### RESEARCH ARTICLE

## Building Fe atom-cluster composite sites using a site occupation strategy to boost electrochemical oxygen reduction

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### Funding information

Guangdong Basic and Applied Basic Research Foundation, Grant/Award Number: 2022A1515011677; the National Natural Science Foundation of China, Grant/Award Numbers: 22109100, 22075203; Shenzhen Science and Technology Project Program, Grant/Award Number: JCYJ2021032409420401; Natural Science Foundation of SZU, Grant/Award Number: 000002111605

### Abstract

The high-temperature pyrolysis process for preparing M-N-C single-atom catalyst usually results in high heterogeneity in product structure concurrently contains multiscale metal phases from single atoms (SAs), atomic clusters to nanoparticles. Therefore, understanding the interactions among these components, especially the synergistic effects between single atomic sites and cluster sites, is crucial for improving the oxygen reduction reaction (ORR) activity of M-N-C catalysts. Accordingly, herein, we constructed a model catalyst composed of both atomically dispersed FeN4 SA sites and adjacent Fe clusters through a site occupation strategy. We found that the Fe clusters can optimize the adsorption strength of oxygen reduction intermediates on FeN<sub>4</sub> SA sites by introducing electron-withdrawing -OH ligands and decreasing the d-band center of the Fe center. The as-developed catalyst exhibits encouraging ORR activity with halfwave potentials  $(E_{1/2})$  of 0.831 and 0.905 V in acidic and alkaline media, respectively. Moreover, the catalyst also represents excellent durability exceeding that of Fe–N–C SA catalyst. The practical application of Fe(Cd)–CN<sub>x</sub> catalyst is further validated by its superior activity and stability in a metal-air battery device. Our work exhibits the great potential of synergistic effects between multiphase metal species for improvements of single-atom site catalysts.

### **KEYWORDS**

d-band center, metal clusters, oxygen reduction reaction, single-atom catalyst, site occupations strategy

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### WILEY-CARBON ENERGY 1 | INTRODUCTION

Proton-exchange membrane fuel cells (PEMFCs) are highefficiency, renewable electrochemical energy conversion devices that require highly active and durable cathode catalysts for the oxygen reduction reaction (ORR).<sup>1-3</sup> Platinum-group metals possess the highest ORR kinetic activity and are currently used as the cathode catalysts in PEMFC.<sup>4–6</sup> Yet, the high expense, scarcity, and low poisoning tolerance of Pt have prompted the search focusing on preparing electrocatalysts with low-cost earth-abundant materials.<sup>4,7-9</sup> Among various substitutes, metal-nitrogen-carbon (M-N-C) catalysts (i.e., Fe-N-C) prepared via pyrolysis are regarded as the most promising material because of their best performance under acidic conditions.<sup>10–15</sup> However, the high pyrolysis temperature of M-N-C catalysts generally results in highly heterogeneous structures containing metal single atoms (SAs), metal nanoparticles (NPs), and metal atomic clusters (ACs).<sup>16–22</sup> Thus, the effects of the different constituents for ORR are still debated, especially the synergies between these components.<sup>23,24</sup> Although previous investigations have demonstrated that the electronic interactions between SA sites and metal NPs/ACs can improve the intrinsic activity of SA sites, however, these synergies have only been proved in alkaline solution because these metal NPs/ ACs are unstable in acidic media.<sup>25–30</sup> Currently, encapsulating these metal NPs and ACs into graphene layer is effective to enhance their ORR stability in an acidic medium.<sup>31–36</sup> Unfortunately, the electron penetration between SAs and NPs/ACs becomes really weak if the layer number of graphite carbon is greater than three, owing to the rapid decline in electron potential with thickness of graphite-carbon layer.<sup>31,37</sup> It suggests that the synergistic effects between metal SAs and metal NPs/ACs will also become more insignificant.<sup>25,35,38</sup> Furthermore, previous strategies for constructing these composite catalyst composed of metal SAs and NPs/ACs are typically to increase the metal content in the catalyst precursors.<sup>39</sup> This leads to the formation of a large number of metal NPs and ACs, both of which are not active for the ORR, thus reducing metal atoms that would be available for the SA sites formation.<sup>39,40</sup> Thus, the development of a new strategy to introduce acid-stable metal NPs/ACs NPs or ACs into SA catalysts, without sacrificing active SA sites, is essential to elucidating the role of interactions between multiphase metal species.

In this work, we constructed a catalyst composed of both atomically dispersed FeN<sub>4</sub> sites and adjacent Fe clusters, which is achieved via pyrolyzing dopingcontrollable FeCd-codoped Zn-zeolitic imidazolate framework (ZIF) precursor. Both Fe<sup>3+</sup> and Cd<sup>2+</sup> are encapsulated in situ in the pores of ZIF-8, and Cd<sup>2+</sup>

competes with Fe<sup>3+</sup> to reduce the amount of Fe precursor, leading to the formation of complex sites of Fe ACs and Fe SAs (denoted as Fe(Cd)-CN<sub>x</sub>) after carbonization. Synergistic effect of Fe SAs and ACs, the as-obtained Fe(Cd)-CN<sub>x</sub> catalyst exhibited an ultrahigh ORR performance with half-wave potential  $(E_{1/2})$  of 0.905 and 0.831 V in alkaline and acidic media, respectively. Additionally, Fe(Cd)-CN<sub>x</sub> also shows outstanding longterm stability, with only a 17 mV positive shift in halfwave potential after 10,000 cycles in harsh acidic media. In addition, when used as catalysts in liquid or flexible solid-state rechargeable metal-air cells, the corresponding electrodes fabricated with the  $Fe(Cd)-CN_r$  catalyst exhibit high power density and outstanding long-term cycle stability, superior to state-of-the-art catalysts.

