Role of Local Carbon Structure Surrounding FeN₄ Sites in Boosting the Catalytic Activity for Oxygen Reduction

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Supporting Information

ABSTRACT: Development of effective nonprecious metal and nitrogen codoped carbon catalysts for the oxygen reduction reaction (ORR) requires a fundamental understanding of the mechanisms underlying their catalytic activity. In this study, we employed the first-principles density functional theory calculations to predict some key parameters (such as activation energy for O–O bond breaking and free-energy evolution as a function of electrode potential) of ORR on three FeN₄-type active sites with different local carbon structures. We find that the FeN₄ site surrounded by eight carbon atoms and at the edge of micropores has the lowest activation energy (about 0.20 eV) for O–O bond breaking among the three FeN₄-type active sites for promoting a direct four-electron ORR. Consequently, our computational results suggest that introduction of micropores in the nonprecious metal catalysts could enhance their catalytic activity for ORR through facilitating the formation of FeN₄=C₈ active sites with high specific activity.

1. INTRODUCTION

A class of pyrolyzed transition metal and nitrogen-derived carbon materials (denoted as TM–N–C) has shown promise as economical yet effective electrocatalysts for the oxygen reduction reaction (ORR) in acid media.1–6 For example, a Fe–N–C catalyst derived from polyaniline and iron was found to exhibit an ORR activity with a half-wave potential (E₁/₂) by only 59 mV more negative relative to that of a commercial Pt/C and with a H₂O₂ yield below 1%.4 Recently, the half-wave potential for ORR in the Fe–N–C catalyst has been improved by another 20–30 mV.5,8 Moreover, a bimetallic (Fe,Mn)–N–C catalyst has been demonstrated to possess improved durability with only 4% activity loss after 9000 potential cycles in acid.6 Despite much progress, there still exists a considerable performance gap between these TM–N–C catalysts and the state-of-the-art platinum group metal (PGM) based catalysts.8 Consequently, it is imperative to acquire fundamental understanding on the mechanisms underlying various synthesis procedures that improve the catalytic performance of the TM–N–C catalysts.9–13

It has been recognized that increasing the microporosity in the TM–N–C catalysts by using microporous carbon black as supports14 ammonia or oxygen etching15,16 or sacrificial support method17,18 could lead to pronounced improvement in the ORR activity of the catalysts. A simple explanation to this enhancement in ORR activity might be that the introduced pores enlarge the total area of exposed surface and thus increase the number of accessible active sites in the TM–N–C catalysts.19 However, quantitative characterization results reveal clearly that the catalytic activity of the Fe–N–C catalysts for ORR is actually correlated with the specific area of those micropores with a size of 5–15 Å rather than the total area of the exposed surface.14,20–22 Hence, this experimental finding strongly suggests that the micropores in the TM–N–C catalysts could host highly active sites for catalyzing ORR. Inspired by this insightful experimental result, we carried out a first-principles density functional theory (DFT) study on how the ORR activity can be enhanced on the FeN₄ moieties formed on the edge of micropores as compared to those formed within a graphene layer.

2. COMPUTATIONAL METHOD

In this study, we performed spin-polarized DFT23,24 calculations using the Vienna ab initio simulation package (VASP) code.25,26 A projector augmented wave (PAW) pseudopotential27,28 was used to describe the core electrons, and a plane wave basis set with a kinetic energy cutoff of 400 eV was used to expand the wave functions. Electronic exchange and correlation was described within the framework of the generalized gradient approximation (GGA) of Perdew, Burke.
Figure 1. Atomistic structures of the ORR active site (a) FeN$_4$−C$_{10}$ (b) FeN$_4$−C$_{12}$, and (c) FeN$_4$−C$_9$ and O$_2$ adsorption with (d) an end-on configuration on FeN$_4$−C$_{10}$, (e) an end-on configuration on FeN$_4$−C$_{12}$ and (f) a side-on configuration on FeN$_4$−C$_9$. In the figure, the gray, blue, orange, red, and white balls represent C, N, Fe, O, and H atoms, respectively.

and Ernzerhof (PBE) functionals. The Brillouin zone was sampled using a Monkhorst−Pack $4 \times 4 \times 1$ k-point grid for active site FeN$_4$−C$_{10}$ $3 \times 3 \times 1$ for FeN$_4$−C$_{12}$, and $4 \times 3 \times 1$ for FeN$_4$−C$_9$. The atomic positions were optimized until the forces were below 0.02 eV/Å during structural optimization. The transition state of the chemical reactions was located using the climbing image nudged elastic band (CI-NEB) method with six intermediate images and with a convergence of 0.05 eV/Å for the force components both along and perpendicular to the tangent of the reaction path. Zero-point energy (ZPE) corrections were included in all energies reported in this work. ZPE corrections were calculated as $ZPE = \sum \frac{1}{2} \hbar \nu_i$, where $\hbar$ is Planck’s constant and $\nu_i$ is the frequency of the $i$th vibrational mode of binding molecules.

