

Why high-spin wins: “Spin state locking” governs the oxygen reduction mechanism of Fe-N-C catalysts

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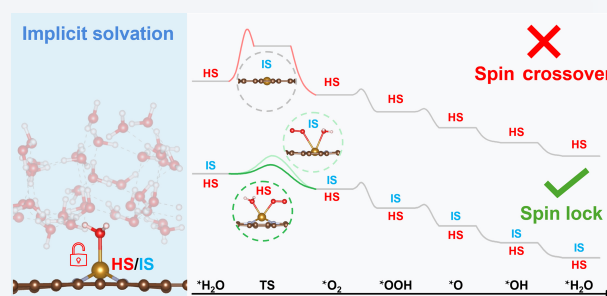
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ABSTRACT: Experimentally synthesized Fe-N-C catalysts invariably exhibit mixed Fe spin states, making it impossible to distinguish the individual contributions of different spin configurations to oxygen reduction reaction (ORR) activity. This has led to conflicting reports, while conventional simulations fail to capture the ORR mechanism under such complexity, creating a significant knowledge gap. Here, we uncover a “spin state locking” mechanism that resolves this puzzle. Using constant-potential *ab initio* molecular dynamics, we demonstrate that adsorbed H₂O kinetically locks the Fe spin state throughout the ORR cycle, preventing spin crossover and confirming that multiple spin states actively contribute to catalysis. By directly comparing kinetics across spin states, we find that high-spin (HS) Fe(II) exhibits superior activity with a half-wave potential of 0.73 V (vs. standard hydrogen electrode (SHE)), far exceeding that of intermediate-spin (IS) FeN₄ (0.46 V). Surprisingly, although OH-coordinated Fe(III) is thermodynamically predicted to be highly active, its kinetic barrier for O₂ activation results in a poor half-wave potential of only −0.1 V. Our work not only establishes the crucial role of spin state locking in Fe-N-C ORR mechanism but also provides the first unambiguous differentiation of how each spin component contributes in mixed-spin catalysts. These insights fundamentally advance the understanding of spin-dependent electrocatalysis.



KEYWORDS: spin state, oxygen reduction reaction, molecular dynamics simulation, Fe-N-C catalysts

1 Introduction

Fe-N-C catalysts are considered promising candidates to replace precious platinum-based catalysts in fuel cells for commercial deployment, owing to their excellent oxygen reduction reaction (ORR) activity and relatively low cost [1–3]. Over the past decade, numerous theoretical and experimental studies have been conducted to investigate the origin of its high activity and the structure of its active sites [4–6]. These works reveal that Fe-N-C materials contain rich FeN_x moieties, in which the coordination, valence state, spin state, and local environment of iron are highly dependent on the synthesis conditions. Among these factors, the spin state of Fe represents a critical parameter that significantly

influences catalytic activity and mechanism, yet it remains difficult to accurately characterize with conventional experimental techniques. To date, many studies have reported the impact of spin configuration on the adsorption strength of oxygen-contained intermediates [7–10], and have proposed various strategies for enhancing the ORR performance of Fe-N-C through spin-state modulation [11–17]. However, because the synthesis process inevitably results in the presence of multiple Fe spin states within the Fe-N-C system (Table S1 in the Electronic Supplementary Material (ESM)), current research struggles to accurately distinguish the contributions of different Fe spin states to catalytic performance.

Mössbauer spectroscopy is the most widely used technique for characterizing Fe spin states in Fe-N-C catalysts. Early studies have clearly established that multiple spin states coexist in these materials [18–20]. Although experimental modulation of spin states is possible by adjusting the relative proportions of these states, achieving a uniform spin configuration remains unattainable. As a result, the correlation between Fe spin state and catalytic activity remains unresolved and highly debated. This controversy stems

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mainly from two issues: (1) Numerous experimental reports on spin characterization and regulation in Fe-N-C present contradictory findings due to the spin multiplicity of Fe, and (2) changes in spin state induced by ligands or dopants are often accompanied by alterations in valence or local chemical environment, making it difficult to isolate the spin effect alone.

As summarized in Table S1 in the ESM, extensive experimental studies on Fe-N-C catalysts clearly identified mixed spin states of Fe according to various characterization techniques. Although many studies (as briefly summarized in Table 1) have successfully modulated Fe spin states and enhanced ORR activity through ligand engineering or doping, there is considerable disagreement over which spin state is responsible for high ORR activity. This inconsistency arises because such modifications affect not only spin but also charge, valence, and local environment of Fe, complicating the decoupling of individual factors. Therefore, experimentally distinguishing the ORR activity of specific Fe spin states while excluding other influences is nearly impossible. Moreover, although Mössbauer spectroscopy can resolve the coexistence of different Fe spin species, current *operando* techniques are unable to directly track spin evolution of individual Fe sites during the ORR process, leaving the spin-dependent reaction pathway experimentally inaccessible. This fundamental limitation highlights the need for a theoretical framework capable of decoupling spin-specific catalytic contributions under reaction conditions.

In theoretical studies, the spin crossover (SCO) effect based on thermodynamic principles is often adopted as the theoretical foundation for mechanistic calculations, meaning that most catalytic reaction studies consider only the lowest-energy spin states of reactants and products [35]. It is well known in coordination chemistry that SCO phenomena are primarily triggered by factors such as temperature, pressure, light irradiation, and gas adsorption [36, 37]. Theoretical studies on FeN₄ suggest that the bare Fe site adopts an intermediate-spin (IS) state ($S = 1$) as its lowest-energy configuration, whereas upon OH adsorption, the Fe center (FeN₄*OH) transitions to a high-spin (HS) state (Fe(III), $S = 5/2$) rather than the expected intermediate-spin ($S = 3/2$) or low-spin ($S = 1/2$) states [38–40]. This implies that ligand-induced crystal field distortion alters the electron occupancy of all Fe 3d orbitals, thereby triggering the SCO effect. Under the assumption of SCO, all

Fe spin states in Fe-N-C are expected to convert to the same spin state to reach the lowest energy after adsorption-desorption of ORR intermediates. This contradicts the experimentally observed phenomenon in which Fe-N-C retains a coexistence of multiple spin states even after catalyzing ORR [6].

Moreover, a theoretical work by Liu et al. shows that the ORR pathway on FeN₄ does not involve a bare FeN₄ site; instead, H₂O desorption and O₂ adsorption are kinetically coupled [41]. This means that the coordination number of Fe in FeN₄ does not change during ORR, casting doubt on the SCO assumption and significantly undermining the persuasiveness of related theoretical studies. Therefore, to thoroughly elucidate the intrinsic relationship between Fe spin state and ORR activity, it is essential to fundamentally distinguish the ORR pathways of Fe under different spin configurations while excluding interference from other confounding factors.

To elucidate the ORR mechanism of Fe-N-C under mixed spin states, this study employs constant-potential density functional theory molecular dynamics (CP-DFT-MD) simulations to investigate the ORR kinetics on FeN₄C₁₀ with different Fe spin states. By calculating the reaction barriers under various spin configurations and ligand environments, we can identify the rate-determining steps (RDS) and clarify how spin states influence ORR activity of Fe-N-C. Finally, we analyze the origins of inconsistencies among experimental findings and discuss the underlying causes.

2 Calculation method

Spin-polarized DFT calculations were performed by using the Vienna *ab initio* simulation package (VASP) [42–44]. In our DFT calculation, the exchange-correlation effect was treated by the general gradient approximation with the Perdew–Burke–Ernzerhof (GGA-PBE) formalism [45]. The van der Waals interaction of adsorbates was described by the empirical correction in Grimme’s scheme (DFT-D3) [46]. The DFT + *U* method was employed to deal the strong correlation effect in Fe with the $U_{\text{eff}} = U - J$ value set as 4.03 eV [39]. The electron–nuclei interaction was described by the projector-augmented wave (PAW) pseudopotential [42]. The energy cutoff of the plane-wave basis set was set to 550 eV. The *k*-point sampling in Brillouin zone was gamma-centered $5 \times 3 \times 1$ mesh for constant potential calculation and single gamma point for reaction barrier calculation. The implicit solvation based on modified Poisson–Boltzmann equation was applied to describe the response behavior of electrolyte with respect to applied potential [47–49]. The dielectric constant and Debye length of implicit electrolyte were set to 80 and 3 Å, respectively [50]. The detailed information for kinetic energy profiles, reaction free energy, and microkinetic simulations method is provided in the ESM.

