

Inverse opal structured Fe single-atom catalyst enables highly stable rechargeable Zn–air batteries and energy saving chlor-alkali electrolysis

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ABSTRACT: Developing active and durable air cathodes for oxygen reduction reaction (ORR) is pivotal for rechargeable aqueous Zn–air battery (A-ZAB) and chlor-alkali electrolysis. Fe-N-C single-atom catalysts have shown great promise, yet the critical role of the carbon support structure remains underexplored. Herein, we report the Fe single-atom on hierarchically ordered porous carbon (Fe-N-HOC) with an inverse opal structure. Fe-N-HOC features high-density Fe-N₄ sites and delivers highly active ORR performance in alkaline media, attaining substantially enhanced half-wave potential ($E_{1/2}$) of 0.90 V. Density functional theory (DFT) calculations manifest that the curved configuration Fe-N₄ enhances electron transfer, weakens the binding strength of oxygen intermediates, and reduces the energy barrier of *OH desorption significantly by 0.79 eV relative to planar analogues, boosting ORR kinetics. Consequently, Fe-N-HOC delivers excellent durability, with only 8 mV loss in $E_{1/2}$ after 50,000 cycles. In practical applications, A-ZAB with Fe-N-HOC achieves remarkable cycling for 1600 h at 5 mA·cm⁻². Fe-N-HOC-based quasi-solid-state ZAB (QSS-ZAB) also exhibits large peak power density of 216.7 mW·cm⁻² and extended cycle life (> 130 h) across the current densities of 0.5–2.0 mA·cm⁻². Furthermore, in chlor-alkali electrolysis, the Fe-N-HOC||RuO₂ system operates at 1.62 V for large current density of 300 mA·cm⁻² with minimal performance decay. This work presents a multi-dimensional modification strategy encompassing morphology control, element doping, and electronic tuning, providing crucial guidance for the development of efficient catalysts in energy conversion and storage systems.

KEYWORDS: inverse opal structure, single-atom catalyst, oxygen reduction reaction, Zn–air battery, chlor-alkali electrolysis

1 Introduction

The escalating environmental crises arising from unsustainable fossil fuel exploitation have made the development of advanced

energy conversion and storage technologies an urgent global priority [1, 2]. Among the diverse range of candidates, fuel cells and metal–air batteries stand out as exceptionally promising options, boasting high theoretical energy densities, environmental benignity, and economic viability [3–5]. The chlor-alkali industry, one of the most important chemical processes, is now being renewed by the advanced oxygen depolarized cathode (ODC) technology, which reduces energy consumption by > 30% [6, 7]. Nevertheless, the cathodic oxygen reduction reaction (ORR) with sluggish kinetics imposes a critical bottleneck that severely constrains overall energy conversion efficiency of both systems [8, 9]. Although noble metal catalysts, particularly platinum-based materials, have long served as

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the benchmark ORR catalysts, their exorbitant cost, insufficient long-term stability, and susceptibility to impurity poisoning have hindered their widespread industrial deployment [10–12]. The recent emergence of single-atom catalysts (SACs), which maximize atomic utilization efficiency and enable precise active-site tuning, has reinvigorated the pursuit of sustainable, earth-abundant alternatives for replacing noble metals in these critical applications [13–17].

While the coordination structure of the metal center has been widely explored, the essential role of the support in SACs cannot be overlooked [18–20]. Beyond providing a stable platform for dispersion, the support also participates in regulating the reaction microenvironment [21–24]. This regulation critically governs the mass and electron transport behavior near the active sites, as well as the conversion pathways of reactants and intermediates [25]. Notably, carbon materials have been widely accepted as an ideal platform for creating high-performance electrocatalyst supports due to the excellent conductivity, high specific surface area, and abundant pore structures [26]. Strategic engineering of carbon-based supports represents a pivotal approach for advancing ORR catalytic activity, because the reaction rates are often constrained by mass transport limitations [27]. Unfortunately, conventional microporous carbons suffer from restricted ion transport pathways, whereas microporous counterparts exhibit insufficient surface areas [28]. Thus, the optimization of pore architecture requires sufficiently confined pores to maximize surface area while simultaneously accommodating unimpeded diffusion of reactant molecules and electrolyte ions.

On the other hand, the architecture also influences the charge distribution within the catalysts [29, 30]. The curvature-induced enhancement of local electric field can modulate the adsorbate-surface binding energy by tuning the polarizability and dipole moment of the adsorbates, thereby simultaneously regulating both the catalytic reaction selectivity and activity [31–33]. So, catalysts with tunable curvature can not only enrich surface ion concentration and capture reaction intermediates but also facilitate electron transport [34]. Although significant progress has been made in previous studies, fully harnessing the potential of electric fields in electrocatalysis still faces numerous challenges. The precisely tailored structures provide a novel platform to overcome these bottlenecks and establish rational design principles for interfacial electric field modulation, thereby elucidating their impact on electrocatalytic reaction pathways and activity. Among various morphologies and architectures, the inverse opal structure is considered one of the ideal models for designing high-performance, long-lasting industrial-grade electrocatalysts [35, 36]. The inverse opal structure is a skeletal framework characterized by three-dimensionally ordered, periodically arranged macropores, and interconnected voids and windows, with smaller mesopores or micropores in its framework walls [37]. Their high specific surface area fully exposes active sites, and the site density (SD) per unit projected area/volume significantly exceeds that of traditional nanoparticles or films, thereby boosting mass activity [38]. The well-ordered, interconnected pore network establishes efficient transport pathways, reducing mass transfer resistance [39]. The continuous cross-linked monolithic skeleton provides direct pathways for electron transport, reducing interfacial resistance between particles. Moreover, the biomimetic cellular architecture imparts excellent mechanical stability, enabling it to withstand internal reaction stresses and resist catalyst agglomeration, detachment, and structural degradation [40]. More importantly, single atoms

anchored on the inverse opal-structured carbon skeletons experience tensile and compressive strains induced by the surrounding curvature, which may further optimize their electronic distribution to accelerate the ORR kinetics.

This study presents the high-performance Fe single-atom on hierarchically ordered porous carbon (Fe-N-HOC) with the inverse opal structure. The unique architecture features a large specific surface area, abundant available Fe-N₄ active sites. According to density functional theory (DFT) calculations, Fe-N₄ curve configuration renders higher adsorption free energy of all ORR intermediates than the plane one, indicating easier desorption from the inverse opal structure. Especially, the Fe-N₄ curve configuration noticeably lowers the energy barrier of rate-determining step (RDS, *OH desorption) by 0.79 eV relative to planar analogues. Consequently, Fe-N-HOC exhibits exceptional 4e⁻-dominant ORR activity, achieving a high half-wave potential (*E*_{1/2}) of 0.90 V. Notably, Fe-N-HOC delivers a remarkable turnover frequency (TOF) of 12.70 e⁻·s⁻¹·site⁻¹ at 0.85 V, 58-fold enhancement compared to commercial Pt/C (0.22 e⁻·s⁻¹·site⁻¹). Fe-N-HOC powered rechargeable aqueous Zn-air battery (A-ZAB) delivers high power density of 248.2 mW·cm⁻², and ultralong cycling stability exceeding 1600 h. The quasi-solid-state ZAB (QSS-ZAB) also exhibits remarkable cycling life (> 130 h). Remarkably, Fe-N-HOC||RuO₂ chlor-alkali electrolyser maintains excellent cycle stability for over 206 and 124 h at the high current density of 100 and 300 mA·cm⁻², respectively, underscoring the great potential for practical chlor-alkali electrolysis. This work provides a promising paradigm for the rational design of high-performance SACs with carefully designed architectures.

2 Experimental

2.1 Chemicals and reagents

Ferric chloride hexahydrate (FeCl₃·6H₂O, analytical reagent (AR), ≥ 99.0%), methanol (CH₃O, AR, ≥ 99.5%), isopropanol (C₃H₈O, AR, ≥ 99.5%), zinc acetate (C₄H₆O₄Zn, AR, ≥ 98.0%), polytetrafluoroethylene (PTFE, ~ 5 μm), and potassium hydroxide (KOH, AR, ≥ 85.0%) were purchased from the Sinopharm Chemical Reagent Co., Ltd. Formaldehyde solution (37 wt.%), potassium persulfate (K₂S₂O₈, ≥ 99.0%), polyvinyl pyrrolidone (PVP, ≥ 98.0%), o-phenylenediamine (o-PD, C₆H₈N₂, AR, 98.0%), and RuO₂ (≥ 99.0%) were acquired from Shanghai Macklin Biochemical Technology Co., Ltd. Pluronic F127 and Pt/C (20 wt.%) were obtained from Sigma-Aldrich. Phenol (≥ 99%), Nafion 117 solution, and polyethylenimine (PEI, *M*_w = 100,000 g·mol⁻¹) were purchased from Aladdin.

2.2 Synthesis of HOC

First, 0.96 g F127 and 15 mL H₂O were placed in a 50 mL beaker. Subsequently, 0.6 g phenol, 15 mL 0.1 M NaOH solution, and 2.1 mL formaldehyde solution were added to an oil bath preheated to 68 °C. After stirring uniformly for 30 min, the fully dissolved F127 solution was added to the above mixture. After continuous stirring for 4 h, 50 mL of deionized water was introduced into the solution, and stirring was continued for another 2 h. Separately, 100 mg polystyrene (PS) spheres were dissolved in 20 mL deionized water, and a milky white emulsion was formed via ultrasonication for 30 min. Then, 50 mg polyethylenimine (PEI) was added to this emulsion, and after thorough mixing by ultrasonication, the mixture was stirred for 2 h. Subsequently, the emulsion was

transferred into a three-necked flask, and continuous stirring was maintained at 68 °C for 12 h. Afterward, the resulting product was subjected to centrifugation and drying, followed by heat treatment at 900 °C for 2 h under a nitrogen atmosphere to obtain HOC.

2.3 Synthesis of Fe-N-HOC

Firstly, 50 mg HOC was dispersed in a solution containing 0.2 mmol o-phenylenediamine and mixed uniformly by ultrasonication. Then, it was mixed with a 0.03 mmol $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solution and stirred for 30 min, followed by stirring uniformly in the dark for 12 h. The product was obtained after vacuum filtration with deionized water and vacuum drying. Subsequently, the product was precisely mixed with urea at a predetermined mass ratio (1:5) and thoroughly ground to ensure the formation of a homogeneous mixture. Finally, the mixture was pyrolyzed at 900 °C for 2 h under a nitrogen atmosphere, yielding the Fe-N-HOC catalyst.

2.4 Synthesis of N-HOC

For comparison, the N-HOC reference sample was prepared using the identical procedure as that for Fe-N-HOC, except that $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was not added during the synthesis.

