

## PAPER

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## Single iron site catalysts with increased metal-site loading via a high-temperature imprinting approach for proton exchange membrane fuel cells†

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Fe–N–C materials have been widely accepted as the most promising catalysts to replace Pt in future fuel cells. However, the loading of active atomic Fe sites in catalysts remains insufficient (<1.0 wt%) due to Fe agglomeration and carbothermal reduction during the synthesis at elevated heating temperatures (>900 °C). Here, we explored an active-site imprinting approach to convert less active ZnN<sub>x</sub> or nitrogen vacancies (V–N<sub>x</sub>) into FeN<sub>4</sub>. We demonstrated that the reaction barrier of ZnN<sub>4</sub> to FeN<sub>4</sub> (trans-metalation) pathways is significantly lower than that of V–N<sub>4</sub> to FeN<sub>4</sub> (metalation) ones, indicating the importance of forming high-loading ZnN<sub>4</sub> sites first. FeCl<sub>2</sub> precursors are preferable over FeCl<sub>3</sub> during active-site imprinting despite their relatively high boiling point. Eventually, the high-temperature active-site imprinting strategy based on a vacuum-sealed reaction system enables an Fe–N–C catalyst containing exceptionally high atomic Fe site loading up to 5.65 wt%. The resulting catalyst exhibited encouraging ORR activity and stability in challenging acidic media.

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## Introduction

Atomically dispersed metal sites (ADMSS)<sup>1,2</sup> have shown significant benefits for energy-conversion related electrocatalytic reactions, including the oxygen reduction reaction (ORR),<sup>3</sup> oxygen evolution reaction (OER),<sup>4,5</sup> hydrogen evolution reaction (HER),<sup>6,7</sup> and CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR).<sup>8</sup> Especially for the ORR<sup>9–12</sup> in challenging acidic electrolytes, nitrogen-coordinated Fe atoms embedded into a carbon support (Fe–N–C) have emerged as the most promising ADMSS among the platinum group metal-free (PGM-free) catalysts.<sup>13,14</sup> These Fe–N–C catalysts have exhibited considerable performance in proton-exchange membrane fuel cells (PEMFCs), and have potential to replace Pt soon.<sup>13,15–17</sup> In particular, over the past decade, significant progress has been made in

enhancing the acidic ORR activity of Fe–N–C catalysts by increasing the abundance of atomically dispersed Fe as FeN<sub>4</sub>.<sup>17,18</sup> However, most Fe–N–C materials reported to date achieve an Fe content of less than 1 wt% (ref. 19) through conventional high-temperature treatment methods. Adding excess Fe site sources often leads to the clustering of Fe atoms, resulting in inactive aggregates such as metallic iron, iron carbide, and iron nitride, in turn, causing activity decline. This phenomenon is associated with the carbothermal reduction catalyzed by the Fe element at elevated temperatures, described as the dilemma of Fe–N–C catalysts.<sup>20</sup> Therefore, innovative synthetic chemistry and approaches are highly desired to significantly increase Fe site loadings in catalysts for improved mass activity.

Recent studies indicate that decoupling the formation of FeN<sub>4</sub> sites from the high-temperature pyrolysis process is an effective strategy for achieving high-density FeN<sub>4</sub> active sites. This method employs less-noble metals, *e.g.*, Zn<sup>21</sup> or Mg,<sup>22</sup> to induce MN<sub>x</sub> sites or protonated nitrogen-vacancy (V–N<sub>x</sub>) sites. These sites are then converted into FeN<sub>4</sub> through subsequent metallization (eqn (1)) or trans-metalation reaction (eqn (2)), referred to as active site imprinting methods. Given that Zn and Mg exhibit lower catalytic activity for carbothermal reduction than Fe, this approach enables the attainment of a higher number of FeN<sub>4</sub> sites in catalysts.