#### **RESULTS AND DISCUSSION** 2

#### 2.1 Synthesis and characterization

The synthetic schematic of Fe SCs and FeN<sub>4</sub> composite sites is depicted in Figure 1A. In detail, we used a ZIF-8 as host to in situ trap metal precursor  $(Cd(NO_3)_2)$ ,  $Fe(acac)_3$  in their cages during ZIF crystallization. The results of X-ray diffraction (XRD) (Figure S1) demonstrated that the crystal structure of Fe, Cd@ZIF-8 resembles that of the original ZIF-8, suggesting that Fe<sup>3+</sup> and Cd<sup>2+</sup> are encapsulated in the ZIF-8 micropores. Thereafter, the Fe,Cd@ZIF-8 precursors were calcined in inert N2 at 950°C for carbonization, followed by Zn and Cd removal to obtain the atomically dispersed FeN<sub>4</sub> SAs and adjacent Fe ACs on a nitrogen-doped carbon framework. The preparation of Fe,Cd@ZIF-8 by adding  $Cd(NO_3)_2$  is advantageous in the following terms: (1) the easy evaporation of Cd favors the creation of porous structures during the pyrolysis process due to its low boiling point; (2) both  $Fe^{2+}$  and  $Cd^{2+}$  are in situ encapsulated in the ZIF-8 micropores, and Cd<sup>2+</sup> competes with Fe<sup>3+</sup> to reduce the amount of Fe precursor Fe precursors, resulting in the formation of Fe ACs during carbonization. The morphological structures of the obtained samples were characterized by scanning electron microscopy and transmission electron microscopy (TEM) (Figures 1B–D and S2–S4). The Fe– $CN_r$  catalyst preserves the rhombic dodecahedral shape of ZIF-8 well, indicating the efficiency of using ZIF-8 as a precursor to achieve catalyst with uniform morphology. Moreover, the Cd–CN<sub>x</sub> and Fe(Cd)–CN<sub>x</sub> catalysts also retain their rhombic dodecahedral morphology because the Cd(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O molecules were also encapsulated in ZIF-8 micropores. Furthermore, no obvious metal particles were observed in the TEM image of  $Fe(Cd)-CN_x$ 



**FIGURE 1** Synthetic procedure and structural characterizations. (A) Schematic illustration for the preparation of  $Fe(Cd)-CN_x$ . (B, C) Field emission scanning electron microscopy image of  $Fe(Cd)-CN_x$ . (D) TEM image of  $Fe(Cd)-CN_x$ . (E) Aberration-corrected HAADF-STEM, (F) yellow dash area displaying the enlarged aberration-corrected HAADF-STEM image, and (G) elemental mapping of  $Fe(Cd)-CN_x$ .

samples, which ruled out the formation of Fe NPs. The subangstrom resolution aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was carried out to further study the distribution of Fe species at the atomic scale. The coexistence of Fe SAs and Fe ACs was observed on the carbon backbone (Figure 1E). The magnified image in Figure 1, more clearly, shows that several Fe atoms (indicated by red circles) tightly surround a AC (indicated by green circle) with distances less than 0.6 nm, suggestin the successful construction of the complex sites of Fe ACs and satellite Fe SAs. The short lattice spacing enables rapid electron transfer from ACs to SAs. The corresponding elemental mapping (Figure 1G) reveals the uniform distribution of C, N, and Fe.

# 2.2 | Electronic and coordination structures

XRD was performed to evaluate the crystalline phases. As seen in Figures S1 and 2A, no diffraction peaks associated

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with Fe crystalline substances were found in the XRD patterns, excluding the existence of Fe NPs. Furthermore, no distinct differences were found among the resultant  $Fe(Cd)-CN_x$ ,  $Fe-CN_x$ ,  $Cd-CN_x$ , and  $CN_x$  catalysts, while characteristic peaks of amorphous and graphitized carbon were clearly observed.<sup>41,42</sup> As the Raman spectra (Figure 2B) show, Fe(Cd)– $CN_x$  has a peak intensity ratio  $(I_D/I_G)$  of D and G bands than Fe–CN<sub>x</sub>, while Cd–CN<sub>x</sub> has a lower  $I_D/I_G$  ratio than  $CN_x$ . These suggest that the introduction of Cd can enhance the graphitization and electrical conductivity of the carbonaceous materials. N<sub>2</sub> adsorption/desorption measurements (Figures 2C, S5 and Table S1) were performed to analyze the surface area and the corresponding pore size distribution. As shown in Figures 2C and S5, the N<sub>2</sub> sorption isotherms and pore structure of Fe(Cd)– $CN_x$  hardly deviate from those of the pristine Fe-CN<sub>x</sub>, as the Cd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O anchored in ZIF-8

micropores will be decomposed upon thermal treatment and, therefore, has no effect on the pore structure. These results suggest that the role of Cd in Fe(Cd)–CN<sub>x</sub> is not to regulate the pore structure and increase the specific surface. These catalysts were also investigated by thermal weight analysis (Figure S6). The Fe(Cd)–CN<sub>x</sub> and Cd–CN<sub>x</sub> have greater weight loss than Fe–CN<sub>x</sub> and CN<sub>x</sub>, respectively, which further proved that there was Cd<sup>2+</sup> volatilization in addition to Zn<sup>2+</sup> volatilization during the carbonization process.