3 Results and discussion

3.1 “Spin state locking” induced by H₂O adsorption on FeN₄

The bare FeN₄ site is generally regarded as the active center and starting point of the ORR pathway in Fe-N-C, involving three key intermediates: *OOH, *O, and *OH. From a thermodynamic stability perspective, the bare FeN₄ tends to adopt an IS state, while those intermediates prefer an HS state, as shown in Fig. 1(a) and Fig. S1 in the ESM. However, to more realistically account for the

Table 1 Spin manipulation on Fe-N-C and ORR Performance

Method	Spin	$E_{1/2}$ (V)	Ref.
Ligands	IS → HS	0.86 → 0.89 (alkaline)	[21]
Ligands	LS → IS	0.89 → 0.91 (alkaline)	[22]
N doping	IS → LS	0.90 → 0.92 (alkaline)	[23]
Ligands	IS → HS	0.91 → 0.92 (alkaline)	[24]
S doping	HS → LS	0.79 → 0.86 (alkaline)	[25]
Cluster	LS → IS	0.87 → 0.90 (alkaline)	[26]
DACs	LS → IS	0.87 → 0.93 (alkaline)	[27]
Cluster	HS → IS	0.77 → 0.80 (acid)	[28]
DACs	LS → IS	0.79 → 0.84 (alkaline)	[29]
Configuration	IS → HS	0.76 → 0.90 (acid)	[30]
N doping	LS → IS	0.82 → 0.90 (alkaline)	[31]
Ligands	HS → LS	0.79 → 0.85 (acid)	[32]
TACs	IS → LS	0.79 → 0.93 (alkaline)	[33]
Loading density	LS → HS	0.75 → 0.82 (acid)	[34]

non-electrochemical steps and their kinetic barriers in ORR, we also need to consider the adsorption and desorption of H_2O and O_2 on Fe. As shown in Fig. S2 in the ESM, adsorbed H_2O and O_2 stabilize the HS state of FeN_4 . If $\text{FeN}_4^*\text{H}_2\text{O}$ and FeN_4^*O_2 are included in the ORR pathway, SCO effects would arise during the H_2O desorption and O_2 adsorption steps. Nevertheless, calculations of the adsorption energies of H_2O and O_2 reveal that, even considering SCO, FeN_4 exhibits strong adsorption toward both H_2O and O_2 within the ORR potential range (Fig. S3 in the ESM). This implies that in explicit solvation, bare FeN_4 sites cannot exist stably and individually within the ORR potential window. Consequently, whether the SCO effect should be considered in mechanistic studies of ORR remains a subject of debate.

To address this question, we calculated the H_2O desorption energy barriers for the HS and IS states in Figs. 1(b) and 1(c). It shows that within 0.0–0.8 V vs. standard hydrogen electrode (SHE), H_2O desorption barrier on HS FeN_4 is as high as 0.7–0.9 eV, while that for the IS state is lower (0.4–0.7 eV). This suggests that in room-temperature, FeN_4 sites are fully occupied by adsorbed H_2O , making desorption from the catalytic site difficult. Furthermore, according to the work by Liu et al., the H_2O desorption and O_2 adsorption processes on FeN_4 proceed synchronously rather than stepwise [41]. Based on this conclusion, the Fe center of FeN_4 in ORR does not undergo a transition between four-coordination and five-coordination, and its spin state should remain unchanged (Fig. 1(d)).

To verify this hypothesis, we calculated the energy barrier for the O_2 – H_2O displacement reaction on HS and IS FeN_4 , as shown in Figs. 1(e) and 1(f). The results show that, with the coupled H_2O desorption and O_2 adsorption, the displacement kinetic barrier is significantly lower than that for standalone H_2O desorption (Figs. 1(b) and 1(c)). The energy barrier is 0.17–0.37 eV for the HS state and 0.19–0.53 eV for the IS state, with the projected Fe spin moment remaining unchanged during the displacement process at

different electrode potentials (Fig. S4 in the ESM). Figure S5 in the ESM further analyzes the projected density of states (PDOS) of the initial, intermediate, and final states at different electrode potentials. For the HS FeN_4 system, the spin state remains $S = 2$ throughout the reaction process. Although slight redistributions of Fe 3d orbital occupancies (e.g., among $d_{x^2-y^2}$, d_{z^2} , and d_{yz} orbitals) are observed during the reaction, the overall electronic structure and spin configuration remain unchanged, indicating no significant alteration in the electronic state of the Fe center. For the IS FeN_4 system, the initially adsorbed H_2O state maintains a spin configuration of $S = 3/2$ across all four simulated electrode potentials, instead of $S = 1$. This behavior can be attributed to d-orbital electron depletion induced by electrode potentials above the zero-charge potential, as demonstrated in our previous study [39]. Moreover, no spin crossover is observed throughout the displacement and reaction processes, confirming the robustness of the spin-locked configuration within the considered potential range.

To further evaluate the stability of the spin-locked state against thermal fluctuations, additional constant-potential DFT-MD simulations were performed for the $^*\text{H}_2\text{O} + \text{O}_2 \rightarrow ^*\text{O}_2 + \text{H}_2\text{O}$ reaction step at $U = 0.0$ V under 300, 400, and 500 K, considering both HS and IS configurations. The corresponding free-energy profiles are shown in Fig. S6 in the ESM. The results indicate that the reaction barriers remain nearly unchanged with increasing temperature for both spin states, suggesting that the reaction kinetics are insensitive to thermal effects within the studied range. More importantly, the projected spin states of the adsorbed O_2 and Fe center remain unchanged throughout the simulations, and no spin crossover or spin-state exchange events are observed, demonstrating that the spin-locked configurations are thermally stable up to 500 K. Therefore, both HS and IS Fe can be considered as individual ORR sites with distinct activities. We term this phenomenon, where the adsorption of H_2O leads to a fixed spin state, as “spin state locking”, meaning that regardless of the initial

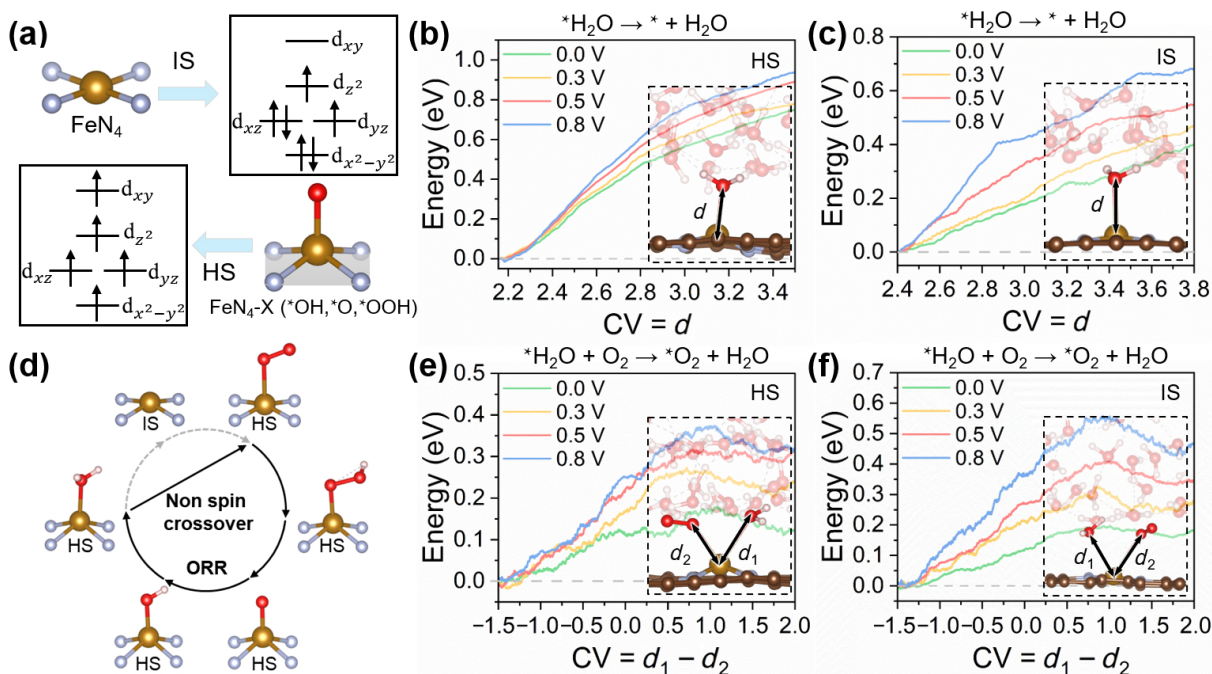


Figure 1 (a) Schematic diagram of spin states of bare FeN_4 and FeN_4 with adsorption intermediates. ((b) and (c)) Potential dependent kinetic energy barrier curves of $^*\text{H}_2\text{O} \rightarrow ^* + \text{H}_2\text{O}$ for (b) HS state and (c) IS state. (d) Schematic illustration of the spin-state evolution of FeN_4 during ORR. ((e) and (f)) Potential dependent kinetic energy barrier curves of $^*\text{H}_2\text{O} + \text{O}_2 \rightarrow ^*\text{O}_2 + \text{H}_2\text{O}$ for (e) HS state and (f) IS state (the insets are structures of transition state and coordination variation (CV)).

spin state of Fe in Fe-N-C, once Fe contacts H₂O, its spin state becomes locked by H₂O, and subsequent ORR reactions proceed exclusively within that corresponding spin state.