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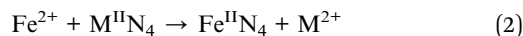
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Fellinger *et al.* pioneered a low-temperature active-site imprinting strategy, in which the initially formed  $\text{MgN}_4$  sites were converted into  $\text{FeN}_4$  moieties *via* ion exchange using  $\text{FeCl}_2$  in methanol.<sup>22</sup> However, this method was inefficient for achieving a high density of  $\text{FeN}_4$  when using  $\text{ZnN}_4$ . Furthermore, a more efficient system for  $\text{ZnN}_4$ -based trans-metalation was developed using  $\text{FeCl}_3/\text{LiCl}$  low-temperature molten salt precursors, achieving an atomically dispersed Fe loading of 3.12 wt%.<sup>21</sup> Unlike the trans-metalation mechanism, Stahl *et al.* reported a metallization method involving the exchange of Fe and protons between  $\text{FeCl}_2$  and V-N<sub>4</sub> with tributyl amine as a promoter.<sup>23</sup> However, the ORR activity of the Fe-N-C catalysts commonly requires activation through acid workup and a second high-temperature treatment, aiming to activate Fe ions adsorbed on the N sites in the form of iron oxide and form active  $\text{FeN}_4$  sites.<sup>20</sup>

High-temperature active-site imprinting offers an alternative route to achieve a high density of  $\text{FeN}_4$ . F. Jaouen *et al.* recently reported a chemical vapor deposition (CVD) method to form Fe-N-C ORR catalysts, proposing that the  $\text{FeN}_4$  sites are primarily formed through high-temperature trans-metalation involving the exchange of Fe and Zn between  $\text{ZnN}_4$  and  $\text{FeCl}_3$ .<sup>24</sup> Kucernak reported a high  $\text{FeN}_4$  loading of 7 wt%, achieved by selective removal of  $\text{Zn}^{2+}$  ions from V-N<sub>4</sub> prior to metalation,<sup>25</sup> suggesting a metalation-based pathway. However, the reaction pathways during  $\text{FeN}_4$  formation remain unclear.

Herein, we reported a high-temperature active-site imprinting method in a closed reaction system with a controlled temperature gradient. Theoretical and experimental research demonstrated that this method can simultaneously utilize  $\text{ZnN}_4$  and V-N<sub>4</sub> to form dense  $\text{FeN}_4$  sites. We also elucidated a lower reaction barrier of trans-metalation compared to metalation. Additionally, a stoichiometric amount of the Fe precursor is determined during high-temperature active-site imprinting, effectively preventing the Fe-N-C catalyst's deactivation caused by Fe particle agglomeration. The newly obtained Fe-N-C catalyst achieved an exceptional loading of 5.65 wt% atomic Fe in the form of  $\text{FeN}_4$  sites, exhibiting considerable ORR performance under acidic conditions.

## Results and discussion

High-temperature active-site imprinting involves the reaction between pre-synthesized Zn-N-C and anhydrous iron(II) chloride ( $\text{FeCl}_2$ ) or iron(III) chloride ( $\text{FeCl}_3$ ), obtaining the corresponding  $\text{Fe}^{\text{II}}\text{-N-C}$  or  $\text{Fe}^{\text{III}}\text{-N-C}$  samples. This process was conducted in a hermetically sealed silica glass ampoule, exposed to a temperature gradient from 720 to 760 °C (Fig. 1). The temperature gradient was employed to intensify gas-phase disturbance, thereby accelerating the reaction rate. The temperature gradient, fluctuating slightly above and below the boiling point of zinc chloride ( $\text{ZnCl}_2$ ) in the hotter and colder zones of the ampoule, would facilitate the separation of the newly formed  $\text{ZnCl}_2$  from Fe-N-C. The disappearance of  $\text{FeCl}_2$

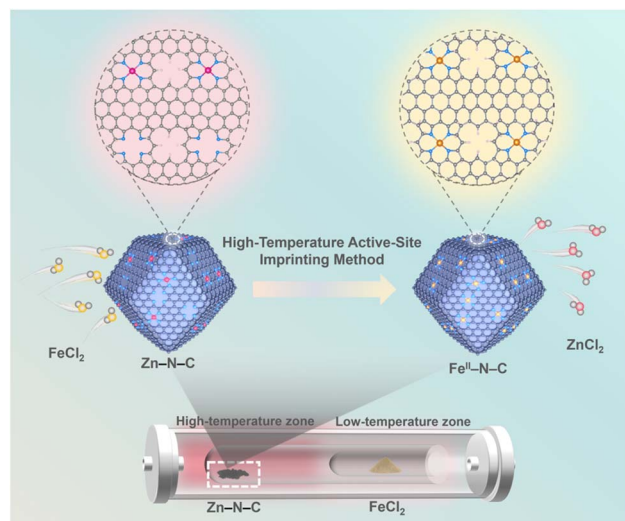
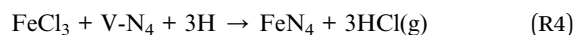
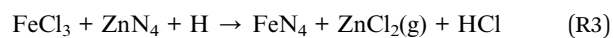
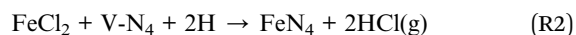
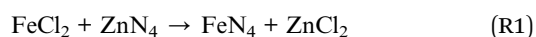