2.5 Characterizations

X-ray diffraction (XRD) patterns were recorded on a Rigaku-Dmax2500 diffractometer. X-ray photoelectron spectroscopy (XPS) and Raman spectra were collected on an ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Scientific) and LabRAM HR800, respectively. Nitrogen adsorption/desorption isotherms were obtained on an ASAP 2020 physical adsorption analyzer. The morphology of the electrocatalysts was observed by scanning electron microscopy (SEM, Sigma 500, Zeiss) and transmission electron microscopy (TEM, JEM-2100F). The energy-dispersive X-ray spectrometry (EDX) was observed by America-ThermoFisher-Talos F200S/FEI Tecnai G2 F20 X-Twin. Aberration-corrected high-angle annular dark-field scanning TEM (AC-HAADF-STEM) images were obtained using a Titan Cubed Themis G260-300 microscope. Inductively coupled plasma mass spectrometry (ICP-MS, Thermo iCAP RQ) was used to determine the metal content in the electrocatalyst.

2.6 Electrochemical measurements

Electrochemical measurements, including linear sweep voltammetry (LSV) and cyclic voltammetry (CV), were performed using an electrochemical workstation, Chenhua (CHI 760E), with a three-electrode configuration. All electrochemical tests were performed on a CHI 760E electrochemical workstation with rotating equipment. ORR measurements were all performed in O_2 -saturated 0.1 M KOH solution. Graphite rod and Ag/AgCl (KCl-saturated) were used as counter electrode and reference electrode, respectively. Then, a working electrode with a catalyst loading of $0.255 \text{ mg} \cdot \text{cm}^{-2}$ was obtained by pasting the electrocatalyst onto a rotating disk electrode (RDE, diameter (d) = 5.0 mm) or a rotating ring disk electrode (RRDE, d = 5.61 mm).

3 Results and discussion

3.1 Synthesis and structural characterization

Figure 1(a) schematically illustrates the synthesis route of Fe-N-

HOC. Firstly, ordered PS spheres were synthesized according to the previously reported literature (Fig. S1 in the Electronic Supplementary Material (ESM)) [41]. PEI-coated PS spheres were added into the phenol-formaldehyde-sodium hydroxide solution, followed by pyrolysis under nitrogen atmosphere to prepare HOC with a pore size of approximately 100 nm (Fig. S2 in the ESM). Using o-PD as the nitrogen source and iron chloride as the iron source, metal-o-phenylenediamine coordination complex was introduced by wet-chemistry metal-ion impregnation. Then carbonization was conducted with urea under nitrogen atmosphere to obtain the Fe-N-HOC.

SEM (Fig. 1(b)) and TEM (Fig. 1(c) and Fig. S3 in the ESM) images reveal that Fe-N-HOC exhibits a regular inverse opal structure with uniform pore size around 100 nm. A characteristic mesoporous architecture with pore diameter of approximately 100 nm is evident (Fig. 1(d)). The high-resolution TEM (HRTEM) image exhibits interlayer spacings of 0.34 and 0.35 nm, which belongs unquestionably to the (002) crystal plane of graphitic carbon (Fig. 1(e)). The EDX elemental mapping images illustrate the uniform distributions of C, N, and Fe in Fe-N-HOC (Fig. 1(f)). The AC-HAADF-STEM image of Fe-N-HOC reveals a host of bright dots representing Fe single-atoms (SAs), verifying the successful synthesis of SAC (Fig. 1(g)).

The XRD patterns reveal two distinct diffraction peaks at 23° and 43°, which are attributed to the lattice planes of carbon of (002) and (101) (Fig. 2(a)). As shown in Fig. S4 in the ESM, the intensity ratios (I_D/I_G) of Fe-N-HOC and N-HOC are determined to be 0.99 and 1.01, respectively. This indicates that Fe doping has no effect on the disordered/defective structures of carbon support. The XPS survey spectrum confirms the successful doping of Fe and N elements in Fe-N-HOC (Fig. S5 in the ESM). The well-defined pyridinic N, Fe-N_x, pyrrolic N, and graphitic N at 397.4, 399.0, 400.1, and 400.9 eV can be observed in high-resolution N 1s XPS spectrum of Fe-N-HOC (Fig. 2(b)) [42]. In comparison with N-HOC, the emergence of a new characteristic peak corresponding to the metal-N species confirms the anchoring of the Fe-N coordination structure on the HOC (Fig. S6 in the ESM). For Fe 2p spectrum, the signals located at 710.9 eV ($\text{Fe}^{2+} 2p_{3/2}$), 724.2 eV ($\text{Fe}^{2+} 2p_{1/2}$), 714.5 eV ($\text{Fe}^{3+} 2p_{3/2}$), and 727.6 eV ($\text{Fe}^{3+} 2p_{1/2}$) are clearly certified as shown in Fig. 2(c), suggesting Fe^{2+} and Fe^{3+} are present in Fe-N-HOC [43]. The Brunauer-Emmett-Teller (BET) surface area of Fe-N-HOC is $1071 \text{ m}^2 \cdot \text{g}^{-1}$ (Fig. S7(a) in the ESM). In addition, the Barrett-Joyner-Halenda (BJH) model and non-local DFT (NLDFT) model reveal the coexistence of micropores (85.5%) and mesopores (15.5%) in Fe-N-HOC (Fig. S7(b) and Table S1 in the ESM). Fe-N-HOC's unique structure not only facilitates the exposure of active sites but also enables efficient mass transfer.

We performed the valence states analysis using X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). The Fe K-edge XANES spectra show that Fe-N-HOC closely resembles FePc (Pc stands for phthalocyanine), confirming the +2 of Fe (Fig. 2(d)). Moreover, the Fourier-transform EXAFS (FT-EXAFS) spectra of Fe-N-HOC exhibit a dominant peak (at 1.50 Å), similar to that of FePc, confirming the predominant Fe-N coordination (Fig. 2(e)) [44]. Moreover, no Fe-Fe scattering is observed, confirming that the metal species exist in atomically dispersed state throughout the support. EXAFS fitting results indicate that the Fe atoms are coordinated by four nitrogen atoms, with a corresponding average bond length of 1.96 Å (Figs. 2(f) and 2(g) and Table S2 in the ESM). The wavelet

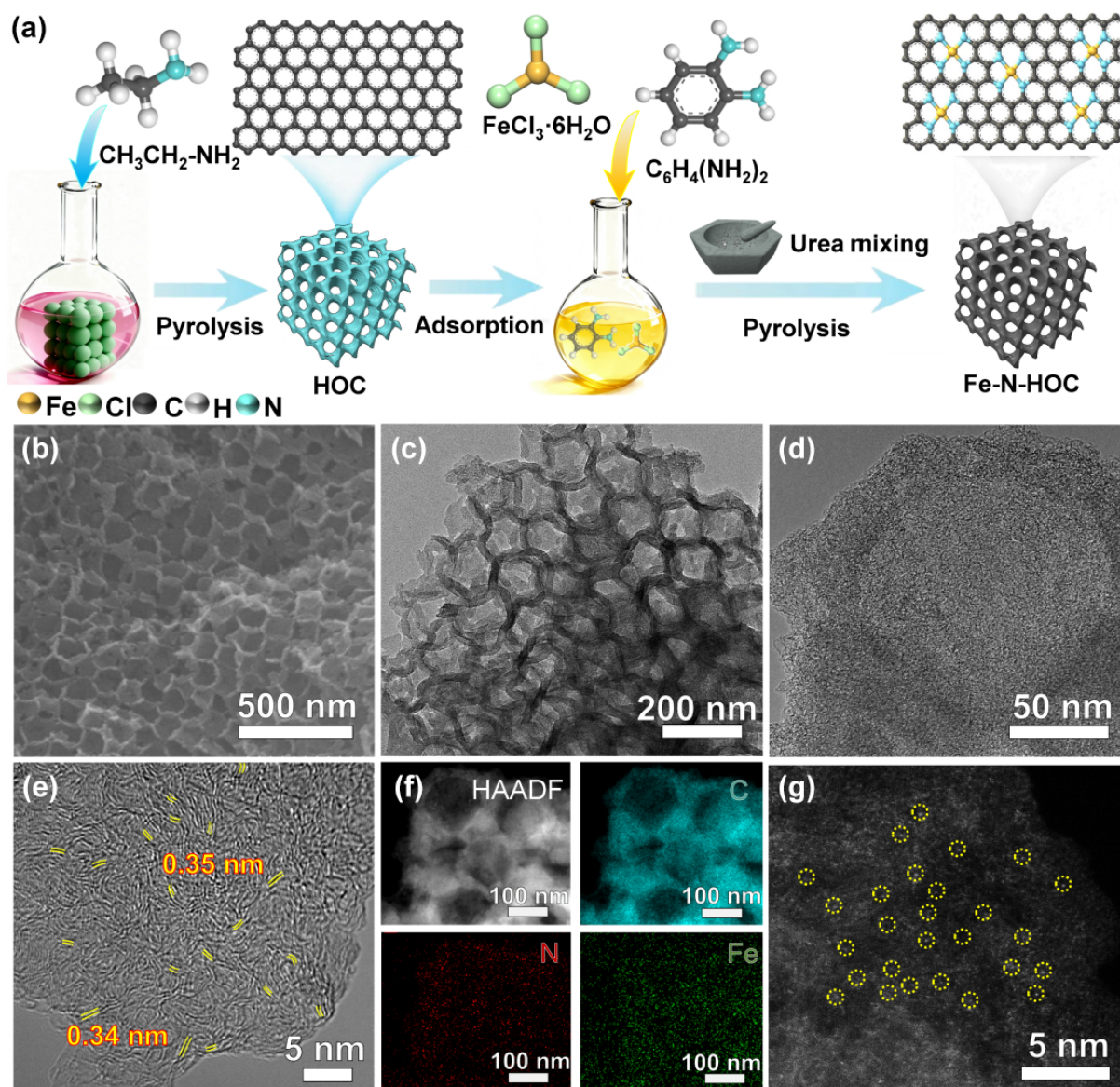


Figure 1 (a) Schematic illustration of the synthetic process of Fe-N-HOC. (b) SEM, ((c) and (d)) TEM, and (e) HRTEM images of Fe-N-HOC. (f) HAADF-STEM and the corresponding EDX mapping images of C, N, and Fe. (g) AC HAADF-STEM image of Fe-N-HOC.

transform (WT)-EXAFS contour plots of Fe-N-HOC exhibit the dominant maximum at approximately $4.8 \text{ \AA}^{-1}$ in k -space. These features correspond to the Fe-N coordination in Fe-N-HOC and align remarkably well with the FePc reference (Fig. 2(h)). The combined evidence from the local coordination environment analysis provides definitive evidence for the successful formation of SAC.