However, from an experimental perspective, Fe-N-C catalysts are typically exposed to air after synthesis, which may lead to pre-adsorption of O₂ on the Fe active sites [51]. This raises an important question of whether O₂ adsorption can induce a similar spin-locking effect as observed for H₂O. To address this issue, we additionally investigated the O₂-involved ligand-exchange process. DFT-MD simulations for the $^*O_2 + H_2O \rightarrow ^*H_2O + O_2$ exchange process show that the system maintains its initial spin configuration throughout the entire reaction coordinate, and no spin crossover events are observed, as shown in Fig. S7 in the ESM. In addition, comparison of reaction pathways reveals that direct O₂ desorption is kinetically unfavorable with a high barrier of approximately 0.8 eV, whereas the H₂O-assisted ligand-exchange pathway significantly lowers the barrier to 0.3 eV for HS state and 0.4 eV for IS state. These results indicate that O₂ removal proceeds predominantly via a ligand-exchange mechanism rather than direct desorption, and this process remains governed by the same spin-locking behavior.

The discovery of the “spin state locking” mechanism implies that, in Fe-N-C catalysts with mixed spin states, Fe atoms with different spin states all contribute to the ORR. This also suggests that, to gain a deeper understanding of the ORR on Fe-N-C, it is

necessary to conduct independent studies on the ORR kinetics of Fe sites with different spin states, which will be discussed in next section.

3.2 Comparison of ORR kinetics on HS and IS FeN₄

Based on the premise of “spin state locking”, we separately investigated the ORR reaction pathways and free energies of HS and IS Fe on FeN₄ sites. In acidic condition, we calculated the kinetic barriers of the four electrochemical steps involved in these two pathways (HS and IS paths) at electrode potentials of 0.0, 0.3, 0.5, and 0.8 V vs. SHE (Figs. S8 and S9 in the ESM). To clearly present the results, we summarized the barrier data for all reaction steps and performed fitting analysis, as shown in Figs. 2(a) and 2(b). The results indicate that for the HS state, the reaction step with the highest barrier within the potential range of 0–0.65 V is $^*H_2O + O_2 \rightarrow ^*O_2 + H_2O$. When the potential exceeds 0.65 V, the highest barrier step shifts to $^*OOH + (H^+ + e^-) \rightarrow ^*O + H_2O$. In contrast, for the IS state, the step $^*H_2O + O_2 \rightarrow ^*O_2 + H_2O$ exhibits the highest barrier across all simulated potentials. This comparison clearly distinguishes HS from IS due to their different energy barriers in ORR process, confirming the spin-dependent ORR mechanism in Fe-N-C. Notably, two proton-coupled electron transfer (PCET) steps were found to be effectively barrierless within the investigated potential range, which differs from the alkaline ORR calculations reported by Yan et al., where finite activation barriers were obtained

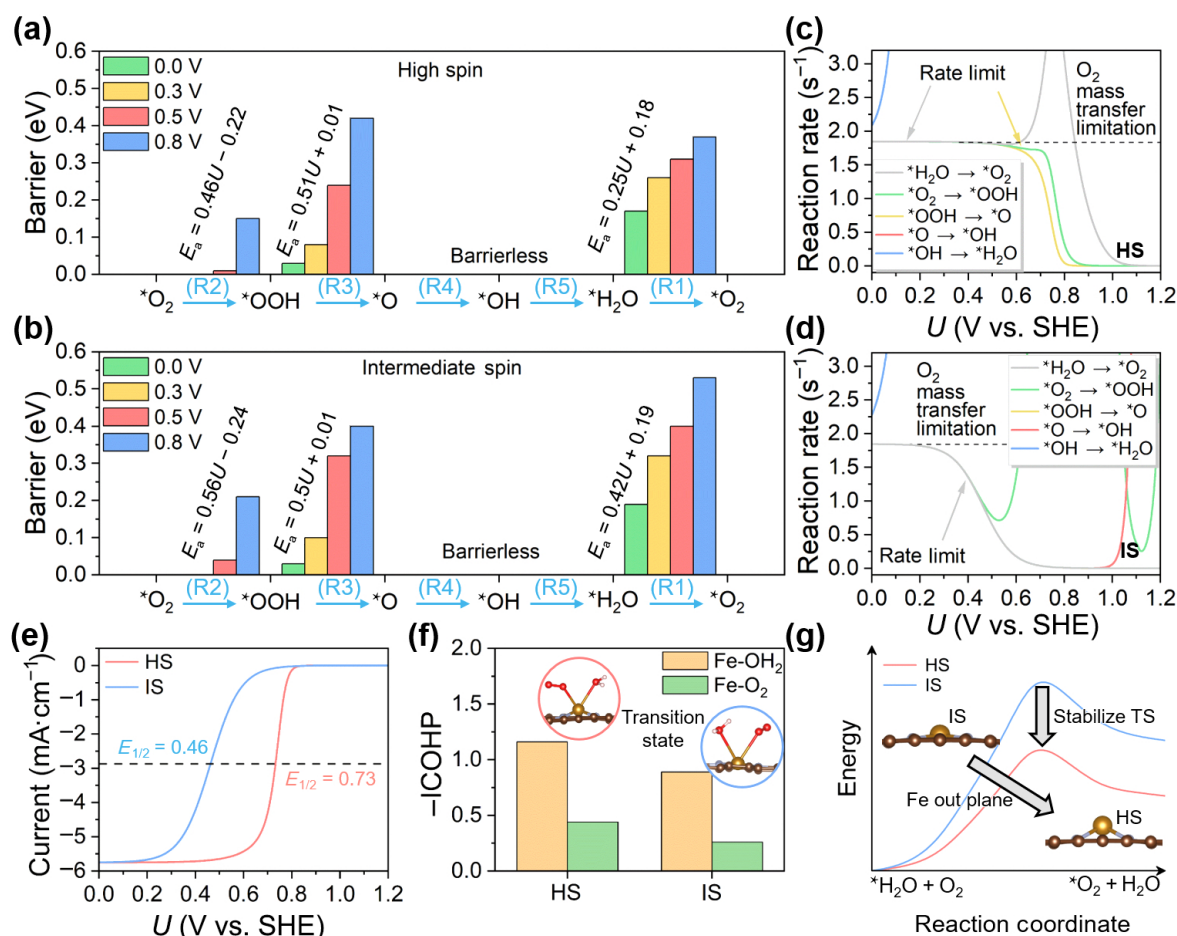


Figure 2 ((a) and (b)) Energy barrier for all of ORR steps under different potentials on (a) HS and (b) IS FeN₄. ((c) and (d)) Potential dependent reaction rate for each step of (c) HS and (d) IS FeN₄. (e) Simulated ORR polarization current density. (f) COHP analysis of the transition state in the reaction $^*H_2O + O_2 \rightarrow ^*O_2 + H_2O$. (g) Schematic diagram of spin state reducing reaction barrier.

for all PCET steps [52]. This difference mainly arises from the distinct proton sources considered in the two studies. In the present work, proton transfer occurs from H_3O^+ under acidic conditions, whereas in the alkaline model of Yan et al., proton transfer is coupled with H_2O dissociation, introducing an additional kinetic penalty. Consequently, partial protonation steps in acidic media can exhibit negligible activation barriers, which are consistent with previous acidic ORR simulations performed by Liu et al. [41].

Due to differences in the specific steps involved in these two reaction pathways, the actual RDS cannot be directly derived from kinetic barriers alone. Therefore, considering factors such as mass transport and collision frequency, we further employed rate equations (Eqs. (S3)–(S18) in the ESM) to investigate the overall ORR kinetic behavior, as shown in Figs. 2(c) and 2(d). These results demonstrate that for the HS state, the RDS of ORR at potentials below 0.5 V is the O_2 – H_2O displacement; when the potential exceeds 0.5 V, it switches to the protonation-then-dehydration of $^*\text{OOH}$. For the IS state, regardless of the applied potential, the RDS remains the O_2 – H_2O displacement. Consequently, the catalytic activities of the HS and IS states are governed by the protonation-then-dehydration of $^*\text{OOH}$ and the O_2 – H_2O displacement step, respectively. The simulated polarization current densities show that the half-wave potentials for the HS and IS states are 0.73 and 0.46 V, respectively (Fig. 2(e)). The former closely aligns with the typically reported experimental half-wave potential range of 0.75–0.8 V for FeN_4 in acidic conditions [28, 30, 32]. Notably, the kinetic barriers for each electrochemical step are nearly identical between the HS and IS states. This indicates that the difference in their catalytic activities stems from the ease of the non-electrochemical O_2 – H_2O displacement step.

