top of the catalyst. The remaining space is filled with implicit solution modeled as a continuous dielectric medium with point ionic charges. This implicit solution serves to balance the extra charges in the explicit region and introduces a region with a flat electrostatic potential profile that can be used to extract the relative electrode potential. The structure is evolved using AIMD with an enhanced sampling technique, and the electron number changes under potentiostat.

In this work, we perform CP-HS-DM simulation using Vienna Ab initio Simulation Package (VASP),^{37,38} leveraging the VASPsol^{39,40} implicit solvation model. We have implemented the cp-AIMD method as a patch to the VASP code (the patch file is available to the readers upon reasonable request). To compute the free energy profile, we employed thermodynamic integration. Specifically, we first run slow-growth simulation⁴¹ to obtain a preliminary profile and then run blue moon simulation^{42,43} to obtain a more accurate one. To model the acidic conditions, we add one H to the explicit water molecules. The details of our calculations can be found in the [Supporting Information \(SI\)](#).

RESULTS AND DISCUSSION

Our study first focuses on $U = 0.5$ V vs SHE because it is within the typical range of working potentials.^{12,44,45} Our cp-AIMD simulations show that when Fe–N–C is in contact with water, a H_2O molecule is adsorbed onto the Fe site. When we intentionally desorb H_2O via slow growth, another H_2O molecule will occupy the Fe site (see [SI Section 3](#)). This result indicates that before ORR, the Fe site is already occupied by a H_2O molecule, consistent with a recent paper.²⁹

Then how does the adsorption of O_2 take place? We find that the adsorption of O_2 occurs concertedly with H_2O desorption. As shown in [Figure 1c](#), as the O_2 in the solvent approaches the Fe to form the Fe–OO bond, it displaces the adsorbed H_2O to break the Fe–OH₂ bond. Eventually, the O_2 replaces the H_2O and becomes adsorbed on the Fe. During this process, the Fe atom remains bonded with the adsorbate(s) (either H_2O or O_2 or both), which lowers the energy cost and results in a barrier of 0.45 eV, as shown in

[Figure 1b](#). Particularly, at the transition state, both H_2O and O_2 are bonded to the Fe site. These results suggest a different reaction mechanism from the commonly accepted one: the steps $^*\text{H}_2\text{O} \rightarrow ^* + \text{H}_2\text{O}$ and $\text{O}_2 + ^* \rightarrow ^*\text{OO}$ steps are not separate; instead, they occur simultaneously and thus should be written together as $^*\text{H}_2\text{O} + \text{O}_2 \rightarrow ^*\text{O}_2 + \text{H}_2\text{O}$ ([Figure 1a](#)).

We further study the subsequent steps, i.e., $^*\text{OO} + \text{H}^+ + \text{e}^- \rightarrow ^*\text{OOH}$, $^*\text{OOH} + \text{H}^+ + \text{e}^- \rightarrow ^*\text{O} + \text{H}_2\text{O}$, $^*\text{O} + \text{H}^+ + \text{e}^- \rightarrow ^*\text{OH}$, and $^*\text{OH} + \text{H}^+ + \text{e}^- \rightarrow ^*\text{OH}_2$. These are electrochemical steps. [Figure 2](#) shows the $^*\text{OOH} + \text{H}^+ + \text{e}^- \rightarrow ^*\text{O} +$

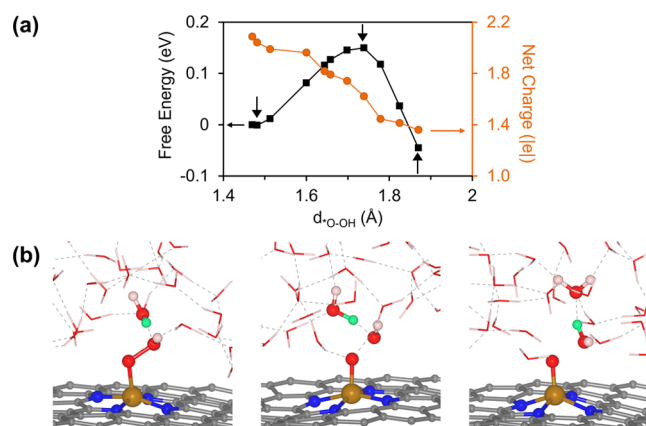


Figure 2. (a) $^*\text{OOH} + \text{H}^+ + \text{e}^- \rightarrow ^*\text{O} + \text{H}_2\text{O}$ free energy profile and net charge evolution at $U = 0.5$ V vs SHE. (b) Representative structures chosen from the reaction coordinate values marked by arrows. The proton transferred to $^*\text{OOH}$ is highlighted in green.