X-ray photoelectron spectroscopy (XPS) was used to examine the surface composition. Figure S7 indicates the typical signals of Fe, C, N, and O for these four catalysts, and Table S2 shows the Fe, C, N, and O contents of  $Fe(Cd)-CN_x$  and  $Fe-CN_x$  catalysts (Supporting Information). The high-resolution N 1s spectrum of  $Fe(Cd)-CN_x$  was deconvoluted into four



**FIGURE 2** Structure characterizations of the catalysts. (A) XRD patterns, (B) Raman spectra, (C)  $N_2$  adsorption and desorption curves, (D) high-resolution N 1s XPS spectra, and (E) high-resolution Fe 2p XPS spectra of Fe(Cd)–CN<sub>x</sub>, Fe–CN<sub>x</sub>, Cd–CN<sub>x</sub>, and CN<sub>x</sub>. (F) Normalized Fe K-edge XANES spectra of Fe(Cd)–CN<sub>x</sub> and Fe foil. (G) EXAFS fitting curve for Fe(Cd)–CN<sub>x</sub> and Fe foil. (H, I) Fe K-edge EXAFS for the (H) resultant Fe foil reference and (I) Fe(Cd)–CN<sub>x</sub>.

peaks (Figure 2D and Table S3), name, pyridine-N (~398.4 eV), Fe-N (~399.1 eV), graphite-N (~400.7 eV), and oxidized-N (~404.1 eV). The high relative content of pyridine-N (28.7%) and graphite-N (48.0%) in  $Fe(Cd)-CN_x$  catalysts contributes to enhanced ORR kinetics. Pyridine N usually supplies coordination sites for Fe atoms to form  $Fe-N_x$ . Graphite N influences the electronic structure and geometry of the carbon framework; meanwhile, the graphite N fraction shows an active role in improving the ultimate current density and catalytic stability of ORR catalysts. 43-45 The formation of N-doped graphite carbon is further confirmed by the peak at 284.8 eV of the C bonded to N in the C 1s spectrum (Figure S8). The presence of Fe-N fraction in  $Fe(Cd)-CN_x$  is also demonstrated by the XPS spectra shown in Figure 2D. The XPS Fe 2p peak of Fe(Cd)– $CN_x$  (Figure 2E) shows a 0.40 eV shift to a higher bonding energy compared to the sample without the introduction of  $Cd(Fe-CN_x)$ . Thus, the negative shift may be due to the introduction of Fe AC. Additionally, the spectrum of  $Fe(Cd)-CN_x$  can be deconvoluted into two sets of doublet peaks assigned to the Fe<sup>2+</sup> (722.68 eV for  $2p_{1/2}$  and 709.58 eV for  $2p_{3/2}$ ) and the ionic  $\text{Fe}^{3+}$  (724.08 eV for  $2p_{1/2}$  and 710.98 eV for  $2p_{3/2}$ ). The characteristic peaks of Cd were absent in the XPS spectra of all four obtained catalysts (Figure S9), which are consistent with inductively coupled plasma-mass spectrometry (ICP-MS) results with ultra-low Cd content (Table S4). The measured Fe and Cd loadings of Fe(Cd)-CN<sub>x</sub> by ICP-MS in Table S4 were, respectively, 0.8160 and 0 wt%, indicating that Cd<sup>2+</sup> was removed almost completely pyrolysis. Therefore, the effect of  $Cd^{2+}$  on the catalytic performance is negligible. Elemental analysis (Table S5) shows slight compositional variation between samples, with Fe(Cd)- $CN_x$  having high N and C content.

X-ray absorption spectroscopy was used to investigate the electronic structure and coordination environment of Fe atoms in the catalysts. In the Fe K-edge X-ray absorption near-edge structure (XANES) spectrum in Figure 2F, the Fe(Cd)-CN<sub>x</sub> catalyst has a higher nearedge absorption than the Fe foil, reflecting an oxidation state of Fe greater than 0, consistent with XPS results. The Fe coordination environment was determined from the Fourier transform curves of the Fe K-edge  $k^2$ weighted extended X-ray absorption fine structure (EXAFS) data in Figures 2G and S10. The Fe–N scattering path can be mainly attributed to the main peak at 1.4 Å observed in Fe(Cd)–CN<sub>x</sub>. The weak peak at 2.4 Å corresponds to the Fe-Fe coordination, which indicates the presence of some Fe ACs.46 The Fe-Fe bond of Fe(Cd)– $CN_x$  has a slight difference compared to that of Fe foil (2.2 Å) in R-value, probably due to the different 5 of 11

degree of coordination between the bulk Fe and the Fe clusters. The average Fe-N coordination number (CN) based on data fitting was 4 (Table S6), indicating that a typical Fe-N<sub>4</sub> structure is the main active center of the Fe(Cd)- $CN_x$  catalyst. These coordinatively unsaturated Fe sites facilitate efficient catalytic ORR.42 Also, the Fe-Fe CN is  $1.1 \pm 1.0$ , which implies the presence of a certain number of Fe ACs. Wavelet transform (WT) analysis was conducted to gain further insight into the k-space resolution, and the WT contour plots showed that there were dispersed FeN<sub>4</sub> SA sites and adjacent Fe ACs coexisting in the Fe(Cd)- $CN_x$  catalyst.<sup>47</sup> The maximum intensity of around  $3.5 \text{ Å}^{-1}$  in k-space indicated the dominance of Fe-N coordination, while the second highest intensity of about  $5.8 \text{ Å}^{-1}$  was attributed to Fe–Fe scattering (Figure 2H,I). The negative *k*-value shift in the Fe–Fe bond of the Fe foil ( $\approx 7.6 \text{ Å}^{-1}$ ) may be due to the different CNs between bulk Fe and Fe ACs.<sup>48,49</sup> Thus. there are dispersed FeN<sub>4</sub> SA sites and adjacent Fe clusters coexisting in the Fe(Cd)- $CN_x$  catalyst.