Fig. 1 Schematic illustration of the high-temperature active-site imprinting process.

and the generation of  $\text{ZnCl}_2$  (a greyish-white substance) are clearly observed (Fig. S1†). Such a separation is crucial for promoting the trans-metalation reaction.

### DFT calculations

Before experimental optimization, a density functional theory (DFT) study was conducted to investigate the reaction barrier associated with the coordination of Fe to either V-N<sub>4</sub> or  $\text{ZnN}_4$  sites. According to previous studies,<sup>26–28</sup> we constructed an  $\text{FeN}_4\text{-C}_{12}$  model with a pyrrole-like  $\text{FeN}_4$  moiety bridging two adjacent zigzag graphitic edges (Fig. S2†). The corresponding V-N<sub>4</sub> models without Fe atomic centers were also constructed to study the reaction barrier of metalation compared to trans-metalation. We proposed the following reaction steps to delineate the interaction between the Fe resource and the Zn-N-C precursor:



where the H element comes from the carbon support.

We model the adsorptions of  $\text{FeCl}_2$  and  $\text{FeCl}_3$  molecules on  $\text{ZnN}_4$  or V-N<sub>4</sub> sites, including the transition state where the V-N<sub>4</sub> sites anchor the Fe-Cl, Zn-Cl, and H-Cl intermediates, as well as the formation of  $\text{FeN}_4$  sites (Fig. 2a, b and S2a, b†). The DFT results (Fig. 2c and Table S1†) reveal that the activation energies follow the sequence reaction (R1) (0.14 eV) < reaction (R2) (0.93 eV) < reaction (R3) (1.23 eV) < reaction (R4) (1.82 eV), indicating that  $\text{FeCl}_2$  is a more favorable precursor compared to  $\text{FeCl}_3$ . The activation barrier for reaction (R1) is significantly lower than that for other reaction pathways, because its transition state



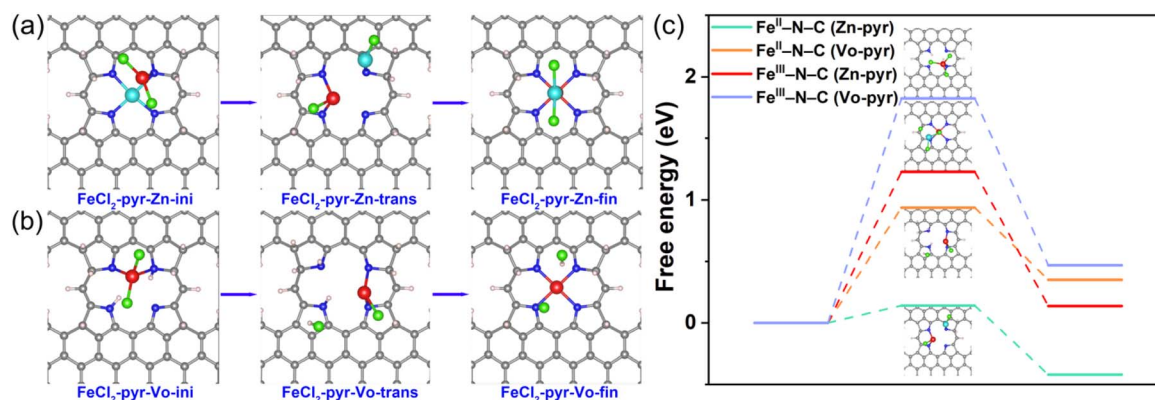


Fig. 2 (a and b) The DFT theoretical calculation model for reactions between (a) FeCl<sub>2</sub> and ZnN<sub>4</sub> and (b) FeCl<sub>2</sub> + V-N<sub>4</sub> + 2H. (c) Energy diagram for the trans-metalation and metalation reactions, including the transition states; the inset shows the adsorption geometries of various transition states.

does not involve the H atoms from the carbon support. For both FeCl<sub>2</sub> and FeCl<sub>3</sub>, the formation energies of FeN<sub>4</sub> following trans-metalation pathways are lower than that for metalation pathways, suggesting that a higher abundance of ZnN<sub>4</sub> motifs can promote the formation of FeN<sub>4</sub> sites.

