

High Durability of Fe–N–C Single-Atom Catalysts with Carbon Vacancies toward the Oxygen Reduction Reaction in Alkaline Media

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Single-atom catalysts (SACs) have attracted extensive interest to catalyze the oxygen reduction reaction (ORR) in fuel cells and metal-air batteries. However, the development of SACs with high selectivity and long-term stability is a great challenge. In this work, carbon vacancy modified Fe-N-C SACs (Fe_H-N-C) are practically designed and synthesized through microenvironment modulation, achieving high-efficient utilization of active sites and optimization of electronic structures. The Fe_H-N-C catalyst exhibits a half-wave potential $(E_{1/2})$ of 0.91 V and sufficient durability of 100 000 voltage cycles with 29 mV $E_{1/2}$ loss. Density functional theory (DFT) calculations confirm that the vacancies around metal-N₄ sites can reduce the adsorption free energy of OH*, and hinder the dissolution of metal center, significantly enhancing the ORR kinetics and stability. Accordingly, Fe_H-N-C SACs presented a highpower density and long-term stability over 1200 h in rechargeable zinc-air batteries (ZABs). This work will not only guide for developing highly active and stable SACs through rational modulation of metal-N₄ sites, but also provide an insight into the optimization of the electronic structure to boost electrocatalytical performances.

such as fuel cells and metal-air batteries.^[1-5] Platinum (Pt)-based catalysts are mainly used to catalyze the ORR at the cathode.^[6,7] However, high costs and natural scarcity of Pt-based catalysts preclude their practical applications.^[8] To replace platinum group metals (PGMs), alternative non-noble electrocatalysts with high catalytic activity and long durability such as transition metal-nitrogen-carbon (TM-N-C, where TM-N-C refers to as the transition metal (TM, such as Fe, Co, Ni, Cu, and Mn) and nitrogen (N) co-doped on the carbon supports) catalysts are highly demanded to be developed as costeffective catalysts for ORR.^[9]

Single-atom catalysts (SACs) have been widely used in catalysis and electrochemical devices due to their maximum atom utilization efficiency, exceptional electronic structure, homogeneous active centers, and unsaturated coordination environment.^[10–12] To enhance the ORR

1. Introduction

Electrocatalytic oxygen reduction reaction (ORR) is an important process in electrochemical energy storage and conversion

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mizing their geometric and electronic properties.^[13,14] However, achieving highly active SACs faces several challenges,
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activity of SACs, the intrinsic activity and the site density

of active sites should be rationally exploited, further opti-

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including the stabilization of isolated metal center at atomic scale,^[15,16] the simultaneous formation of inactive metal species and less-active sites during calcination.^[17,18] and the low utilization of active sites covered by carbon framework.^[19] More importantly, the electrochemical performance of SACs toward ORR is closely related to the local environment of active metals and their electronic interaction with the supports. Modulating the electronic structures of metal atoms including the center atoms,^[20] coordinated atoms,^[21] the coordination numbers,^[22,23] and the nature of first and second coordination spheres to the center atoms^[24] can tune the charge density redistribution and the d orbital states of the metal active sites. In addition, great attentions have been paid on the development of various catalysts with optimized defects as efficient catalysts for numerous applications, including Fe-N-C SACs with carbon vacancies for ORR,[25] NiFe-layered double hydroxide (LDH) with NiFe vacancies for nucleophile oxidation reaction,^[26] Pt/Ni-N-C SACs with carbon vacancies for ORR,^[27] carbon nitride with nitrogen vacancies for photocatalytic H2O2 evolution,[28] Ir SACs with oxygen vacancies for oxygen evolution reaction,^[29] Pt SACs with sulfur vacancies for photocatalytic hydrogen evolution,^[30] Pt SACs with carbon vacancies for photocatalytic CO₂ methanation,^[31] and Pt SACs with carbon vacancies for electrocatalytic hydrogen evolution.^[32] In particular, engineering the local defects surrounding single-atom active sites can optimize the adsorption energy for the intermediates on the surface of the metal active sites.^[15,33,34] So far, most SACs focused on enhancing the electrocatalytic activity, which cannot meet the long-term stability for practical applications such as ZABs. Therefore, it is highly desirable to rationally design and synthesize SACs with optimized electronic structure and enhanced functionalities, achieving superior activity and durability.

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Herein, we presented a facile approach to design TM-N-C SACs toward cost-effective, efficient, and durable electrocatalysts through highly utilizing M-N₄ active sites, engineering defects, and optimizing electronic structures. By using theoretical prediction and experimental verification, we demonstrated atomic-level vacancy regulation of TM-N-C SACs to control chemical environment and electronic structure of the active metal center, optimizing the adsorption of oxygen intermediates and enhancing ORR performances. The as-synthesized Fe_H-N-C catalysts with carbon vacancies exhibited superior ORR activities and stability compared with commercial Pt/C and other reference samples. In addition, Fe_H-N-C catalyst displayed a high durability for ORR of 50 000 cycles with no significant loss of $E_{1/2}$ and up to 100 000 cycles with $E_{1/2}$ loss of 29 mV. DFT calculations confirmed that carbon vacancies modulate the electronic structure around Fe-N4 sites and further reduce the adsorption free energy of OH*. The rechargeable ZABs assembled using Fe_H-N-C as the air cathode delivered excellent long-cycling life over 1200 h. This work elucidates new insights that the optimal utilization of Fe-N-C SACs with well-defined electronic structures can enhance electrochemical catalytic stability toward ORR, opening a new avenue for preparing long-life PGM-free catalysts for practical applications.