3.2 Electrocatalytic performance toward ORR

The electrocatalytic ORR activity and stability of Fe-N-HOC, N-HOC (Fig. S8 in the ESM), and Pt/C were evaluated. ORR cathodic peaks observed in CV curves are located at 0.88, 0.84, and 0.87 V for Fe-N-HOC, N-HOC, and benchmark Pt/C, respectively (Fig. S9 in the ESM). LSV curves unveil that Fe-N-HOC possesses the most positive $E_{1/2}$ of 0.90 V, which is larger than Pt/C (0.86 V), N-HOC (0.83 V), and previously reported catalysts (Fig. 3(a) and Table S3 in the ESM). As shown in Fig. 3(b), Fe-N-HOC achieves a kinetic current density (J_k) of $20.70 \text{ mA}\cdot\text{cm}^{-2}$ at 0.85 V, representing a 7-

and 4-fold enhancement over $2.83 \text{ mA}\cdot\text{cm}^{-2}$ (N-HOC), and $5.60 \text{ mA}\cdot\text{cm}^{-2}$ (Pt/C), respectively. Moreover, Fe-N-HOC's Tafel slope is $59 \text{ mV}\cdot\text{dec}^{-1}$, which is smaller than $64 \text{ mV}\cdot\text{dec}^{-1}$ (N-HOC) and $76 \text{ mV}\cdot\text{dec}^{-1}$ (Pt/C), indicating accelerated ORR kinetics for Fe-N-HOC (Fig. 3(c)). Fe-N-HOC exhibits a TOF of $12.7 \text{ e}\cdot\text{s}^{-1}\cdot\text{site}^{-1}$ and a significant mass activity of $21.93 \text{ A}\cdot\text{mg}^{-1}$ at 0.85 V. This corresponds to an improvement by a factor of ~ 58 in TOF and a factor of ~ 199 in mass activity relative to the commercial Pt/C (TOF: $0.22 \text{ e}\cdot\text{s}^{-1}\cdot\text{site}^{-1}$; mass activity: $0.11 \text{ A}\cdot\text{mg}^{-1}$), as illustrated in Fig. 3(d). Fe-N-HOC has the highest double-layer capacitance (C_{dl}) value of $22.8 \text{ mF}\cdot\text{cm}^{-2}$, which exhibits a 4.4-fold higher than of commercial Pt/C ($5.2 \text{ mF}\cdot\text{cm}^{-2}$) and 10.9-fold higher than of N-HOC ($2.1 \text{ mF}\cdot\text{cm}^{-2}$, Fig. S10 in the ESM), delivering a larger electrochemical surface area (ECSA) and a greater number of exposed active sites for Fe-N-HOC [45]. The accessible active SD of Fe-N-HOC was quantitatively determined via the nitrite reduction stripping measurement [46]. As illustrated in Fig. S11 in the ESM, the SD is as high as $8.2 \times 10^{19} \text{ sites}\cdot\text{g}^{-2}$, which is higher than

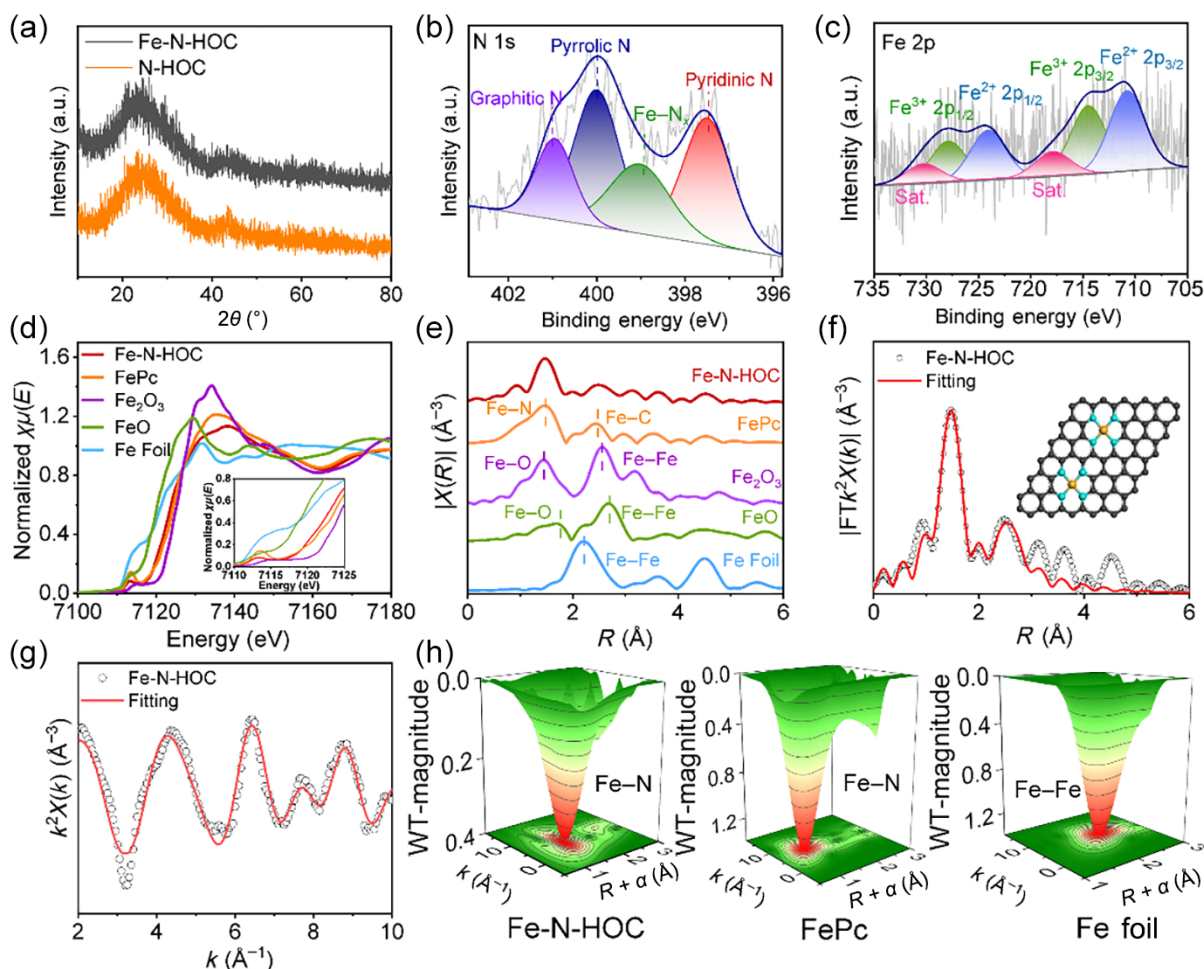


Figure 2 (a) XRD patterns of Fe-N-HOC and N-HOC. (b) High-resolution N 1s and (c) Fe 2p spectra of Fe-N-HOC. (d) XANES spectra of Fe K-edge of Fe-N-HOC, Fe foil, FeO, Fe₂O₃, and FePc. (e) Fourier-transformed Fe K-edge EXAFS spectra of Fe-N-HOC, Fe foil, FeO, Fe₂O₃, and FePc. ((f) and (g)) Least squares fitting curves of FT-EXAFS spectra of Fe-N-HOC at R- and k-space. (h) WT-EXAFS plots of Fe-N-HOC and the references.

previously reported catalysts (Table S4 in the ESM). The Koutecky–Levich (K–L, Fig. 3(e)) equation reveals that Fe-N-HOC has a four-electron transfer pathway. Remarkably, the electron transfer number (*n*) based on the rotating ring-disk electrode (RRDE) measurement is quantitatively determined to be 3.99 at the potential range of 0.2 to 0.8 V (Fig. 3(f) and Fig. S12 in the ESM). The H₂O₂ yield (H₂O₂%) of Fe-N-HOC is below 3.5% within 0.2–0.8 V, far lower than that of Pt/C (7.0%). Taken together, the above evidence conclusively demonstrates that Fe-N-HOC proceeds via a highly selective four-electron pathway for ORR.

During the chronoamperometry test, the ORR current density of Pt/C decreases significantly, with a current density retention rate of only 78% (Fig. 3(g)). In contrast, the ORR current density retention of Fe-N-HOC is 92%, indicating better durability. Conspicuously, the LSV curves of Fe-N-HOC show an extremely small *E*_{1/2} decay of merely 8 mV even after 50,000 CV cycles (Fig. 3(h)). Morphological and compositional analyses were conducted on Fe-N-HOC after accelerated durability test (ADT). SEM and mapping images confirm that the structural integrity of Fe-N-HOC remains well preserved after ADT (Figs. S13 and S14 in the ESM). Clearly, its phase composition is well-preserved, indicating excellent structural integrity of Fe-N-HOC (Fig. S15 in the ESM). Furthermore, the XPS spectra of Fe-N-HOC after ADT exhibit no significant binding energy shifts in the N 1s and Fe 2p spectra (Fig. S16 in the ESM),

indicating the well-preserved Fe and N valence states. These results demonstrate that Fe-N-HOC possesses excellent morphological and structural stability. In addition, Fe-N-HOC shows better methanol tolerance capacity than Pt/C (Fig. 3(i)). Accordingly, Fe-N-HOC holds immense potential for practical applications in methanol fuel cells.

3.3 Theoretical insights

We used the *in situ* attenuated total reflection-surface enhanced infrared absorption spectroscopy (ATR-SEIRAS) to systematically elucidate the ORR process and the adsorption behavior of oxygen intermediates. As the applied potential from open circuit voltage (OCV) to 0.2 V, a marked characteristic absorption band (at 1108 cm⁻¹) corresponding to the O=O stretching vibration mode in *OOH intermediate appeared in Fe-N-HOC, confirming that ORR follows the associative mechanism (Fig. 4(a)) [47]. Another absorption band at ~3746 cm⁻¹ is observed, corresponding to O–H stretching vibration of surface-adsorbed *OH intermediates (Fig. 4(b)) [48, 49]. With the decrease of applied potential, the continuous intensification of the *OH absorption band is observed, indicating the *OH intermediates accumulation and signifying that *OH desorption may be the RDS [50].