### 2.3 | Electrocatalytic ORR performance

Electrocatalytic ORR performance of Fe(Cd)-CN<sub>n</sub>, Fe-CN<sub>n</sub> Cd-CN<sub>x</sub>, FeCd-CN<sub>x</sub>, and CN<sub>x</sub> were evaluated and compared with commercial Pt/C in both O<sub>2</sub>-saturated acid  $(0.1 \text{ M HClO}_4)$  and alkaline (0.1 M KOH) electrolyte. The polarization curves in Figure 3A show the order of ORR activity:  $Fe(Cd)-CN_x > Fe-CN_x \gg Fe-Cd-CN_x \gg Cd CN_x$  with  $E_{1/2}$  evaluated at 0.831, 0.785, 0.605, and 0.451 V, respectively. The  $Fe(Cd)-CN_x$  possesses better ORR activity than Fe-CN<sub>x</sub> and FeCd-CN<sub>y</sub> implying the essential synergetic roles of SA sites and adjacent Fe clusters in improving ORR activity in acidic media. The ultra-low current density of Cd-CN<sub>x</sub> and the similar performance comparable to CN<sub>x</sub> indicate that the Cd site is ineffective in the acidic ORR reaction. As seen in Figure 3B, Fe(Cd)– $CN_x$ has the smallest Tafel plot slope (67.89 mV dec<sup>-1</sup>) among all these electrocatalysts, which further supports its ability to accelerate the reaction kinetics. Notably,  $Fe(Cd)-CN_x$ displays a decent  $j_k$  of 21.57 mA cm<sup>-2</sup> for ORR, which is approximately six times larger than that of Fe-CN<sub>x</sub> at 3.67 mA cm<sup>-2</sup>, as depicted in Figure 3C. The highest  $j_k$  of  $Fe(Cd)-CN_r$  in an acidic solution indicates the outstanding intrinsic ORR activity of the designed active site.<sup>50</sup> During the potential from 0.2 to 1.0 V, the  $H_2O_2$  yield was kept below 1% and the electron transfer number (n) was about 4, suggesting that the ORR on Fe(Cd)-CN<sub>x</sub> proceeds through a four-electron transfer pathway, as measured by the rotating ring-disk electrode (RRDE) (Figure 3D).<sup>51</sup> Fe(Cd)- $CN_x$  exhibited the greatest stability after 10,000 potential cycles between 0.6 and 1.0 V in 0.1 M HClO<sub>4</sub>, with



FIGURE 3 Electrochemical ORR performance of the catalysts in acidic and alkaline solutions. (A) Linear sweep voltammetry (LSV) curves of Fe(Cd)-CN<sub>x</sub>, Fe-CN<sub>x</sub>, Cd-CN<sub>x</sub>, FeCd-CN<sub>x</sub>, and 20% Pt/C in O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> solution, and (B) corresponding Tafel plots obtained from the RDE polarization curves. (C) Comparison of the kinetic current density  $(j_k)$  and  $E_{1/2}$  of Fe(Cd)-CN<sub>x</sub>, Fe-CN<sub>x</sub>, Cd-CN<sub>x</sub>, FeCd-CN<sub>x</sub>, CN<sub>x</sub>, and Pt/C. (D)  $H_2O_2$  yield and electron transfer number (n) in 0.1 M HClO<sub>4</sub> solution. (E) Rotating disk electrode (RDE) polarization curves of  $Fe(Cd)-CN_x$  and  $Fe-CN_x$  obtained before and after ADT (10K cycles between 0.6 and 1.0 V in O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub>). (F) LSV curves of Fe(Cd)-CN<sub>x</sub>, Fe-CN<sub>x</sub>, Cd-CN<sub>x</sub>, FeCd-CN<sub>x</sub>, CN<sub>x</sub>, and 20% Pt/C in O<sub>2</sub>-saturated 0.1 M KOH solution. (G) Corresponding Tafel plots obtained from the RDE polarization curves. (H)  $H_2O^-$  yield and electron transfer number (n) in 0.1 M KOH solution. (I) RDE polarization curves of  $Fe(Cd)-CN_x$  and  $Fe-CN_x$  obtained before and after ADT (10K cycles between 0.6 and 1.0 V in O2-saturated 0.1 M KOH).

an  $E_{1/2}$  loss of only 17 mV, much lower than that of the corresponding Fe– $CN_x$  catalyst (29 mV) (Figure 3E).

Apart from the outstanding ORR performance in acid conditions, Fe(Cd)– $CN_x$  also performed well in alkaline conditions (Figure 3F). The onset potential  $(E_{onset})$  of 0.992 V and the half-wave potential  $(E_{1/2})$  of 0.905 V for  $Fe(Cd)-CN_x$  are much higher than those of  $Fe-CN_x$  $(E_{\text{onset}} = 0.923 \text{ V}; E_{1/2} = 0.852 \text{ V})$  and Pt/C  $(E_{\text{onset}} = 0.9 \text{ V};$  $E_{1/2} = 0.774$  V). As shown in Figure 3G, Fe(Cd)–CN<sub>x</sub> has the lowest Tafel slope, indicating its fast ORR reaction kinetics in basic conditions. The excellent mass transfer capability of Fe(Cd)-CN<sub>x</sub> is also supported by its highest limiting current density  $(5.8 \text{ mA cm}^{-2})$ , superior to the value of Pt/C ( $4.9 \text{ mA cm}^{-2}$ ) (Figure 3F). In the RRDE test, the  $H_2O^-$  yield of the Fe(Cd)-CN<sub>x</sub> catalyst was below 5% and the electron transfer number was above 3.8 (Figure 3H), indicating a four-electron ORR process. In the accelerated stability test, the Fe(Cd)- $CN_x$  catalyst also exhibited excellent stability in alkaline conditions (Figure 3I), with only 6 mV  $E_{1/2}$  decay.<sup>52</sup> We have carried out the methanol tolerance tests; unlike the Pt-based materials, this  $Fe(Cd)-CN_x$  catalyst showed good tolerance ability to methanol (Figure S11). These results indicate that satellite Fe-N<sub>4</sub> sites around Fe clusters have higher stability in both acidic and basic solutions compared to isolated Fe-N<sub>4</sub> sites.

