

Central electron-enriched NO-FeN₄ sites as superior acidic oxygen reduction reaction electrocatalysts for proton exchange membrane fuel cells

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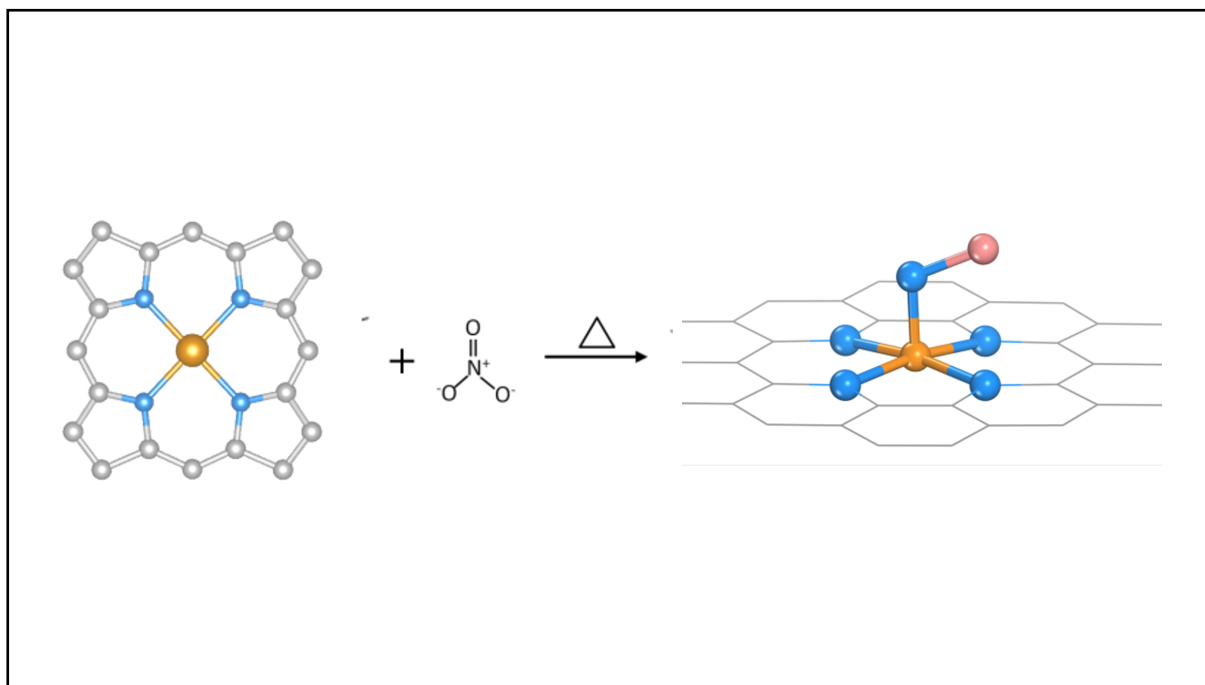
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Graphical abstract



Restricted synthesis of new FeN₄ structures.

Public summary

- A central electron-enriched FeN₄ structure was established by the NO (nitrogen oxide) group directly modifying the Fe central, which exhibited three times higher mass activity compared to the traditional FeN₄ sample.
- The PEMFC assembled with the as-prepared electrocatalyst exhibits a much-enhanced peak power density (>725 mW·cm⁻²), providing a new approach to rationally designing advanced M-N_x nonnoble electrocatalysts for the oxygen reduction reaction.

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Central electron-enriched NO-FeN₄ sites as superior acidic oxygen reduction reaction electrocatalysts for proton exchange membrane fuel cells

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Supporting Information

Abstract: Developing noble-metal-free catalysts, especially for iron-nitrogen on carbon (FeNC) materials, has been an urgent demand for wide applications of proton exchange membrane fuel cells (PEMFCs). However, the inferior oxygen reduction reaction (ORR) activity of traditional iron-nitrogen sites in acidic conditions seriously impedes the further improvement of their performance. Herein, we synthesized FeN₄ with NO (nitric oxide) group axial modification (denoted as NO-FeN₄) on a large scale through a confined small molecule synthesis strategy. Benefitting from the strong electron-withdrawing effect of the NO group, the central electron-rich FeN₄ site exhibits ultrahigh ORR activity with a three times higher mass activity (1.1 A·g⁻¹ at 0.85 V) compared to the traditional FeN₄ sample, as well as full four-electron reaction selectivity. Moreover, the PEMFC assembled with the as-prepared electrocatalyst also exhibits a greatly enhanced peak power density (>725 mW·cm⁻²). This work provides a new approach to rationally design advanced M-N_x nonnoble electrocatalysts for the ORR.

Keywords: large-scale customization; oxygen reduction reaction; proton exchange membrane fuel cell; confined small molecule synthesis

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1 Introduction

Proton exchange membrane fuel cells (PEMFCs) have been regarded as the most promising low-carbon energy conversion technology because of their amazing energy density, high efficiency, and environmental protection characteristics^[1–3]. However, the sluggish oxygen reduction reaction largely impedes its wide application in PEMFC cathodes^[4–5]. Noble metals with high activity, such as platinum, account for a high proportion of the cost of fuel cells, and this problem will become increasingly obvious with large-scale industrialization. Therefore, the development of nonprecious metal catalyst substitutes has become an important issue. Among many substitutes, atomically FeN₄ catalysts are favored by researchers due to their activity with promotion potential and low cost^[6–8]. However, further requirements for selectivity and activity per unit are still driving the design and development of FeN₄ with new configurations.