3. RESULTS AND DISCUSSION

Several models involving FeN$_4$ moieties embedded in carbon have been proposed to explain the activity of the Fe−N−C catalysts for ORR in acid. In a previous study, we predicted that the four-electron OOH dissociation pathway is both thermodynamically and kinetically favorable on the FeN$_4$ site embedded in an otherwise intact graphitic layer and surrounded by 10 carbon atoms (denoted as FeN$_4$−C$_{10}$, Figures 1a and S1a). In the present study, we used this FeN$_4$−C$_{10}$ site to study the ORR activity of the Fe−N−C catalysts in the region far away from micropores. Regarding the active sites hosted by micropores, we constructed a FeN$_4$−C$_{12}$ site (Figures 1b and S1b) near micropores and with a FeN$_4$ moiety bridging two adjacent zigzag graphitic edges with a porphyrin-like architecture and a FeN$_4$−C$_9$ site (Figures 1c and S1c) on the edge of micropores and with a FeN$_4$ moiety bridging two adjacent armchair-like graphitic edges. It is noted that FeN$_4$−C$_{12}$ was identified as the primary active site in the Fe−N−C catalysts by Jaouen et al. from their analysis of X-ray absorption near-edge structure (XANES) results, whereas FeN$_4$−C$_9$ was proposed to be the ORR active site by Dodelet et al. based on X-ray photoelectron and diffraction characterization results. Recent XANES studies indicated that the catalytic activity of the Fe−N−C catalysts varied with the amount of the three different types of FeN$_4$ moieties in the sample. The formation energies of these three FeN$_4$ active sites have been calculated in this study and are presented in Figure S2. Our calculation results suggest that it is indeed energetically favorable to form a FeN$_4$−C$_{10}$ site from a perfect graphene layer, whereas both FeN$_4$−C$_{12}$ and FeN$_4$−C$_9$ active sites are stable only if proper pore structures have already been present in the graphene layer.

In acid media, a four-electron pathway of ORR on an active site starts from adsorption of the O$_2$ molecule, undergoes a series of elementary reactions involving OOH, O, and OH, and ends with desorption of H$_2$O. Hence, we calculated the adsorption energies of the ORR species (O$_2$, OOH, O, OH, and H$_2$O) on the three FeN$_4$-type active sites and presented our results in Table 1. It should be noted that, for each ORR species, there are several different adsorption configurations on the FeN$_4$-type active site. In this work, we examined various possible adsorption configurations with the central Fe as the adsorption site (Figure S3) and located the most stable one (Figure S4) for each adsorption system in our restricted search. Correspondingly, the predicted lowest adsorption energy is reported in Table 1.

<table>
<thead>
<tr>
<th>Species</th>
<th>FeN$<em>4$−C$</em>{10}$</th>
<th>FeN$<em>4$−C$</em>{12}$</th>
<th>FeN$_4$−C$_9$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$</td>
<td>−0.95</td>
<td>−0.63</td>
<td>−1.67</td>
</tr>
<tr>
<td>OOH</td>
<td>−1.71</td>
<td>−1.41</td>
<td>−1.97</td>
</tr>
<tr>
<td>O</td>
<td>−4.12</td>
<td>−3.89</td>
<td>−4.37</td>
</tr>
<tr>
<td>OH</td>
<td>−2.69</td>
<td>−2.38</td>
<td>−2.83</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>−0.13</td>
<td>−0.27</td>
<td>−0.21</td>
</tr>
</tbody>
</table>

*Negative value of adsorption energy indicates attractive interaction between the ORR species and the ORR active sites.*
comparable to those predicted for O₂ on Pt catalysts (-0.69 eV on Pt(111) and -1.10 eV on Pt(100)). Moreover, our DFT results in Table 1 indicate that the binding of H₂O on the FeN₄-type active sites is weaker than the solvation stabilization energy of bulk water by about 0.40 eV. Consequently, we predict here that FeN₄−C₁₀, FeN₄−C₁₂, and FeN₄−C₈ active sites are able to attract reactant O₂ to initiate the ORR as well as release product H₂O to complete the ORR.