To elucidate the influence of HS/IS state FeN_4 on the H_2O – O_2 displacement, we compared the geometric and electronic structures of the transition state. Bonding analysis reveals that the HS state forms stronger bonds with both H_2O and O_2 compared to the IS state (Fig. 2(f)). This suggests that the HS state more effectively promotes the attack of the reactant O_2 to the product H_2O absorbed on Fe, while simultaneously stabilizing the transition state and lowering the reaction energy barrier (Fig. 2(g)). This behavior can be further rationalized by examining the entire ligand-exchange pathway. Additional COHP analysis in Fig. S10 in the ESM shows that HS state exhibits intrinsically stronger interactions with oxygen-containing adsorbates throughout the reaction coordinate. In the initial state, the Fe– H_2O bonding strength is significantly higher on HS-Fe than on IS-Fe (–ICOHP = 1.48 vs. 0.60, ICOHP = integrated crystal orbital Hamilton population). Similarly, in the final state, the Fe– O_2 interaction is also substantially stronger on HS-Fe (–ICOHP = 2.75 vs. 1.44). In the transition state, HS-Fe further enhances the formation of the Fe– O_2 interaction (–ICOHP = 0.44 vs. 0.26), while the difference in Fe– H_2O bonding strength is reduced (–ICOHP = 1.16 vs. 0.89), indicating a more facile displacement of the coordinated H_2O molecule. This phenomenon can be intuitively understood from the transition-state structure: In the HS state, the Fe atom tends to shift away from the graphene plane and toward the solution phase. As shown in Fig. S11 in the ESM, the Fe atom in the HS state is displaced from the plane by an average distance of 0.7 Å, with an average Fe– H_2O bond length of 2.09 Å. In contrast, the Fe atom in the IS state deviates by only 0.15 Å, and the Fe– H_2O bond length increases to 2.40 Å.

According to the PDOS analysis in Fig. S12 in the ESM, the d_{xy} orbital of Fe is empty in the IS state but half-occupied in the HS

state. Since the d_{xy} orbital participates in dsp^2 hybridization and forms bonds with the four N atoms, its occupation implies the filling of Fe–N antibonding orbitals. To alleviate the resulting structural instability, the Fe atom moves out of the plane, which elongates the Fe–N bond length and lowers the energy of the antibonding orbitals. This phenomenon has been discussed and described in detail in our previous work [40]. Such adaptive structural distortion also unexpectedly enhances the axial adsorption to reactant (O_2) and product (H_2O), effectively reducing the H_2O – O_2 displacement barrier and thereby leading to the superior performance observed for the HS state. Notably, a recent experimental study independently demonstrated that the spin state of Fe strongly influences both Fe– H_2O and Fe– O_2 interactions, providing direct experimental evidence for the spin-dependent adsorbate binding behavior proposed in our work [53]. The excellent agreement between experiment and theory further confirms that the spin state governs ORR activity by modulating the interaction strength between Fe active sites and oxygen-containing species. Taken together, these results demonstrate that Fe(II) centers with identical coordination environments can exhibit markedly different ORR activities depending on their spin state. Our simulations reveal that HS-Fe(II) is intrinsically more active than IS-Fe(II), indicating that HS Fe sites contribute more significantly to ORR in Fe–N–C catalysts containing mixed-spin Fe populations.

Furthermore, we investigated the competing two-electron ORR pathway involving H_2O_2 formation. The calculated activation barriers for the $^*\text{OOH}$ hydrogenation step ($^*\text{OOH} + \text{H}^+ + \text{e}^- \rightarrow ^*\text{H}_2\text{O}_2$) are approximately 0.10–0.70 and 0.07–0.60 eV for the HS and IS states, respectively, over the potential range of 0–0.8 V, as shown in Fig. S13 in the ESM. In contrast, the competing $^*\text{OOH}$ dissociation step leading to the four-electron pathway exhibits substantially lower barriers of only about 0.03–0.40 eV for both spin states (Figs. 2(a) and 2(b)). These results indicate that the four-electron pathway is kinetically favored over the two-electron pathway throughout the investigated potential range. Moreover, the barriers for H_2O_2 formation are nearly identical for the HS and IS states, suggesting that the spin state has little influence on the electrochemical proton–electron transfer step of the two-electron pathway, consistent with the negligible spin dependence observed for the electron-transfer steps in the four-electron ORR pathway.

3.3 ORR kinetics in FeN_4^*OH : Influence of axial ligand

Axial ligand engineering is a widely employed experimental strategy for spin-state modulation in Fe–N–C catalysts, which can convert original IS or LS Fe(II) into HS Fe(III) [22, 54, 55]. Some studies have shown that OH adsorption occurs on the back side of Fe–N–C during the ORR, resulting in the actual catalytic site becoming $\text{Fe(III)N}_4^*\text{OH}$ [4, 5, 56]. Therefore, to fully elucidate the ORR mechanism of Fe–N–C, we must compare the ORR kinetics of Fe(II) and Fe(III) under identical conditions. In the $\text{X}^*\text{Fe(III)N}_4^*\text{OH}$ (X refers to ORR intermediates), Fe resides in an octahedral crystal field, where DFT calculation confirms that the IS state exhibits the highest stability (Fig. 3(a)) [39, 40]. As mentioned earlier, the spin state of Fe remains unchanged throughout the reaction process. Therefore, in FeN_4^*OH , Fe is expected to maintain the IS state during ORR. This model system allows us to clarify the regulatory mechanism of axial ligands on ORR activity while excluding interference from spin-state alternation.

We calculated the kinetic barriers of ORR on IS- FeN_4^*OH via

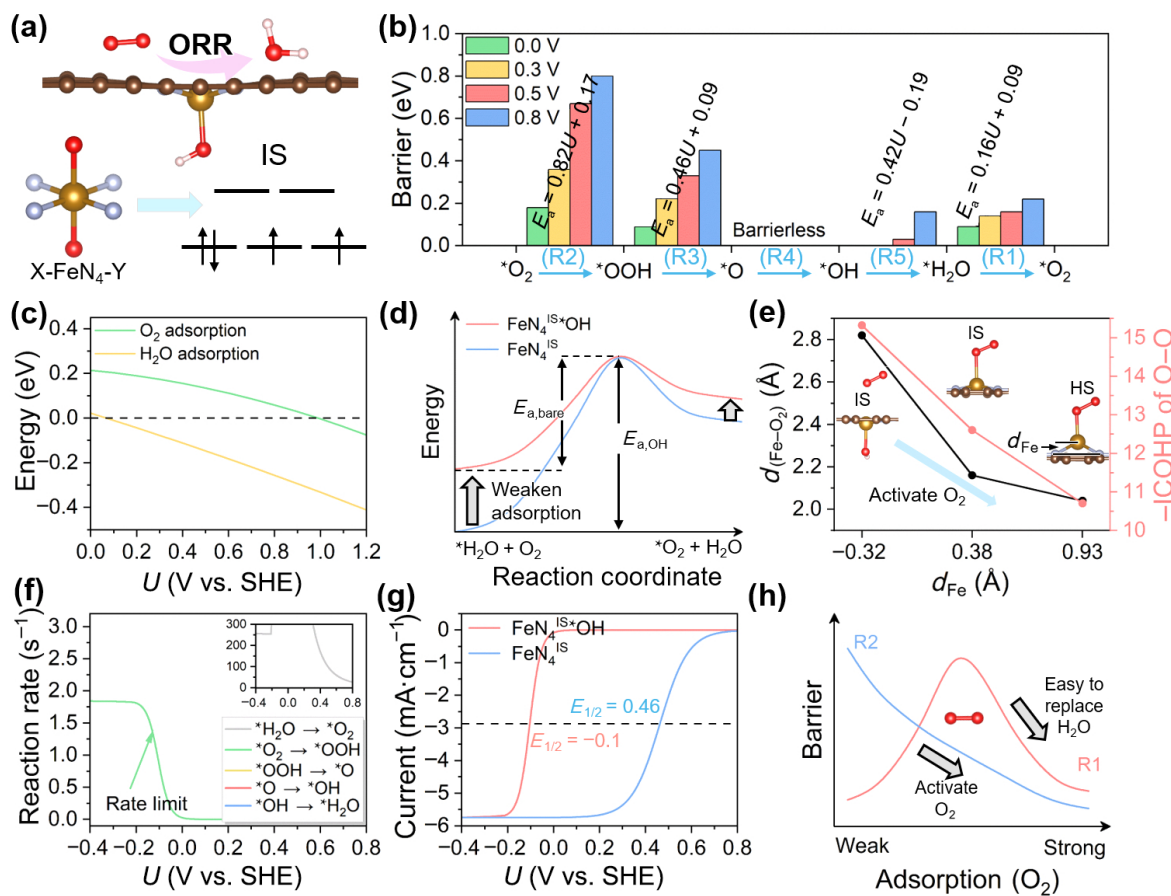


Figure 3 (a) Schematic diagram of the ORR reaction of FeN₄*OH and the spin state of the intermediate. (b) Energy barriers for all of ORR steps under different potentials (c) Potential dependent H₂O and O₂ adsorption energy in FeN₄*OH. (d) Schematic diagram of ligand modification reducing reaction barrier. (e) The relationship between the out-of-plane displacement of Fe and the Fe–O₂ bond length and –ICOHP of O–O. (f) Potential dependent reaction rate for each step. (g) Simulated ORR polarization current density. (h) Schematic diagram of the relationship between reaction barrier and O₂ adsorption strength.