FeN₄ with a conventional planar configuration has been studied as a potential cathode catalyst for PEMFCs for many years^[9–11]. Nevertheless, this planar four-coordinate structure is easily attacked by protons or free radicals in acidic environ-

ments, causing leaching of iron ions in the FeN₄ site and oxidation of the surrounding carbon structure^[12–13]. In addition, exposed Fe active centers are easily poisoned in the electrolyte solution, resulting in a decline in both stability and selectivity^[14]. Therefore, effectively regulating the local coordination structure and electronic structure to obtain a new FeN₄ configuration arouses the extensive interest of researchers. For instance, most current reported regulation strategies are focused on heteroatom doping carbon substrates^[15–16], fabricating carbon structure disorder^[17], and introducing multiple active sites^[18]. In these excellent works, it is worth noting that high-temperature thermal activation plays an important role in enhancing catalytic activity and stability. However, because high temperature greatly accelerates the diffusion of ions, the original structure of sites is often changed after thermal activation. Therefore, it is difficult to customize FeN₄ sites with a specific structure on a large scale^[19–21].

Herein, by using confinement space and specific adsorption of NO to hemin, we developed an NO (nitrogen oxide) group axial-modified central electron-enriched FeN₄ structure (denoted as NO-FeN₄) with excellent ORR mass activity and selectivity for the first time. This specific FeN₄ site with a

modified electronic structure shows complete 4-electron reaction selectivity and high mass activity, which paves the way for designing advanced ORR electrocatalysts for PEMFCs.

2 Experiments

2.1 The synthesis of NO-FeN₄ product

All of the chemicals were of analytical grade and used without further purification. In a typical synthesis, 1 mmol hemin and 1 mmol Zn(NO₃)₂ were dissolved in 25 mL dimethylformamide under vigorous stirring for 30 min, and then 600 mg commercial activated carbon black (Ketjenblack EC600JD) and 25 mL dimethylformamide were sonicated for 1 h and dipped into the above solution. The mixed solution was continuously stirred for 4 h at 10 °C for adsorption until most of the hemin was adsorbed onto the carbon black. Then, the carbon black with adsorbed hemin/Zn(NO₃)₂ was separated from the mixture solution by washing with dimethylformamide several times, filtrating and freeze drying for 48 h. The obtained composite was directly pyrolyzed (at 650 °C for 2 h, heating rate of 10 °C·min⁻¹, in an Ar atmosphere). Then, the pyrolyzed product was leached in 0.5 mol·L⁻¹ H₂SO₄ at 80 °C for 8 h to remove inactive iron and zinc species. The leached sample was washed to neutral with water and alcohol several times and dried in vacuum at 60 °C overnight to generate the carbon-supported NO-FeN₄ catalyst. For comparison, carbon black with only adsorbed hemin was also prepared under similar conditions, and the resultant sample was denoted as carbon black-supported FeN₄.

2.2 Fabrication of the working electrode for ORR catalytic activity testing

To prepare the working electrode, 4 mg catalysts mixed with 40 µL Nafion solution (Sigma Aldrich, 5 wt%) were dispersed into 1 mL isopropanol and water mixture solution (volume ratio 3 : 1) and sonicated for at least 60 min to form a homogeneous catalyst ink. A certain volume of catalyst ink was then drop-cast onto the glassy carbon electrode with a 0.6 mg·cm⁻² loading for all samples.

2.3 Fabrication of single PEMFC battery

The catalyst inks were prepared by using catalyst, isopropanol, deionized water and Nafion solution (Sigma Aldrich, 5 wt%) with a weight ratio of 1/90/30/11. The catalyst inks were ultrasonicated for 1 h and then brushed on carbon paper with an effective area of 5 cm² until the loading reached 4 mg·cm⁻². With a similar preparation process, commercial Pt/C (20 wt%) ink was dispersed on carbon paper with a loading of 0.2 mg Pt cm⁻² as the anode. Using a thermocompressor, the prepared cathode and anode were then pressed onto the two sides of a Nafion 211 membrane (DuPont) at 130 °C and 5 MPa for 5 min to fabricate membrane electrode assemblies (MEAs). The MEA was measured in a single-cell and condition-controlled fuel cell test station (Scribner 850e, Scribner Associates). The flow rates of H₂ and O₂ were both 400 mL·min⁻¹, and the relative humidity was 100% during the PEMFC tests. During the test, the cell and input fuel temperature were maintained at 80 °C, and the back pressure was set at 0.2 MPa.