2. Results and Discussion

2.1. Theoretically Understanding of TM-N-C Structure for **Oxygen Reduction Reaction**

Although TM-N-C SACs have exhibited good activities for ORR, the search of highly active and stable catalysts is still based on trial-and-error approaches.^[35] It results in the unclear and empirical acquisition for the determination of MN₄ active sites and reaction mechanisms. Therefore, it is of great significance to deeply understand the effect of center metal atoms from MN₄ active sites to further enhance the electrocatalytic activity of TM-N-C SACs and to examine the relationships between the structure of SACs and the electrochemical performances at the molecular level with regard to metal centers.

In alkaline mediate, O2 molecules can react with two H2O molecules through four-electron pathway to generate OH-(Figure 1a).^[36] The free energy diagrams of ORR on TM-N-C are systematically investigated through DFT calculations. As shown in Figure 1b and Figure S1, Supporting Information, the potential-determining step of ORR on Mn-N-C and Fe-N-C is the formation of the last OH-, while the generation of the adsorbed O* is the potential-determining step on Ni–N–C and Cu–N–C. This is consistent with the adsorption strength of ORR intermediates on TM-N-C. O2 molecules can be easily activated on Mn-N-C and Fe-N-C because of the strong adsorption ability of ORR intermediates (Figure S2 and Table S1, Supporting Information). The strong adsorption ability of OH* on the surface hinders the desorption process to form the final product. Moreover, the O-O bond of OOH* is hard to break on Co-N-C, Ni-N-C, and Cu-N-C due to the weak adsorption capability of ORR intermediates, resulting in the formation of the adsorbed O* as the potential-determining step. It is clearly observed that the ΔG of potential-determining step of ORR increases in the order of Fe-N-C < Co-N-C < Mn–N–C < Cu–N–C < Ni–N–C, indicating that Fe–N–C exhibits the best electrochemical catalytic activity. Based on the Sabatier principle, the ideal ORR catalyst should be effective to activate O2 and noble enough to release the O-containing species from the surface.^[37] A volcano relationship was found between the adsorption energy of OH* and the ΔG of potential-determining step (Figure 1c), in which Fe-N-C is situated at the top, revealing the favorable adsorption strength of ORR intermediates and the efficient catalyst for ORR. Furthermore, the effect of graphitic-N near the Fe-N-C structure on the catalytic activity of Fe-N-C was also considered. As shown in Figure S3, Supporting Information, the reaction free energy of ORR on Fe-N-C with nearby graphitic-N is similar to that on pristine Fe-N-C, indicating that graphitic-N has a marginal effect on the reaction free energies of ORR on Fe-N-C.

To investigate the origin of the interaction between ORR intermediates and TM-N-C, we calculated the partial density of states (PDOS) for transition metal atoms (Figure 1d). It can be clearly observed that the d-band of central metal shifts to left relative to the Fermi level as the central metals vary from Mn to Cu. A downshift of the d states leads to a downward shift of the antibonding states, revealing the formation of weaker bonds. The strength of O-M bonds has been proved





Figure 1. The influence of center atoms in TM–N–C structures for ORR. a) The atomic structures of ORR intermediates on Fe–N–C. b) The free energy diagram of ORR on TM–N–C under the electrode potential of 0 V at pH = 13. c) The volcano relationship between the adsorption energy of OH* and the ΔG of potential-determining step under the electrode potential of 0 V at pH = 13. d) The PDOS of central metal atoms in TM–N–C. e) The PDOS of OH* adsorbed on TM–N–C. f) d–p orbital hybridization between central metal atom and O atom. g) PDOS of d_{y2} and d_{y2} orbitals for TM–N–C.

to be dependent on the coupling between the 2p states from oxygen and the d states from metal.^[38] As shown in Figure 1e. the mixing between the O-2p and M-3d states becomes small as the central metals vary from Mn to Cu, suggesting that the adsorption strength becomes weak. For a transition metal anchored by four nitrogen atoms, the coordination environment can be approximated as the D_{4h} crystal field (Figure 1f). Five *d* orbitals are arranged into four d states: $d_{x^2-y^2}$, d_{xy} , d_{z^2} , and $d_{xz/yz}$ (twofold degenerate). Based on the orbital symmetry, the d-p hybridization scenario can be predicted as: i) The d_{z^2} orbital hybridizes with the p_z orbital of O, forming σ and σ^* bonds with strong energy splitting. ii) The twofold $d_{xz/yz}$ mixes with the $p_{x/y}$ to form two relatively weak π and π^* bonds. iii) d_{xy} and $d_{x^2-y^2}$ are not active compared to the other d states and are considered as non-bonding. Therefore, the d-p hybridization can be classified the electronic states as σ , σ^* , π , π^* , and non-bonding d_{xy} and $d_{x^2-y^2}$ states. As shown in Figure 1g, for Mn, only partial π^* states are slightly filled. As the central metal varying from Mn to Cu, the π^* and σ^* are gradually occupied, indicating that the adsorption strength of ORR intermediates becomes weaker. From the discussion above, it was known that Fe–N–C exhibits the best catalytic activity due to the favorable adsorption strength of reaction intermediates, which results from the special electronic structures.