# 2.4 | Density functional theory (DFT) calculations

To further reveal the synergistic effect between Fe SAs and ACs, theoretical calculations were carried out. The two ideal models represent Fe SA sites (FeN<sub>4</sub>/C) and Fe AC (Fe<sub>4</sub>N<sub>6</sub>/C with an atomic number set to four based on HAADF-STEM and EXAFS results). A FeN<sub>4</sub> model with closely adjacent Fe<sub>4</sub>N<sub>6</sub> sites was constructed on a carbon substrate to simulate the SA/AC hybrid (Figure S13). The advantage of the Fe atom-cluster interactions toward anchoring OH ligand at FeN<sub>4</sub> sites is revealed, and we found that OH shows a strong tendency to absorb on the FeN<sub>4</sub> sites adjacent to Fe<sub>4</sub>N<sub>6</sub> with an exothermic energy of -3.30 eV compared to the case on the pure FeN<sub>4</sub> (-3.22 eV). The electron-withdrawing -OH ligand as an excellent energy regulator can effectively weaken the adsorption energy and bonding strength between Fe and ORR intermediates.<sup>53–54</sup> More importantly, the introduction of Fe clusters can also decrease the d-band center of Fe. The partial density of states (pDOS) of Fe (Figure 4A) shows that the  $FeN_4/Fe_4N_6$  (-5.687 eV) exhibits a lower d-band center than  $FeN_4$  (-3.004 eV), suggesting the weakened absorption energy of ORR intermediates. It is well known that FeN<sub>4</sub> is located on the left leg of the volcano diagram, implying that the excessively high Fe-O binding strength limits their intrinsic activity. Thus, the weakened Fe-O bond coupling with the OH ligand confers the high ORR performance of the FeN<sub>4</sub>-OH/Fe<sub>4</sub>N<sub>6</sub> catalyst. Then, we furthermore calculated Gibbs free energy profiles (Figure 4B) for ORR elementary steps on FeN<sub>4</sub>-OH/Fe<sub>4</sub>N<sub>6</sub> site and FeN<sub>4</sub> site to systematically explore the adsorption-desorption properties on these two sites. The Gibbs free energy

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diagram at *U* of 1.23 V shows that the extremely strong absorption of oxygen species at the Fe–N<sub>4</sub> site prevents the final protonation of OH (rate-determining step). However, OH can optimize the adsorption of O-containing species on FeN<sub>4</sub>–OH/Fe<sub>4</sub>N<sub>6</sub> site, leading to a noticeable reduction in the energy barrier by 0.13 eV, indicating that its intrinsic activity was improved. Moreover, the FeN<sub>4</sub>–OH/Fe<sub>4</sub>N<sub>6</sub> site shows a quite low overpotential of 0.4 V, while this value turns out to be 0.51 V for the FeN<sub>4</sub> site, which verified the superiority of the FeN<sub>4</sub>–OH/Fe<sub>4</sub>N<sub>6</sub> site in ORR catalysis. These results suggest that the Fe atom–cluster interactions coupling with OH ligand can play a promotional role in facilitating the intrinsic ORR properties of FeN<sub>4</sub>.

### 2.5 | Zinc-air battery performance

Driven by the increasing demand for flexible and portable electronic devices, an all-solid zinc-air battery was further fabricated with a Fe(Cd)- $CN_x$ -coated carbon paper cathode, nickel foam anode, and hydrogel electrolyte (Figure S16). The Fe(Cd)- $CN_x$ -based all-solid-state zinc-air cell has an open circuit potential (OCP) of 1.47 V and a peak power density of  $37.5 \text{ mW cm}^{-2}$ , which are higher than those of commercial Pt/C (1.42 V and  $28 \text{ mW cm}^{-2}$ ) (Figure 5F,G). The cycle stability of Fe (Cd)-CN<sub>x</sub>-based solid-state Zn-air battery was also evaluated. This battery maintains a stable discharge charge potential at a cycling rate of  $2 \text{ mA cm}^{-2}$  for nearly 23.5 h (Figure 5H), which is higher than that of Pt/C (13.7 h). The Fe(Cd)- $CN_x$ -based solid-state Zn-air battery also did not show an obvious overpotential shift after continuous operation for 10.5 h at a high current density



**FIGURE 4** Theoretical analysis of the active site. (A) pDOS of modeling structure of  $Fe-N_4$  and  $FeN_4/Fe_4N_6$ . (B) Free energy diagram of ORR for  $Fe-N_4$  and  $FeN_4-OH/Fe_4N_6$  at 1.23 V.

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of 5 mA cm<sup>-2</sup> (Figure S17). In contrast, the voltage gap of Pt/C sharply increased after 2.5 h, further implying the long-term stability of Fe(Cd)–CN<sub>x</sub>. Figure 5I shows the cycling stability performance at different bending angles (Figure S18) and shows that two series-connected Fe(Cd)–CN<sub>x</sub>-based solid-state zinc–air cells can successfully light up red LEDs in both flat and bent states, demonstrating the battery's excellent flexibility and potential application in flexible wearable electronic device.