3 Results and discussion

3.1 Coordination structure analysis of central electron-enriched NO-FeN₄ sites

In this work, central electron-enriched NO-FeN₄ sites with optimized electronic configurations were prepared by adsorption of hemin and zinc nitrate into the mesopores of carbon black (Ketjenblack EC600JD) and rapid heat treatment. Through in situ mass spectrometry, we found that nitrate can rapidly generate a large number of nitric oxide groups (NO) with 650 °C fast pyrolysis treatment, and the generated NO groups tend to adsorb onto the central atom of porphyrin iron^[22] (Supporting information Fig. S1a). In contrast, in Fig. S1b, nitric oxide cannot be detected at 30 *m/z* for FeN₄ precursors without adding nitrate (denoted as FeN₄). The detailed structural features of the as-prepared NO-FeN₄ electrocatalysts were investigated by X-ray diffraction (XRD) and Raman spectroscopy. As shown in Figs. S2 and S3, both NO-FeN₄ and FeN₄ show only two distinct peaks at approximately 26.2° and 43.2°, which could be ascribed to the characteristic (002) and (100) planes of graphitic carbon^[23]. Meanwhile, the Raman spectra of the NO-FeN₄ and FeN₄ samples (Fig. S4) also display similar D-band (1326 cm⁻¹) for lattice defects and G-band (1585 cm⁻¹) for sp² hybrid carbon atoms. Additionally, the *I_G/I_D* ratios of NO-FeN₄ and FeN₄ were 0.81 and 0.83, respectively, indicating the similar graphitization degrees of the two catalysts^[24]. These results suggest that no obvious Fe-based compounds exist in either the NO-FeN₄ or FeN₄ electrocatalysts. Moreover, the morphology and microstructure were also investigated by transmission and scanning electron microscopy. As shown in Figs. 1b and S5, the NO-FeN₄ electrocatalyst displays a spherical porous carbon structure, and no obvious nanoparticles could be found, indicating that the Fe atoms might be confined in carbon pores in atomically dispersed forms. Further investigation by high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) in Fig. 1c showed that many bright spots were homogeneously distributed in the porous carbon framework, confirming the atomically dispersed FeN₄ sites existing in the NO-FeN₄ sample. The corresponding energy-dispersive spectroscopy (EDS) mapping (Fig. 1d) shows that only Fe, N, and C are uniformly dispersed in the carbon framework, and no Zn can be detected, indicating that Zn has little residue after the wash and heat treatment processes. This conclusion can also be confirmed by X-ray photoelectron spectroscopy (XPS) analysis in Fig. S6. Similarly, FeN₄ samples prepared without confined NO treatment, which are denoted as FeN₄, are also presented in Figs. S1a, S3–4, S6, and S8–9. After systematic characterizations, the traditional FeN₄ sample seems to have similar features to NO-FeN₄ in terms of phase composition, morphology structure, and element distributions. Thus, it can be easily concluded that confined small molecule synthesis has no obvious effect on morphology and element distributions and that Fe atoms might form as single FeN₄ sites or clusters in the NO-FeN₄ sample. The detailed carbon structure was also investigated to exclude its influence on catalyst performance. Brunauer-Emmett-Teller (BET) analysis was also presented to analyze the

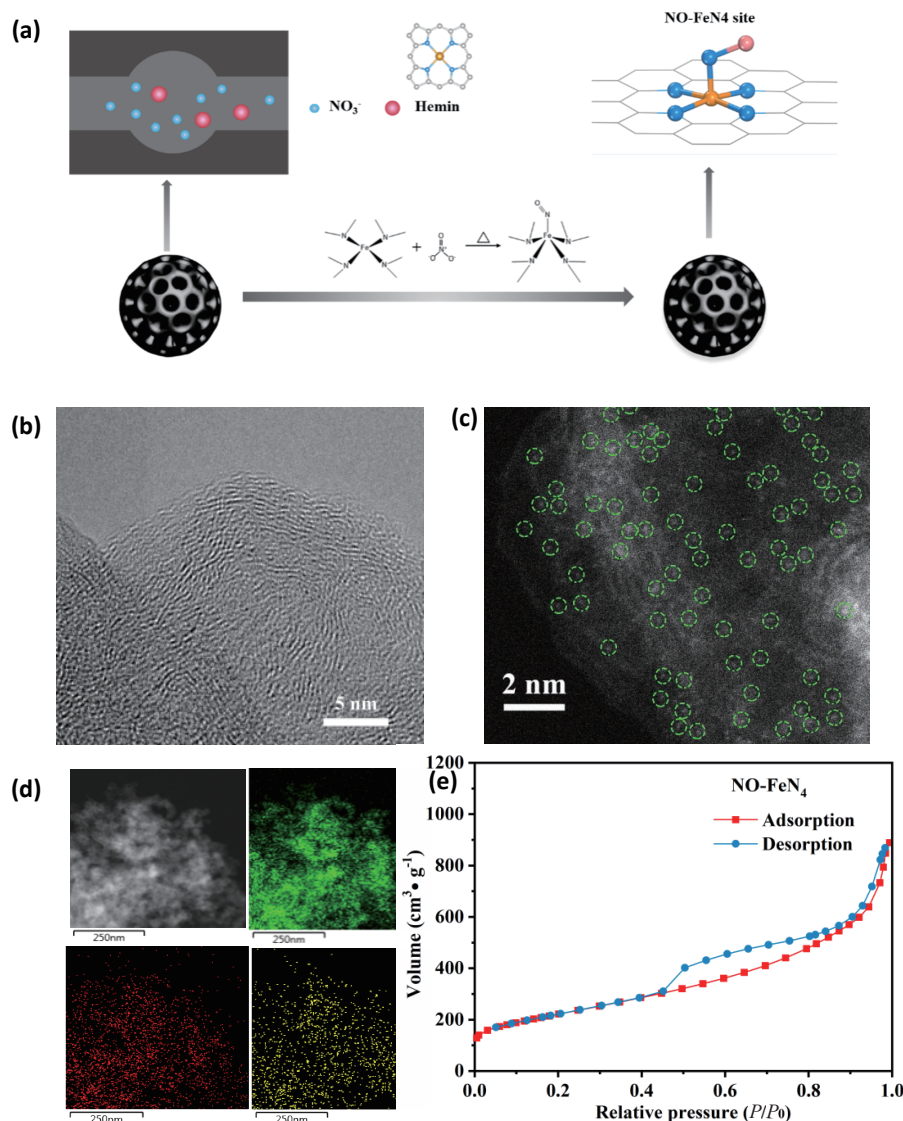


Fig. 1. (a) Schematic representation of the synthesis for NO-FeN₄. (b) HRTEM images of NO-FeN₄ material. (c) HAADF-STEM images of NO-FeN₄. (d) Elemental mapping images for the NO-FeN₄. (e) N₂ adsorption/desorption isotherms and corresponding pore size distribution curves (inset) of as-prepared NO-FeN₄ product.