### Morphology and structure characterization

Based on the DFT calculation, FeCl<sub>2</sub> was initially selected as the vapor-phase Fe resource for preparing Fe<sup>II</sup>-N-C catalysts. To attain a high density of ZnN<sub>4</sub> sites in the Zn-N-C precursor, the pyrolytic temperature was controlled at 900 °C.<sup>29,30</sup> Temperatures exceeding this threshold could significantly induce nitrogen dopants depletion, whereas temperatures below it might lead to insufficient carbonization with poor electrical conductivity.<sup>16</sup> Scanning electron microscope (SEM) images show that the synthesized Fe<sup>II</sup>-N-C is a regular dodecahedron (Fig. 3a). The transmission electron microscopy (TEM) images show that the as-synthesized Zn-N-C retained the pristine morphology of ZIF-8 with a uniform size of approximately 150 nm (Fig. 3b and S3a, b†). The EDS mapping images of Zn-N-C revealed that only atomically dispersed Zn element was present without other metals (Fig. S3c and d†). In contrast, the presence of the Fe element was apparent in the Fe<sup>II</sup>-N-C catalyst (Fig. 3d).

The atomic-resolution high-angle annular dark-field scanning TEM (HAADF-STEM) image shows isolated single Fe atoms throughout the Fe<sup>II</sup>-N-C catalyst without agglomerated metal clusters or particles detected (Fig. 3c). The XRD (Fig. 3e) and Raman (Fig. 3f) results reveal that Zn-N-C and Fe<sup>II</sup>-N-C exhibit similar diffraction peaks at 25.0° and 43.0° and comparable *I*<sub>D</sub>/*I*<sub>G</sub> values.<sup>31</sup> This indicates that high-temperature active-site imprinting does not change the basic structure of the carbonaceous skeleton. The nitrogen adsorption-desorption isotherms (Fig. 3g) are type I isotherms with limited hysteresis for Zn-N-C and Fe<sup>II</sup>-N-C, indicating predominant microporous structures. The Brunauer-Emmett-Teller specific surface areas (SSAs) were slightly increased from 1076 m<sup>2</sup> g<sup>-1</sup> for Zn-N-C to 1180 m<sup>2</sup> g<sup>-1</sup> for Fe<sup>II</sup>-N-C. Their micropore volumes are 0.761 and 1.047 cm<sup>3</sup> g<sup>-1</sup>, respectively (Fig. S4†). The increase in SSAs and micropore

volumes for Fe<sup>II</sup>-N-C suggests that vaporized FeCl<sub>2</sub> may unblock the channels of the carbon support that are initially not gas-phase accessible in the Zn-N-C precursor. This phenomenon may be attributed to the intercalation effect of FeCl<sub>2</sub> into graphitic carbon accompanied by the formation of gaseous ZnCl<sub>2</sub>.<sup>32</sup>

