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# Axial heteroatom (P, S and Cl)-decorated Fe single-atom catalyst for the oxygen reduction reaction: a DFT study†

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An FeN<sub>4</sub> single-atom catalyst (SAC) embedded in a graphene matrix is considered an oxygen reduction reaction (ORR) catalyst for its good activity and durability, and decoration on the Fe active site can further modulate the performance of the FeN<sub>4</sub> SAC. In this work, the axial heteroatom (L = P, S and Cl)-decorated FeN<sub>4</sub> SAC (FeN<sub>4</sub>L) and pure FeN<sub>4</sub> were comparatively studied using density functional theory (DFT) calculations. It was found that the rate-determining step (RDS) in the ORR on pure FeN<sub>4</sub> is the reduction of OH to H<sub>2</sub>O in the last step with an overpotential of 0.58 V. However, the RDS of the ORR for the axial heteroatom-decorated FeN<sub>4</sub>L is the reduction of O<sub>2</sub> to OOH in the first step. The axial P and S heteroatom-decorated FeN<sub>4</sub>P and FeN<sub>4</sub>S exhibit lower activity than pure FeN<sub>4</sub> since the overpotentials of the ORR on FeN<sub>4</sub>P and FeN<sub>4</sub>S are 1.02 V and 1.09 V, respectively. Meanwhile, FeN<sub>4</sub>Cl exhibits the best activity towards the ORR since it possesses the lowest overpotential (0.51 V). The main reason is that the axial heteroatom decoration alleviates the adsorption of all the species in the whole ORR, thus modulating the free energy in every elementary reaction step. A volcano relationship between the d band center and the ORR activity can be determined among the axial heteroatom-decorated FeN<sub>4</sub>L SACs. The d band center of the Fe atom in various FeN<sub>4</sub>L SACs follows the order of FeN<sub>4</sub> > FeN<sub>4</sub>Cl > FeN<sub>4</sub>S > FeN<sub>4</sub>P, whereas the overpotential of the ORR on various catalysts follows the order of FeN<sub>4</sub>Cl > FeN<sub>4</sub> > FeN<sub>4</sub>S ≈ FeN<sub>4</sub>P. ΔG(\*OH) is a simple descriptor for the prediction of the ORR activity of various axial heteroatom-decorated FeN<sub>4</sub>L, although the RDS in the ORR is either the first step or the last step. This paper provides a guide to the design and selection of the ORR over SACs with different axial heteroatom decorations, contributing to the rational design of more powerful ORR electrocatalysts and achieving advances in electrochemical conversion and storage devices.

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## Introduction

A typical example of a clean energy conversion technology is the proton exchange membrane fuel cell (PEMFC). To ensure energy conversion, the sluggish oxygen reduction reaction (ORR) at the cathode needs a powerful electrocatalyst.<sup>1</sup> Currently, the most efficient catalyst for the ORR is platinum group metals (PGMs). However, their major drawbacks (such as huge overpotential, scarcity, and high cost) limit their commercialization. One effective way to address this issue is to

explore alternatives to non-precious metal catalysts. Carbon materials doped with metals and heteroatoms have drawn much interest from researchers as promising and exceptional electrocatalysts to efficiently reduce the overpotential of the ORR. Overall, heteroatom dopants (such as N, B, P, and S) can produce charged active sites and cause the polarization of the carbon skeleton, which can effectively reduce the overpotential of the ORR and improve the slow kinetics of the ORR.<sup>2–4</sup> As opposed to PGMs and carbon-based metal-free catalysts, single-atom catalysts (SACs) have emerged as a frontier in the field of ORR electrocatalysts owing to their large specific surface area, maximum atomic efficiency, high selectivity, and long-term operational endurance. DFT calculations have been widely and significantly successful in research studies on the ORR mechanism<sup>5</sup> since it can greatly save experimental costs and accurately predict the components with high activity. Graphene with defects is one of the numerous substrates that can make an excellent SAC substrate. The electrocatalytic activity of the ORR can be increased by monitoring the d-orbital electrons of the central transition metal (TM) through the coordination of

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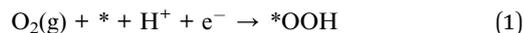

four N atoms,<sup>6</sup> and the atomically dispersed TMN<sub>4</sub> site has been considered as the active sites for ORR.<sup>7–9</sup> Both experimental studies and DFT calculations have shown that the SACs based on non-precious TM (TM = Fe, Co, Mn, Ni, Zn, *etc.*<sup>2,10–12</sup>) on nitrogen-doped carbon support can significantly enhance the ORR electrocatalytic activity. Among the aforementioned SACs, the single-atom Fe–N–C catalyst exhibits considerable activity and remarkable selectivity for the ORR,<sup>9,13,14</sup> which is even comparable to the commercial platinum catalysts. Furthermore, our previous experiments have proved that the activity and stability of FeN<sub>4</sub> is as good as the platinum catalyst for ORR.<sup>15,16</sup> The FeN<sub>4</sub> catalyst has been reported as a possible replacement for Pt-based catalysts because of its good activity and durability, and the decoration on the Fe active site can further improve the performance of SACs through modulating the electronic and geometric structure.<sup>17,18</sup> Thus, the rational design of carbon-based ORR catalysts with low cost, as well as high activity, selectivity, and durability, is of great significance. Lin *et al.*<sup>19</sup> synthesized a new SAC, and each Fe atom is coordinated with five N atoms rather than four N, resulting in a 3D Fe–N<sub>5</sub> coordination site. By using DFT calculations, they discovered that the axially coordinated pyridine could positively regulate the binding strength of oxygen on the 2D Fe–N<sub>4</sub> site to a higher level. Other scholars came to similar results that were well-researched.<sup>20,21</sup> In addition, SACs exhibited good activity for electrochemical N<sub>2</sub> reduction,<sup>22</sup> CO<sub>2</sub> reduction,<sup>23–25</sup> lithium–sulfur batteries,<sup>26</sup> NO electroreduction<sup>27,28</sup> and CO detection.<sup>29</sup> Thus, the study on axial heteroatom-decorated Fe SAC for ORR is important, and this paper can shed light on the rational design of SAC catalysts with good performance.