2.2. Synthesis and Characterization

The synthesis strategy for Fe_H –N–C catalyst is schematically presented in **Figure 2**a. ZnFe-Zeolite imidazolate frameworks (ZnFe-ZIFs), dispersed uniformly in methanol solution, were added into a solution containing tannic acid (TA). Subsequently, chemical etching occurred between ZnFe-ZIF particles and TA, engineering defects and removing unstable and less-active

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Figure 2. Synthetic and characterizations of SACs. a) Schematic illustration of synthesis procedure for Fe_H-N-C catalysts. b) HAADF image, c) STEM element mapping images, and d) aberration-corrected HAADF-STEM. e) XANES spectra and f) Fourier-transform EXAFS spectra in *R*-space of Fe_H-N-C , Fe foil, FeO, Fe_2O_3 , and Fe phthalocyanine (FePc) at iron K-edge. Corresponding FT-EXAFS fitting of iron K-edge in *R*-space of Fe_H-N-C and FePc of Fe_H-N-C . g) EPR spectrum of Fe_H-N-C .

metal species during subsequent pyrolysis. As shown in scanning electron microscopy (SEM) images of Figure S4a,b, Supporting Information, the particle size of the polyhedralstructured ZnFe-ZIFs with smooth surfaces is about 400 nm. The X-ray diffraction (XRD) pattern for ZnFe-ZIFs shown in Figure S5, Supporting Information, agrees well with that of the as-prepared bimetallic ZIFs,^[39] confirming the formation of bimetallic ZIF structures. This synthetic approach can be extended to the fabrication of other bimetallic ZIFs with different components. The SEM images in Figure S4, Supporting Information, and XRD patterns in Figure S5, Supporting Information, show the successful preparation of ZnCo-ZIFs, ZnNi-ZIFs, ZnCu-ZIFs, and ZnMn-ZIFs. Through a chemical etching process by using tannic acid, hollow structured ZIFs (HZFZ) with smooth surfaces can be obtained, as presented from SEM images in Figure S6, Supporting Information. To further confirm the morphology transformation from solid structure ZIFs to hollow structured ZIFs, ex situ TEM was used to monitor the morphology of ZnFe-ZIFs with different etching

time. As shown in Figure S7, Supporting Information, stable hollow structured ZIFs can be achieved at the etching time of 10 min. The XRD results in Figure S8, Supporting Information, show the crystalline nature of hollow structured ZIFs, which is similar with that of bimetal ZIFs in Figure S5, Supporting Information. The as-prepared hollow bimetallic ZIF materials were converted into hollow carbonaceous nanocomposites at 800 °C under an Ar atmosphere. The obtained carbon materials are denoted transitional single-atom hollow carbon materials (M_H-N-C, M, such as Fe, Co, Ni, Cu, and Mn). The low-magnification and high-magnification TEM image (Figure S9, Supporting Information), high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image (Figure 2b) of Fe_H-N-C particles showed the hollow structure of the as-prepared carbon materials is maintained and no iron aggregates are observed, indicating the uniform distribution of iron species in the carbon matrix. As shown in energy-dispersive X-ray spectroscopy (EDS) images (Figure 2c), elements (iron, nitrogen, oxygen, and carbon) are homogeneously



distributed in the whole carbon framework, identifying the well-dispersed metal single atoms and N dopant. From aberration-corrected HAADF-STEM images in Figure 2d, the bright dots (highlighted by red circles) can be detected, revealing the formation of atomic iron. In addition, the solid structured SACs (Fe_S–N–C) can be achieved through the direct calcination of ZnFe-ZIF particles. TEM image in Figure S10a, Supporting Information, and HAADF image in Figure S10b, Supporting Information, showed that the polyhedral structure remained very well after calcination. The single atoms were distributed uniformly within the carbon framework, as presented from the aberration-corrected HAADF-STEM images in Figure S10c,d, Supporting Information. Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis of Fe_H–N–C particles determined that the iron content was ultralow to ~0.2 wt%.

XRD measurement was performed to investigate the phase structure of M_H-N-C particles (Figure S11, Supporting Information). The peaks around 25.7° and 43.6° in the XRD pattern of M_H–N–C particles fit the (002) and (100) planes of graphitic carbon. XPS measurements were also used to determine the chemical environment of Fe_H-N-C particles. The high-resolution Fe 2p spectrum (Figure S12a, Supporting Information) can be well fitted with Fe²⁺ and Fe³⁺ species. From the N 1s spectrum in Figure S12b, Supporting Information, three peaks at 398.5, 400.0, and 401.2 eV can be deconvoluted, corresponding to pyridinic N, Fe-N, and graphitic-N.^[40] X-ray absorption nearedge structure (XANES) and extended X-ray absorption fine structure measurements (EXAFS) were conducted to investigate the chemical state and coordination environment of Fe atoms in the Fe_H-N-C particles. As shown in the XANES spectra (Figure 2e), the comparison of near-edge adsorption energy with reference to iron phthalocyanine (FePc), FeO, Fe₂O₃, and Fe foil implies that the Fe single atoms in Fe_H–N–C particles are positively charged, which agrees well with previous results.^[41,42] Furthermore, the EXAFS spectra in Figure 2f show the same peak at ≈1.49 Å of FePc and Fe_H-N-C corresponding to the Fe-N coordination. Compared with the spectra of Fe_H-N-C and Fe foil, no Fe-Fe peak around 2.22 Å is observed in Fe_H-N-C, indicating that Fe single atoms are atomically dispersed.^[43,13] Furthermore, the EXAFS fitting curve in R space (Figure 2f and Table S2, Supporting Information) and in k-space (Figure S13, Supporting Information) unveils an average Fecoordinated number of \approx 3.8, thus suggesting a dominating Fe-N₄ configuration in the carbon frameworks. The electron paramagnetic resonance (EPR) pattern of Fe_H-N-C showed a stronger peak signal at the g-value of 2.005 g, demonstrating the successful introduction of carbon vacancies in bulk phase of carbon-based materials,^[32,44,45] which is coincided well with our etching strategy (Figure 2g).