CP-DFT-MD simulation (Figs. S14 and S15 in the ESM), as summarized in Fig. 3(b). It shows that, compared to IS FeN₄ with the same spin state (0.19–0.53 eV), the kinetic barrier for the H₂O–O₂ displacement step on IS FeN₄*OH is significantly reduced to 0.09–0.22 eV. We further found that FeN₄*OH exhibits relatively weak adsorption toward both H₂O and O₂: The adsorption energy of H₂O ranges from 0 to –0.4 eV, and that of O₂ ranges from 0.22 to –0.05 eV (Fig. 3(c)). In contrast, HS FeN₄ shows much stronger adsorption, with adsorption energies for both H₂O and O₂ consistently below –0.6 eV. For IS FeN₄, the adsorption energies of both H₂O and O₂ are below –0.2 eV (Fig. S16 in the ESM). Since the reaction barrier is determined by the energy difference between transition state and initial state, weakening the adsorption strength of H₂O and raising the energy of the initial state can also lower the reaction barrier, as illustrated in Fig. 3(d). Additionally, within the potential range of 0–0.8 V, the reaction barrier for the protonation of *O₂ to form *OOH on FeN₄*OH increases significantly to 0.18–0.8 eV, whereas for HS and IS FeN₄, the barriers are as low as 0.01–0.15 and 0.04–0.21 eV, respectively, at potentials of 0.5–0.8 V. Thus, it can be concluded that introducing OH as an axial ligand weakens the binding affinity of Fe toward O₂ and H₂O while substantially increasing the difficulty of O₂ adsorption and activation.

To further elucidate the influence of the OH ligand on ORR kinetics, we again examined the geometric and electronic structures

of reaction intermediates. By analyzing the O₂ adsorption structure on FeN₄*OH (Fig. 3(e)), we find that the axial OH ligand pulls the Fe center toward the ligand side and away from the O₂ adsorption side. This pulling effect of the axial OH ligand causes the Fe–O₂ bond length on the opposite side to increase to 2.82 Å, thereby significantly weakening O₂ activation. In contrast, in HS FeN₄, the occupation of Fe–N antibonding orbitals displaces the Fe center by 0.93 Å from the graphene plane. This structural distortion shortens the Fe–O₂ bond length to 2.04 Å, which not only favors O₂ activation but also facilitates H₂O–O₂ displacement. The difference in O₂ activation capability directly determines the energy barrier for the protonation of O₂ to form OOH, resulting in a notably higher barrier for FeN₄*OH in the R2 reaction step (protonation of *O₂). Polarization current derived from rate equations further shows that the RDS on IS FeN₄*OH remains the R2 step (Fig. 3(f)), with a corresponding half-wave potential of –0.1 V (Fig. 3(g)). Compared to bare IS FeN₄ ($E_{1/2} = 0.46$ V), axial ligand modification lowers ORR activity, which is attributed to the weakened adsorption and activation capability of the Fe center toward O₂.

This conclusion is inconsistent with the prevalent consensus in much of the literature, which posits that axial ligands enhance ORR activity by weakening OH adsorption and thus facilitating OH desorption [56–59]. Indeed, when we isolate the *OH + (H⁺ + e[–]) → * + H₂O reaction step (an electrochemical step) without considering the H₂O desorption step (a non-electrochemical step), OH

modification does significantly lower the reaction barrier for this specific step (Fig. S17 in the ESM). However, this simplified approach yields controversial conclusions because it fails to accurately reflect the complete ORR pathway. In our monolayer FeN_4 model, which accounts for the full ORR pathway, we propose that strong adsorption of both H_2O and O_2 at the active site is beneficial for the ORR. On the one hand, it promotes O_2 activation during adsorption; on the other hand, it lowers the energy barrier for the $\text{H}_2\text{O}-\text{O}_2$ displacement reaction, as illustrated in Fig. 3(h). Although H_2O adsorbs readily, the subsequently adsorbed O_2 is rapidly consumed in the ORR process. The spin state exerts its influence by altering the catalyst structure, specifically, the out-of-plane displacement of the Fe center, thereby bringing the Fe atom closer to the solution and enhancing the adsorption and activation of O_2 . However, it is reasonable to hypothesize that excessively strong adsorption energies for H_2O and O_2 are not always advantageous, as this could hinder the desorption of the product H_2O and lead to catalyst deactivation. These results clearly confirm that $\text{IS-Fe(III)N}_4^*\text{OH}$ is less ORR-active than IS-Fe(II)N_4 .

To examine whether the effect of OH functionalization can be generalized to other axial ligands, we further investigated the first proton-coupled electron transfer step of ORR ($^*\text{O}_2 + (\text{H}^+ + \text{e}^-) \rightarrow ^*\text{OOH}$) on FeN_4 sites coordinated with Cl and N ligands. The calculated free-energy profiles and kinetic barriers at 0.0 V are shown in Fig. S18 in the ESM. Both Cl- and N-coordinated FeN_4 exhibit noticeable activation barriers for $^*\text{OOH}$ formation, similar to the OH-functionalized Fe(III)N_4 site (Fig. S18(a) in the ESM). In contrast, the bare four-coordinate FeN_4 catalyst shows a barrierless pathway for this step, indicating a fundamentally different reaction energetics in the absence of axial coordination. To further elucidate the origin of this behavior, we analyzed the $\text{Fe}-\text{O}_2$ bonding interactions using COHP and structural parameters (Fig. S18(b) in the ESM). The results show that axial ligands (OH, Cl, and N) consistently lead to elongated $\text{Fe}-\text{O}_2$ bond lengths and weakened $\text{Fe}-\text{O}_2$ bonding interactions compared with bare FeN_4 . Consequently, O_2 activation is suppressed, resulting in an increased kinetic barrier for $^*\text{OOH}$ formation. These results suggest that the influence of axial ligands on ORR activity is not specific to OH, but rather represents a general effect of axial coordination, which modulates $\text{Fe}-\text{O}_2$ bonding strength and thereby alters O_2 activation kinetics.

3.4 Implication of our work to experiments and perspective of spin-dependent ORR activity

In many combined theoretical-experimental studies, theoretical calculations often rely on simplified PCET models and the computational hydrogen electrode (CHE) method, without strictly

accounting for kinetic barriers and non-electrochemical steps, which may introduce certain misinterpretations. As shown in Fig. 4, the limiting potentials obtained from reaction free-energy analysis for HS-FeN_4 , IS-FeN_4 , and $\text{IS-FeN}_4^*\text{OH}$ are 0.96, 0.83, and 0.94 V, respectively. These values are all close to experimental measurements in Table 1, potentially resulting in misleading interpretation of ORR mechanism on Fe-N-C. Our study implies the significance of considering the spin and potential-dependent non-electrochemical barrier in ORR simulations.

In addition, spin states determined by Mössbauer spectroscopy usually represent a superposition of multiple components, suggesting the co-existence of multiple spin states and FeN_x moieties. Therefore, it is not feasible to measure the ORR activity of individual spin states experimentally. Our simulation clearly revealed that the ORR activity follows the order HS-Fe(II)N_4 ($E_{1/2} = 0.73$ V vs. SHE) > IS-Fe(II)N_4 ($E_{1/2} = 0.46$ V vs. SHE) > $\text{IS-Fe(III)N}_4^*\text{OH}$ ($E_{1/2} = -0.10$ V vs. SHE) in Fe-N-C. Although previous studies have suggested that Fe-N-C systems could possess an exceptionally rich variety of active sites, such as FeN_3 , FeN_5 , pyrrolic $\text{FeN}_4\text{C}_{12}$, and defective sites [60–63], and that these sites may also exhibit high ORR activity, our results clearly identify pyridinic HS-Fe(II)N_4 as an ORR-active site and classify IS-Fe(II)N_4 and $\text{IS-Fe(III)N}_4^*\text{OH}$ as ORR-inactive sites in realistic Fe-N-C with multiple Fe spin states. Our simulation can also be a standard research paradigm for studying spin-dependent ORR mechanisms in other types of active sites in Fe-N-C.

Finally, we discuss the potential connection between our results and experimental observations. Our results indicate that, in the electrochemical step of ORR, the IS and HS states have nearly identical barriers. Therefore, the difference in their ORR activity primarily stems from the non-electrochemical step, namely the $\text{H}_2\text{O}-\text{O}_2$ exchange (Figs. 2(a) and 2(b)), which is determined by the degree of Fe's out-of-plane displacement. This change in ORR activity, which is highly sensitive to the position of Fe atoms, is difficult to verify experimentally. This is because, in actual Fe-N-C synthesis, the surrounding structure and position of Fe atoms are often influenced by many complex factors, rather than by a single property such as spin state.