In this work, DFT calculations were performed to investigate the effect of different axial heteroatom decorations on the activity of FeN<sub>4</sub>L towards ORR. The binding energy and cohesion energy, which describe the stability of the heteroatom-decorated FeN<sub>4</sub>L, were first studied. Then, the overpotentials of ORR catalyzed by pure FeN<sub>4</sub> and various FeN<sub>4</sub>L were evaluated. Furthermore, the relationship between the overpotential and the OH adsorption free energy ( $\Delta G(*OH)$ ) were studied, since  $\Delta G(*OH)$  is a good descriptor for ORR activity.<sup>30–32</sup> An accurate quantitative description of the ORR activity trends was elucidated with the help of the adsorption free energy of the reaction intermediate, d-band center, partial density of states, differential charge density and Bader charge of the heteroatom-decorated Fe atom.

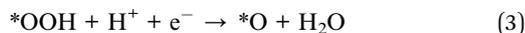
## Computational methods

The spin-polarized DFT calculations were performed by using the Vienna *Ab initio* Simulation Package (VASP).<sup>33,34</sup> The Kohn–Sham wave functions were expanded in a plane wave basis set with a cutoff energy of 500 eV. The projector-augmented wave (PAW) method and PBE potential for the exchange–correlation function were used.<sup>35</sup> The  $3 \times 3 \times 1$  Monkhorst–Pack *k*-point mesh was used to sample the Brillouin zone.<sup>36</sup> All atoms were allowed to relax until the forces fell below  $0.02 \text{ eV } \text{Å}^{-1}$ . A vacuum region of  $15 \text{ Å}$  was created to ensure negligible interaction between mirror images.

The ORR occurs *via* the following steps:



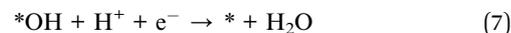
$$\Delta G(1) = G(*OOH) - G(\text{O}_2) - \frac{1}{2}G(\text{H}_2) - G(*) + eU \quad (2)$$



$$\Delta G(2) = G(*O) + G(\text{H}_2\text{O}) - G(*OOH) - \frac{1}{2}G(\text{H}_2) + eU \quad (4)$$



$$\Delta G(3) = G(*OH) - G(*O) - \frac{1}{2}G(\text{H}_2) + eU \quad (6)$$



$$\Delta G(4) = G(*) + G(\text{H}_2\text{O}) - G(*OH) - \frac{1}{2}G(\text{H}_2) + eU \quad (8)$$

where \* represents the preferable adsorption site for intermediates, and  $G(*)$ ,  $G(*OOH)$ ,  $G(*O)$  and  $G(*OH)$  are the Gibbs free energies of the clean catalyst, and the catalyst adsorbed with \*OOH, \*O and \*OH, respectively.  $G(\text{H}_2\text{O})$  and  $G(\text{H}_2)$  are the Gibbs free energies of H<sub>2</sub>O and H<sub>2</sub>, respectively.

The Gibbs free energy ( $\Delta G$ ) diagram of the ORR was calculated using the computational hydrogen electrode (CHE) model proposed by Nørskov *et al.*,<sup>37</sup> where the free energy of ( $\text{H}^+ + \text{e}^-$ ) under standard conditions is equal to the value of  $1/2\text{H}_2$ . The free energy change ( $\Delta G$ ) of the primitive step of the ORR is calculated according to the following equation.

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta \int C_{\text{Pd}}dT + \Delta G_{\text{U}} + \Delta G_{\text{pH}} \quad (9)$$

where  $\Delta E$  is the total energy difference between the reactants and products of the reactions,  $\Delta ZPE$  is the zero-point energy correction,  $\Delta S$  is the vibrational entropy change and  $T$  is temperature with the value of 298.15 K.  $\Delta \int C_{\text{Pd}}dT$  is the difference in enthalpic correction,  $\Delta G_{\text{U}} = -eU$ , where  $e$  is the elementary charge,  $U$  is the electrode potential, and  $\Delta G_{\text{pH}}$  is the correction of the  $\text{H}^+$  free energy.

The overpotential for ORR ( $\eta_{\text{ORR}}$ ) is calculated according to the following equation:

$$\eta_{\text{SHE}} = 1.23 \text{ V} + \Delta G_{\text{max}}/e \quad (10)$$

where 1.23 V is defined as the equilibrium potential of the overall 4-electron ORR at the standard state, and  $\Delta G_{\text{max}}$  represents the maximum  $\Delta G$  associated with the proton–electron-transfer steps.

The binding energies ( $E_{\text{Binding}}$ ) of the axial heteroatom with FeN<sub>4</sub> and the adsorption energy ( $E_{\text{ads}}$ ) of the intermediates in ORR have been calculated according to formulas (11) and (12):

$$E_{\text{Binding}} = E_{\text{FeN}_4\text{X}} - E_{\text{FeN}_4} - E_{\text{X}} \quad (11)$$

$$E_{\text{ads}} = E_{\text{system}} - E_{\text{C}} - E_{\text{species}} \quad (12)$$



where  $E_{\text{FeN}_4\text{X}}$ ,  $E_{\text{FeN}_4}$  and  $E_{\text{X}}$  are the total electronic energies (non-ZPE corrected) of the system,  $\text{FeN}_4$  and heteroatoms, respectively.  $E_{\text{system}}$ ,  $E_{\text{C}}$  and  $E_{\text{species}}$  denote the total electronic energy (non-ZPE corrected) of the adsorption system, the individual surface and adsorbate, respectively.

## Result and discussion

A  $6 \times 6$  graphene supercell containing 72 carbon atoms was used as the basis for the construction of the axial heteroatom-decorated  $\text{FeN}_4$  SAC. A double carbon atom vacancy was constructed at the center of graphene. Then, an Fe atom was embedded in the center of the double vacancy, and the four closest C atoms surrounding the vacancy were replaced by four N atoms, resulting in a structural model of the  $\text{FeN}_4$  catalyst.