Following four-electron pathways of ORR, the O−O bond in the adsorbed O₂ must be broken through either direct dissociation of O₂ or dissociation of OOH, which is after O₂ is protonated. It is noted that this O−O bond breaking process is not influenced by the external electrode potential. In Table 2 we report our calculated activation energies for the two types of O−O bond breaking reactions (O₂ vs OOH) on the three FeN₄-type active sites. Our results show that the activation energy for the direct O₂ dissociation reaction is always higher than that for the OOH dissociation reaction on the FeN₄ sites. In addition, the activation energy for the O₂ hydrogenation reaction to form OOH was found to be quite low (for example, 0.04 eV on FeN₄−C₈). It is thus inferred from our DFT calculation that the OOH dissociation pathway would be kinetically more feasible than the O₂ dissociation pathways for ORR on the FeN₄-type active sites.

Our calculation results in Table 2 also indicate that the OOH dissociation reaction on FeN₄−C₈ requires an activation energy of only 0.20 eV, which is appreciably lower by at least 0.36 eV than those on the other two FeN₄-type active sites. In addition, we find that the central Fe of FeN₄−C₈ is fully capable of breaking the OOH molecule into O and OH on itself (Figure 2c, Figure S5, Table S2). In contrast, the OOH dissociation reaction on both FeN₄−C₁₀ and FeN₄−C₁₂ is predicted to require transportation of product OH to the top of the adjacent carbon (Figure 2a and 2b). Consequently, our DFT calculations predict the O−O bond breaking of ORR is fairly easier on FeN₄−C₈ than on FeN₄−C₁₀ and FeN₄−C₁₂ sites, apparently relating to the relatively stronger O₂ adsorption on FeN₄−C₈ than the other sites.

Besides the potential-independent O−O bond breaking reaction, the four-electron pathways of ORR include several protonation reactions (such as O₂ protonation, OH protonation, and O protonation) whose activation energies vary with external electrode potential. Examining this effect of electrode potential on ORR, we predicted the free energy evolution following the OOH dissociation ORR pathway on the three FeN₄-type active sites. These free energy landscapes were calculated using the adsorption energies given in Table 1 and a computational approach (see “Free energy calculation” in Supporting Information) proposed by Nørskov et al. The step of OOH dissociation into O and OH is included in this diagram. The free energy change and activation energy of this nonelectrochemical step are independent of the electrode potential. Hence, Figure 3 depicts the same reaction pathway adopted in other studies. Our results indicate that all of the elementary ORR reactions will be exergonic and thus thermodynamically favorable below a limiting electrode potential, whereas some reactions involving charge transfer will become endergonic above this limiting electrode potential. In Figure 3 we plot the free energy evolution for ORR under an

![Figure 2](image1.png)  
**Figure 2.** Atomistic structures of the initial state, transition state, and final state for the OOH dissociation reaction on (a) FeN₄−C₁₀, (b) FeN₄−C₁₂, and (c) FeN₄−C₈ active sites. In the figure, the gray, blue, yellow, red, and white balls represent C, N, Fe, O, and H atoms, respectively.

![Figure 3](image2.png)  
**Figure 3.** Calculated free energy evolution diagrams for the O₂ reduction through an OOH dissociation pathway on the active sites FeN₄−C₁₀, FeN₄−C₁₂, and FeN₄−C₈ at a temperature of 300 K and under an electrode potential of 0.69 V in acid medium.
optimized structures, the lengths of the Fe−N bond in FeN₄₋₋C₁₀ and FeN₄₋₋C₈ are calculated to be 1.90 Å, which is about 6% shorter than the Fe−N bond length of 2.02 Å in FeN₄₋₋C₁₂. It is noted that the Fe−N bond length in the FeN₄₋₋C₁₂ site is very close to 1.99 Å as previously predicted for an isolated Fe−porphyrin molecule. In such a square planar ligand field of FeN₄ moieties, the 3dₓᵧ, 4s, 4pₓ, and 4pᵧ orbitals of the central Fe would participate in the formation of four Fe−N bonding orbitals with the hybrid 2p orbitals of the surrounding N, whereas the other four 3d orbitals (dₓz, dᵧz, and dₓᵧ) of Fe would transform into four nonbonding d-type orbitals and interact with the electronic orbitals of adsorbates. Illustrating this point, we plot in Figure 4 the partial density of states (pDOS) for the elements in the three FeN₄ active sites. It can be seen in the upper panels of Figure 4 that N 2p orbitals mainly overlap the Fe 3dₓᵧ orbitals to form the Fe−N bonds in the clean FeN₄ active sites.