However, fortunately, a recent study by Zhao et al. published in *Nature*, which reported excellent ORR activity for Fe-N-C supported on curved substrates, aligns well with our theoretical perspective [64]. This confirms that, even without chemical modifications such as ligands or doping, adjusting the magnitude of the out-of-plane displacement of the Fe atom in Fe-N-C via spherical carbon substrates can indeed significantly enhance ORR activity. Furthermore, a very recent study by Wan et al. demonstrated that increasing the density of active sites can induce a spin-state transition of Fe centers from low-spin to high-spin,

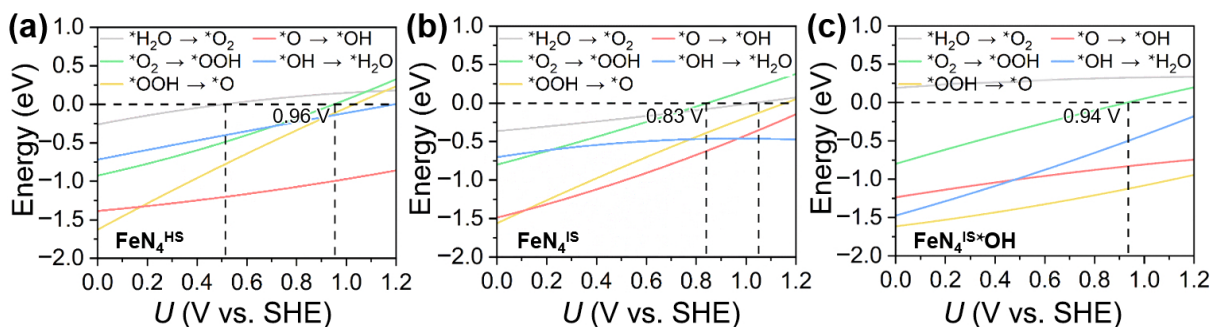


Figure 4 Potential dependent ORR reaction free energy in (a) FeN_4^{HS} , (b) FeN_4^{IS} , and (c) $\text{FeN}_4^{\text{IS}^*\text{OH}}$.

thereby lowering the kinetic barrier of the $\text{H}_2\text{O}-\text{O}_2$ displacement process and enhancing ORR activity. This result further supports the role of spin-state modulation in governing catalytic kinetics in Fe-N-C systems [34]. Moreover, Yi et al. showed that highly graphitized carbon frameworks can act as a macromolecular ligand, reconstructing the electronic structure of FeN_4 sites and inducing a spin-state transition from $S = 0$ to $S = 1$ without altering the FeN_4 coordination environment [53]. This electronic reconstruction selectively suppresses water adsorption via Pauli repulsion while promoting O_2 activation. Collectively, these studies consistently support our theoretical conclusion that the superior ORR activity of high-spin Fe sites originates from their favorable reaction energetics, which can be effectively tuned through out-of-plane structural distortion and extended electronic modulation without modifying the intrinsic FeN_4 structure. In addition, Lai et al. compared the influence of spin states on acetalization reactions using the same experimental conditions in a $[\text{Fe}(\text{NH}_2\text{trz})_3](\text{NO}_3)_2$ dual-state system [36]. They found that the high activity of the HS Fe essentially originates from a more favorable geometric structure to catalytic reaction formed under that specific spin state. This conclusion also matches our findings that the superior ORR activity of HS FeN_4 stems from the out-of-plane protruding feature of the Fe atom. Therefore, we can assert that the microscopic structure of catalysts serves as the critical bridge linking spin state and activity.

4 Conclusions

In this work, we investigated the ORR mechanisms on Fe-N-C catalysts with mixed Fe spin states using CP-DFT-MD and microkinetic modeling. We demonstrate that the ORR on FeN_4 does not proceed via a bare active site. Instead, H_2O desorption and O_2 adsorption are kinetically coupled, forming a $\text{H}_2\text{O}-\text{O}_2$ displacement process. This mechanism suppresses spin crossover effect and causes “spin state locking” effect on Fe in ORR pathways, resulting in spin-dependent activity. Although the HS and IS FeN_4 sites exhibit similar kinetic barriers for most electrochemical steps, their ORR activities differ substantially due to the non-electrochemical $\text{H}_2\text{O}-\text{O}_2$ displacement step. The HS state shows lower barrier for this process, resulting in a higher half-wave potential (0.75 V vs. SHE) that closely matches experimental values under acidic conditions. This enhanced activity originates from the larger out-of-plane displacement of the Fe center in the HS state, which strengthens axial adsorption of H_2O and O_2 , stabilizes the co-adsorbed transition state, and facilitates $\text{H}_2\text{O}-\text{O}_2$ exchange. By introducing axial OH ligands, we further decoupled ligand effects from spin effects. Axial coordination stabilizes the IS state and weakens adsorption of H_2O and O_2 , which lowers the barrier for H_2O displacement but significantly suppresses O_2 activation and increases the protonation barrier of $^*\text{O}_2$. Consequently, the RDS shifts, leading to an overall decrease in ORR activity. Our study clearly reveals the ORR activity of various active sites in pyridinic Fe-N-C: HS-Fe(II)N_4 ($E_{1/2} = 0.73$ V vs. SHE) $>$ IS-Fe(II)N_4 ($E_{1/2} = 0.46$ V vs. SHE) $>$ $\text{IS-Fe(III)N}_4\text{OH}$ ($E_{1/2} = -0.10$ V vs. SHE).

Our work fundamentally reveals, for the first time, how Fe-N-C with mixed spin states catalyze ORR via “spin state locking” mechanism, which has been never explored in early studies. It clarifies that the spin-state-induced activity regulation essentially originates from enhanced activity driven by subtle structural distortions of crystal field on Fe. Our study not only fills a critical gap between experimental and theoretical understanding of ORR mechanism on Fe-N-C but also suggests that the “spin state locking”

mechanism may represent a generic phenomenon in magnetic M-N-C catalysts, thereby offering a paradigm for simulating spin-dependent catalytic mechanism on single-atom-catalysts.

Electronic Supplementary Material: Supplementary material (computational method, constant-potential free energy diagrams, constant potential kinetic integration curve, and Table S2) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908988>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of Competing Interest

All the contributing authors report no conflict of interests in this work.

Author contribution Statement

C. Z. designed the project. M. Y. Y. performed the simulation, data analysis, and manuscript writing. M. Y. Y., X. Y. Z., F. W., E. J. K., and C. Z. participated in the discussion and manuscript revision. All the authors have approved the final manuscript.

Use of AI statement

During the preparation of this work, the authors used ChatGPT (OpenAI) for language polishing and improving the clarity and readability of the manuscript. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

References

- [1] Singh, B.; Gawande, M. B.; Kute, A. D.; Varma, R. S.; Fornasiero, P.; McNeice, P.; Jagadeesh, R. V.; Beller, M.; Zbořil, R. Single-atom (iron-based) catalysts: Synthesis and applications. *Chem. Rev.* **2021**, *121*, 13620–13697.
- [2] Liu, K.; Fu, J. W.; Lin, Y. Y.; Luo, T.; Ni, G. H.; Li, H. M.; Lin, Z.; Liu, M. Insights into the activity of single-atom Fe-N-C catalysts for oxygen reduction reaction. *Nat. Commun.* **2022**, *13*, 2075.
- [3] Amaro-Gahete, J.; Salatti-Dorado, J. A.; Benítez, A.; Esquivel, D.; García-Caballero, V.; López-Haro, M.; Delgado, J. J.; Cano, M.; Giner-Casares, J. J.; Romero-Salguero, F. J. Surface diels-alder adducts on multilayer graphene for the generation of edge-enriched single-atom FeN_4 sites for ORR and OER electrocatalysis. *Sustain. Energy Fuels* **2022**, *6*, 1603–1615.
- [4] Zhao, K. M.; Wu, D. X.; Wu, W. K.; Nie, J. B.; Geng, F. S.; Li, G.; Shi, H. Y.; Huang, S. C.; Huang, H.; Zhang, J. et al. Identifying high-