Fig. 1 shows the top and side views of  $\text{FeN}_4$ ,  $\text{FeN}_4\text{P}$ ,  $\text{FeN}_4\text{S}$ , and  $\text{FeN}_4\text{Cl}$ . The metal and the four coordinated N atoms almost remain in place in the pure  $\text{FeN}_4$ , while a slight deviation from the original plane can be determined after the axial heteroatom decoration. The Bader charge in Fig. S1<sup>†</sup> shows that the central Fe atom in  $\text{FeN}_4$ ,  $\text{FeN}_4\text{P}$ ,  $\text{FeN}_4\text{S}$ , and  $\text{FeN}_4\text{Cl}$  loses electrons ( $-1.03e$ ,  $-0.86e$ ,  $-1.06e$ , and  $-1.15e$ ; the negative value represents the deficiency of electrons), and electrons are transferred to the surrounding coordinated nonmetal atoms, where the P, S, and Cl atoms get  $0.04e$ ,  $0.44e$ , and  $0.54e$ , respectively.

As shown in Table 1, the binding energy between the heteroatom and Fe are all negative with values of  $-1.79$  eV,  $-3.30$  eV, and  $-2.97$  eV, respectively, indicating that these structures can be stabilized. Thus, the subsequent adsorption of the ORR intermediates can be carried out on these structures.

The optimized structures of the  $^*\text{OOH}$ ,  $^*\text{O}$ , and  $^*\text{OH}$  intermediates adsorbed on  $\text{FeN}_4$ ,  $\text{FeN}_4\text{P}$ ,  $\text{FeN}_4\text{S}$ , and  $\text{FeN}_4\text{Cl}$  are depicted in Fig. S2.<sup>†</sup> The Fe atom is located at the center of the double vacant graphene in the  $\text{FeN}_4$ ,  $\text{FeN}_4\text{P}$ ,  $\text{FeN}_4\text{S}$ , and  $\text{FeN}_4\text{Cl}$  systems. The bond lengths between the central Fe and 4 coordinated N atoms are almost similar, and the deviation of the central Fe atom from the graphene plane became smaller

Table 1 Binding energy ( $E_{\text{Binding}}$ ) between the axial heteroatom and Fe in different  $\text{FeN}_4\text{L}$

System	$\text{FeN}_4\text{P}$	$\text{FeN}_4\text{S}$	$\text{FeN}_4\text{Cl}$
$E_{\text{Binding}}$ (eV)	$-1.79$	$-3.03$	$-2.97$

compared with the pure  $\text{FeN}_4$ . Table 2 lists the bond lengths between the central Fe and various O atoms from the  $^*\text{OOH}$ ,  $^*\text{O}$ ,  $^*\text{OH}$  intermediates and the inter-bond lengths of various ORR intermediates as well. For the adsorbed  $^*\text{OOH}$  intermediates on various axial heteroatom  $\text{FeN}_4\text{L}$ , the bond lengths of Fe–O follow the order of  $\text{FeN}_4\text{S} > \text{FeN}_4\text{P} > \text{FeN}_4\text{Cl} > \text{FeN}_4$ , and the values are  $2.02$  Å,  $1.95$  Å,  $1.86$  Å, and  $1.80$  Å, respectively. This is consistent with the fact that the relatively large binding energy usually corresponds to a short distance. For the  $^*\text{O}$  intermediates, a similar phenomenon can also be observed. The bond lengths of Fe–O follow the order of  $\text{FeN}_4\text{S} > \text{FeN}_4\text{P} = \text{FeN}_4\text{Cl} > \text{FeN}_4$ , and the values are  $1.69$  Å,  $1.68$  Å,  $1.68$  Å, and  $1.65$  Å, respectively. Similarly, for the  $^*\text{OH}$  intermediate, the bond lengths of Fe–O follow the order of  $\text{FeN}_4\text{S} > \text{FeN}_4\text{P} > \text{FeN}_4\text{Cl} > \text{FeN}_4$ , and the values are  $1.94$  Å,  $1.92$  Å,  $1.87$  Å, and  $1.83$  Å, respectively. Thus, it can be concluded that the axial heteroatom decoration of  $\text{FeN}_4\text{L}$  leads to a decreased binding between various ORR intermediates and axial heteroatom-decorated Fe SACs.

The free energy changes ( $\Delta G$ ) on the different catalysts are shown in Fig. 2. The  $\Delta G$  for each elementary step at the active sites of various  $\text{FeN}_4\text{L}$  are based on the following four reactions: (1)  $\text{O}_2$  adsorbs at the active site and hydrogenates to form  $^*\text{OOH}$ ; (2)  $^*\text{OOH}$  continues to hydrogenate to form  $^*\text{O}$ ; (3)  $^*\text{O}$  continues to combine with  $\text{H}^+$  and forms  $^*\text{OH}$ ; (4)  $\text{H}_2\text{O}$  is produced through hydrogenation of  $^*\text{OH}$  and eventually desorbs.

At the ORR equilibrium potential, all four  $\Delta G$  values are negative, indicating that each reaction of the ORR is thermodynamically favoured to occur. For a perfect ORR catalyst,  $\Delta G$  should be  $-1.23$  eV for each elementary reaction step involving electron transfer, causing zero overpotential (Fig. 2a). The rate-

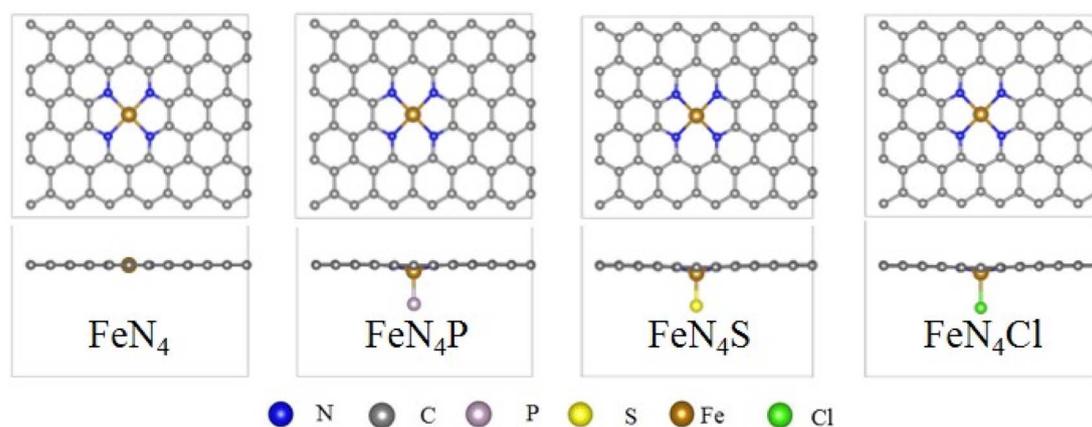


Fig. 1 Top and side views of the optimized  $\text{FeN}_4$ ,  $\text{FeN}_4\text{P}$ ,  $\text{FeN}_4\text{S}$ , and  $\text{FeN}_4\text{Cl}$ , respectively.