The porosity of M_H –N–C particles was studied by nitrogen adsorption–desorption analysis. The M_H –N–C particles display mixed type I and IV isotherms (Figure S14a, Supporting Information). From the low-pressure region of the isotherms, the sharp adsorption reveals the presence of plentiful micropores, while in the medium-pressure region the hysteresis loop can be attributed to the existence of the mesopores with the carbon framework. The pore size distribution of M_H –N–C particles was then analyzed based on the isotherms (Figure S14b, Supporting Information), which shows that most peaks centered

in the range of micropores. The majority of MN₄ active sites are usually hosted on the micropores in the TM-N-C catalysts.^[46,47] On the basis of the aforementioned adsorption isotherm of Fe_H-N-C, Co_H-N-C, Ni_H-N-C, Cu_H-N-C, and Mn_H-N-C, similar Brunauer-Emmett-Teller (BET) surface areas and dominate micropores are presented in Table S3, Supporting Information. As shown in Figure S15, Supporting Information, MN₄ active sites in micropores of M-N-C catalysts have porphyrin-like MN₄ structure.^[48] It also reveals that the smaller micropores (7 Å) could be filled by Fe-N₄ sites because of the similar size between the smaller micropores and the diameter of Fe-N₄ sites. Moreover, the larger micropores (12Å) could be partially covered by Fe-N₄ sites, leading to the generation of defects formed near Fe-N4 sites. The defect level of carbon materials can be characterized by an I_D/I_C value (I_D and I_C represents the intensity of Raman D- and G-bands of carbon materials) in Raman spectra (Figure S16, Supporting Information). The ratios for Fe_H-N-C, Co_H-N-C, Ni_H-N-C, Cu_H-N-C, and Mn_H-N-C were 1.33, 1.30, 1.33, 1.29, and 1.28, respectively. This suggests the similar defect levels of these carbon materials, excluding the influence of carbon supports on electrochemical performance. To highlight the role of Fe-N₄ sites and defect engineering around Fe-N₄ sites, we also synthesized a control sample of nitrogen-doped carbon (H-N-C) without iron single atoms. Compared with H–N–C, the I_D/I_G value of Fe_H–N–C is larger, indicating more defect contents in Fe_H-N-C catalysts.

Significantly, our synthetic strategy can be extended to prepare other transition metal SACs (including but not limited to Co, Ni, Cu, and Mn). These SACs have been prepared using the similar synthesis approach. TEM images of Cu_H-N-C in Figure S17, Supporting Information, Mn_H–N–C in Figure S18, Supporting Information, Co_H-N-C in Figure S19, Supporting Information, and Ni_H-N-C in Figure S20, Supporting Information, showed the formation of hollow structures. The EDS mapping images show that metal (Cu, Co, Mn, and Ni), carbon, nitrogen, and oxygen elements are homogeneously distributed in the carbon matrix. The XPS results verify that the single atoms in M_H -N-C (M = Co/Ni/Cu/Mn) have positive charge (Figure S21, Supporting Information). The atomically dispersed single atoms in M_H -N-C (M = Co/Ni/Cu/Mn) are also determined by high-resolution HAADF-STEM (Figure S22, Supporting Information), presenting uniform atomic dispersion of the metal atoms on the carbon frameworks.

2.3. Electrochemical Performance of ORR

The electrocatalytic activity of the Fe_H–N–C catalysts was evaluated by cyclic voltammetry (CV) and linear scan voltammetry (LSV) measurements. The CV curves reveal a significant reduction peak for Fe_H–N–C (Figure S23, Supporting Information), indicating an excellent ORR electrocatalytic activity. **Figure 3**a presents the LSV curves of H–N–C, Fe_H–N–C, and 20% Pt/C catalysts. The Fe_H–N–C catalyst exhibits a high $E_{1/2}$ of 0.91 V (vs RHE), which are superior to the state-of-the-art 20% Pt/C (0.87V vs RHE), H–N–C (0.77 V vs RHE) without Fe–N₄ sites and most of PGM-free Fe-based ORR electrocatalysts (Table S4, Supporting Information). These results further demonstrate the importance of maximizing the utilization of Fe–N₄ active ADVANCED SCIENCE NEWS _____



Figure 3. Electrochemical performances and the kinetics for atomically dispersed M_H-N-C (M = Fe/Co/Ni/Cu/Mn) catalysts. a) Polarization ORR profiles for the fabricated Fe-based cathodes in comparison with H-N-C and commercial Pt/C. b) Kinetic current density (J_k) at 0.80, 0.85, and 0.90 V. c) Tafel profile kinetics for ORR. d) Polarization ORR profiles for the fabricated atomically dispersed M_H-N-C (M = Fe/Co/Ni/Cu/Mn) catalysts. e) Kinetic current density (J_k) at 0.80, 0.85, and 0.90 V. f) Calculated transferred electron numbers and HO_2^- yields for fabricated catalysts. g) Accelerated robustness measurements for Fe_H-N-C . h) $E_{1/2}$ loss compared with recently reported excellent catalysts (Table S4, Supporting Information). Conditions for ORR: current normalized by the area of the RDE and RRDE electrode, O_2 saturated 0.1 M KOH.

sites and defect engineering. The kinetic current density (J_k) at 0.90 V for Fe_H–N–C (7.00 mA cm⁻²) is also 3.8 times higher than that of 20% Pt/C (1.82 mA cm⁻²) (Figure 3b). The ORR kinetics was further investigated by the Tafel plot (Figure 3c). The Fe_H–N–C catalysts show a smaller Tafel slope than that of commercial Pt/C, revealing a better ORR kinetics of Fe_H–N–C. In addition, as shown in Figure S24, Supporting Information, the Fe_S–N–C SACs also exhibited inferior activity than Fe_H–N–C SACs.