X-ray photoelectron spectroscopy (XPS) N 1s spectra of Zn-N-C and Fe<sup>II</sup>-N-C (Fig. 4a) reveal N-H species at 400.68 eV and N-M at 399.7 eV. In comparison, Fe<sup>II</sup>-N-C preserves similar proportions of N-H and N-M components to Zn-N-C. However, the N-M signal of Fe<sup>II</sup>-N-C slightly shifts towards a higher bond energy due to the stronger electronic interaction in Fe-N compared to Zn-N. XPS comparison shows a significant decrease in the Zn signal (Fig. S5†) and an increase in the Fe signal in the Fe<sup>II</sup>-N-C catalyst (Fig. 4c). Owing to the limited penetration depth of XPS, the Zn and Fe contents were further quantified using ICP-OES (Fig. 4b). Fe<sup>II</sup>-N-C demonstrates a considerably high Fe loading of 5.3 wt%, while the residual Zn content decreases from 3.86 wt% to 0.65 wt%. The increase in the number of Fe atoms exceeds the number of removed Zn atoms, suggesting that the Fe atoms likely occupy unoccupied V-N<sub>4</sub> cavities as well. Therefore, the high-temperature active-site imprinting process can simultaneously utilize ZnN<sub>4</sub> and V-N<sub>4</sub> sites to form dense FeN<sub>4</sub>. To further confirm the reaction mechanism, we employed online mass spectrometry to analyze the gas composition from the FeCl<sub>2</sub> and Fe<sup>II</sup>-N-C mixture and the pure ZnCl<sub>2</sub> control at elevated temperatures. As depicted in Fig. 4d, distinct signals for Zn and Cl atoms appeared when the heating temperature exceeded ~650 °C. This may be due to ZnCl<sub>2</sub> dissociating into Zn and Cl atoms,<sup>33,34</sup> which have lower volatilization temperatures. Additionally, ZnCl<sub>2</sub> molecules are prone to condensation before entering the pipeline ahead of the mass spectrometer, thus making them difficult to detect. This result is consistent with the experimental observation of the white ZnCl<sub>2</sub> precipitate that appeared in the low-temperature zone of the quartz tube after the reaction (Fig. 1).

X-ray absorption fine structure (XAFS) analyses, comprising X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS), were conducted to investigate the coordination environment and valence state of