**Table 2** Bond length (Å) between the ORR intermediates OOH, O, and OH and the central active Fe site

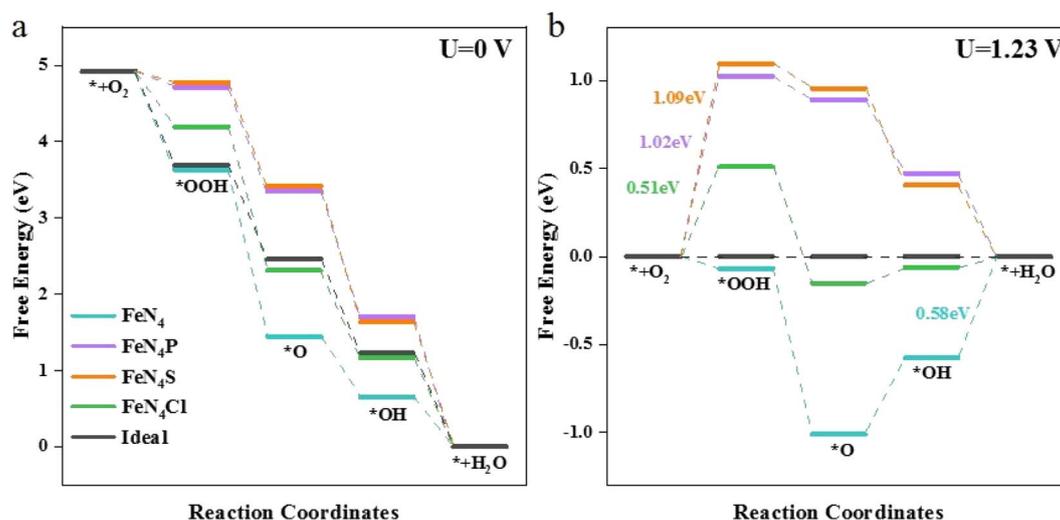
System	Bond length/Å					
	*OOH			*O	*OH	
	$d_{\text{Fe-O}}$	$d_{\text{O-O}}$	$d_{\text{O-H}}$	$d_{\text{Fe-O}}$	$d_{\text{Fe-O}}$	$d_{\text{O-H}}$
FeN <sub>4</sub>	1.80	1.47	0.98	1.65	1.83	0.98
FeN <sub>4</sub> P	1.95	1.45	0.98	1.68	1.92	0.98
FeN <sub>4</sub> S	2.02	1.44	0.98	1.69	1.94	0.97
FeN <sub>4</sub> Cl	1.86	1.47	0.98	1.68	1.87	0.98

determining step (RDS) of ORR on FeN<sub>4</sub> differs from that on the axial heteroatom-decorated FeN<sub>4</sub>L, as illustrated in Fig. 2. The RDS is defined by eqn (10). For FeN<sub>4</sub>, the reaction is determined by the last step of ORR, *i.e.*, the formation of H<sub>2</sub>O from \*OH ( $\Delta G(4)$ ). However, for the axial heteroatom-decorated FeN<sub>4</sub>P, FeN<sub>4</sub>S, and FeN<sub>4</sub>Cl, the reaction is controlled by the first proton–electron transfer step ( $\Delta G(1)$ ), *i.e.*, the protonation of oxygen to \*OOH. At 1.23 V, the two steps of hydrogenation of \*O and the formation of H<sub>2</sub>O from \*OH are free energy increasing processes at the FeN<sub>4</sub> active site, with the largest free energy increase for \*OH. This suggests that the \*OH removal step is the RDS with an overpotential of 0.58 V. Whereas the energy of the first step for FeN<sub>4</sub>P, FeN<sub>4</sub>S, and FeN<sub>4</sub>Cl is 1.02 eV, 1.09 eV, and 0.51 eV, respectively. The FeN<sub>4</sub>Cl has the lowest overpotential, indicating that the axial Cl decoration contributed the most to the ORR activity of FeN<sub>4</sub>L compared to the pure FeN<sub>4</sub> structure, the P and S heteroatom-decorated FeN<sub>4</sub>L.

Fig. 3 delves deeper into the ORR catalytic cycle and the optimized conformation of the ORR intermediates on FeN<sub>4</sub> and FeN<sub>4</sub>Cl to reveal the origin of their high ORR activity (FeN<sub>4</sub>P and FeN<sub>4</sub>S in Fig. S3†). As a transition metal element, the central Fe atom can transfer partial electrons throughout the ORR process, resulting in stronger binding to diverse intermediates. Thus,

the obtained conclusion is consistent with the above calculation results, *i.e.*, at the central iron atom, some electron transfer occurs, followed by hydroxide ion desorption. On the contrary, after the central iron atom has been axially decorated with heteroatoms, a portion of the electrons are transferred to the heteroatoms. The electrons provided by the iron atom to the oxygen reduction intermediates are reduced, and the binding becomes weaker, making desorption of the hydroxide ion easier on FeN<sub>4</sub>X. Conversely, the adsorption of O<sub>2</sub> to generate OOH is the most difficult step in the entire ORR process.