BET surface area and pore size distribution of NO-FeN₄ and its contrast. In Fig. 1e, NO-FeN₄ exhibits a surface area of 760.7 m²·g⁻¹, which is comparable to that of the FeN₄ sample (794.5 m²·g⁻¹). In addition, the isotherm hysteresis loops of the NO-FeN₄ and FeN₄ samples exhibit obvious type-IV isotherms, indicating the same mesoporous carbon configuration of the two catalysts^[25]. Moreover, the corresponding pore size distribution also confirms that these two catalysts both have a large number of mesopores with a diameter of approximately 3.2 nm (Fig. 1e inset). Comprehensive analysis of the results above, it can be concluded that NO-FeN₄ catalysts have no significant difference in phase, element composition, morphology or detailed carbon structure properties. Therefore, the specific modified FeN₄ sites might play a key role in enhancing ORR activities.

To evaluate the local atomic structure around the NO-FeN₄ catalyst, X-ray absorption structure (XAS) measurements were performed. As shown in Fig. 2a and b, the XANES spectra of both the NO-FeN₄ and FeN₄ samples present simi-

lar preedge peaks at 7113.6 eV compared with the standard heme precursor, suggesting their similar main structure of a typical square-planar Fe-N₄ structure (*D*_{4h} symmetry)^[26]. However, the negative energy shifting of the absorption edge (Fig. 2c), as well as the lower white-line intensity (Fig. 2b) of NO-FeN₄, suggests that its 3d orbital electron density is higher than that of the FeN₄ sample, which means that the enrichment of d-electrons in the Fe center of NO-FeN₄ catalysts occurs^[27]. Moreover, an in-depth investigation of NO-FeN₄ was also performed, as shown in Fig. 2d. From Fourier transform (FT) plots of the Fe K-edge results in R-space, NO-FeN₄ presented one main peak at 1.51 Å, which was considered to be an elongated Fe-N shell compared with the FeN₄ sample at 1.48 Å. To further reveal the local coordination structure of Fe atoms, Fe K-edge EXAFS spectra of NO-FeN₄ and FeN₄ catalysts were both fitted. As shown in Fig. S10, NO-FeN₄ exhibited an Fe-N/O bond length of 2.03 Å ± 0.03 Å with a N/O coordination number of 5.6 ± 0.6, which is different from that of the FeN₄ sample (2.00 Å ± 0.03 Å, 6.4 ± 0.6),

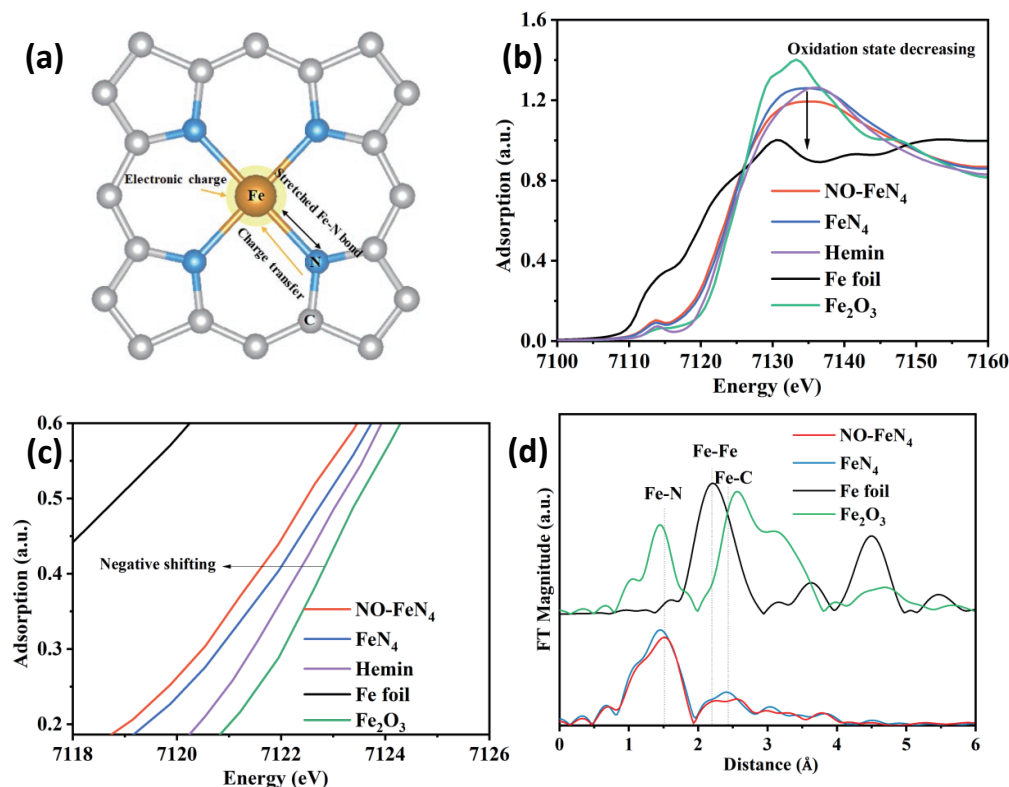


Fig. 2. (a) Schematic illustration of electronic structure for NO-FeN₄. (b) and (c) Fe K-edge X-ray absorption near edge structures (XANES). (d) The Fe K-edge extended XAFS oscillation function of NO-FeN₄ and FeN₄ samples.

demonstrating that increased Fe–N/O bond length has an obvious effect on the coordination number of Fe center atoms, which might change the adsorption/desorption energy of reactants. Based on the XAFS results, NO-FeN₄ has a larger bond length than FeN₄, which provides the opportunity to discuss the structure–function relationship between the bond length and the catalytic activity. As is well known, the metal iron center can act as an oxygen molecule adsorption center during the ORR process^[26]. Therefore, the intrinsic ORR catalytic activity of the FeN₄ materials is highly dependent on the nature of the Fe center. In fact, due to the stretched Fe–N bond length, NO-FeN₄ with an electron-rich Fe atom center could suppress the Fe-to-ligand back-donation between the Fe atom center and its adsorbed oxygen species, causing enhancement of the Fe^{2+/3+} redox potential and reducing site-blocking effects on the ORR^[28]. As far as we know, the scaled customization of the FeN₄ structure in the high-temperature pyrolysis process is still a great challenge. As shown in Fig. S11, the NO-FeN₄ site can be customized on a large scale during the pyrolysis process owing to the confinement space and specific adsorption of NO to hemin.