DFT calculations were employed to elucidate the ORR mechanism of Fe-N-HOC. Based on the aforementioned

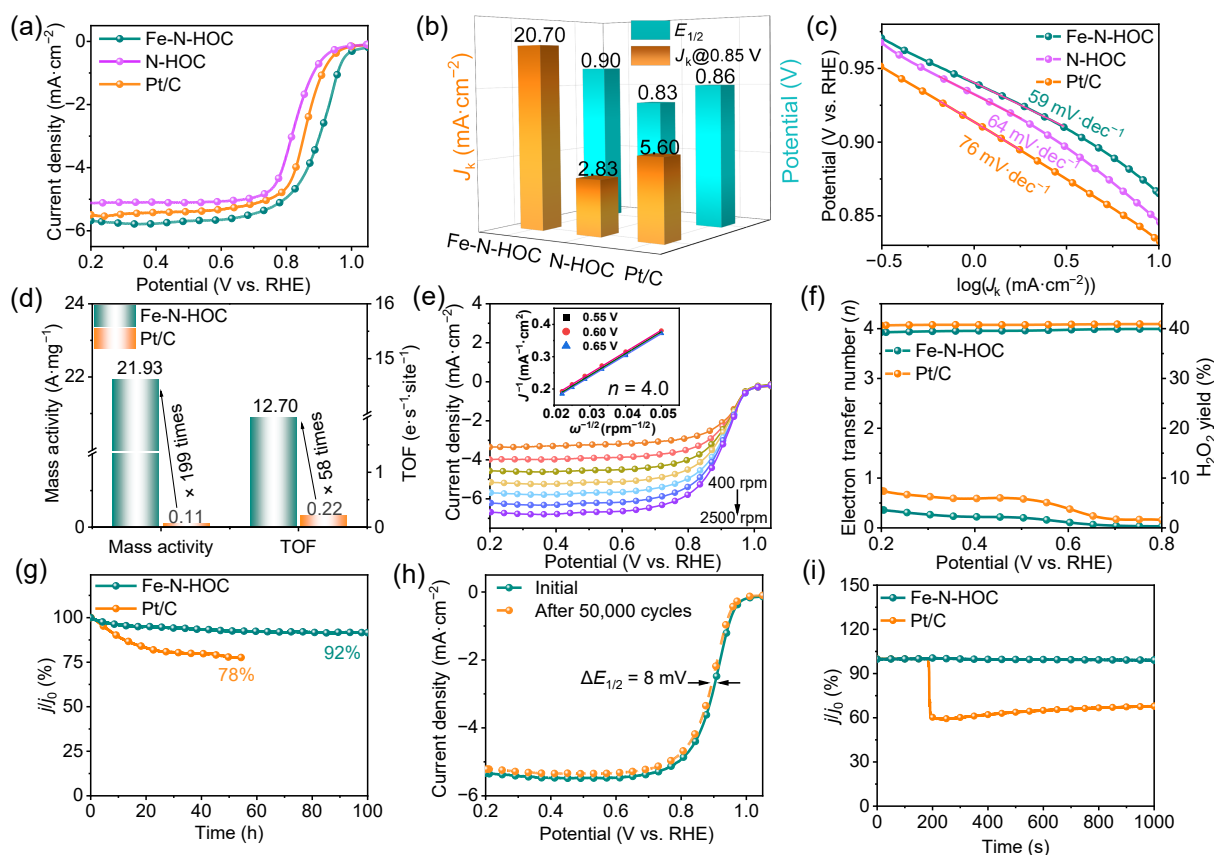


Figure 3 (a) ORR polarization curves and (b) $E_{1/2}$ and $J_k@0.85\text{ V}$ of Fe-N-HOC, N-HOC, and Pt/C. (c) The corresponding Tafel plots of Fe-N-HOC, N-HOC, and Pt/C were recorded in O_2 -saturated 0.1 M KOH. (d) TOF and mass activity of Fe-N-HOC and Pt/C. (e) LSV curves of Fe-N-HOC obtained at different rotating speeds (inset: K-L plots). (f) H_2O_2 yield and n for Fe-N-HOC and Pt/C. (g) Chronoamperometric curves of Fe-N-HOC and Pt/C in O_2 -saturated 0.1 M KOH. (h) ORR polarization curves of Fe-N-HOC before and after 50,000 cycles in O_2 -saturated 0.1 M KOH. (i) Methanol tolerance of Fe-N-HOC and Pt/C.

characterization results, Fe-N-HOC with plane structure (named Fe- N_4 plane), and bending curvature to mimic the inverse opal structure (named Fe- N_4 curve, Fig. S17 in the ESM) were constructed. Figure 4(c) displays the differential charge density for the two models, where obvious charge transfer between Fe and N atoms in both configurations can be observed. However, the Fe atoms in the Fe- N_4 curve lose more electrons (-1.19e) than the Fe- N_4 plane (-1.09e , Fig. 4(d)). Specifically, the higher electron loss from Fe atom in the Fe- N_4 curve configuration than Fe- N_4 plane results in weakened adsorption of oxygen intermediates, thereby enhancing the overall kinetics of ORR.

The adsorption configurations of oxygen intermediates ($^*\text{OOH}$, $^*\text{O}$, and $^*\text{OH}$) onto both Fe- N_4 curve and Fe- N_4 plane were illustrated (Fig. 4(e) and Fig. S18 in the ESM). At electrode potential (U) = 0 V, the free energy curve for the Fe- N_4 site exhibits a decreasing trend, indicating that each electron transfer step on Fe- N_4 curve configuration is exothermic and thermodynamically spontaneous (Fig. 4(f) and Table S5 in the ESM). For Fe- N_4 plane configuration, the ORR pathway involves both endothermic and exothermic elementary steps. It is noteworthy that $^*\text{OH}$ desorption is an endothermic process and is thus non-spontaneous. In addition, Fe- N_4 curve configuration exhibits a weaker binding strength of oxygen intermediates, as evidenced by its systematically higher adsorption energies compared to Fe- N_4 plane configuration. The adsorption free energy of oxygen intermediates on Fe- N_4 curve configuration is universally higher than that on Fe- N_4 plane counterpart under $U = 1.23\text{ V}$. It means that the ORR intermediate

is more likely to desorb from Fe- N_4 curve configuration (Fig. 4(g) and Table S6 in the ESM). Additionally, the ORR pathway for both configurations involves the endothermic steps: $^*\text{O} \rightarrow ^*\text{OH}$ and $^*\text{OH} \rightarrow \text{H}_2\text{O}$. In addition, the steps $\text{O}_2 \rightarrow ^*\text{OOH}$ and $^*\text{OOH} \rightarrow ^*\text{O}$ are exothermic steps. $^*\text{OH}$ deprotonation is the RDS in both configurations. Significantly, Fe- N_4 curve has a much lower $^*\text{OH}$ desorption energy (1.09 eV) than Fe- N_4 plane (1.88 eV). It is demonstrated that $^*\text{OH}$ desorbs more easily from Fe- N_4 curve configuration, suggesting that the enhanced kinetics.

3.4 Zn-air battery performance

Inspired by the favorable ORR activity and stability, Fe-N-HOC was used as an air cathode catalyst in A-ZAB to assess the application potential in energy devices. The OCV of A-ZAB assembled with Fe-N-HOC is 1.50 V, higher than noble metal-based system (1.46 V, Fig. 5(a)). Fe-N-HOC-based A-ZAB delivers substantially enhanced peak power density ($248.2\text{ mW}\cdot\text{cm}^{-2}$), which is higher than that of reported SACs (Table S7 in the ESM) and Pt/C-based A-ZAB ($193.3\text{ mW}\cdot\text{cm}^{-2}$, Fig. 5(b)). Fe-N-HOC-based one delivers a large specific discharge capacity ($826.2\text{ mAh}\cdot\text{g}^{-1}$ at $10\text{ mA}\cdot\text{cm}^{-2}$), exceeding Pt/C-based one ($769.3\text{ mAh}\cdot\text{g}^{-1}$, Fig. 5(c)). Fe-N-HOC-based system consistently delivers higher discharge voltages than Pt/C-based A-ZAB as presented in Fig. S19 in the ESM, as the current density is enhanced from 1 to $50\text{ mA}\cdot\text{cm}^{-2}$. Clearly, the former displays 1.26 V, while the latter drops to only 1.07 V at $50\text{ mA}\cdot\text{cm}^{-2}$. Notably, the discharge voltage rapidly reverts to its initial value when the current density decreases.