Table 3 demonstrates that the adsorption of various intermediates of the ORR on FeN<sub>4</sub>, FeN<sub>4</sub>P, FeN<sub>4</sub>S, and FeN<sub>4</sub>Cl is an exothermic process. The adsorption of OOH was strongest on the FeN<sub>4</sub> active site with an adsorption energy of  $-1.68$  eV, moderate adsorption energy of  $-1.12$  eV on FeN<sub>4</sub>Cl, and the smallest adsorption energy on the FeN<sub>4</sub>S surface with a value of  $-0.53$  eV. Meanwhile, it is  $-0.60$  eV on FeN<sub>4</sub>P. Correspondingly, O also exhibited the strongest adsorption on the FeN<sub>4</sub> active site with  $-4.36$  eV, followed by FeN<sub>4</sub>Cl at  $-3.52$  eV. The adsorption energies on the FeN<sub>4</sub>P and FeN<sub>4</sub>S surfaces are also relatively strong at  $-2.46$  eV and  $-2.41$  eV, respectively. Similarly, the exothermic processes that occur during the OH intermediate adsorption on the surfaces of FeN<sub>4</sub>, FeN<sub>4</sub>P, FeN<sub>4</sub>S, and FeN<sub>4</sub>Cl are all thermodynamically advantageous. \*OH has the highest adsorption energy ( $-2.73$  eV) on FeN<sub>4</sub>, the lowest ( $-1.68$  eV) on FeN<sub>4</sub>P, and  $-1.74$  eV and  $-2.23$  eV on FeN<sub>4</sub>S and FeN<sub>4</sub>Cl, respectively. In comparison, OOH, O, and OH on FeN<sub>4</sub> have the strongest adsorption. Meanwhile, FeN<sub>4</sub>P, FeN<sub>4</sub>S, and FeN<sub>4</sub>Cl, which were decorated by axial heteroatoms, decreased the adsorption of the oxygen-containing ORR intermediates to varying degrees. Furthermore, the adsorption energy of the \*O intermediate was higher than both \*OOH and \*OH on the same catalyst. This indicated that the dissociation of OOH in the first step is relatively simple, and that the hydrogenation reaction of \*O occurring in the latter step is also favored by the strong adsorption of the intermediate O.<sup>32</sup>



**Fig. 2** Free energy diagrams for the ORR on FeN<sub>4</sub>, FeN<sub>4</sub>P, FeN<sub>4</sub>S, FeN<sub>4</sub>Cl, and the ideal catalyst at (a)  $U = 0$  V and (b)  $U = 1.23$  V.



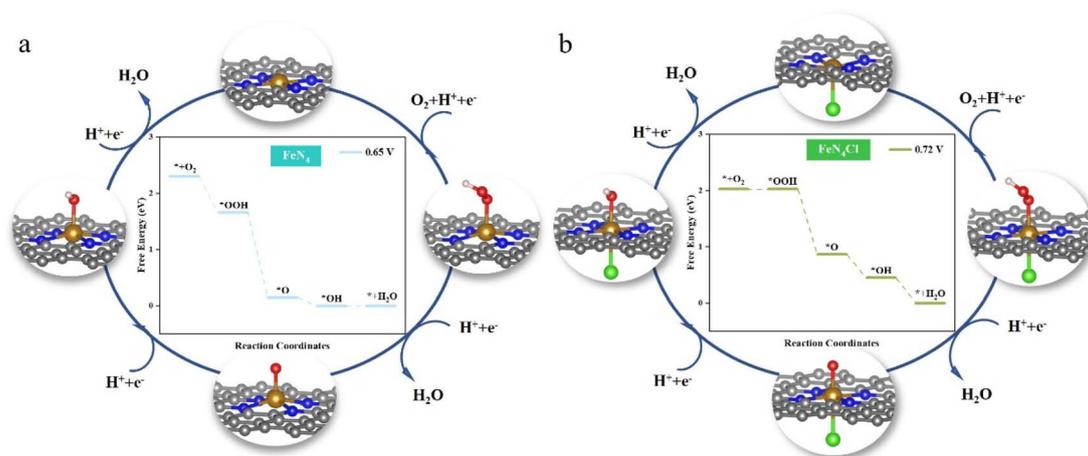


Fig. 3 Schematic diagram of the cycle of the ORR. The middle diagram shows  $\Delta G$  of the ORR at different potentials on (a)  $\text{FeN}_4$  and (b)  $\text{FeN}_4\text{Cl}$ . For  $U < 0.65$  V and  $U < 0.72$  V, all steps on  $\text{FeN}_4$  and  $\text{FeN}_4\text{Cl}$  are thermodynamically accessible.

Table 3 The adsorption energy ( $E_{\text{ads}}$ ) of OOH, O, and OH on  $\text{FeN}_4$ ,  $\text{FeN}_4\text{P}$ ,  $\text{FeN}_4\text{S}$ , and  $\text{FeN}_4\text{Cl}$

System	Adsorption energy/eV		
	*OOH	*O	*OH
$\text{FeN}_4$	-1.68	-4.36	-2.73
$\text{FeN}_4\text{P}$	-0.60	-2.46	-1.68
$\text{FeN}_4\text{S}$	-0.53	-2.41	-1.74
$\text{FeN}_4\text{Cl}$	-1.12	-3.52	-2.23

The reaction free energy of the elementary reaction in ORR is determined by the adsorption free energy ( $\Delta G_{\text{ads}}$ ) of the intermediate species, \*OH, \*O and \*OOH (abbreviated as  $\Delta G(*\text{OH})$ ,  $\Delta G(*\text{O})$ , and  $\Delta G(*\text{OOH})$ ).<sup>38</sup> The  $\Delta G_{\text{ads}}$  of \*OOH, \*O, and \*OH can be calculated according to the following equations:

$$\Delta G(*\text{OOH}) = G(*\text{OOH}) - G(*) - 2G(\text{H}_2\text{O}) + \frac{3}{2}G(\text{H}_2) \quad (13)$$

$$\Delta G(*\text{O}) = G(*\text{O}) - G(*) - G(\text{H}_2\text{O}) + G(\text{H}_2) \quad (14)$$

$$\Delta G(*\text{OH}) = G(*\text{OH}) - G(*) - G(\text{H}_2\text{O}) + \frac{1}{2}G(\text{H}_2) \quad (15)$$

Table S1† lists the calculated  $\Delta G(*\text{OH})$ ,  $\Delta G(*\text{O})$ , and  $\Delta G(*\text{OOH})$  on various catalysts.  $\Delta G(*\text{OH})$  is the variable used to describe the ORR overpotential because RDS is related to either  $\Delta G(*\text{OH})$  or  $\Delta G(*\text{OOH})$ . As  $\Delta G(*\text{OH})$  becomes more negative, the strength of the bond between \*OH and the catalyst increases.