3.2 Electron structure analysis of central electron-enriched NO-FeN₄ sites

It has been widely recognized that the NO group has a strong electron absorption effect^[29], while the electronic structure and valence state around the Fe center have been systematically studied by soft X-ray absorption near-edge spectroscopy (XANES) and X-ray photoelectron spectroscopic (XPS) analysis. As shown in Fig. 3a, the normalized XANES spectrum of NO-FeN₄ at the Fe L₃ edge has a lower peak intensity and

a negative energy shift compared to that of the FeN₄ electrocatalyst, indicating that more electrons occupy the Fe 3d orbitals of NO-FeN₄, which is consistent with the Fe K-edge result above. Moreover, in Fig. 3b, the C K-edge XANES spectra of the NO-FeN₄ and FeN₄ products exhibit a δ^*C-C transition centered at ~ 303.5 eV and a $\pi^*C=C$ transition at ~ 295.6 eV, which represent typical sp²-hybridized carbon^[30]. The increased $\pi^*C=C$ intensity for NO-FeN₄ suggests that it has fewer electrons in the C 2p orbitals than FeN₄. This phenomenon hints that more electrons might flow into the Fe center of NO-FeN₄, demonstrating a stronger charge transfer effect. In addition, N K-edge XANES and XPS spectra can also verify the findings discovered above. As shown in Fig. 3c, the N K-edge of NO-FeN₄ represents two typical spectroscopic features: the 1s $\rightarrow\pi^*$ transition in the region of 393.0–401.0 eV and the 1s $\rightarrow\sigma^*$ transition at 401.0–410.0 eV. Specifically, peak **a** can be ascribed to the π^* transition of Fe-bonded pyrrole-type N at 398.5 eV, and **b** can be assigned to the π^* transition of graphitic-type N-groups at 401.5 eV^[31]. Notably, peak **a** of NO-FeN₄ exhibits lower absorption intensity in the two resonances. This result suggests that the formation of the Fe–N–C chemical bond in NO-FeN₄ has a stronger charge transfer effect. Furthermore, in Fig. 3d, the X-ray photoelectron spectroscopy (XPS) spectra of N 1s also reveal that the Fe-pyrrolic N peak in NO-FeN₄ shifts to a higher binding energy (399.1 eV) compared with FeN₄ materials (398.8 eV)^[32]. In Fig. S12, the core-level scan spectrum of Fe 2p shows that the Fe 2p^{3/2} peak of NO-FeN₄ has a slight negative shift compared with that of FeN₄. These results confirm that a faster electron transfer pathway has formed between the Fe center