To investigate its behaviors in a real fuel cell device, the performance of  $Fe(Cd)-CN_x$  as an anodic catalyst under an  $H_2/O_2$  fuel cell was also tested. As shown in Figure S19, the open-circuit voltage reaches as high as 0.99 V in 1.0 bar  $H_2-O_2$  condition with  $Fe(Cd)-CN_x$  as cathode, implying high intrinsic ORR activity. Moreover, the maximum power density reaches 562 mW cm<sup>-2</sup> with Fe(Cd)–CN<sub>x</sub> as a cathode in 1.0 bar H<sub>2</sub>–O<sub>2</sub>, which is obviously better than the Fe–CN<sub>x</sub> (235 mW cm<sup>-2</sup>). These results strongly imply that Fe(Cd)–CN<sub>x</sub> can serve as a competitive ORR catalyst to replace Pt.

### 3 | CONCLUSIONS

In summary, a site occupation strategy was presented to construct atomically dispersed  $FeN_4$  SA sites and tightly surrounding Fe cluster sites for ORR in acidic media. The DFT calculations reveal that the iron clusters



**FIGURE 5** Performance of assembled Zn-air battery. (A) The structural illustration of rechargeable Zn-air battery. (B) Open-circuit potential (inset: photo of open-circuit voltage of  $Fe(Cd)-CN_x$ -based battery). (C) Discharging polarization curves and the corresponding power densities. (D) Specific capacity of Zn-air battery at 5 mA cm<sup>-2</sup>. (E) Cycling tests at the current density of 5 mA cm<sup>-2</sup> of  $Fe(Cd)-CN_x$ -based battery and Pt/C-based battery (inset: cyclic amplification). (F) OCP measurement of solid-state Zn-air battery. (G) Discharging polarization curves and the corresponding power densities. (H) Cycling tests at the current density of 2 mA cm<sup>-2</sup> of  $Fe(Cd)-CN_x$  solid battery and Pt/C-based solid battery (20 min for each cycle). (I) Cycling tests at the current density of 1 mA cm<sup>-2</sup> of  $Fe(Cd)-CN_x$  solid battery at different bending angles. Voltage gap increase indicates the superstability of  $Fe(Cd)-CN_x$ .

introduce the high electron negativities -OH species into the metal center (FeN<sub>4</sub> sites), which can act proactively as an energy level modifier to empower easy intermediate desorption. Furthermore, the introduction of Fe clusters is also able to reduce the d-band center of the Fe center to weaken the Fe-O bond, facilitating the desorption of OH to free up active sites for subsequent reactions. Benefiting from these attributes, the  $FeCd-CN_x$  catalyst shows impressive catalytic activity for ORR and excellent long-term operational stability. To demonstrate practical applications, this catalyst has also been successfully applied to effective air cathodes of rechargeable liquid or flexible solid-state ZAB. Thus, our work opens a new way to manipulate the catalytic performance of single-atom site catalysts based on atomic structure design.

### ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (22109100, 22075203), Guangdong Basic and Applied Basic Research Foundation (2022A1515011677), Shenzhen Science and Technology Project Program (JCYJ2021032409420401), and Natural Science Foundation of SZU (000002111605). Thanks to Chuan Shi and Wei Zhang for their technical guidance in sample characterization and Shenzhen University Electron Microscopy Center.

### CONFLICT OF INTEREST STATEMENT

The authors declare that there are no conflicts of interests.

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### REFERENCES

- 1. Zhu C, Shi Q, Xu BZ, et al. Hierarchically porous M–N–C (M = Co and Fe) single-atom electrocatalysts with robust  $MN_x$  active moieties enable enhanced ORR performance. *Adv Energy Mater.* 2018;8(29):1801956.
- Yuan K, Sfaelou S, Qiu M, et al. Synergetic contribution of boron and Fe–N<sub>x</sub> species in porous carbons toward efficient electrocatalysts for oxygen reduction reaction. *ACS Energy Lett.* 2018;3(1):252-260.
- Li J, Li W, Mi H, et al. Bifunctional oxygen electrocatalysis on ultra-thin Co<sub>9</sub>S<sub>8</sub>/MnS carbon nanosheets for all-solid-state zinc-air batteries. J Mater Chem A. 2021;9(39):22635-22642.
- Zhu J, Xie M, Chen Z, et al. Pt–Ir–Pd trimetallic nanocages as a dual catalyst for efficient oxygen reduction and evolution reactions in acidic media. *Adv Energy Mater.* 2020;10(16):1904114.
- 5. Zhu X, Tan X, Wu KH, et al. Intrinsic ORR activity enhancement of Pt atomic sites by engineering the d-band

## CARBON ENERGY-WILEY

center via local coordination tuning. *Angew Chem Int Ed.* 2021;60(40):21911-21917.