The adsorption free energy is not equivalent to the adsorption energy, but reflects the trend of the binding strength of the same substance on different substrates. An appropriate catalyst should have a reasonable  $\Delta G_{\text{ads}}$  to make sure that the

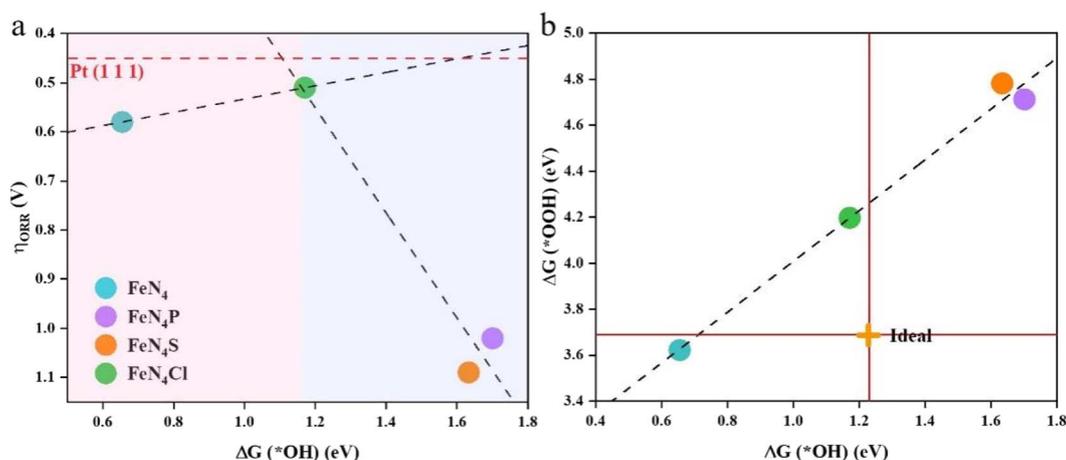


Fig. 4 (a) Volcano plot between the theoretical overpotential ( $\eta_{\text{ORR}}$ ) and the adsorption free energy of \*OH for the ORR on various catalysts. The red dashed line represents the ORR overpotential on Pt(111). (b) The relationship between the adsorption free energy of \*OOH and \*OH. The ideal intersection point is marked with an orange cross.



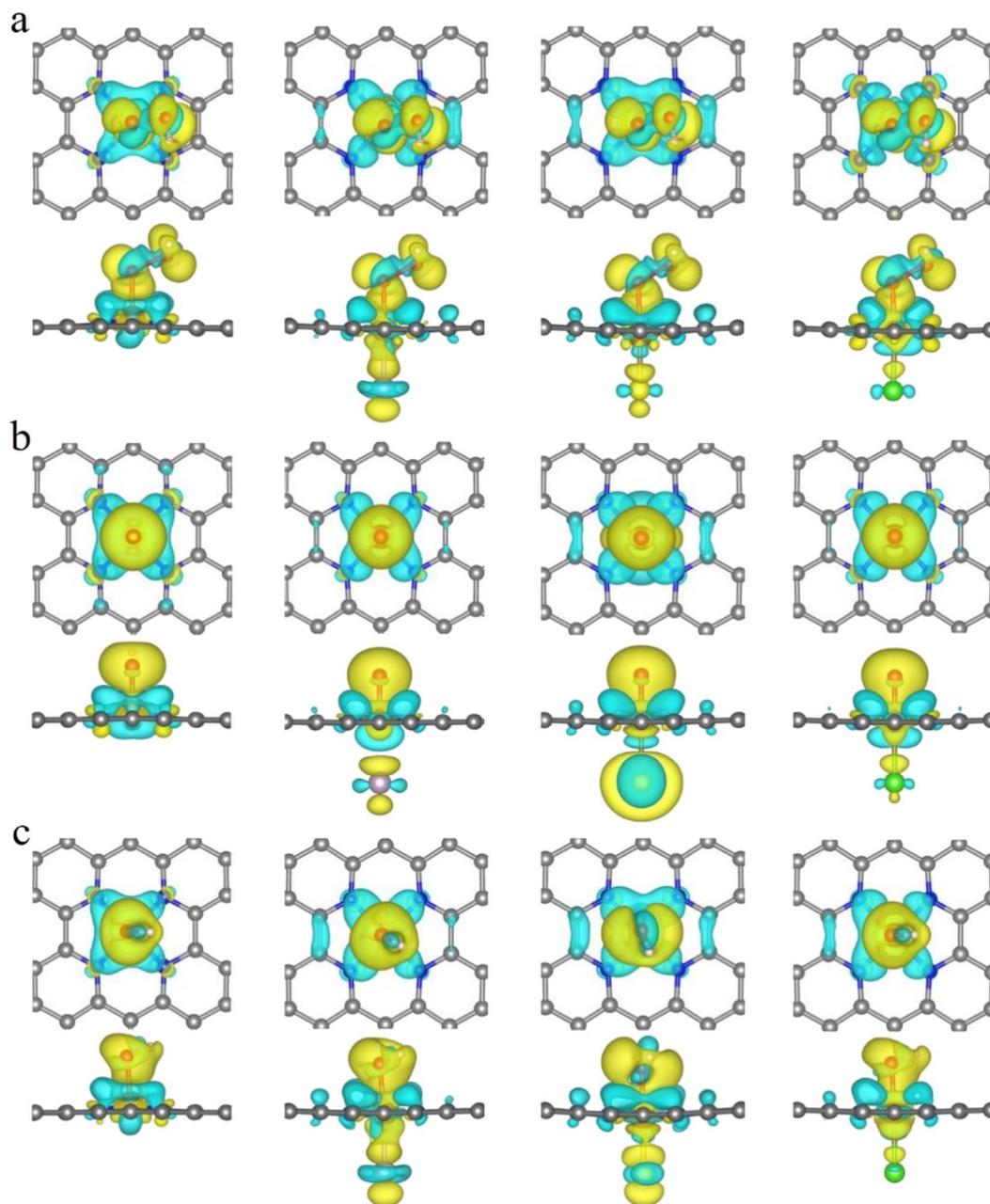


Fig. 5 The differential charge density of FeN<sub>4</sub>, FeN<sub>4</sub>P, FeN<sub>4</sub>S and FeN<sub>4</sub>Cl for (a) \*OOH, (b) \*O and (c) \*OH, respectively. The isosurface is 0.002 e Å<sup>-3</sup>.