To highlight the influence of center atoms in TM–N–C structures for ORR, other transitional metal SACs including Co_H – N–C, Ni_H–N–C, Cu_H–N–C, and Mn_H–N–C were also tested. As presented in LSV measurements in Figure 3d, the comparison of kinetic current density in Figure 3e, the Tafel slope in Figure S25, Supporting Information, Fe_H–N–C SACs exhibit the best ORR activity among all M_H –N–C SACs. This elucidates that iron single atoms with Fe–N₄ sites in Fe_H–N–C SACs are more active than other transitional single atoms with M–N₄ sites in M_H –N–C SACs (M = Co, Ni, Cu, and Mn). The ORR selectivity of the as-prepared catalysts was further evaluated by the rotating ring disk electrode (RRDE) measurements. In the potential range of 0.2–0.9 V, the HO₂⁻ yield of Fe_H–N–C (Figure 3f) remains extremely low yield (<1%), guaranteeing a high selectivity toward OH⁻. Compared with other SACs and commercial Pt/C catalysts, a lower HO₂⁻ yield of Fe_H–N–C can also be obtained, indicating that Fe_H–N–C undertook a more efficient catalytic process. Based on RRDE results, the electron transfer number (*n*) for the as-prepared catalysts at various potentials revealed a four-electron reduction pathway, which are also consistent with the Koutecký–Levich (K–L) methods (Figures S26–S28,

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Supporting Information). The active site density was calculated from reversible nitrite poisoning.^[13] The in situ nitrite poisoning was used to quantify the accessible $Fe-N_4$ sites on the Fe_H-N-C . As shown in Figure S29, Supporting Information, the Fe_H-N-C catalyst has a site density of 8.47×10^{18} sites per g. After a fast accelerated durability test (ADT) of 10 000 cycles (Figure 3g) for Fe_H–N–C catalysts, no obvious decay in $E_{1/2}$ is detected, indicating the excellent stability. An $E_{1/2}$ loss of only 3 mV has been achieved after 30 000 cycles, which is much lower than that of commercial Pt/C (30 mV). In particular, even after 100000 cycles, Fe_H-N-C catalysts still exhibited excellent stability, as evidenced by an $E_{1/2}$ loss of only 29 mV. This exceeds the values of the vast majority of previously reported PGM-free catalysts under similar conditions (Figure 3h). Additionally, aberrationcorrected HAADF-STEM images after ADT test (Figure S30, Supporting Information) demonstrate that atomic dispersion of iron atoms still maintained, further demonstrating the excellent durability of Fe₁₁-N-C.

2.4. Zn-Air Batteries System Analysis

Inspired by the outstanding ORR performances of Fe_H-N-C catalysts, primary and rechargeable ZABs were assembled using Fe_H-N-C as cathodes. A high open-circuit potential of up to 1.53 V (Figures S31 and S32, Supporting Information) and a peak-power density as high as 225 mW cm⁻² (Figure 4a) were achieved, which is superior to commercial Pt/C (118 mW cm⁻²) and other recent-reported M-Nx/catalysts (Table S5, Supporting Information). Figure 4b shows the capacities at various discharge current densities ranging from 2 to 200 mA cm⁻². The capacity can be well recovered when the current density is reversed back to 2 mA cm⁻². Even at high current densities of 200 mA cm⁻², no significant decrease of discharge voltage is observed. At a current density of 10 mA cm⁻², the specific capacity of Fe_H-N-Cbased ZAB (Figure 4c) was estimated to be 814 mAh g_{Zn}^{-1} , which is higher than that of the Pt/C-based ZAB (758 mAh g_{Zn}^{-1}). The cycling performance of $Fe_H-N-C + RuO_2$ (with a mass ratio of



Figure 4. Electrochemical performances of primary and rechargeable ZABs under commercially available conditions. a) Discharge polarization curves and corresponding power density curves of primary ZABs with Fe_H-N-C and Pt/C. b) Galvanostatic discharge curves of Fe_H-N-C -based and Pt-based ZAB with a voltage range of 0.6–1.4 V for various current densities from 5 to 200 mA cm⁻². c) Galvanostatic discharge curves of Fe_H-N-C and Pt/C at a current density of 10 mA cm⁻². d) Galvanostatic discharge/charge cycling performance of rechargeable ZAB based on $Fe_H-N-C+RuO_2$ and $Pt/C+RuO_2$ at a current density of 5 mA cm⁻². e) The corresponding discharge voltage stability graphs. f) Voltage efficiency graphs of $Fe_H-N-C+RuO_2$ at 100, 300, 500, 700, 900, and 1200 h during the cycling test. (Time constraint = 40 min per cycle).



1/1)-based ZAB was investigated by galvanostatic dischargecharge cycles (Figure 4d). Stable cycling performance for both discharge and charge processes can be observed over 1200 h (1800 cycles) for Fe_H –N–C + RuO₂-based ZAB, which is superior to recently reported M–N_x/catalysts (Table S6, Supporting Information). Under the same test conditions, the discharge voltage of Pt/C + RuO₂-based ZAB (Figure 4e) dropped evidently within 100 h, confirming the outstanding stability of Fe_H –N–C in practical ZABs. Moreover, Figure 4f shows that negligible changes of voltage efficiency during discharge and charge processes can be achieved over 1200 h. In addition, the ZABs with Fe_H –N–C catalysts as the cathode could power a red light-emitting diode (Figure S33, Supporting Information).