- 6. Gong L, Liu J, Li Y, et al. An ultralow-loading platinum alloy efficient ORR electrocatalyst based on the surface-contracted hollow structure. *Chem Eng J.* 2022;428:131569.
- Zadick A, Dubau L, Sergent N, Berthomé G, Chatenet M. Huge instability of Pt/C catalysts in alkaline medium. ACS Catal. 2015;5(8):4819-4824.
- Kim J, Hong Y, Lee K, Kim JY. Highly stable Pt-based ternary systems for oxygen reduction reaction in acidic electrolytes. *Adv Energy Mater*. 2020;10(41):2002049.
- Kluge RM, Haid RW, Riss A, et al. A trade-off between ligand and strain effects optimizes the oxygen reduction activity of Pt alloys. *Energy Environ Sci.* 2022;15(12):5181-5191.
- Xia BY, Yan Y, Li N, Wu HB, Lou XW, Wang X. A metal-organic framework-derived bifunctional oxygen electrocatalyst. *Nat Energy*. 2016;1(1):15006.
- 11. Zhu C, Li H, Fu S, Du D, Lin Y. Highly efficient nonprecious metal catalysts towards oxygen reduction reaction based on three-dimensional porous carbon nanostructures. *Chem Soc Rev.* 2016;45(3):517-531.
- Wang J, Kim J, Choi S, Wang H, Lim J. A review of carbonsupported nonprecious metals as energy-related electrocatalysts. *Small Methods*. 2020;4(10):2000621.
- Lin L, Zhu Q, Xu AW. Noble-metal-free Fe–N/C catalyst for highly efficient oxygen reduction reaction under both alkaline and acidic conditions. *J Am Chem Soc.* 2014;136(31): 11027-11033.
- 14. Shu C, Tan Q, Deng C, et al. Hierarchically mesoporous carbon spheres coated with a single atomic Fe–N–C layer for balancing activity and mass transfer in fuel cells. *Carbon Energy*. 2022;4(1):1-11.
- Jiménez-Morales I, Reyes-Carmona A, Dupont M, et al. Correlation between the surface characteristics of carbon supports and their electrochemical stability and performance in fuel cell cathodes. *Carbon Energy*. 2021;3(4):654-665.
- Guan Y, Li N, He J, et al. Tuning and understanding the electronic effect of Co-Mo-O sites in bifunctional electrocatalysts for ultralong-lasting rechargeable zinc-air batteries. *J Mater Chem A*. 2021;9(38):21716-21722.
- Jiao L, Wan G, Zhang R, Zhou H, Yu SH, Jiang HL. From metal-organic frameworks to single-atom fe implanted N-doped porous carbons: efficient oxygen reduction in both alkaline and acidic media. *Angew Chem Int Ed.* 2018;57(28): 8525-8529.
- Kim J, Yoo JM, Lee HS, Sung YE, Hyeon T. Single-atom M–N–C catalysts for oxygen reduction electrocatalysis. *Trends Chem.* 2021;3(9):779-794.
- 19. Lai Q, Zheng L, Liang Y, He J, Zhao J, Chen J. Metal-organicframework-derived Fe–N/C electrocatalyst with fivecoordinated Fe– $N_x$  sites for advanced oxygen reduction in acid media. *ACS Catal*. 2017;7(3):1655-1663.
- 20. Wu L, Li J, Shi C, et al. Rational design of the FeS<sub>2</sub>/NiS<sub>2</sub> heterojunction interface structure to enhance the oxygen electrocatalytic performance for zinc–air batteries. *J Mater Chem A*. 2022;10(31):16627-16638.
- 21. Yan L, Xie L, Wu XL, et al. Precise regulation of pyrrole-type single-atom  $Mn-N_4$  sites for superior pH-universal oxygen reduction. *Carbon Energy*. 2021;3(6):856-865.

ZHOU ET AL.

## WILEY-CARBON ENERGY-

- Zhang M, Li H, Chen J, et al. High-loading Co single atoms and clusters active sites toward enhanced electrocatalysis of oxygen reduction reaction for high-performance Zn-air battery. *Adv Funct Mater.* 2023;33(4):2209726.
- Tang H, Zeng Y, Liu D, et al. Dual-doped mesoporous carbon synthesized by a novel nanocasting method with superior catalytic activity for oxygen reduction. *Nano Energy*. 2016;26: 131-138.
- 24. Xiao M, Zhu J, Ma L, et al. Microporous framework induced synthesis of single-atom dispersed Fe–N–C acidic ORR catalyst and its in situ reduced Fe–N<sub>4</sub> active site identification revealed by X-ray absorption spectroscopy. *ACS Catal.* 2018;8(4):2824-2832.
- Wang Y, Cui X, Zhang J, et al. Advances of atomically dispersed catalysts from single-atom to clusters in energy storage and conversion applications. *Prog Mater Sci.* 2022;128:100964.
- Patniboon T, Hansen HA. Acid-stable and active M–N–C catalysts for the oxygen reduction reaction: the role of local structure. *ACS Catal.* 2021;11(21):13102-13118.
- 27. Zitolo A, Goellner V, Armel V, et al. Identification of catalytic sites for oxygen reduction in iron- and nitrogen-doped graphene materials. *Nat Mater.* 2015;14(9):937-942.
- Lu Z, Wang B, Hu Y, et al. An isolated zinc-cobalt atomic pair for highly active and durable oxygen reduction. *Angew Chem Int Ed.* 2019;58(9):2622-2626.
- 29. Ku YP, Ehelebe K, Hutzler A, et al. Oxygen reduction reaction in alkaline media causes iron leaching from Fe–N–C electrocatalysts. *J Am Chem Soc.* 2022;144(22):9753-9763.
- Li Y, Zhu X, Li L, et al. Study on the structure-activity relationship between single-atom, cluster and nanoparticle catalysts in a hierarchical structure for the oxygen reduction reaction. *Small.* 2022;18(7):2105487.
- Liu L, Liao Y, Yue S, et al. Hierarchal porous graphene-structured electrocatalysts with Fe–N<sub>5</sub> active sites modified with Fe clusters for enhanced performance toward oxygen reduction reaction. ACS Appl Mater Interfaces. 2022;14(37):42038-42047.
- Liu M, Lee J, Yang TC, et al. Synergies of Fe single atoms and clusters on N-doped carbon electrocatalyst for pH-universal oxygen reduction. *Small Methods*. 2021;5(5):2001165.
- Xiao M, Xing Z, Jin Z, et al. Preferentially engineering FeN<sub>4</sub> edge sites onto graphitic nanosheets for highly active and durable oxygen electrocatalysis in rechargeable Zn-air batteries. *Adv Mater*. 2020;32(49):2004900.
- Fan L, Zhang L, Li X, et al. Controlled synthesis of a porous single-atomic Fe–N–C catalyst with Fe nanoclusters as synergistic catalytic sites for efficient oxygen reduction. *Inorg Chem Front*. 2022;9(16):4101-4110.
- 35. Yan L, Li P, Zhu Q, et al. Atomically precise electrocatalysts for oxygen reduction reaction. *Chem.* 2023;9(2):280-342.
- 36. Bai J, Fu Y, Zhou P, et al. Synergies of atomically dispersed Mn/Fe single atoms and Fe nanoparticles on N-doped carbon toward high-activity eletrocatalysis for oxygen reduction. ACS Appl Mater Interfaces. 2022;14(26):29986-29992.
- 37. Ao X, Zhang W, Li Z, et al. Markedly enhanced oxygen reduction activity of single-atom Fe catalysts via integration with Fe nanoclusters. *ACS Nano*. 2019;13(10):11853-11862.
- 38. Kou Z, Zang W, Ma Y, et al. Cage-confinement pyrolysis route to size-controlled molybdenum-based oxygen electrode