Figure 4. Calculated partial density of states (pDOS) for Fe, N, and O in the relaxed FeN₄₋₋C₁₀, FeN₄₋₋C₁₂, and FeN₄₋₋C₈ sites (upper panels), and the adsorption of the O₂ molecule on these three FeN₄-type active sites (lower panels). In the lower panels, O₁ refers to the O atom close to the Fe atom whereas O₂ refers to the other O atom away from the Fe atom in an end-on O₂ adsorption configuration; the two O atoms are equivalent in a side-on O₂ adsorption configuration.

Therefore, our DFT predictions calculate that although all three FeN₄-type active sites are able to catalyze the four-electron ORR under their respective thermodynamic limiting electrode potentials, the OOH dissociation pathway requires the lowest activation energy (about 0.20 eV) on FeN₄₋₋C₈ which lies on the edge of micropores in the graphitic layer whereas the highest activation energy (about 0.72 eV) on FeN₄₋₋C₁₂ which has a porphyrin-like structure. These theoretical predictions agree well with a previous experimental finding that the Fe−N−C catalysts containing the FeN₄₋₋C₁₀ and/or FeN₄₋₋C₈ moieties exhibited enhanced catalytic activity for ORR than the sample containing the porphyrin-like FeN₄₋₋C₁₂ moieties. Consequently, it could be a practical route to enhance the activity of Fe−N−C catalysts for ORR through controlled fabrication of these highly active FeN₄₋₋C₈ sites using metal−organic frameworks.

In order to understand the predicted local carbon structure−dependent ORR activity, we further performed analysis on the geometric and electronic structures of the three FeN₄-type active sites. All three FeN₄ moieties are found to have a planar structure embedded in a graphene layer and with a nearly square ligand field (as shown in Figure 1a−c). In their fully optimized structures, the lengths of the Fe−N bond in FeN₄₋₋C₁₀ and FeN₄₋₋C₈ are calculated to be 1.90 Å, which is about
can be broken fairly easily (with an activation energy of 0.20 eV and final O−O separation of 2.53 Å) on the central Fe atom of FeN4−C8, which is thus predicted to possess enhanced ORR activity than other possible active sites. This result confirms our previous proposal that the side-on adsorption configuration of O2 and OOH would favor easy O−O bond scission on FeN4 macrocyclic complexes.

Comparing the calculated binding strength of various ORR species on the three FeN4-type active sites (Figure S8) we established a linear scaling relation between the adsorption energy of ORR species and the number of local carbon atoms immediately adjacent to the FeN4 moiety. Our finding here is in support of the previous proposition that the position of the nonbonding Fe 3d orbitals could be tuned by the degree of π-electron delocalization on the carbon plane with sp²-hybridized graphitic carbon atoms and is related to the adsorption energy of ORR species. 10,43 In this study we find that a lower number of local carbon atoms around a FeN4 moiety (i.e., the FeN4−C8 on the edge of micropores) results in a Fe 3da5 and/or 3dx2−y2 orbital near the Fermi energy, strong binding of ORR species, easy O−O bond breaking, and thus enhanced ORR activity.

4. CONCLUSIONS
In conclusion, we predicted the adsorption energies of ORR species, activation energy for O−O bond breaking, and free-energy evolution of ORR on three FeN4-type active sites with different local carbon structures using first-principles DFT calculations. Our DFT calculations reveal that the FeN4−C8 sites hosted by micropores could favorably promote the four-electron ORR below a limiting electrode potential of 0.54 V and break the O−O bond in the adsorbed OOH with a pretty low activation energy of 0.20 eV. Consequently, our theoretical study suggests that introduction of micropores in the nonprecious Fe−N−C catalysts could enhance their intrinsic catalytic activity for ORR through generating the FeN4−C8 active sites with high specifivity. Therefore, this computational study provides useful guidance to the rational design and controlled synthesis of nonprecious metal and nitrogen-derived carbon electrocatalysts.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b00913.

Extended simulation cells; formation energy of the FeN4 active site; locating the most stable adsorption configuration; atomistic structures of the optimized configurations of various ORR species adsorbed on the three FeN4-type active sites; free energy calculation; determination of the final state for the O2 and OOH dissociation reaction; predicted activation energies of the two different pathways for O2 and OOH dissociation on FeN4−C10, FeN4−C12, and FeN4−C16; electronic structures for O2−FeN4 systems and FeN4 sites; pDOS for decomposed d orbitals of Fe in the FeN4-type active sites; scaling relation for adsorption energies (PDF).

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**Notes**
The authors declare no competing financial interest.

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