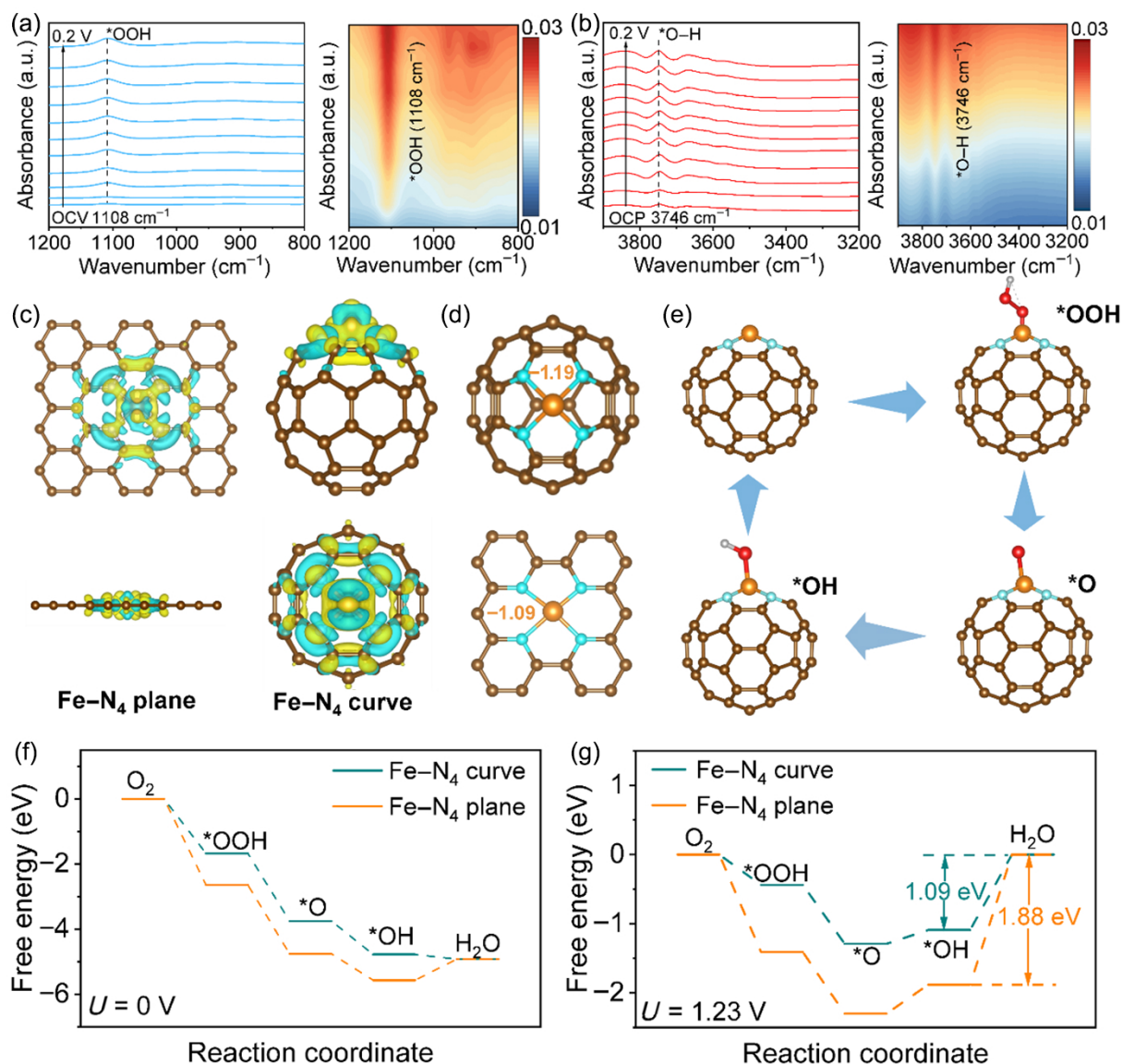


Figure 4 ((a) and (b)) *In situ* ATR-SEIRAS spectra and the corresponding contour images of Fe-N-HOC in O₂-saturated 0.1 M KOH solution from the OCV to 0.2 V (vs. reversible hydrogen electrode (RHE)). (c) Charge density difference of Fe-N₄ plane and Fe-N₄ curve (yellow: electron accumulation and cyan: electron depletion). (d) Bader charge of Fe-N₄ curve and Fe-N₄ plane. Negative value indicates the loss of electron, while positive value indicates the gain of electron. (e) The adsorption configurations of *OOH, *O, and *OH on Fe-N₄ curve. ((f) and (g)) Gibbs free-energy diagrams of Fe-N₄ plane and Fe-N₄ curve at the electrode potential of $U = 0$ and 1.23 V.

Consequently, these results demonstrate excellent rate capability and remarkable reversibility of Fe-N-HOC-based system.

Fe-N-HOC-based A-ZAB maintains remarkable cycling durability at 5.0 mA·cm⁻² over 1600 h of continuous charge-discharge cycling (Fig. 5(d)). Fe-N-HOC-based A-ZAB maintains a minimal charge-discharge voltage gap of merely 0.87 V after 400 h of cycling. This voltage gap then decreased to 0.85 V after an additional 400 h of cycling. The assembly maintained this 0.85 V voltage gap following 1200 h of galvanostatic charge-discharge. Notably, after an extended cycling test of 1600 h, the voltage gap increased by a mere 0.01 V, resulting in a final value of 0.86 V. In summary, the overall increment of the voltage gap remains as low as 0.01 V during the whole operation process (Fig. S20(a) in the ESM). In comparison, Pt/C-based A-ZAB suffers from a pronounced voltage gap (over 1.1 V) and a charge-discharge cycling stability limited to merely 458 h. Clearly, Fe-N-HOC-based

system exhibits a voltage efficiency of 57.65% after 200 h with a constant current density of 5.0 mA·cm⁻², while it maintains 53.68% following 1600 h of cycling. Notably, the voltage efficiency degrades by only 4% (Fig. S20(b) in the ESM). The above results conclusively validate the exceptional cycling stability of Fe-N-HOC-based system. During galvanostatic charge-discharge cycling, Fe-N-HOC-based one delivers a stable discharge voltage at approximately 1.1 V at 5.0 mA·cm⁻². In contrast, Pt/C-based A-ZAB suffers a marked decline in the following 100 h operation (Fig. S20(c) in the ESM). Collectively, these findings highlight the considerable promise of Fe-N-HOC as a higher-performance and stability catalyst for A-ZAB.

QSS-ZABs have emerged as an ideal candidate to overcome the performance limitations of aqueous batteries and propel the advancement of flexible energy devices toward practical application. Taking advantage of the excellent electrochemical reaction performance of Fe-N-HOC, we fabricated the QSS-ZAB using Fe-

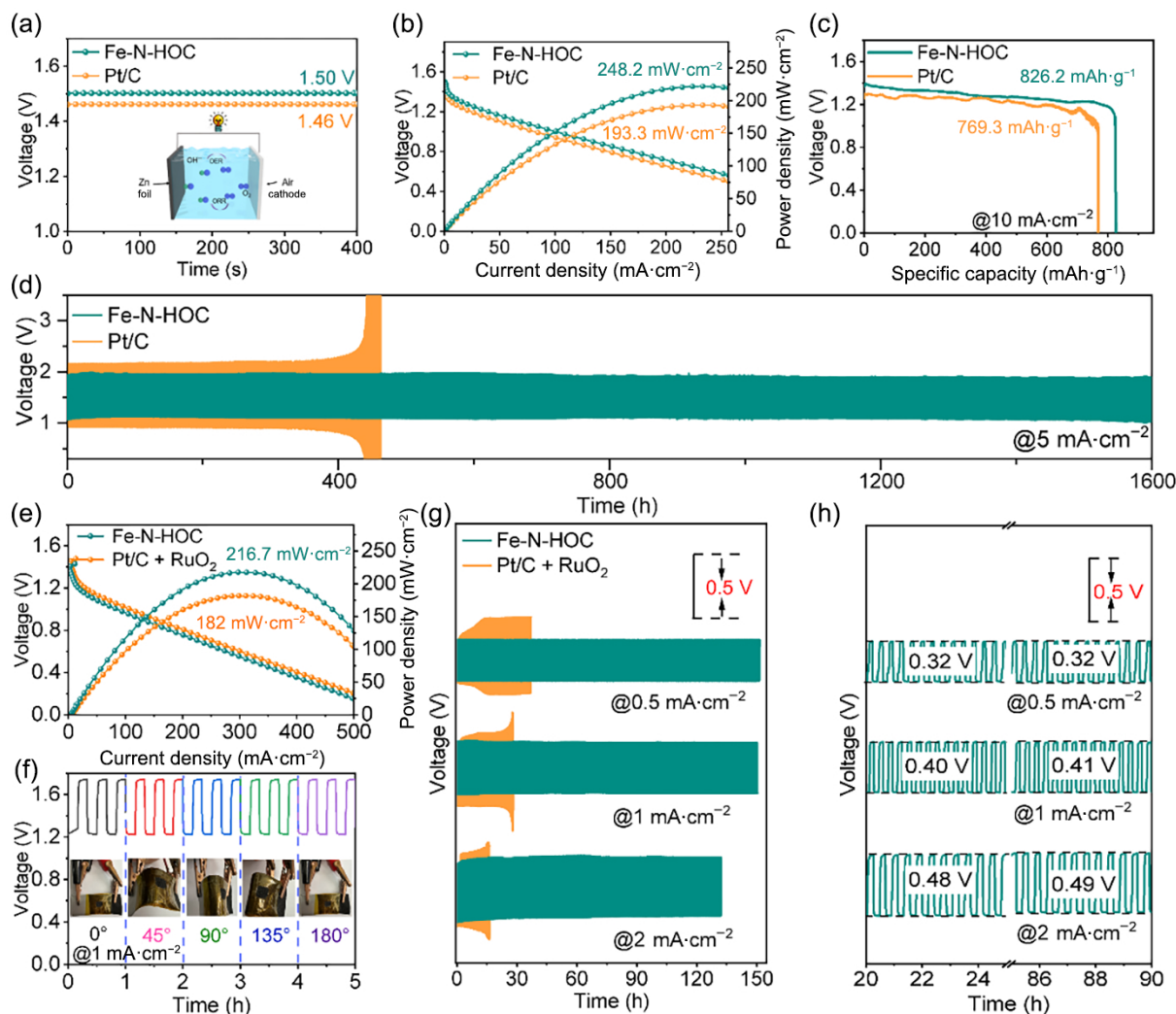


Figure 5 (a) OCV of Fe-N-HOC- and Pt/C-based A-ZABs. The inset is the scheme of A-ZAB. (b) Discharge curves and power density plots of A-ZABs assembled by Fe-N-HOC and Pt/C. (c) Discharge curves of A-ZABs assembled by Fe-N-HOC and Pt/C as air cathode catalysts, at a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$. (d) Galvanostatic charge-discharge cycling curves of A-ZABs assembled by Fe-N-HOC and Pt/C, at a current density of $5.0 \text{ mA}\cdot\text{cm}^{-2}$. (e) Discharge curves and power density plots of QSS-ZABs using Fe-N-HOC and Pt/C + RuO_2 . (f) Cycling curves of QSS-ZAB assembled with Fe-N-HOC at different bending angles. (g) Galvanostatic charge-discharge cycling at the current densities of 0.5, 1.0, and $2.0 \text{ mA}\cdot\text{cm}^{-2}$ for QSS-ZABs assembled with Fe-N-HOC and Pt/C + RuO_2 . (h) The corresponding charge-discharge voltage gap of assembled QSS-ZAB at around 20 and 90 h.

N-HOC. Due to the sluggish kinetics of oxygen evolution reaction (OER), we replaced it with the efficient iodine oxidation reaction (IOR) by introducing KI into the electrolyte. As shown in Fig. S21(a) in the ESM, LSV curves demonstrate that the potential of IOR is negatively shifted by 349 mV relative to that of OER at $10 \text{ mA}\cdot\text{cm}^{-2}$. Significantly, Fe-N-HOC-based QSS-ZAB shows an OCV (1.48 V), surpassing Pt/C + RuO_2 -based QSS-ZAB (1.43 V, Fig. S21(b) in the ESM). Fe-N-HOC-based QSS-ZAB displays an outstanding peak power density of $216.7 \text{ mW}\cdot\text{cm}^{-2}$ at $308.4 \text{ mA}\cdot\text{cm}^{-2}$, which is higher than that of Pt/C + RuO_2 -based QSS-ZAB ($182 \text{ mW}\cdot\text{cm}^{-2}$, Fig. 5(e)). Fe-N-HOC-based QSS-ZAB also delivers transcendent rate capability (Fig. S21(c) in the ESM), exhibiting consistently higher discharge voltages than noble metal counterparts across the current densities ranging from 0.5 to $10 \text{ mA}\cdot\text{cm}^{-2}$. Additionally, Fe-N-HOC-based QSS-ZAB's discharge voltage achieves 1.35 V, even at $10 \text{ mA}\cdot\text{cm}^{-2}$, which is higher than noble metal system (1.21 V). Additionally, Fe-N-HOC-based system delivers a high specific capacity of $796.5 \text{ mAh}\cdot\text{g}^{-1}$, larger than Pt/C + RuO_2 ($734.1 \text{ mAh}\cdot\text{g}^{-1}$), evidencing Fe-N-HOC's superior

discharge performance (Fig. S21(d) in the ESM). It is noteworthy that the cycling performance was remarkably stable under various bending conditions, from 0° to 180° , indicating excellent mechanical robustness of Fe-N-HOC-based QSS-ZAB (Fig. 5(f)).