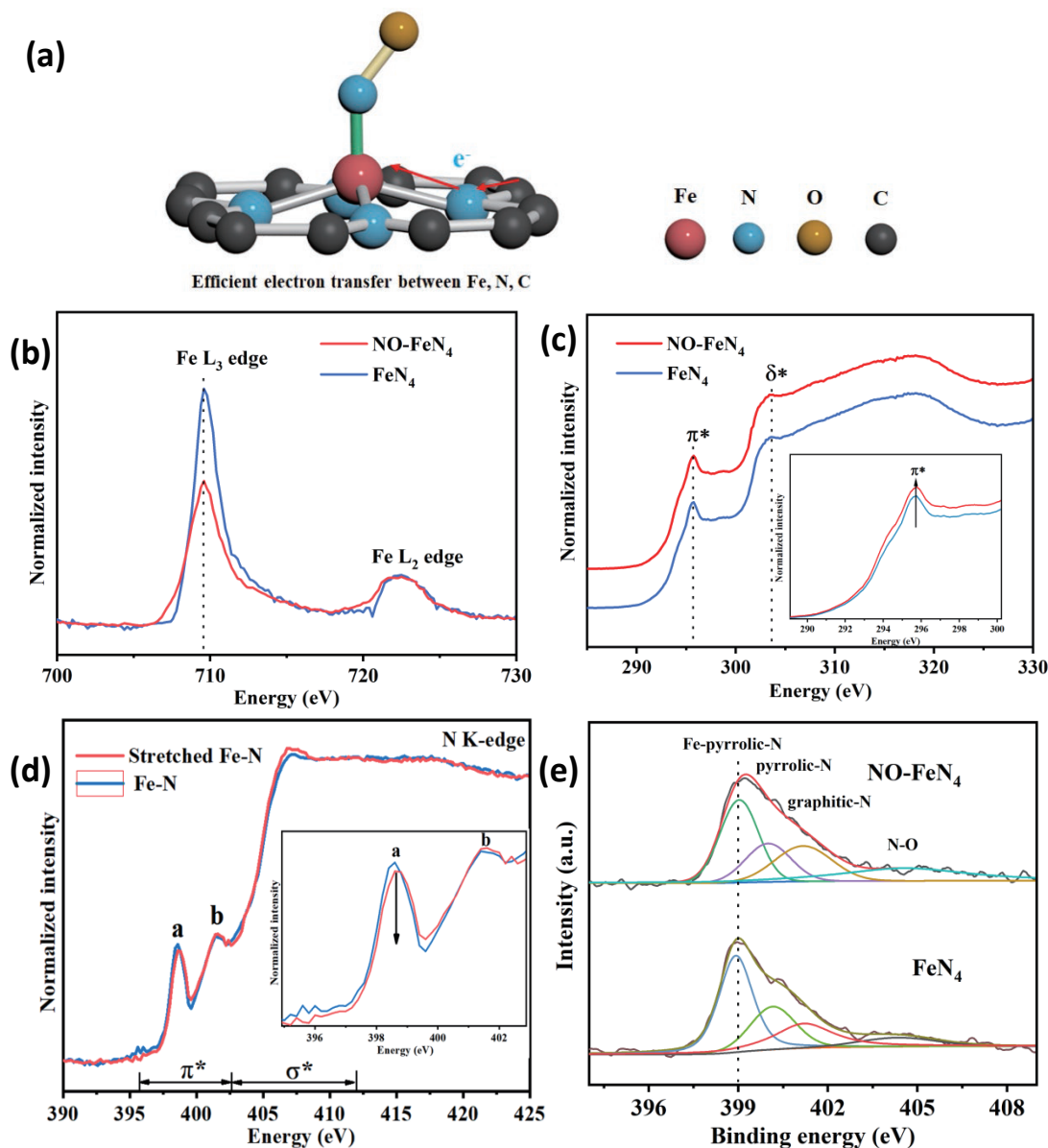


Fig. 3. (a) Electron transfer diagram of N, C adjacent to Fe central of NO-FeN₄. (b) Soft-XAS spectra of Fe L-edge, (c) C K-edge and (d) N K-edge of NO-FeN₄ and FeN₄. (e) XPS spectra of N 1s of NO-FeN₄.

and its substrate due to the strong electron absorption effect of NO. This suggests establishing a fast electron transport pathway between the substrate and the active sites.

To verify the ORR activity of the NO-FeN₄ and FeN₄ electrocatalysts, rotating ring-disk electrode (RRDE) measurements were first performed in an acidic medium. As shown in Fig. 4a, the linear scan sweep voltammetry (LSV) curves exhibited a positive onset potential of 0.90 V and a half-wave potential of 0.82 V for NO-FeN₄, which is much higher than that of the FeN₄ electrocatalyst (0.75 V) and close to that of commercial Pt/C. To quantitatively evaluate the ORR activity of the as-prepared NO-FeN₄ sample, Tafel slopes and electrochemical impedance spectroscopy (EIS) were also performed, as shown in Fig. 4b and Fig. S13. NO-FeN₄ has a relatively small Tafel slope value (77 mV/dec) compared to that of FeN₄ (90 mV/dec) and Pt/C (110 mV/dec). Moreover, it also shows the smallest semicircle, which represents the min-

imum interface charge transfer resistance, indicating the extremely high kinetic activity for the NO-FeN₄ sample. In Fig. 4c, the mass activity at 0.85 V was also calculated to demonstrate the high catalytic activity of the NO-FeN₄ sample. In Fig. 4d, NO-FeN₄ exhibits the largest mass activity of 9.3 A·g⁻¹. Moreover, the turnover frequency (TOF) of NO-FeN₄ is 1.14 e⁻·s⁻¹·site⁻¹. It is 1.375 times that of the FeN₄ sample, indicating that the Fe-N bond length endows its ultrahigh intrinsic activity. Moreover, the peroxide (H₂O₂) generation percent and electron transfer number were also evaluated using the RRDE technique. As shown in Fig. 4d, NO-FeN₄ exhibited a relatively low H₂O₂ yield ranging from 1.3% to 1.8%, and the corresponding electron transfer number exceeded 3.97 below 0.8 V, suggesting its high selectivity and a direct four-electron pathway. These results revealed that NO-FeN₄ could suppress the generation of H₂O₂ and reduce the Fenton reaction during the ORR process. As shown in Fig. 4e,