adsorption of intermediates is neither too high nor too low. The correlation between the ORR overpotential and the Gibbs free energy of the \*OH intermediates can be seen in Fig. 4a. The overpotential and  $\Delta G(*OH)$  have a perfect volcanic relationship, and the catalytic process will be hindered by too strong or too weak interactions between the catalysts and intermediates. The inflection point of the volcano diagram is the turning point for both strong and weak adsorption of OH. The ORR process is constrained in the strong binding region (the left pink zone of the volcano diagram) by the reduction of \*OH to H<sub>2</sub>O in the last step. The limit of the catalytic process in the weak binding zone (the right blue zone of the volcano diagram) is the first step of

O<sub>2</sub> reduction to \*OOH. Among all the studied catalysts here, FeN<sub>4</sub>Cl is nearly at the top of the volcano diagram, and is closest to the theoretical overpotential of Pt(111).<sup>37</sup> This indicates that FeN<sub>4</sub>Cl possesses a comparable catalytic activity with Pt(111). For the ideal ORR electrocatalyst,  $\Delta G(*OH)$  should be 1.23 eV and  $\Delta G(*OOH)$  should be 3.69 eV. As shown in Fig. 4b, a proportional relationship  $\Delta G(*OOH) = 1.10\Delta G(*OH) + 3.41$  with a coefficient of determination  $R^2 = 0.98$  can be determined, indicating a strong linear relationship between the adsorption free energy of \*OH and \*OOH. The axial heteroatoms decoration of FeN<sub>4</sub> with Cl, P, and S elements can effectively tune the binding energy of \*OH and \*OOH, with FeN<sub>4</sub>Cl being closer to



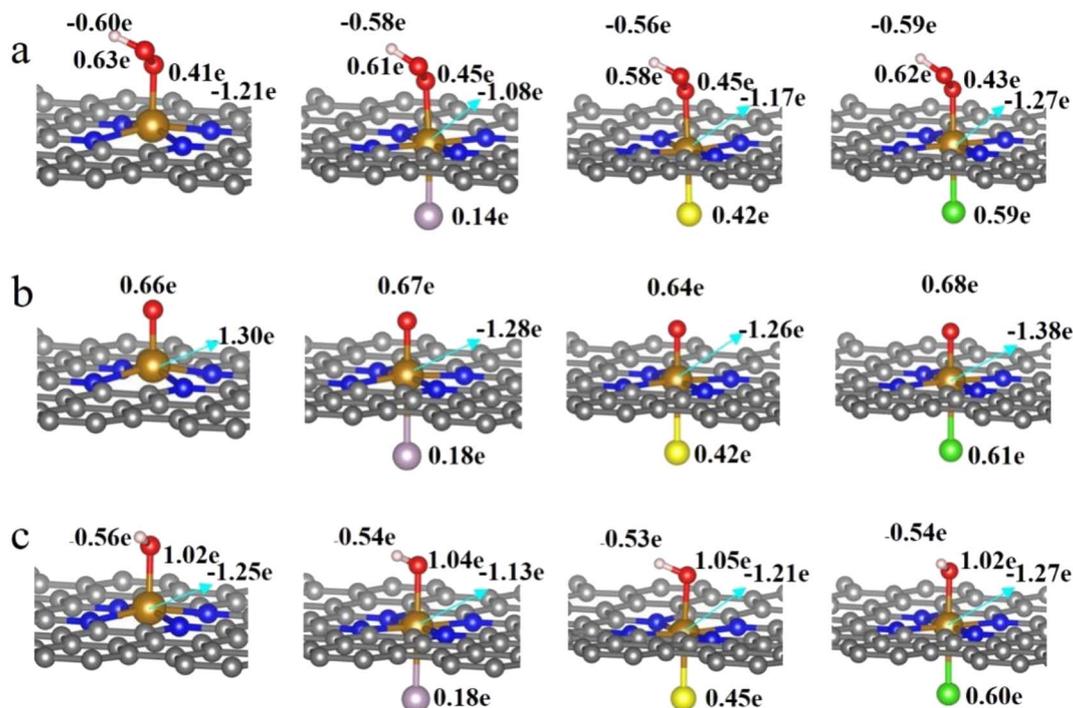


Fig. 6 Bader charge analysis of FeN<sub>4</sub>, FeN<sub>4</sub>P, FeN<sub>4</sub>S and FeN<sub>4</sub>Cl for (a) \*OOH, (b) \*O and (c) \*OH, respectively.

the ideal electrocatalyst value than FeN<sub>4</sub>P and FeN<sub>4</sub>S, indicating that the Cl heteroatom decoration can enhance the electrocatalytic activity of FeN<sub>4</sub> more effectively than both P and S heteroatoms. Thus, the evaluation of ORR activity *via*  $\Delta G(*OH)$  is applicable for the axial heteroatom-decorated FeN<sub>4</sub>L,

although the RDS is either the last step for pure FeN<sub>4</sub> or the first step for various FeN<sub>4</sub>L.

The electronic properties of a substance have a significant impact on its catalytic activity. The study of the electronic properties of catalysts can provide a greater understanding of