To experimentally validate the exceptional durability of QSS-ZAB, galvanostatic charge-discharge cycling was conducted. Fe-N-HOC-based QSS-ZAB exhibits excellent reversibility over cycles exceeding 152, 151, and 132 h at 0.5, 1.0, and $2.0 \text{ mA}\cdot\text{cm}^{-2}$, respectively (Fig. 5(g)). Notably, Fe-N-HOC-based QSS-ZAB displays a voltage gap of only 0.32 V at $0.5 \text{ mA}\cdot\text{cm}^{-2}$, surpassing the performance of most reported catalysts (Fig. 5(h) and Table S8 in the ESM). Notably, the voltage gap remains essentially unchanged even after 90 h of continuous operation. The Pt/C + RuO_2 -based QSS-ZAB functions for merely 37 h at $0.5 \text{ mA}\cdot\text{cm}^{-2}$, during which its voltage gap significantly increases from 0.44 to 0.62 V. At $1.0 \text{ mA}\cdot\text{cm}^{-2}$, Pt/C + RuO_2 -based QSS-ZAB sustains cycling for merely 28 h, accompanied by an increase in the voltage gap from 0.58 to 0.62 V. Under the same experimental conditions, voltage gap of Fe-N-HOC-based QSS-ZAB increases by merely 0.01 V.

Even more impressively, after 90 h of operation at a large current density of $2.0 \text{ mA}\cdot\text{cm}^{-2}$, the voltage gap negligibly increases from 0.48 to 0.49 V. The Pt/C + RuO_2 -based QSS-ZAB demonstrates limited stability at $2.0 \text{ mA}\cdot\text{cm}^{-2}$, with its cycle life limited to a short duration of only 17 h. These results demonstrate the excellent cycling stability of QSS-ZAB assembled with Fe-N-HOC, providing new support for the long-term endurance of wearable electronic devices.

3.5 Fe-N-HOC application in chlor-alkali electrolysis

We performed chlor-alkali electrolysis of Fe-N-HOC using ODC in high-concentration NaOH solution, and the test was conducted at 25 and 80 °C, respectively. As confirmed by Fig. 6(a), Fe-N-HOC-based ODC exhibits superior performance to Pt/C regardless of whether the tests are conducted at 25 or 80 °C. Clearly, the potential required for Fe-N-HOC-based ODC to reach $100 \text{ mA}\cdot\text{cm}^{-2}$ is 0.73 V (Fig. 6(b)), 80 mV higher than 0.65 V (Pt/C) at 25 °C. Notably, when electrolyte temperature is increased to 80 °C, both Fe-N-HOC and Pt/C-based ODC performance improve markedly. The former one exhibits a potential of only 0.89 V to reach $100 \text{ mA}\cdot\text{cm}^{-2}$, significantly outperforming Pt/C, which requires 0.87 V. Fe-N-HOC-based ODC delivers substantially enhanced potential of 0.82 V at $300 \text{ mA}\cdot\text{cm}^{-2}$ relative to the benchmark Pt/C of 0.76 V. Notably, at 25 °C, Fe-N-HOC-based ODC's Tafel slope is $72 \text{ mV}\cdot\text{dec}^{-1}$, which is substantially lower than $89 \text{ mV}\cdot\text{dec}^{-1}$ of Pt/C-

based one (Fig. 6(c)). Upon elevating the electrolyte temperature to 80 °C, Fe-N-HOC-based ODC's Tafel slope is measured to be $129 \text{ mV}\cdot\text{dec}^{-1}$, far below that of Pt/C-based one ($152 \text{ mV}\cdot\text{dec}^{-1}$), thereby demonstrating superior reaction kinetics. Fe-N-HOC-based ODC can operate stably for $\sim 130 \text{ h}$ at $300 \text{ mA}\cdot\text{cm}^{-2}$ under 80 °C, with a minimal decay of only $7 \text{ mA}\cdot\text{cm}^{-2}$ (Fig. 6(d)). By contrast, Pt/C-based ODC exhibits a significant current density decay after 60 h of test. The prepared Fe-N-HOC is promising as an ODC candidate for chlor-alkali electrolysis to produce caustic soda, showing remarkable superiority to conventional chlor-alkali processes (Table S9 in the ESM).

To elucidate the industrial application of Fe-N-HOC in chlor-alkali electrolysis, Fe-N-HOC-based ODC was integrated with RuO_2 -based anode to construct two-electrode chlor-alkali flow cell (Fe-N-HOC|| RuO_2 , Fig. 6(e)). As expected, Fe-N-HOC|| RuO_2 system presents better chlor-alkali electrolysis performance compared to Pt/C|| RuO_2 at 25 and 80 °C (Fig. 6(f)). Fe-N-HOC|| RuO_2 needs a cell voltage of only 1.97 V to reach the current density of $150 \text{ mA}\cdot\text{cm}^{-2}$, which is significantly lower than that of Pt/C|| RuO_2 (2.52 V) at 25 °C. Remarkably, the Fe-N-HOC|| RuO_2 achieves a $150 \text{ mA}\cdot\text{cm}^{-2}$ at a significantly lower cell voltage of 1.56 V at 80 °C. In contrast, Pt/C|| RuO_2 requires 1.63 V to attain the same current density. Significantly, at 80 °C, Fe-N-HOC|| RuO_2 reaches $300 \text{ mA}\cdot\text{cm}^{-2}$ at a two-electrode cell voltage of 1.62 V, representing a reduction of $\sim 0.11 \text{ V}$ compared to noble metal-

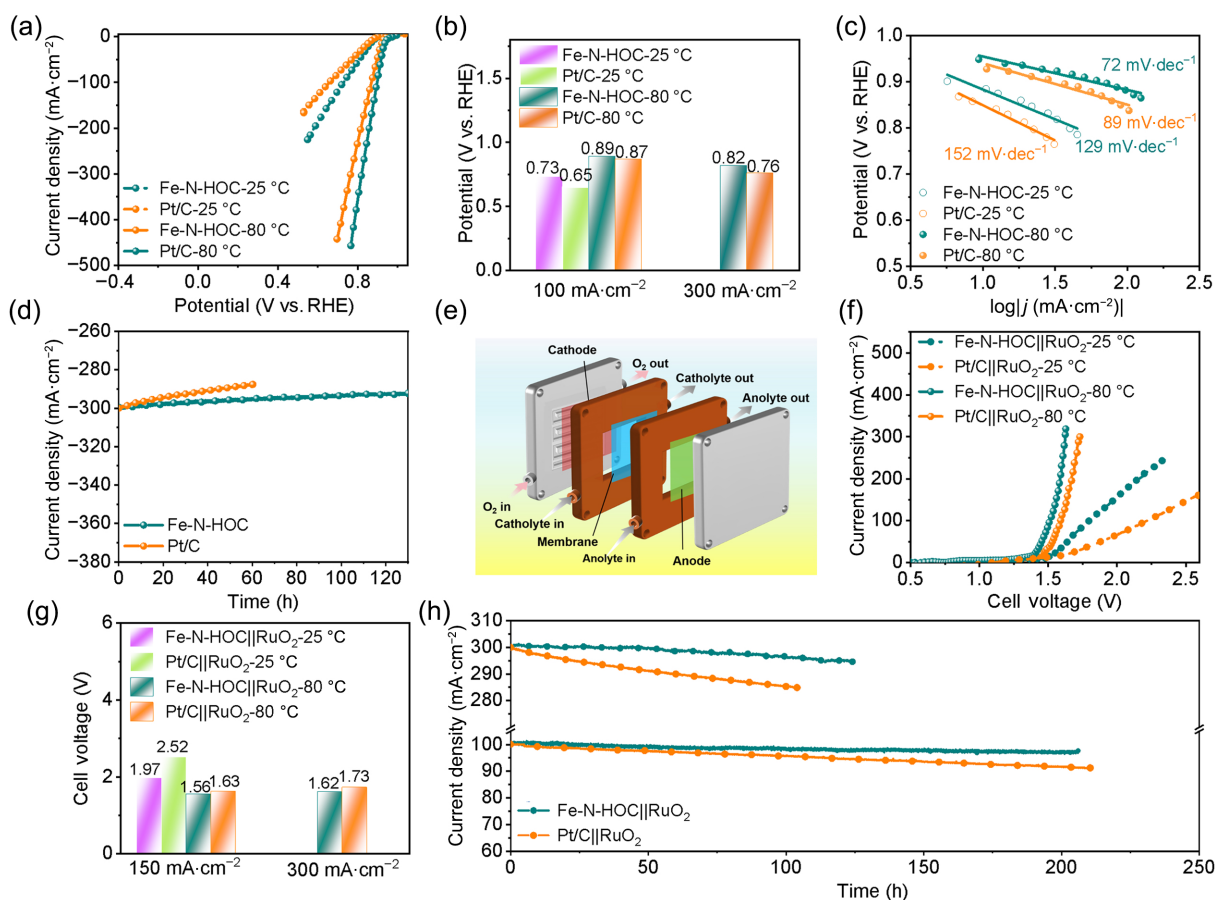


Figure 6 (a) ORR LSV curves of Fe-N-HOC and Pt/C-based ODCs measured in 30 wt.% NaOH solution at 25 and 80 °C. (b) Potential comparison diagram at the current density of 100 and $300 \text{ mA}\cdot\text{cm}^{-2}$. (c) Tafel plots of Fe-N-HOC- and Pt/C-based ODCs in 30 wt.% NaOH at 25 and 80 °C. (d) Chronoamperometric curves of Fe-N-HOC- and Pt/C-based ODCs recorded in 30 wt.% NaOH at 80 °C. (e) Schematic diagram of a two-electrode flow cell simulating the industrial chlor-alkali process. (f) LSV curves of Fe-N-HOC|| RuO_2 and Pt/C|| RuO_2 two-electrode chlor-alkali flow cells measured at 25 and 80 °C. (g) Cell voltage comparison diagram at the current density of 150 and $300 \text{ mA}\cdot\text{cm}^{-2}$. (h) Chronoamperometric responses of Fe-N-HOC|| RuO_2 and Pt/C|| RuO_2 two-electrode chlor-alkali flow cell.

based one (1.73 V, Fig. 6(g)). Fe-N-HOC||RuO₂ attains substantially enhanced stability for 206 h, with negligible current density decay at 100 mA·cm⁻². In contrast, Pt/C||RuO₂ counterpart suffers a current density decay (9 mA·cm⁻²) under the same condition (Fig. 6(h)). Fe-N-HOC||RuO₂ exhibits a slight current density decay of only 5 mA·cm⁻² at 300 mA·cm⁻². In contrast, Pt/C||RuO₂ shows a 15 mA·cm⁻² current density decay within just 100 h. Collectively, the high activity and superior stability of two-electrode flow cell position Fe-N-HOC make it a promising oxygen cathode catalyst in chlor-alkali electrolysis.