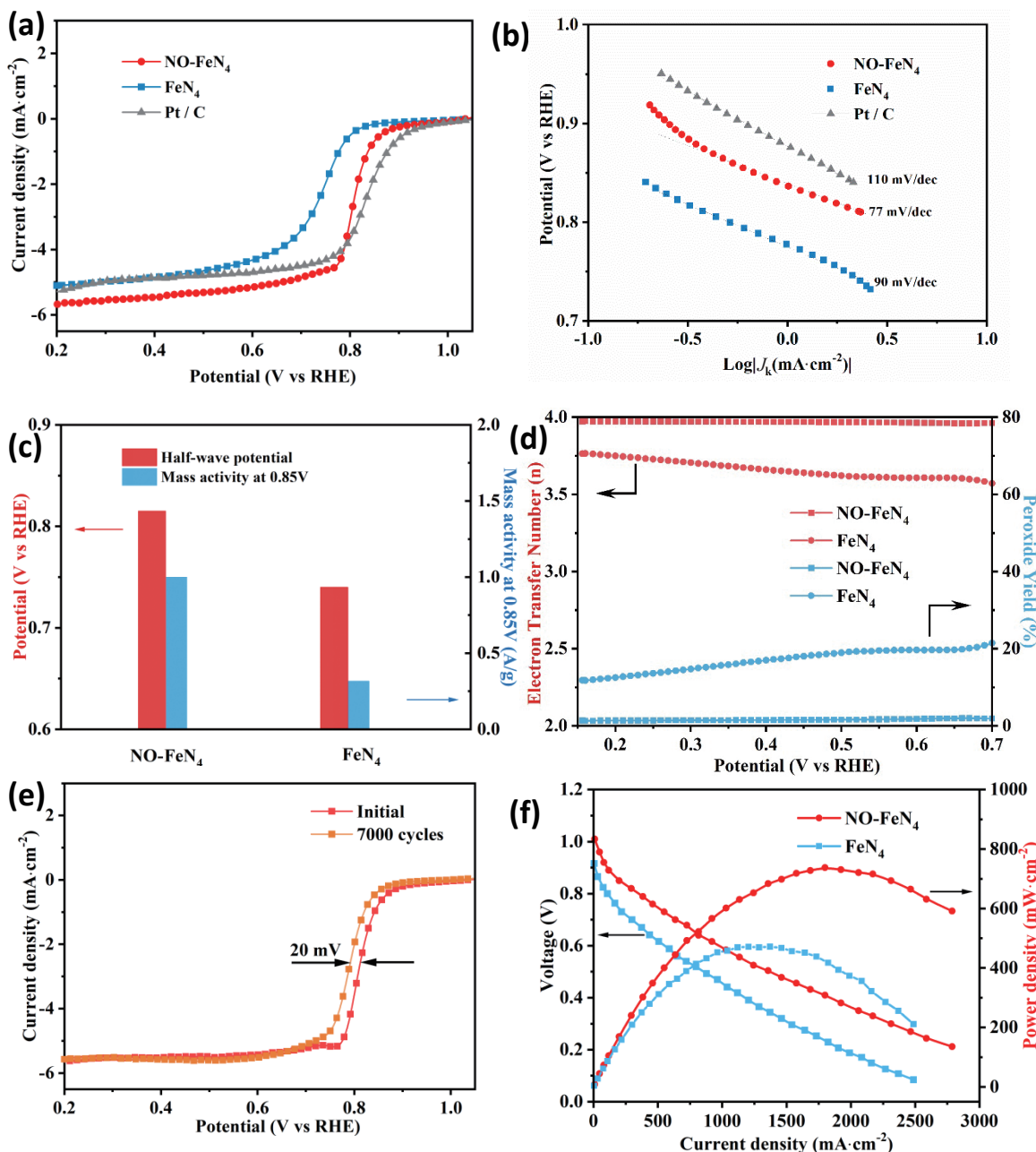


Fig. 4. Electrocatalytic performance. (a) ORR polarization curves and (b) corresponding Tafel plots of NO-FeN₄ and FeN₄ in O₂-saturated 0.5 mol·L⁻¹ H₂SO₄ and 20% Pt/C in 0.1 mol·L⁻¹ HClO₄ under a rotating rate of 1600 r·min⁻¹. (c) Comparison of mass activity at 0.85 V and half-wave potential of NO-FeN₄ and FeN₄ catalysts. (d) Peroxide yield and electron transfer number of NO-FeN₄ and FeN₄ sample during ORR process. (e) LSV curves of NO-FeN₄ catalysts before and after 7000 CV cycles. (f) Polarization and power density curves of NO-FeN₄ and FeN₄ based membrane electrode assemblies in PEMFCs. Cell temperature: 80 °C; RH: 100%; H₂/O₂: 1.5 bar.

only a 20 mV loss can be detected after 7000 CV cycles for NO-FeN₄ in O₂-saturated 0.5 mol·L⁻¹ H₂SO₄. However, the half-wave potential of the FeN₄ sample decreased by 47 mV under the same conditions (Fig. S14). These results prove that NO-FeN₄ exhibits significantly enhanced catalytic activity as well as stability and could be a promising cathode electrocatalyst for PEMFCs. The excellent ORR activity of the NO-FeN₄ sample was also demonstrated by integrating it into membrane-electrode assemblies (MEAs) with a total catalyst loading of 4.0 mg·cm⁻² for PEMFC testing. As shown in Fig. 4f,

under the test condition of 1.5 bar H₂/O₂ back pressure, the NO-FeN₄ exhibited an open-circuit potential of 1.01 V and generated a current density of 355 mA·cm⁻² at 0.8 V and 1828 mA·cm⁻² at 0.4 V, which surpasses the FeN₄ catalyst. Moreover, the corresponding peak power density of NO-FeN₄ reached 735 mW·cm⁻², which was much higher than that of FeN₄ (481 mW·cm⁻²), indicating its broad application prospects in PEMFCs.

The specific reaction mechanism of NO-FeN₄ was further investigated by operando XAFS tests. As shown in Fig. 5a,

operando XAS tests were conducted on a three-electrode system by using a gas diffusion electrode composited with NO-FeN₄ as a cathode in fluorescence mode. In Fig. 5b, the first derivative of the XANES spectra of NO-FeN₄ at the open circuit exhibited obvious positive energy shifting compared to the dry powder sample, indicating that the adsorption of oxygen species in the electrolyte may lead to an increase in the oxidation state for central Fe atoms, while excessive impurity adsorption in the electrolyte may be harmful to the fast oxygen reduction reaction FeN₄ sites. Additionally, Fig. 5c shows the normalized XANES spectra of the Fe K-edge for NO-FeN₄, and the adsorption edge exhibited negative shifting along with the decrease in applied potential, indicating that the ORR is closely related to the Fe²⁺/Fe³⁺ redox potential. Notably, the adsorption edge of 1.0 V and 1.0 V after cycles coincide, which proves that NO-FeN₄ has good cycle stability. As the adsorption of reactants at FeN₄ sites plays a key role in the ORR process, a surface-sensitive delta-mu ($\Delta\mu$) technique in the X-ray absorption near-edge spectra (XANES) region was used to study the adsorption state of reactants at the NO-FeN₄ sites. For example, in 0.5 mol·L⁻¹ H₂SO₄, the experimental $\Delta\mu$ spectrum is obtained by subtracting the region of the Fe K-edge at 0.1 and 1.0 V (or 0.9, 0.7, and 0.3 V). As shown in Fig. 5d, the corresponding $\Delta\mu$ -XANES also shows that NO-FeN₄ exhibited a significant increase in $|\Delta\mu|$ between 0.7 and 0.9 V, which means that it could decompose adsorbed oxygen molecules at a relatively

high potential, avoid the influence of adsorbed impurities, and improve the ORR activity^[33]. Since most FeN₄ catalysts are easily poisoned by impurities at the beginning of the reaction process, a low reaction potential is required to decompose impurities and conduct an oxygen reduction reaction. Therefore, the high reaction potential of NO-FeN₄ indicates that it is not easily poisoned, leading to a higher reaction activity and stability. In conclusion, all the above results demonstrate that NO-FeN₄ exhibits accelerated kinetics and relatively high stability for oxygen reduction under acidic conditions.