H_2O step as an example. In this step, as the $^*\text{O}$ –OH bond breaks, the proton attacks the generated OH to form H_2O . During this process, the system gradually acquires excessive electron concentrating on the higher O, which attracts the proton closer and facilitates the H_2O formation. Consequently, the barrier is low, only 0.15 eV. It is worth noting that this change in electron number cannot be observed in the conventional constant-charge simulation, thereby necessitating the use of the constant-potential method as we employed here. Additionally, the Fe–N–C surface exhibits a positive charge under 0.5 V. This is because its potential of zero charge (PZC) is lower than 0.5 V. In other words, at a charge-neutral state,

the Fermi level of Fe–N–C is higher than that of the electrode. To align the Fermi levels, Fe–N–C has to lose electrons, thereby acquiring a positive charge. Another interesting finding is that at the initial state, the proton is located closer to the higher O than the lower O in the $^*\text{O}-\text{OH}$ on Fe–N–C. This contrasts the Co–N–C catalyst, where the proton prefers the lower O.²⁰ Therefore, after the proton attacks the closer O, Fe–N–C will generate H_2O , whereas Co–N–C will produce H_2O_2 . This explains the difference in ORR selectivity observed for these two catalysts.

Figure 3 provides a comprehensive summary of the energy barriers for all ORR steps. Note that the $^*\text{O} + \text{H}^+ + \text{e}^- \rightarrow$

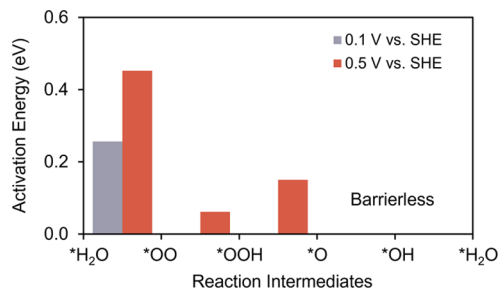


Figure 3. Energy barriers for all of the ORR steps under different potentials.

$^*\text{OH}$ and $^*\text{OH} + \text{H}^+ + \text{e}^- \rightarrow ^*\text{OH}_2$ steps do not have barriers because in our simulations (without geometric constraint), the protons spontaneously diffuse to the adsorbates, completing the steps (see SI Section 5). The comparison shows that the $^*\text{H}_2\text{O} + \text{O}_2 \rightarrow ^*\text{O}_2 + \text{H}_2\text{O}$ step has the highest activation energy and is thus the rate-limiting step. This finding contrasts the common belief based on thermodynamic considerations that the hydrogenation step is rate-limiting.

To check if our conclusion still holds at a lower potential, we also study ORR at $U = 0.1$ V vs SHE. This potential is chosen because it is not too low to be unrealistic but low enough to show a significant difference.^{12,44,45} As shown in Figure 3, we find that all electrochemical steps become barrierless while the $^*\text{H}_2\text{O} + \text{O}_2 \rightarrow ^*\text{O}_2 + \text{H}_2\text{O}$ step still has a barrier of 0.26 eV. Therefore, the rate-limiting step is still $^*\text{H}_2\text{O} + \text{O}_2 \rightarrow ^*\text{O}_2 + \text{H}_2\text{O}$.

It is interesting to see that the activation energy of $^*\text{H}_2\text{O} + \text{O}_2 \rightarrow ^*\text{O}_2 + \text{H}_2\text{O}$ noticeably decreases when the potential is decreased (Figure 3). This challenges the conventional view that it is a thermal step (as it does not explicitly involve electron(s)) and should be potential-independent. To understand the origin, we calculate the adsorption energies of O_2 and H_2O on Fe–N–C under different potentials (without solvent molecules for simplicity). As shown in Figure 4a, decreasing

the potential enhances the O_2 adsorption while weakening the H_2O adsorption. Therefore, the lower barrier at the lower potential can be explained by the stronger driving force provided by the enhanced binding with O_2 and the weakened binding with H_2O .