- spin hydroxyl-coordinated Fe^{3+}N_4 as the active centre for acidic oxygen reduction using molecular model catalysts. *Nat. Catal.* **2025**, *8*, 422–435.
- [5] Mineva, T.; Matanovic, I.; Atanassov, P.; Sougrati, M. T.; Stievano, L.; Clémancey, M.; Kochem, A.; Latour, J. M.; Jaouen, F. Understanding active sites in pyrolyzed Fe-N-C catalysts for fuel cell cathodes by bridging density functional theory calculations and ^{57}Fe Mössbauer spectroscopy. *ACS Catal.* **2019**, *9*, 9359–9371.
 - [6] Abdiaziz, K.; Ni, L. M.; Demirbas, D.; Haak, H.; Reijerse, E.; Theis, P.; Jiang, W.; Chabbra, S.; Lunkenbein, T.; Kramm, U. I. et al. Reversibly redox-active iron oxide structures in FeNC catalysts identified by microscopy and spectroelectrochemical EPR and Mössbauer methods. *J. Am. Chem. Soc.* **2026**, *148*, 3995–4007.
 - [7] Zhang, Z. R.; Ma, P. Y.; Luo, L.; Ding, X. L.; Zhou, S. M.; Zeng, J. Regulating spin states in oxygen electrocatalysis. *Angew. Chem., Int. Ed.* **2023**, *62*, e202216837.
 - [8] Li, J. S.; Ma, J. J.; Ma, Z. A.; Zhao, E. L.; Du, K.; Guo, J. X.; Ling, T. Spin effect on oxygen electrocatalysis. *Adv. Energy Sustain. Res.* **2021**, *2*, 2100034.
 - [9] Bates, J. S.; Johnson, M. R.; Khamespanah, F.; Root, T. W.; Stahl, S. S. Heterogeneous M-N-C catalysts for aerobic oxidation reactions: Lessons from oxygen reduction electrocatalysts: Focus review. *Chem. Rev.* **2023**, *123*, 6233–6256.
 - [10] Shen, H. J.; Thomas, T.; Rasaki, S. A.; Saad, A.; Hu, C.; Wang, J. C.; Yang, M. H. Oxygen reduction reactions of Fe-N-C catalysts: Current status and the way forward. *Electrochem. Energy Rev.* **2019**, *2*, 252–276.
 - [11] Song, K. X.; Yang, B. B.; Zou, X.; Zhang, W.; Zheng, W. T. Unified ORR mechanism criteria via charge-spin-coordination of Fe functional units. *Energy Environ. Sci.* **2024**, *17*, 27–48.
 - [12] Wang, Y. X.; Su, H. Y.; He, Y. H.; Li, L. G.; Zhu, S. Q.; Shen, H.; Xie, P. F.; Fu, X. B.; Zhou, G. Y.; Feng, C. et al. Advanced electrocatalysts with single-metal-atom active sites. *Chem. Rev.* **2020**, *120*, 12217–12314.
 - [13] Yang, X. F.; Wang, A. Q.; Qiao, B. T.; Li, J.; Liu, J. Y.; Zhang, T. Single-atom catalysts: A new frontier in heterogeneous catalysis. *Acc. Chem. Res.* **2013**, *46*, 1740–1748.
 - [14] Qu, G.; Guo, K.; Dong, J. C.; Huang, H. J.; Yuan, P. F.; Wang, Y. J.; Yuan, H. Y.; Zheng, L. R.; Zhang, J. N. Tuning Fe-spin state of FeN_4 structure by axial bonds as efficient catalyst in Li-S batteries. *Energy Storage Mater.* **2023**, *55*, 490–497.
 - [15] Sun, F.; Li, F. H.; Tang, Q. Spin state as a participator for demetalation durability and activity of Fe-N-C electrocatalysts. *J. Phys. Chem. C* **2022**, *126*, 13168–13181.
 - [16] Zhang, J. C.; Li, F. H.; Liu, W.; Wang, Q. L.; Li, X. N.; Hung, S. F.; Yang, H. B.; Liu, B. Modulating spin of atomic manganese center for high-performance oxygen reduction reaction. *Angew. Chem., Int. Ed.* **2024**, *63*, e202412245.
 - [17] Han, X.; Chen, J. X.; He, P.; Lu, J. Harnessing spin effects for heterogeneous single-atom spin catalysis. *Natl. Sci. Rev.* **2024**, *11*, nwae217.
 - [18] Li, J. K.; Sougrati, M. T.; Zitolo, A.; Ablett, J. M.; Oğuz, I. C.; Mineva, T.; Matanovic, I.; Atanassov, P.; Huang, Y.; Zenyuk, I. et al. Identification of durable and non-durable FeN_x sites in Fe-N-C materials for proton exchange membrane fuel cells. *Nat. Catal.* **2021**, *4*, 10–19.
 - [19] Ni, L. M.; Gallenkamp, C.; Wagner, S.; Bill, E.; Krewald, V.; Kramm, U. I. Identification of the catalytically dominant iron environment in iron-and nitrogen-doped carbon catalysts for the oxygen reduction reaction. *J. Am. Chem. Soc.* **2022**, *144*, 16827–16840.
 - [20] Xiao, M. L.; Zhu, J. B.; Ma, L.; Jin, Z.; Ge, J. J.; Deng, X.; Hou, Y.; He, Q. G.; Li, J. K.; Jia, Q. Y. et al. Microporous framework induced synthesis of single-atom dispersed Fe-N-C acidic ORR catalyst and its *in situ* reduced Fe-N_4 active site identification revealed by X-ray absorption spectroscopy. *ACS Catal.* **2018**, *8*, 2824–2832.
 - [21] Li, Z. L.; Zhuang, Z. C.; Lv, F.; Zhu, H.; Zhou, L.; Luo, M. C.; Zhu, J. X.; Lang, Z. Q.; Feng, S. H.; Chen, W. et al. The marriage of the FeN_4 moiety and mxene boosts oxygen reduction catalysis: Fe 3d electron delocalization matters. *Adv. Mater.* **2018**, *30*, 1803220.
 - [22] Zhang, S. R.; Han, Y. T.; Zhang, R.; Zhang, Z. Y.; Sun, G. B. Regulating Fe intermediate spin states via $\text{FeN}_4\text{-Cl-Ti}$ structure for enhanced oxygen reduction. *Adv. Energy Mater.* **2025**, *15*, 2403899.
 - [23] Xia, D. S.; Yang, X.; Xie, L.; Wei, Y. P.; Jiang, W.; Dou, M.; Li, X. N.; Li, J.; Gan, L.; Kang, F. Y. Direct growth of carbon nanotubes doped with single atomic Fe-N₄ active sites and neighboring graphitic nitrogen for efficient and stable oxygen reduction electrocatalysis. *Adv. Funct. Mater.* **2019**, *29*, 1906174.
 - [24] Qiao, J. Y.; Lu, C. J.; Kong, L. Q.; Zhang, J.; Lin, Q. Y.; Huang, H. B.; Li, C. F.; He, W.; Zhou, M.; Sun, Z. M. Spin engineering of Fe-N-C by axial ligand modulation for enhanced bifunctional oxygen catalysis. *Adv. Funct. Mater.* **2024**, *34*, 2409794.
 - [25] Chen, Z. Y.; Niu, H.; Ding, J.; Liu, H.; Chen, P. H.; Lu, Y. H.; Lu, Y. R.; Zuo, W.; Han, L.; Guo, Y. Unraveling the origin of sulfur-doped Fe-N-C single-atom catalyst for enhanced oxygen reduction activity: Effect of iron spinstate tuning. *Angew. Chem.* **2021**, *133*, 25608–25614.
 - [26] Zhang, H. W.; Chen, H. C.; Feizpoor, S.; Li, L. F.; Zhang, X.; Xu, X. F.; Zhuang, Z. C.; Li, Z. S.; Hu, W. Y.; Snyders, R. et al. Tailoring oxygen reduction reaction kinetics of Fe-N-C catalyst via spin manipulation for efficient zinc-air batteries. *Adv. Mater.* **2024**, *36*, 2400523.
 - [27] Yang, G. G.; Zhu, J. W.; Yuan, P. F.; Hu, Y. F.; Qu, G.; Lu, B. A.; Xue, X. Y.; Yin, H. B.; Cheng, W. Z.; Cheng, J. Q. et al. Regulating Fe-spin state by atomically dispersed Mn-N in Fe-N-C catalysts with high oxygen reduction activity. *Nat. Commun.* **2021**, *12*, 1734.
 - [28] Chen, C. J.; Wu, Y. L.; Li, X. L.; Ye, Y. T.; Li, Z. L.; Zhou, Y. F.; Chen, J.; Yang, M. Z.; Xie, F. S. et al. Modulating Fe spin state in FeNC catalysts by adjacent Fe atomic clusters to facilitate oxygen reduction reaction in proton exchange membrane fuel cell. *Appl. Catal. B: Environ.* **2024**, *342*, 123407.
 - [29] Wang, Y. B.; Meng, P. Y.; Yang, Z. H.; Jiang, M.; Yang, J.; Li, H. X.; Zhang, J.; Sun, B. D.; Fu, C. P. Regulation of atomic Fe-spin state by crystal field and magnetic field for enhanced oxygen electrocatalysis in rechargeable zinc-air batteries. *Angew. Chem., Int. Ed.* **2023**, *62*, e202304229.
 - [30] Kim, K.; Kim, G.; Jeong, T.; Lee, W.; Yang, Y.; Kim, B.; Kim, B. H.; Lee, B.; Kang, J.; Kim, M. Activating the Mn single atomic center for an efficient actual active site of the oxygen reduction reaction by spin-state regulation. *J. Am. Chem. Soc.* **2024**, *146*, 34033–34042.
 - [31] Liu, F.; Shi, C. X.; Pan, L.; Huang, Z. F.; Zhang, X. W.; Zou, J. J. Manipulating the spin state to activate the atomically dispersed Fe-N-C catalyst for oxygen reduction. *EES Catal.* **2023**, *1*, 562–570.
 - [32] Shen, D.; Sun, F. F.; Liang, Z. J.; Fu, H. G.; Wang, L. Axial-N induced square-pyramidal crystal field of atomically iron sites for enhancing acidic oxygen reduction. *Angew. Chem., Int. Ed.* **2025**, *64*, e202505937.
 - [33] Song, K. X.; Yang, B. B.; An, W. G.; Liang, Q.; Lin, J. K.; Zhang, H. Y.; Qi, Y. G.; Lai, Y. C.; Chen, Z. J.; Li, W. W. et al. Dynamic spin governing asymmetric coordination fields in trimetallic single-atom catalysts for optimal oxygen reduction. *Angew. Chem., Int. Ed.* **2026**, *65*, e19740.
 - [34] Wan, H.; Hou, X. X.; Chen, S.; Fan, Z. C.; Lin, L.; Yin, Y. X.; Zhao, W. Y.; Hou, L. N.; Yan, H.; Wang, Y. et al. Fe loading triggers high-spin state: Expediting $\text{H}_2\text{O/O}_2$ swap in fuel cell cathodes. *J. Am. Chem. Soc.* **2026**, *148*, 4329–4338.
 - [35] Duan, Z. Y.; Henkelman, G. Surface charge and electrostatic spin crossover effects in CoN_4 electrocatalysts. *ACS Catal.* **2020**, *10*, 12148–12155.
 - [36] Lai, Y. J.; Getzner, L.; Enríquez-Cabrera, A.; Molnár, G.; Routaboul, L.; Bousseksou, A. Spin state-driven modulation of catalytic activity of an iron spin-crossover complex: Toward switchable catalysis. *ChemCatChem* **2025**, *17*, e202500127.