2.5. Theoretical Elucidation of Vacancies in Fe-N-C Catalysts

Based on above discussion, the potential-determining step of ORR on Fe–N–C is the reduction of OH* to form the final product, so the catalytic activity can be enhanced through weakening OH* adsorption. DFT calculations were performed to understand the superior ORR activity. Based on the HAADF, XAFS, XPS, EPR, and Raman characterization results for the Fe_H–N–C catalysts, carbon vacancies could contribute to the catalytic activity of Fe–N–C catalysts. As shown in **Figure 5**a; Figure S34 and Table S7, Supporting Information, six possible single carbon vacancies were considered, and the Gibbs free energy change (ΔG) on the defective Fe–N₄ along the 4 e⁻ ORR process were calculated (Figure 5b and Figure S35, Supporting Information). For sites A, B, C, and F, the adsorption of ORR intermediates becomes strong and the adsorbed OH* is stabilized, indicating that a larger ΔG is needed to remove the OH species. However, the adsorption of ORR intermediates becomes weaker on Fe-N-C with site E compared with that on defect-free Fe–N–C. The ΔG of potential-determining step decrease from -0.37 eV on perfect Fe-N-C to -0.41 eV on site E, resulting in an enhanced catalytic activity. Additionally, in Figure 5c, the PDOS of OH* on Fe-N-C with and without C vacancies presented that the hybridization between Fe-3d and O-2p for Fe-N-C with site B becomes greater than that of Fe-N-C, revealing that the OH* adsorption energy on Fe-N-C with site B becomes stronger. Compared with Fe-N-C, the mixing between Fe-3d and O-2p for Fe-N-C with site E becomes weaker, resulting in weaker adsorption of OH*. The different adsorption property of ORR intermediates on Fe-N-C with and without C vacancy can lead to different ORR kinetics. Furthermore, the ORR reaction process on Fe-N-C with two or four Site E vacancies was further investigated and the corresponding free energy diagram was shown in Figure 5d. The ΔG value of potential-determining step decreased to -0.44 and -0.47 eV on Fe-N-C with two or four Site E vacancies compared with Fe-N-C (-0.41 eV) with single Site E, respectively, indicating higher catalytic activity. A linear relationship between the adsorption energy OH* and the ΔG of the potential-determining step in ORR was found (Figure 5e). Furthermore, the catalytic activity of defective carbon near Fe-N₄ structure was also considered in this work. As shown in Figure S36, Supporting Information, the activation of O2 molecule on the defective carbon was enhanced compared with that on Fe−N₄ structure. However, the reduction of O* and OH* to form OH^- was very hard with ΔG values of 0.76 and 1.53 eV at U = 0 V, which is very high to overcome, indicating that the catalytic activity of defective carbon was low.



Figure 5. The vacancy effects in TM–N–C structures for ORR. a) The atomic structures of Fe–N–C with six single C. b) The free energy diagrams of ORR on Fe–N–C with six C vacancies under the electrode potential of 0 V at pH = 13. c) The PDOS of OH* on Fe–N–C with and without C vacancies. d) The free energy diagrams of ORR on Fe–N–C with two and four Site-E vacancies, inset are the atomic structures of Fe–N–C with two and four Site-E vacancies under the electrode potential of 0 V at pH = 13. e) The relationship between the adsorption energy of OH* and the ΔG of potential determining step on Fe–N–C with six C vacancies. f) The ΔG_{disso} of the Fe atom dissolving from the carbon host into the solvent for Fe–N–C and Fe–N–C with Site-E vacancy at pH = 13.



Synthesis of ZnFe-ZIF: Typically, $Zn(NO_3)_2$ ·6H₂O (0.575 g) and FeSO₄·7H₂O (0.019 g) were dissolved into 50 mL of methanol to form a solution. 50 mL of methanol containing 2-methylimidazole (0.66 g) and PVP (0.6 g) were poured into $Zn(NO_3)_2$ and FeSO₄ solution. The mixture was kept stirring at room temperature for 24 h. The resulting white precipitates were collected by centrifugation, washed with methanol three times, and finally dried at 80 °C overnight.

Synthesis of ZnCo-ZIF: Typically, Zn(NO₃)₂·6H₂O (0.863 g) and Co(NO₃)₂·6H₂O (0.0291 g) were dissolved in 30 mL of methanol to form a solution. 20 mL of methanol containing 2-methylimidazole (1.97 g) was poured into Zn(NO₃)₂ and Co(NO₃)₂ solution. The mixture was kept stirring at room temperature for 24 h. The resulting white precipitates were collected by centrifugation, washed with methanol three times, and finally dried at 80 °C overnight.

Synthesis of ZnNi-ZIF: Typically, Zn(NO₃)₂·6H₂O (0.743 g) and Ni(NO₃)₂·6H₂O (0.145 g) were dissolved in 30 mL of methanol to form a solution. 20 mL of methanol containing 2-methylimidazole (1.97 g) was poured into Zn(NO₃)₂ and Ni(NO₃)₂ solution. The mixture was kept stirring at room temperature for 24 h. The resulting white precipitates were collected by centrifugation, washed with methanol three times, and finally dried at 80 °C overnight.

Synthesis of ZnCu-ZIF: Typically, Zn(NO₃)₂·6H₂O (0.743 g) and Cu(NO₃)₂·2.5H₂O (0.116 g) were dissolved in 30 mL of methanol to form a solution. 20 mL of methanol containing 2-methylimidazole (1.97 g) was poured into Zn(NO₃)₂ and Cu(NO₃)₂ solution. The mixture was kept stirring at room temperature for 24 h. The resulting white precipitates were collected by centrifugation, washed with methanol three times, and finally dried at 80 °C overnight.

Synthesis of ZnMn-ZIF: Typically, Zn(NO₃)₂·6H₂O (0.743 g) and Mn(NO₃)₂·4H₂O (0.125 g) were dissolved in 30 mL of methanol to form a solution. 20 mL of methanol containing 2-methylimidazole (1.97 g) was poured into Zn(NO₃)₂ and Mn(NO₃)₂ solution. The mixture was kept stirring at room temperature for 24 h. The resulting white precipitates was collected by centrifugation, washed with methanol three times, and finally dried at 80 °C overnight.