The much-enhanced ORR performance of NO-FeN₄ can be ascribed to the following features: (i) the highly dispersed FeN₄ sites could significantly improve ORR catalytic activity. (ii) $\Delta\mu$ -XANES analysis shows that NO-FeN₄ sites possess highly reversible Fe²⁺/Fe³⁺ redox potential and are less likely to be affected by adsorbed impurities. (iii) Rapid electron transfer occurs between the Fe center and its coordinated nitrogen and carbon atoms, which greatly expedites the reduction process of adsorption oxygen species. (iv) The porous and highly graphitization carbon configuration increases the utilization and robust ability of electrocatalysts. Benefiting from the combination of highly active sites and open exposure areas, NO-FeN₄ exhibits superior ORR catalytic activity in an acidic medium as well as high power density when integrated into PEMFC systems.

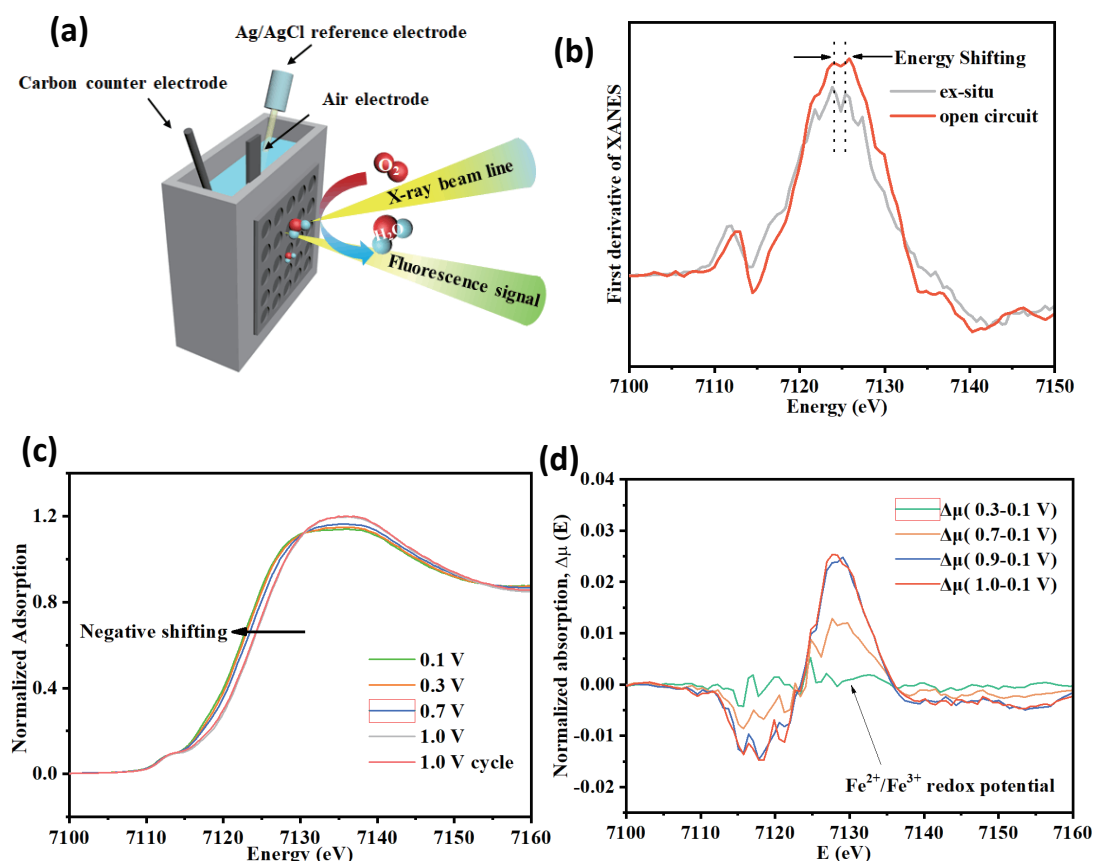


Fig. 5. (a) Schematic of operando XAS measurement device and three-electrode half-cell. (b) First derivative of XANES spectra of NO-FeN₄ for dry powder and operando sample. (c) Operando XANES spectra of Fe K-edge for NO-FeN₄. (d) Normalized difference spectra for Fe K-edge of NO-FeN₄ at different potentials at operando condition.

4 Conclusions

In conclusion, the central electron-enriched NO-FeN₄ structure has been successfully developed as a high-efficiency cathode electrocatalyst. Because the confined small molecule modification significantly increases the charge densities of central iron atoms, the as-prepared electrocatalyst exhibits much enhanced intrinsic catalytic activity, fast electron transfer ability and full four-electron reaction selectivity. Moreover, the as-prepared NO-FeN₄ electrocatalyst shows high mass activity (1.1 A·g⁻¹ at 0.85 V) and TOF activity (1.14 e·s⁻¹·site⁻¹), and its half-wave potential is also close to that of the commercial Pt/C sample. As a result, the PEMFC built by this electrocatalyst has a high power density of 725 mW·cm⁻² at 80 °C, 1.5 bar back pressure, and 100% relative humidity, demonstrating its promising potential in practical applications. This work will pave new avenues for the design of advanced nonnoble electrocatalysts for PEMFCs.

Supporting information

The supporting information for this article can be found online at <https://doi.org/10.52396/JUSTC-2022-0143>. The supporting information includes an experimental section, XPS spectra, TEM images, N₂ physisorption isotherms, LSV curves, structural parameters, and electrochemical performances.

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Conflict of interest

The authors declare that they have no conflict of interest.

Biographies

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