- [37] He, P.; Zhu, S. F. Spin crossover and its application in organometallic catalysis: Concepts and recent progress. *Chem.—Eur. J.* **2024**, *30*, e202403437.
- [38] Zheng, T.; Wang, J. C.; Xia, Z. H.; Wang, G. F.; Duan, Z. Y. Spin-dependent active centers in Fe-N-C oxygen reduction catalysts revealed by constant-potential density functional theory. *J. Mater. Chem. A* **2023**, *11*, 19360–19373.
- [39] Yu, M. Y.; Li, A.; Kan, E. J.; Zhan, C. Substantial impact of spin state evolution in OER/ORR catalyzed by Fe-N-C. *ACS Catal.* **2024**, *14*, 6816–6826.
- [40] Yu, M. Y.; Wu, J. X.; Chen, Y. S.; Du, Y. P.; Li, A.; Kan, E. J.; Zhan, C. Strain-controlled spin regulation in Fe-N-C catalysts for enhanced oxygen reduction reaction activity. *J. Mater. Chem. A* **2024**, *12*, 24530–24541.
- [41] Yu, S.; Levell, Z.; Jiang, Z.; Zhao, X. H.; Liu, Y. Y. What is the rate-limiting step of oxygen reduction reaction on Fe-N-C catalysts. *J. Am. Chem. Soc.* **2023**, *145*, 25352–25356.
- [42] Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **1994**, *50*, 17953–17979.
- [43] Kresse, G.; Furthmüller, J. Efficiency of *ab-initio* total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci* **1996**, *6*, 15–50.
- [44] Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **1999**, *59*, 1758–1775.
- [45] Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- [46] Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comput. Chem.* **2006**, *27*, 1787–1799.
- [47] Mathew, K.; Kolluru, V. S. C.; Mula, S.; Steinmann, S. N.; Hennig, R. G. Implicit self-consistent electrolyte model in plane-wave density-functional theory. *J. Chem. Phys.* **2019**, *151*, 234101.
- [48] Mathew, K.; Sundaraman, R.; Letchworth-Weaver, K.; Arias, T. A.; Hennig, R. G. Implicit solvation model for density-functional study of nanocrystal surfaces and reaction pathways. *J. Chem. Phys.* **2014**, *140*, 084106.
- [49] Gauthier, J. A.; Ringe, S.; Dickens, C. F.; Garza, A. J.; Bell, A. T.; Head-Gordon, M.; Nørskov, J. K.; Chan, K. Challenges in modeling electrochemical reaction energetics with polarizable continuum models. *ACS Catal.* **2019**, *9*, 920–931.
- [50] Hagopian, A.; Doublet, M. L.; Filhol, J. S.; Binniger, T. Advancement of the homogeneous background method for the computational simulation of electrochemical interfaces. *J. Chem. Theory Comput.* **2022**, *18*, 1883–1893.
- [51] Zhang, X.; Zhao, J.; Heng, C. Q.; Lei, Y. Y.; Yu, M. Y.; Xiang, Z. H.; Hu, M. Y.; Zhao, J. Y.; Alp, E. E.; Li, X. N. et al. Identification of *in situ* generated high-spin Fe(II)–N₄ active sites for acidic oxygen reduction reaction via *operando* ⁵⁷Fe Mössbauer spectroscopy. *ACS Catal.* **2026**, *16*, 8996–9007.
- [52] Yan, H. M.; Wang, G.; Lv, X. M.; Cao, H.; Qin, G. Q.; Wang, Y. G. Revealing the potential-dependent rate-determining step of oxygen reduction reaction on single-atom catalysts. *J. Am. Chem. Soc.* **2025**, *147*, 3724–3730.
- [53] Yin, Y. X.; Hou, L. N.; Fan, Z. C.; Lin, L.; Zhao, W. Y.; Mao, L.; Wan, H.; Ge, J. J. Spin-selective water rejection in Fe-N-C catalysts via graphitic macro-ligand engineering. *J. Am. Chem. Soc.* **2026**, *148*, 17083–17093.
- [54] Miao, K. H.; Qin, J. D.; Lai, S. Y.; Luo, M.; Kuchkaev, A.; Yakhvarov, D.; Kang, X. W. Spin regulation of nickel single atom catalyst via axial phosphor-coordination achieves near unity CO selectivity in electrochemical CO₂ reduction. *Adv. Funct. Mater.* **2025**, *35*, 2419989.
- [55] Gallenkamp, C.; Kramm, U. I.; Krewald, V. FeN₄ environments upon reduction: A computational analysis of spin states, spectroscopic properties, and active species. *JACS Au* **2024**, *4*, 940–950.
- [56] Wang, Y.; Tang, Y. J.; Zhou, K. Self-adjusting activity induced by intrinsic reaction intermediate in Fe-N-C single-atom catalysts. *J. Am. Chem. Soc.* **2019**, *141*, 14115–14119.
- [57] Huang, Z.; Tang, Q. Axial coordination effect on the oxygen reduction reaction of FeN₄ electrocatalysts based on grand canonical density functional theory. *J. Phys. Chem. C* **2022**, *126*, 21606–21615.
- [58] Han, Y. H.; Wang, Y. G.; Xu, R. R.; Chen, W. X.; Zheng, L. R.; Han, A. J.; Zhu, Y. Q.; Zhang, J.; Zhang, H. B.; Luo, J. et al. Electronic structure engineering to boost oxygen reduction activity by controlling the coordination of the central metal. *Energy Environ. Sci.* **2018**, *11*, 2348–2352.
- [59] Yang, Z. K.; Wang, Y.; Zhu, M. Z.; Li, Z. J.; Chen, W. X.; Wei, W. C.; Yuan, T. W.; Qu, Y. T.; Xu, Q.; Zhao, C. M. et al. Boosting oxygen reduction catalysis with Fe–N₄ sites decorated porous carbons toward fuel cells. *ACS Catal.* **2019**, *9*, 2158–2163.
- [60] Levell, Z.; Yu, S.; Wang, R. Y.; Liu, Y. Y. What is the “other” site in M-N-C. *J. Am. Chem. Soc.* **2025**, *147*, 603–609.
- [61] Liang, X.; Li, Z. Y.; Xiao, H.; Zhang, T. F.; Xu, P.; Zhang, H.; Gao, Q. M.; Zheng, L. R. Two types of single-atom FeN₄ and FeN₅ electrocatalytic active centers on N-doped carbon driving high performance of the SA-Fe-NC oxygen reduction reaction catalyst. *Chem. Mater.* **2021**, *33*, 5542–5554.
- [62] Li, Y. C.; Liu, X. F.; Zheng, L. R.; Shang, J. X.; Wan, X.; Hu, R. M.; Guo, X.; Hong, S.; Shui, J. L. Preparation of Fe-N-C catalysts with FeN_x (x = 1, 3, 4) active sites and comparison of their activities for the oxygen reduction reaction and performances in proton exchange membrane fuel cells. *J. Mater. Chem. A* **2019**, *7*, 26147–26153.
- [63] Tan, Y.; Fu, J. W.; Luo, T.; Liu, K.; Liu, M. Theoretical insights into the selectivity of single-atom Fe-N-C catalysts for electrochemical NO_x reduction. *J. Am. Chem. Soc.* **2025**, *147*, 4937–4944.
- [64] Zhao, Y. S.; Wan, J. W.; Ling, C. Y.; Wang, Y. L.; He, H. Y.; Yang, N. L.; Wen, R.; Zhang, Q. H.; Gu, L.; Yang, B. L. et al. Acidic oxygen reduction by single-atom Fe catalysts on curved supports. *Nature* **2025**, *644*, 668–675.



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