Synthesis of Hollow ZIF Materials: 10 mL methanol solution containing 100 mg ZIF nanocrystals were incubated in 40 mL of a tannic acid solution (8 g L⁻¹) and aged for 10 min. The hollow ZIF materials were collected by centrifugation and washed with methanol three times, and finally dried at 80 °C overnight.

Synthesis of Single-Atom Catalysts: The as-prepared ZIF nanoparticles were carbonized in flowing Ar in a tube furnace using a heating rate of $2 \,^{\circ}$ C min⁻¹ up to 800 °C, dwell for 3 h.

Characterizations: The morphology and chemical composition of the as-prepared samples were observed by field-emission scanning electron microscopy (FESEM, Zeiss Supra 55VP) and TEM (FEI Themis-Z Double-Corrected 60-300 kV S/TEM). XRD measurements were carried out by using a scanning step of $0.04^\circ~s^{-1}$ in the 2θ range from 10° to 80° (Bruker D8 Discovery XRD). XPS measurements were performed on an ESCALAB250Xi (Thermo Scientific, UK) equipped with mono-chromated Al K alpha (energy 1486.68 eV). The BET specific surface area and single-point pore volume were obtained from nitrogen adsorption isotherms measured at -196 °C using a nitrogen sorption instrument (ASAP 2460 Micropore Physisorption Analyzer). Prior to nitrogen adsorption measurements, the samples were degassed at 250 °C overnight. Raman spectra were obtained from a Renishaw inVia Raman spectrometer system (Gloucestershire, UK) equipped with a Leica DMLB microscope (Wetzlar, Germany) and a Renishaw He-Ne laser source producing 17 mW at 633 nm. X-ray absorption fine structure (XAFS) measurements of Fe, Co, and Ni K-edge were performed at the 1W1B beamline of the Beijing Synchrotron Radiation Facility (BSRF) in transmission mode. The X-ray was monochromatized using a doublecrystal Si (111) monochromator and the energy was calibrated by metal foils. The XAFS data was analyzed using the WinXAS3.1 program. Metal content in catalysts was determined by ICP-OES.

Electrochemical Measurements: All electrochemical measurements were performed on CHI 760E workstation with a standard three-electrode system. The catalyst ink solution containing ethanol and 5 wt% Nafion

To understand the origin of the high stability of Fe-N-C catalysts, the interaction energy (E_{int}) between transition metal and N₄ group was investigated. As shown in Table S8, Supporting Information, the Eint value of Fe in Fe-N-C is the largest among the five TM-N-C SACs studied here, indicating that the Fe atom in Fe-N-C is more stable than other TM-N-C SACs. It is worth-noting that the E_{int} value of Fe in Fe–N–C with site E is larger than that in pristine Fe–N–C, indicating the stability of Fe-N-C can be further improved through the introduction of the vacancy at site E for the carbon structure. The effect of vacancy on the durability of Fe-N-C was also considered based on the free energy (ΔG_{disso}) of the Fe atom dissolving from the carbon host. As shown in Figure 5f and Table S9, Supporting Information, the ΔG_{disso} value of Fe–N–C with site E is larger than that of Fe-N-C, indicating that the vacancy at site E can enhance the stability of Fe-N-C. This is consistent with the higher Eint value of Fe in Fe-N-C with site E (Table S8, Supporting Information) compared with pristine Fe-N-C.

3. Conclusions

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We report the rational design and synthesis of cost-effective single-atom catalysts. Among them, Fe_H-N-C SACs demonstrate outstanding ORR activities and ultra-stable long-term stability. In particular, Fe_H–N–C SACs exhibit ultralow $E_{1/2}$ losses of 29 mV for ORR after 100 000 cycles, which are superior to the commercial Pt/C and most previously reported M-N-C catalysts. When assembled in rechargeable ZABs, it achieved ultralong cycle life over 1200 h with negligible performance degradation, demonstrating a great promise for practical application. Additionally, our experimental results and theoretical calculations reveal that optimizing the electronic structures of M-N₄ moieties for TM-N-C SACs can enhance the intrinsic electrochemical activity. The distinctive features of Fe_H-N-C SACs can be attributed to the optimized local atomic configurations through defect engineering, high utilization of active sites, and the optimization of electronic structures. This strategy could open a new avenue for developing highly durable single-atom catalysts for sustainable energy conversion.

4. Experimental Section

Materials: The chemicals used in this work such as methanol (99%), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O), cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O), nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O), copper nitrate hemi(pentahydrate) (Cu(NO₃)₂·2.5H₂O), manganese nitrate tetrahydrate (Mn(NO₃)₂·24H₂O), iron sulfate heptahydrate (FeSO₄·7H₂O), poly(vinylpyrrolidone) (PVP, M_w \approx 50 000) and 2-methylimidazole were purchased from Sigma-Aldrich and used as received without any further purification. Washing was achieved with ultrapure water and reagent grade ethanol and methanol where required. Ultrapure water was used for solution preparations.

Synthesis of ZIF-8: Typically, $Zn(NO_3)_2$ ·6H₂O (0.89 g) was dissolved in 30 mL of methanol to form a solution. 20 mL of methanol containing 2-methylimidazole (1.97 g) was poured into $Zn(NO_3)_2$ solution. The mixture was kept stirring at room temperature for 24 h. The resulting white precipitates were collected by centrifugation, washed with methanol three times, and finally dried at 80 °C overnight. ADVANCED SCIENCE NEWS _____

was dropped on the glassy carbon (GC) of RDE (5 mm in diameter, PINE Instruments) and RRDE (5.6 mm in diameter, PINE Instruments), giving a catalyst loading of 600 μg cm $^{-2}$. All prepared electrodes were activated before records. Then, oxygen gas is continuously supplied to the test cells. LSV curves of the cathodes were conducted with a scan rate of 5 mV s $^{-1}$ at a rotating speed of 1600 rpm.