The potential-induced change in the binding strength can be attributed to different surface charges under different potentials. Our calculations (without solvent for simplicity) show that the bare Fe–N–C acquires ~ 1 electron as the potential decreases from 0.5 to 0.1 V. This large change in the surface charge results in a significant change in the electronic state occupation, thereby altering the chemical reactivity of Fe–N–C.²¹ But why do O_2 and H_2O have opposite responses to the surface charge? This can be explained by the opposite directions of charge transfer. We find that upon adsorption, O_2 gains electrons from Fe–N–C while H_2O donates electrons (see Figure 4b). Increasing the electronic charges on Fe–N–C will enhance the electron transfer to the adsorbate while suppressing the back-transfer. Therefore, reducing the potential strengthens the binding with O_2 while weakening that with H_2O . This mechanism suggests that to design more active sites for ORR, one may target those that are more negatively charged (under the same electrode potential), because they can have lower activation energies for the rate-limiting step of $^*\text{H}_2\text{O} + \text{O}_2 \rightarrow ^*\text{O}_2 + \text{H}_2\text{O}$.

The charge transfer theory also explains the potential dependence of the adsorption energies of other intermediates ($^*\text{OOH}$, $^*\text{O}$, and $^*\text{OH}$). As shown in Figure S9a, the potential decrease enhances their bindings with the catalyst. This can be attributed to the fact that they all gain electrons from the catalyst (Figure S9b).

Although our focus here is on the acidic conditions, as Fe–N–C is mainly used in proton exchange member fuel cells, it is worth considering other pH conditions. For the same RHE potential, the SHE potentials are lower under alkaline conditions than under acid conditions. In other words, the catalyst surface is more negatively charged under alkaline conditions. According to our findings, a more negatively charged site should have a lower barrier for the $^*\text{H}_2\text{O} + \text{O}_2 \rightarrow ^*\text{O}_2 + \text{H}_2\text{O}$ step. On the other hand, the proton source is a water molecule under alkaline conditions and it is more difficult to donate protons than H_3O^+ . Therefore, compared with acidic conditions, we anticipate that in alkaline conditions the $^*\text{H}_2\text{O} + \text{O}_2 \rightarrow ^*\text{O}_2 + \text{H}_2\text{O}$ step will become easier, whereas the hydrogenation steps will become more difficult.

CONCLUSIONS

In this study, we employed an advanced first-principles model to reveal the rate-limiting step of ORR on Fe–N–C. We discovered a new mechanism that O_2 replaces the preadsorbed

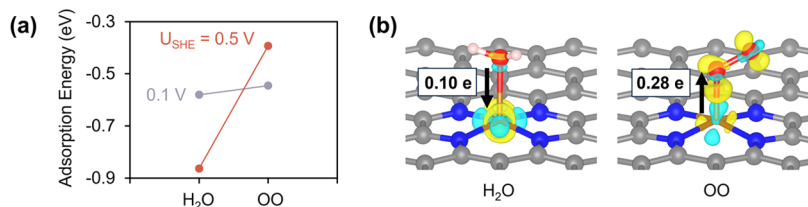


Figure 4. (a) Adsorption energies of H_2O and O_2 on Fe–N–C under different potentials. (b) Isosurfaces of the electronic density change due to the adsorptions. Yellow represents electron accumulation, and cyan represents electron depletion (isovalue = $0.015 \text{ e} \text{ \AA}^{-3}$). The black arrows indicate the directions of the electron transfer, and the numbers show the magnitude of charge transfer using the Bader partition method.

H₂O on Fe through a concerted motion without leaving the Fe site bare. This step was found to have the largest activation energy among the ORR steps. The barrier of this step counterintuitively lowers with decreasing electrode potential, due to the stronger O₂ adsorption and weaker H₂O adsorption when the surface carries more electronic charges. This can be further explained by the fact that O₂ adsorption gains electrons from the surface while H₂O donates electrons to the surface. These results suggest that a more negatively charged site would be more active for the ORR. Our work emphasizes the importance of kinetic information in understanding and designing heterogeneous electrocatalysts.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.3c09193>.

General settings of DFT calculations; details of electronic charge calculation; structure evolution for water adsorption dynamics; details of energy barrier calculations; more reaction kinetics data; and adsorption energies and electronic charge transfer of ORR intermediates (PDF)

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Notes

The authors declare no competing financial interest.

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