4 Conclusions

In conclusion, we successfully anchored atomically dispersed Fe-N₄ sites on a nitrogen-doped carbon support with an inverse opal hierarchical porous structure. This structural design not only maximizes the exposure of active sites (8.2×10^{19} sites·g⁻¹) but also facilitates rapid mass transport and electron transfer, addressing key limitations of traditional carbon-supported catalysts. Consequently, Fe-N-HOC exhibits exceptional ORR performance in alkaline media, achieving $E_{1/2}$ of 0.90 V, a TOF of 12.7 e·s⁻¹·site⁻¹ in 0.1 M KOH, 58 times higher than Pt/C, respectively. More notably, its $E_{1/2}$ decays only 8 mV after 50,000 CV cycles, and it retains 92% of its initial current density after 100 h operation. DFT calculations reveal that the Fe-N₄ curve configuration enhances electron transfer, and the adsorption strength of all ORR intermediates is weakened, which subsequently lowers the energy barrier of RDS (*OH desorption) by 0.79 eV relative to planar one, thereby accelerating ORR kinetics. When deployed in A-ZABs, Fe-N-HOC achieves a remarkable peak power density (248.2 mW·cm⁻²), and maintains stable charge-discharge cycling for over 1600 h with a mere voltage gap variation of 0.01 V. QSS-ZAB not only ensures mechanical flexibility (stable operation at 0°–180° bending angles) but also maintains a cycle life exceeding 130 h at 0.5–2.0 mA·cm⁻², with negligible voltage gap increase. Fe-N-HOC||RuO₂ chlor-alkali flow cell achieves 300 mA·cm⁻² at a low cell voltage of 1.62 V (80 °C) and operates stably for over 124 h with only 5 mA·cm⁻² decay, outperforming Pt/C||RuO₂ counterpart. The exceptional ORR activity, durability, and device-level performance validate a novel paradigm for SACs with tailored porous structures and optimized active-site configurations to develop high-performance catalysts in broader energy conversion and storage applications.

Electronic Supplementary Material: Supplementary material (XRD patterns, XPS spectrum, Raman spectra, SEM images, TEM images, electrochemical testing, and Tables) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908797>.

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.: Data curation, writing – original draft. C. B. W.: Data curation. K. C. F.: Formal analysis, funding acquisition. K. P. G.: Validation. Z. M. W.: Writing – review & editing. P. R. L.: Validation, resources. B. L.: Resources. Z. Y. X.: Resources. T. R. Z.: Validation. L. W.: Resources, supervision, funding acquisition. L. B. Z.: Conceptualization, investigation, writing – review & editing, supervision, funding acquisition. All the authors have approved the final manuscript.

Use of AI statement

None.

References

- [1] 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.
- [2] Seh, Z. W.; Kibsgaard, J.; Dickens, C. F.; Chorkendorff, I.; Nørskov, J. K.; Jaramillo, T. F. Combining theory and experiment in electrocatalysis: Insights into materials design. *Science* **2017**, *355*, eaad4998.
- [3] Li, J. X.; Sun, C. T.; Fan, H. Y.; Dong, F. L.; Lv, Z. H.; Liu, R.; Yang, W. X.; Wang, B. Boosting active site accessibility and alleviating mass transfer resistance for high-performance fuel cells. *Nano Res.* **2025**, *18*, 94907654.
- [4] Lin, C. F.; Cao, X.; Wang, L. L.; Cai, M. L.; Ma, R.; Ma, J. F. S/Cl Co-doped biomass-derived carbon electrocatalysts: Low ΔE of 0.58 V for ORR/OER and application in high-performance zinc-air batteries. *Nano Energy* **2026**, *150*, 111791.
- [5] He, Z. Z.; Xu, N. N.; Wang, Y. D.; Chao, D. L.; Maric, R.; Virkar, A.; Zhou, X. D. Electrode-resolved mechanisms governing performance and durability in zinc-air batteries. *Chem. Eng. J.* **2026**, *527*, 171444.
- [6] Fan, R. Y.; Lu, S. S.; Wang, F. L.; Zhang, Y. S.; Hojamberdiev, M.; Chai, Y. M.; Dong, B.; Zhang, B. Enhancing catalytic durability in alkaline oxygen evolution reaction through squaric acid anion intercalation. *Nat. Commun.* **2025**, *16*, 3407.
- [7] Shu, Y. J.; Ji, J. P.; Liu, J. X.; Mao, Z. X.; Chen, S.; Zhou, M.; Fan, K. C.; Qi, D. C.; Chuang, C. H.; Zhu, Z. J. et al. Oxygenated carbon electrocatalysts for chlorine evolution reaction. *J. Am. Chem. Soc.* **2025**, *147*, 44293–44302.
- [8] Li, H. Q.; Zeng, R.; Shi, Z. X.; Wang, H. S.; Leshchev, D.; Stavitski, E.; Tellez-Cruz, M. M.; Xu, W. X.; Kim, M. J.; Molina Villarino, A. et al. Rational design of high-performance low-loading oxygen reduction catalysts for alkaline fuel cells. *Nat. Mater.* **2026**, *25*, 447–455.
- [9] Yang, J. R.; Li, W. H.; Tang, H. T.; Pan, Y. M.; Wang, D. S.; Li, Y. D. CO₂-mediated organocatalytic chlorine evolution under industrial conditions. *Nature* **2023**, *617*, 519–523.