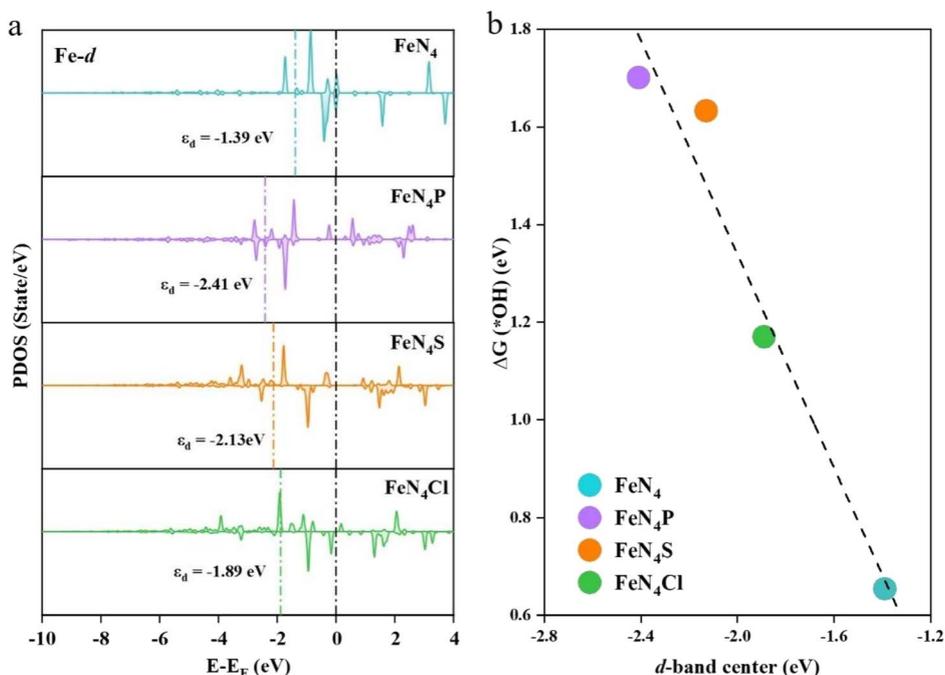


Fig. 7 (a) Projected density of states of the Fe atom on FeN<sub>4</sub>, FeN<sub>4</sub>P, FeN<sub>4</sub>S and FeN<sub>4</sub>Cl, and their corresponding d-band centers. (b) Relationship between the d-band center of the Fe atom in FeN<sub>4</sub>, FeN<sub>4</sub>P, FeN<sub>4</sub>S and FeN<sub>4</sub>Cl and  $\Delta G(*OH)$ .



the origin of the catalytic activity. Therefore, various electronic properties were calculated and analysed to provide insight into the ORR electrocatalytic performances of FeN<sub>4</sub>, FeN<sub>4</sub>P, FeN<sub>4</sub>S, and FeN<sub>4</sub>Cl. The projected density of states (PDOS) was used to evaluate the d-band center of the materials, and the Bader charge and differential charge density of several intermediates were calculated as well.

It is clear from the results of the differential charge density (Fig. 5) that charge transfer and redistribution occur between the ORR intermediates (\*OOH, \*O, \*OH) and the FeN<sub>4</sub>, FeN<sub>4</sub>P, FeN<sub>4</sub>S, and FeN<sub>4</sub>Cl catalysts. The O atom shows the strongest electronegativity compared to the H, C, N and Fe atoms. Thus, as shown in Fig. 6, in the FeN<sub>4</sub> system, the O atom receives electrons from the directly attached Fe and/or H atoms, with OH\*, O\* and OOH\* receiving 0.41e, 0.66e and 1.02e, respectively. When FeN<sub>4</sub> is axially decorated with P, S, and Cl, the electrons obtained by the O atom from the directly attached Fe and/or H atoms are very close to those of FeN<sub>4</sub>, differing only by ±0.01–0.04e.

The d-bands of the Fe atom in FeN<sub>4</sub>, FeN<sub>4</sub>P, FeN<sub>4</sub>S, and FeN<sub>4</sub>Cl are depicted in Fig. 7a. There are some electrons near the Fermi level; thus, it can be deemed that all of the FeN<sub>4</sub>L SACs possess good conductivity. Furthermore, the d-band center of Fe in FeN<sub>4</sub> is –1.39 eV, which is closest to the Fermi energy level ( $E_F$ ) compared with the axial heteroatom-decorated FeN<sub>4</sub>L. The d-band centers of Fe in FeN<sub>4</sub>P, FeN<sub>4</sub>S, and FeN<sub>4</sub>Cl are all farther away from  $E_F$  compared to that in FeN<sub>4</sub>, with the values of –2.41 eV, –2.13 eV and –1.89 eV, respectively. The d-band center theory has successfully described the chemisorption capacity and electrocatalytic properties of transition metals.<sup>39,40</sup> Generally, a more negative d-band center indicates a weaker adsorption. The d-band center of FeN<sub>4</sub>Cl is closest to  $E_F$  among all the axial heteroatom-decorated FeN<sub>4</sub>L, indicating that FeN<sub>4</sub>Cl is the best catalyst for the ORR intermediate adsorption. Fig. 7b shows the scaling relationship between the d-band center of Fe and  $\Delta G(*OH)$ . A negative correlation between the d-band center and  $\Delta G(*OH)$  can be observed, indicating that the intensity of adsorption of OH on Fe atoms increases with the upward shift of the d-band center of the Fe atom, which is consistent with the classical d-band theory.<sup>39,40</sup>

## Conclusions

We performed a detailed calculation and analysis of the structural stability, electronic property, and catalytic activity of both FeN<sub>4</sub> and axial heteroatom-decorated FeN<sub>4</sub>L (L = P, S and Cl) using DFT calculations. Our results show that all of the axial heteroatom-decorated FeN<sub>4</sub>L SACs have good structural stability. The strong adsorption of the reaction intermediates on FeN<sub>4</sub> resulted in suboptimal catalytic activity for ORR, and the RDS of ORR on FeN<sub>4</sub> is the reduction of OH to H<sub>2</sub>O with an overpotential of 0.58 eV. For the axial heteroatom-decorated FeN<sub>4</sub>L, all of the heteroatoms can bind tightly with the central Fe atom in FeN<sub>4</sub>. Meanwhile, the RDS for FeN<sub>4</sub>P, FeN<sub>4</sub>S and FeN<sub>4</sub>Cl is the hydrogenation of O<sub>2</sub> to OOH with the overpotentials of 1.02 V, 1.09 V and 0.51 V, respectively. FeN<sub>4</sub>Cl is nearly at the top of the volcano diagram, and the overpotential

of ORR is closest to Pt(111). The axial Cl heteroatom decoration improves the ORR catalytic activity compared with pure FeN<sub>4</sub>, while the axial P and S heteroatoms have a negative effect on the ORR. The evaluation of ORR activity *via*  $\Delta G(*OH)$  is applicable for the axial heteroatom-decorated FeN<sub>4</sub>L, although the RDS in the ORR is either the first step or the last step.

## Conflicts of interest

There are no conflicts to declare.

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