catalysts: from isolated atoms to clusters and nanoparticles. Nano Energy. 2020;67:104288.

- Zhang W, Fan K, Chuang CH, et al. Molten salt assisted fabrication of Fe@FeSA-N-C oxygen electrocatalyst for high performance Zn-air battery. J Energy Chem. 2021;61:612-621.
- Liang L, Jin H, Zhou H, et al. Cobalt single atom site isolated Pt nanoparticles for efficient ORR and HER in acid media. Nano Energy. 2021;88:106221.
- 41. Li Q, Chen W, Xiao H, et al. Fe isolated single atoms on S, N codoped carbon by copolymer pyrolysis strategy for highly efficient oxygen reduction reaction. *Adv Mater.* 2018;30(25): 1800588.
- 42. Zhang Z, Sun J, Wang F, Dai L. Efficient oxygen reduction reaction (ORR) catalysts based on single iron atoms dispersed on a hierarchically structured porous carbon framework. *Angew Chem Int Ed.* 2018;57(29):9038-9043.
- 43. Chen Z, Liao X, Sun C, et al. Enhanced performance of atomically dispersed dual-site Fe–Mn electrocatalysts through cascade reaction mechanism. *Appl Catal B.* 2021; 288:120021.
- Guo D, Shibuya R, Akiba C, Saji S, Kondo T, Nakamura J. Active sites of nitrogen-doped carbon materials for oxygen reduction reaction clarified using model catalysts. *Science*. 2016;351(6271):361-365.
- 45. Hao X, Jiang Z, Zhang B, et al. N-doped carbon nanotubes derived from graphene oxide with embedment of FeCo nanoparticles as bifunctional air electrode for rechargeable liquid and flexible all-solid-state zinc–air batteries. *Adv Sci.* 2021;8(10):2004572.
- Liu L, Zhao X, Li R, Su H, Zhang H, Liu Q. Subnano amorphous Fe-based clusters with high mass activity for efficient electrocatalytic oxygen reduction reaction. ACS Appl Mater Interfaces. 2019;11(44):41432-41439.
- Fei H, Dong J, Arellano-Jiménez MJ, et al. Atomic cobalt on nitrogen-doped graphene for hydrogen generation. *Nat Commun.* 2015;6:8668.
- Ji S, Chen Y, Fu Q, et al. Confined pyrolysis within metalorganic frameworks to form uniform Ru<sub>3</sub> clusters for efficient oxidation of alcohols. *J Am Chem Soc.* 2017;139(29):9795-9798.
- Gu J, Jian M, Huang L, et al. Synergizing metal-support interactions and spatial confinement boosts dynamics of atomic nickel for hydrogenations. *Nat Nanotechnol.* 2021;16(10):1141-1149.
- Lu F, Fan K, Cui L, et al. Engineering FeN<sub>4</sub> active sites onto nitrogen-rich carbon with tubular channels for enhanced oxygen reduction reaction performance. *Appl Catal B.* 2022;313:121464.
- 51. Xu H, Jia H, Li H, et al. Dual carbon-hosted  $Co-N_3$  enabling unusual reaction pathway for efficient oxygen reduction reaction. *Appl Catal B.* 2021;297:120390.
- Li Z, Ji S, Xu C, et al. Engineering the electronic structure of single-atom iron sites with boosted oxygen bifunctional activity for zinc-air batteries. *Adv Mater.* 2023;35(9): 2209644.
- 53. Yu L, Li Y, Ruan Y. Dynamic control of sacrificial bond transformation in the Fe–N–C single-atom catalyst for molecular oxygen reduction. *Angew Chem Int Ed.* 2021;60(48):25296-25301.
- 54. Nematollahi P, Barbiellini B, Bansil A, et al. Identification of a robust and durable  $FeN_4C_x$  catalyst for ORR in PEM fuel cells

and the role of the fifth ligand. *ACS Catal.* 2022;12(13): 7541-7549.

### SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article. **How to cite this article:** Zhou T, Guan Y, He C, et al. Building Fe atom–cluster composite sites using a site occupation strategy to boost electrochemical oxygen reduction. *Carbon Energy*. 2024;e477. doi:10.1002/cey2.477