For the Tafel plot, the \hat{J}_k was calculated from the mass-transport correction of RDE using Equation (1):

$$J_k = \frac{J \times J_L}{J_L - J} \tag{1}$$

All the electrochemical measurements were recorded against the reversible hydrogen electrode (RHE). Cyclic voltammograms (CVs) at different scan rates (10, 20, 30, 40, 50, and 60 mV s⁻¹) in a non-Faradaic region were delivered to calculate the double layer capacitance (C_{dl}) of the prepared cathodes.

For RRDE, the ring collection efficiency (*N*) is 0.37, the percentage of HO_2^- species and the electron transfer number (*n*) are calculated by the following Equations (2) and (3):

$$HO_{2}^{-}(\%) = 200 \times \frac{I_{R}/N}{I_{D} + I_{R}/N}$$
(2)

$$n = 4 \times \frac{I_{\rm D}}{I_{\rm R}/N + I_{\rm D}} \tag{3}$$

in which I_D is the disk current, I_R is the ring current.

All test data were recorded with the test system reaching steady state. Zn–Air Battery Assembly and Measurements: Primary ZABs were assembled by using polished zinc foil as the anode and aqueous solution containing 6 m KOH as the electrolyte. M_H–N–C or commercial Pt/C coated on carbon paper was used as the air cathode. The total catalyst loading amount on carbon paper was 1 mg cm⁻².

Rechargeable ZABs were assembled by using aqueous solution containing 6 m KOH + 0.2 m zinc acetate as the electrolyte. Fe_H–N–C and RuO₂ (with a mass ration of 1:1) or commercial 20% Pt/C and RuO₂ (with a mass ration of 1:1) coated on carbon paper were used as the air cathode. The total catalyst loading amount on carbon paper was 2.0 mg cm⁻². The galvanostatic discharge/charge cycling stability for the ZABs was performed using a Neware battery testing station system (CT-3008) with a cycling interval of 40 min (20 min for discharging and 20 min for charging) under ambient condition.

Computational Method and Models: All spin-unrestricted DFT calculations were performed by DMol³ code.^[49,50] The generalized gradient approximation and the Perdew-Burke-Ernzerhof (PBE) functional was employed to describe the exchange and correlation effects.^[51] The core electrons were described by the All Electron Relativistic core treat method, which contains all electrons and introduces some relativistic effects into the core.^[52] This method initially neglects the spin-orbit interaction, but retains all other relativistic kinematic effects such as Darwin and massvelocity.^[52] The spin-orbit interaction can be included as a perturbation once the "relativistic" spin-polarized bands and wavefunctions have been obtained.^[52] The basis set was set as double numerical atomic orbital augmented by a polarization function (DNP), which includes a polarization p-function on all hydrogen atoms.^[49] It is one of the best accuracy and highest cost choices in DMol³ code. A smearing of 0.005 Ha orbital occupation was adopted to speed up the electronic convergence. The convergence tolerances of energy, maximum force, and displacement were 1.0×10^{-5} Ha, 0.002 Ha/Å, and 0.005 Å, respectively. A vacuum of 20 Å was added to avoid the artificial interactions between the TM-N-C slabs in adjacent cells. The adsorption energy of adsorbates was calculated as $E_{ad} = E_{sys} - E_{mol} - E_{TM-N-C}$, where E_{mol} , E_{TM-N-C} , and E_{sys} were the total energies of the isolated adsorbate molecule, TM-N-C, and adsorption systems, respectively.^[53] Based on these definitions, a negative E_{ad} value denotes a stable adsorption process. The reaction free energy (ΔG) of the elementary steps was calculated based on the computational hydrogen electrode (CHE) model, which was developed by Nørskov et al.^[54] The CHE model defines that the free energy of a coupled proton/electron in water solution equals to half of that for a gas-phase H_2 .

The ΔG value for elemental step was calculated as: $\Delta G = \Delta E + \Delta E_{ZPE} - \Delta E_{ZPE}$ $T\Delta S + \Delta G_{pH} + \Delta G_{U}$, where the ΔE was the change of *the* total energy, ΔE_{ZPE} was the difference of zero-point energy, ΔS was the change of entropy, and ΔG_{pH} and ΔG_{U} were the free energy contributions related to the pH value and electrode potential U, respectively. The effect of pH on the ΔG of elemental step was obtained by $\Delta G_{pH} = -k_B T \ln[H^+] = pH \times$ $k_{\rm B}$ Tln10. pH value was set as 13 to describe an alkaline media. The effect of electrode potential U for the elementary step involving electron and proton transfer was determined by $\Delta G_U = -neU$, where *n* is the number of electrons transferred. T was the temperature (T is 298.15 K in this work). The water solvent was described by the conductor-like screening model (COSMO), and the dielectric constant was set as 78.54 for water solvent.^[55] The interaction energy between transition metal and N₄ group was calculated as: $E_{int} = E_{TM-N-C} - E_{TM} - E_{N-C}$, where E_{TM-N-C} was the energy of TM–N–C, E_{TM} , and E_{N-C} were the energies of transition metal and N₄-C group from single-point energy calculation.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

carbon vacancies, metal-organic frameworks, oxygen reduction reaction, single-atom catalysts, zinc-air batteries

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