- [10] Lyu, Z. X.; Cai, J. L.; Zhang, X. G.; Li, H. Q.; Huang, H. P.; Wang, S. P.; Li, T. Y.; Wang, Q. X.; Xie, Z. X.; Xie, S. F. Biphasic Pd nanosheets with atomic-hybrid RhO_x/Pd amorphous skins disentangle the activity-stability trade-off in oxygen reduction reaction. *Adv. Mater.* **2024**, *36*, 2314252.
- [11] 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.
- [12] Ji, Y.; Zhong, H. X.; Qiao, L.; Ma, C. N.; Hu, Q. Y.; Nikolaichik, Y.; Chi, K. B.; Zhang, X. B. Atomic-level local-structure engineering of Pt-group oxygen electrocatalysts for fuel cells and water electrolyzers. *Nano Res.* **2026**, *19*, 94908173.
- [13] Lan, L. S.; Wu, Y. G.; Pei, Y. F.; Wei, Y. H.; Hu, T.; Lützenkirchen-Hecht, D.; Yuan, K.; Chen, Y. W. High-density accessible iron single-atom catalyst for durable and temperature-adaptive laminated zinc-air batteries. *Adv. Mater.* **2025**, *37*, 2417711.
- [14] Liu, Y.; Li, R. S.; Xia, J. J.; Shu, C. Y.; Liu, J. H.; Yan, S. X.; Jin, R.; Chen, H. F.; Teng, L. M.; Si, Y. J. et al. Recent progress on understanding of micro- and electronic-structures to synergistically enable the activity and stability for oxygen reduction. *Nano Res.* **2025**, *18*, 94907244.
- [15] Kment, Š.; Bakandritsos, A.; Tantis, I.; Kmentová, H.; Zuo, Y. P.; Henrotte, O.; Naldoni, A.; Otyepka, M.; Varma, R. S.; Zbořil, R. Single-atom catalysts based on earth-abundant metals for energy-related applications. *Chem. Rev.* **2024**, *124*, 11767–11847.
- [16] Ji, S. Q.; Mou, Y. M.; Liu, H. X.; Lu, X.; Zhang, Y. Q.; Guo, C. M.; Sun, K. Z.; Liu, D.; Horton, J. H.; Wang, C. et al. Manipulating the electronic properties of an Fe single-atom catalyst via secondary coordination sphere engineering to provide enhanced oxygen electrocatalytic activity in zinc-air batteries. *Adv. Mater.* **2024**, *36*, 2410121.
- [17] Pang, M. Y.; Yang, M.; Zhang, H. H.; Shen, Y. Q.; Kong, Z.; Ye, J. J.; Shan, C. Y.; Wang, Y.; An, J.; Li, W. S. et al. Synthesis techniques, mechanism, and prospects of high-loading single-atom catalysts for oxygen reduction reactions. *Nano Res.* **2024**, *17*, 9371–9396.
- [18] Xia, H. Y.; Pang, R. Y.; Dong, X. Y. M.; Liu, Q. X.; Chen, J. J.; Wang, E. K.; Li, J. Boosting oxygen reduction reaction kinetics by designing rich vacancy coupling pentagons in the defective carbon. *J. Am. Chem. Soc.* **2023**, *145*, 25695–25704.
- [19] Jiang, P.; Li, P.; Yang, Y.; Chen, C.; Ye, C. L.; Zhang, L.; Hu, H. B.; Zhang, Y.; Zhou, H.; Gao, X. P. et al. Symbiotic topological defect with atomic Fe sites for enhanced electrocatalytic oxygen reduction. *Nano Res.* **2025**, *18*, 94907532.
- [20] Zhao, J. Y.; Li, P.; Fan, K. C.; Wei, W. J.; Lu, F. H.; Zhao, H. M.; Li, B.; Zong, L. B.; Wang, L. B. Spatial confinement of zeolitic imidazolate framework deposits by porous carbon nanospheres for dual-atom catalyst towards high-performance oxygen reduction reaction. *Nano Res.* **2023**, *16*, 11464–11472.
- [21] Kim, J.; Guo, J. L.; Shan, N. N.; Yoo, J.; Martins, P. F. B. D.; Noh, J.; Jung, M.; Zapol, P.; Mun, B. S.; Klie, R. et al. Deciphering catalyst-support interaction via doping for highly active and durable oxygen evolution catalysis. *J. Am. Chem. Soc.* **2025**, *147*, 16340–16349.
- [22] Fan, H. Y.; Liu, Y. R.; Li, J. X.; Lv, Z. H.; Wang, C. L.; Liu, R.; Dong, F. L.; Tian, C. G.; Feng, X.; Yang, W. X. et al. Optimizing the mass transport and atomic Fe intrinsic activity to achieve high-performing fuel cells. *J. Am. Chem. Soc.* **2025**, *147*, 18953–18962.
- [23] Ji, S. Q.; Wang, Y. H.; Liu, H. X.; Lu, X.; Wang, Y.; Tian, X. L.; Zhao, Y. S.; Horton, J. H.; Li, Z. J. Site-specific synergy by heteronuclear microenvironment atomic editing for oxygen reduction reaction. *Nat. Commun.* **2025**, *16*, 11691.
- [24] Zhang, L.; Meng, Q. L.; Zheng, R. X.; Wang, L. Q.; Xing, W.; Cai, W. W.; Xiao, M. L. Microenvironment regulation of M–N–C single-atom catalysts towards oxygen reduction reaction. *Nano Res.* **2023**, *16*, 4468–4487.
- [25] Smith, K. S.; Adjah-Tetteh, C.; He, Z. Z.; Yang, G.; Wang, Y. D.; Bliznakov, S.; Maric, R.; Xu, N. N.; Zhou, X. D. Interface and phase synergy in hierarchically porous $\text{Co} @ (\text{Co-Mn})_3\text{O}_{4-x}$ for high-efficiency and durable rechargeable Zn-air batteries. *J. Phys. Chem. C* **2025**, *129*, 16507–16515.
- [26] Zhong, J. W.; Huang, S. C.; Cao, Y. F.; Pei, K. W.; Zhang, D.; Lin, X. Q.; Long, H.; Chen, H.; Liang, Y. H.; Zhou, X. S. et al. Inner-wrinkled porous carbons via soft-hard coupling assembly strategy for ultrahigh-capacity lithium-ion batteries. *Adv. Funct. Mater.* **2026**, *36*, e14143.
- [27] Bender, J. T.; Sanspeur, R. Y.; Bueno Ponce, N.; Valles, A. E.; Uvodich, A. K.; Milliron, D. J.; Kitchin, J. R.; Resasco, J. How electrolyte pH affects the oxygen reduction reaction. *J. Am. Chem. Soc.* **2025**, *147*, 37819–37832.
- [28] Liu, X. Y.; Lyu, D.; Merlet, C.; Leesmith, M. J. A.; Hua, X.; Xu, Z.; Grey, C. P.; Forse, A. C. Structural disorder determines capacitance in nanoporous carbons. *Science* **2024**, *384*, 321–325.
- [29] Yang, C. W.; Sun, F.; Zhang, Y.; Qu, Z. B.; Zuo, J. Y.; Zhou, W.; Gao, J. H.; Liu, S. Q.; Lu, Y. F. Unveiling the coupling effect of sp^2 domain size and local active sites in switching the selectivity of nanocarbon catalysts toward the oxygen electro-reduction. *Nat. Commun.* **2025**, *16*, 11270.
- [30] Lee, K.; Mehrgardi, M. A.; Zare, R. N. Interfacial curvature, not simply size, controls spontaneous hydrogen peroxide formation in water microdroplets. *J. Am. Chem. Soc.* **2025**, *147*, 33240–33247.
- [31] Wang, B. Q.; Wang, M.; Fan, Z. T.; Ma, C.; Xi, S. B.; Chang, L. Y.; Zhang, M. S.; Ling, N.; Mi, Z. Y.; Chen, S. H. et al. Nanocurvature-induced field effects enable control over the activity of single-atom electrocatalysts. *Nat. Commun.* **2024**, *15*, 1719.
- [32] Jing, C.; Guo, Z. Y.; Yao, Y. J.; Xu, R. J.; Li, D. F.; Li, K. L.; Zhang, Y. X. Curvature-dominated microenvironment modulation enables efficient electrocatalytic oxygen reduction. *Nano Res.* **2026**, *19*, 94908197.
- [33] Xia, H. Y.; Sun, H. N.; Yang, D. Y.; Zhao, J. W.; Gao, G.; Wu, L.; Huang, L.; Jiang, X. E. Curvature-engineered steering of oxygen electroreduction pathways on single-atom catalysts. *Angew. Chem., Int. Ed.* **2026**, *65*, e3924995.
- [34] Yang, X. Y.; Liu, Z.; Guo, C. M.; Li, X. Y.; Deng, Z.; Ye, C. F.; Lyu, J. M.; Yu, S.; Li, Y.; Huang, Y. Y. et al. Engineering bent MoS_2 nanosheets promotes stable electrocatalytic hydrogen evolution at $1.0 \text{ A} \cdot \text{cm}^{-2}$. *ACS Catal.* **2025**, *15*, 20294–20307.
- [35] Sun, C. Z.; Xiao, B. H.; Zhao, Q.; Zong, X. M.; Zeng, Y. X.; Cao, S. S.; Liu, Z. Q. *In situ* reconstructed $\text{Cu/Cu}_{2-x}\text{O/ZnO}$ inverse opals accelerate electrocatalytic nitrate reduction kinetics for high power Zn- NO_3^- battery. *Adv. Mater.* **2025**, *37*, 2510680.
- [36] Zou, S. W.; Xin, Y.; Jin, J. L.; Lin, Z. C.; He, Y. Y.; Liang, J.; Yan, X. J.; Huang, J. M. Inverse opal photonic crystal structured bifacial-iridescent efficient perovskite solar cells and modules. *Adv. Mater.* **2025**, *37*, 2420130.
- [37] Che, M. F.; Chen, X.; Wu, Z. B.; Xu, W. D.; Suh, Y. D.; Wu, S. L.; Liu, X. W.; Huang, W. Dynamic modulation of afterglow emission in polymeric phosphors via inverse opal photonic structures. *Adv. Mater.* **2025**, *37*, 2415835.
- [38] Yu, Y.; Wang, Y. A.; Yang, F.; Feng, D.; Yang, M. Y.; Xie, P. F.; Zhu, Y. Z.; Shao, M. H.; Mei, Y.; Li, J. C. Meso/microporous single-atom catalysts featuring curved Fe–N₄ sites boost the oxygen reduction reaction activity. *Angew. Chem., Int. Ed.* **2025**, *64*, e202415691.
- [39] Yao, W.; Hu, A. Q.; Ding, J. T.; Wang, N. S.; Qin, Z.; Yang, X. F.; Shen, K.; Chen, L. Y.; Li, Y. W. Hierarchically ordered macromesoporous electrocatalyst with hydrophilic surface for efficient oxygen reduction reaction. *Adv. Mater.* **2023**, *35*, 2301894.
- [40] Tian, Q.; Jing, L. Y.; Du, H. N.; Yin, Y. C.; Cheng, X. L.; Xu, J. X.; Chen, J. Y.; Liu, Z. X.; Wan, J. Y.; Liu, J. et al. Mesoporous carbon spheres with programmable interiors as efficient nanoreactors for H_2O_2 electrosynthesis. *Nat. Commun.* **2024**, *15*, 983.
- [41] Chen, K.; Liang, Y. Q.; Pan, D.; Huang, J. H.; Gao, J. Y.; Lu, Z. W.; Liu, X.; Chen, J. X.; Zhang, H.; Hu, X. et al. Mass transportation facilitated porous Fe/Co dual-site catalytic cathodes for ultrahigh-power-density Al-air fuel cells. *Adv. Energy Mater.* **2025**, *15*, 2404140.

- [42] Liu, C. L.; Yang, R. Z.; Wang, J. C.; Liu, B. W.; Chang, X. W.; Feng, P. X.; Zhang, X. Z.; Zhong, L. J.; Zhao, X. L.; Niu, L. et al. Synergistic catalysts with Fe single-atoms and Fe₃C clusters for accelerated oxygen adsorption kinetics in oxygen reduction reaction. *Angew. Chem., Int. Ed.* **2025**, *64*, e202501266.
- [43] Zhao, C.; Chu, B. X.; Nian, H.; Shao, B.; Lu, Y.; Zhang, F. C.; Wang, Y. G.; Xu, Q. Sulfur-mediated microenvironment modulation of high-density Fe–N₄ sites for high-efficiency oxygen reduction and cryotolerant quasi-solid-state zinc–air batteries. *Adv. Mater.* **2025**, *37*, e10621.
- [44] Zhou, Y. Z.; Lu, R. H.; Tao, X. F.; Qiu, Z. J.; Chen, G. B.; Yang, J.; Zhao, Y.; Feng, X. L.; Müllen, K. Boosting oxygen electrocatalytic activity of Fe–N–C catalysts by phosphorus incorporation. *J. Am. Chem. Soc.* **2023**, *145*, 3647–3655.
- [45] Yuan, L. J.; Miao, Z. Y.; Sui, X. L.; Lee, C. F.; Li, Q.; Yin, M. J.; Shen, L. X.; Lu, Y. R.; Zhao, Z. G.; Liu, Y. Z. et al. Janus effect of FeCo dual atom catalyst with Co as active center in acidic oxygen reduction reaction. *Nat. Commun.* **2025**, *16*, 7198.
- [46] Zeng, Y. C.; Li, C. Z.; Li, B. Y.; Liang, J. S.; Zachman, M. J.; Cullen, D. A.; Hermann, R. P.; Alp, E. E.; Lavina, B.; Karakalos, S. et al. Tuning the thermal activation atmosphere breaks the activity–stability trade-off of Fe–N–C oxygen reduction fuel cell catalysts. *Nat. Catal.* **2023**, *6*, 1215–1227.
- [47] Hu, C.; Xing, G. Y.; Han, W. T.; Hao, Y. X.; Zhang, C. C.; Zhang, Y.; Kuo, C. H.; Chen, H. Y.; Hu, F.; Li, L. L. et al. Inhibiting demetalation of Fe–N–C via Mn sites for efficient oxygen reduction reaction in zinc–air batteries. *Adv. Mater.* **2024**, *36*, 2405763.
- [48] Zhang, L. L.; Lei, Y. T.; Wang, X. C.; Lv, E. Y.; Li, J. Z.; Zhang, N.; Wang, D.; Zhao, Y. F.; Shang, H. S.; Zhang, B. Synergistic long-range interaction of CO–Cu dual-atom sites on hollow CeO₂ nanostructures for bifunctional oxygen electrocatalysis. *Adv. Funct. Mater.* **2026**, *36*, e11730.
- [49] Qu, Q. Y.; Mao, Y.; Ji, S. F.; Liao, J. W.; Dong, J. C.; Wang, L. G.; Wang, Q. C.; Liang, X.; Zhang, Z. D.; Yang, J. R. et al. Engineering the lewis acidity of Fe single-atom sites via atomic-level tuning of spatial coordination configuration for enhanced oxygen reduction. *J. Am. Chem. Soc.* **2025**, *147*, 6914–6924.
- [50] Jia, B. B.; Xie, X.; Lin, J.; Wang, H. Q.; Hu, P. F.; Wang, F. Y.; Fan, X. Y.; Zheng, J. L.; Ma, T. Y.; Ye, L. Q. Harnessing pyridinic N vacancy defect in microporous structures to induce the pre-adsorption of oxygen and boost oxygen reduction reaction kinetics. *Angew. Chem., Int. Ed.* **2025**, *64*, e202508674.



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