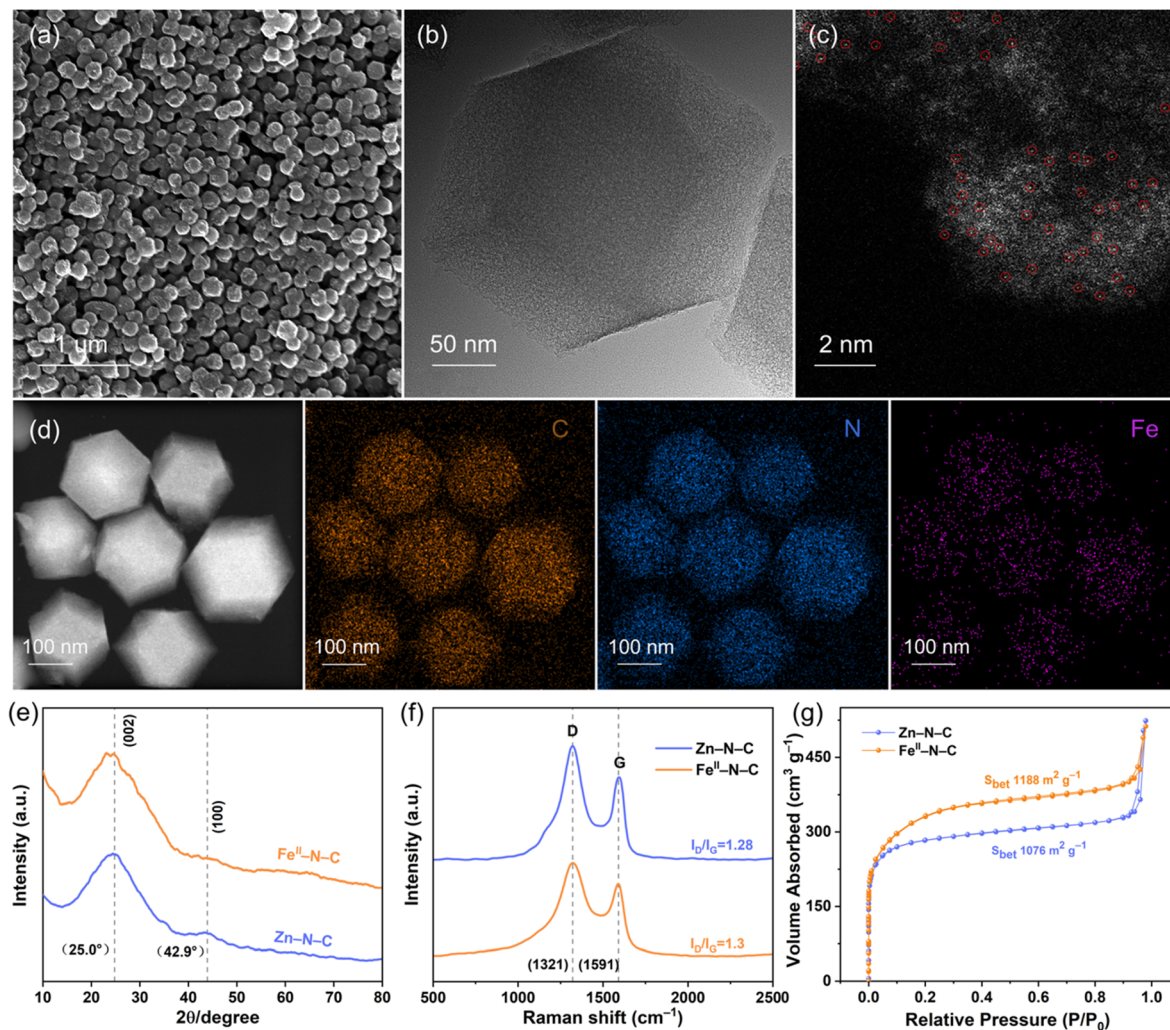


Fig. 3 (a) SEM image of Fe<sup>II</sup>-N-C. (b and d) TEM image and corresponding EDS mapping of Fe<sup>II</sup>-N-C. (c) Atomic-resolution HADDF-STEM image of Fe<sup>II</sup>-N-C. (e) XRD pattern of Fe<sup>II</sup>-N-C. (f) Raman spectrum of Fe<sup>II</sup>-N-C. (g) N<sub>2</sub> isothermal desorption curve of Zn-N-C and Fe<sup>II</sup>-N-C.

the atomically dispersed metal species.<sup>35</sup> The Zn K-edge XANES spectra (Fig. 5a) reveal that the near-edge absorption energy of Zn-N-C is located between those of Zn foil and ZnO, similar to that of Zn phthalocyanine (ZnPc), suggesting the presence of cationic Zn states in the Zn-N-C precursor. The Fourier-transform (FT)  $k^3$ -weighted EXAFS spectra (FT-EXAFS) of Zn-N-C display a distinct peak at approximately 1.5 Å (Fig. 5b), likely ascribed to the Zn-N scattering path originating from atomically dispersed Zn sites. The coordination number and bond length between Zn and N are estimated to be around 4 and 2.01 Å, respectively (Fig. S6 and Table S2†).

The Fe K-edge XANES spectra (Fig. 5d) reveal that the absorption edge position of the Fe<sup>II</sup>-N-C catalyst falls between that of FePc and Fe<sub>2</sub>O<sub>3</sub>, indicating that the valence state of Fe species ranges from +2 to +3. The Fe FT-EXAFS curve (Fig. 5e) of Fe<sup>II</sup>-N-C indicates a scattering path at similar radial distances to that of FePc, likely containing an analogous pyrrolic N coordination environment. A primary peak of Fe<sup>II</sup>-N-C appears at 1.6 Å, representing the first Fe-N or Fe-O coordination. Notably, there is no Fe-Fe scattering peak at ~2.2 Å in the Fe<sup>II</sup>-

N-C catalyst.<sup>36</sup> The wavelet transformed (WT) EXAFS spectra discern the contributions of each pathway not only in *R*-space but also in *k*-space. The  $k^3$ -weighted WT-EXAFS spectra (Fig. 5c) for Fe<sup>II</sup>-N-C exhibit a contour profile in *k*-space aligns well with the FePc pattern, albeit with a subtle shift in the contour intensity maximum exhibits partial characteristics of Fe<sub>2</sub>O<sub>3</sub>. Therefore, the coexistence of Fe-N and Fe-O bonds within the Fe<sup>II</sup>-N-C catalyst is likely.

Quantitative structural configuration information for these samples was extracted by least-squares EXAFS curve fitting analyses (Fig. S7 and Table S2†). The analysis suggests that the primary coordination shell of Fe<sup>II</sup>-N-C is a blend of Fe-N and Fe-O coordination paths, with Fe coordination numbers of 4.0 (N) and 2 (O), respectively. This result implies that the central Fe sites in Fe<sup>II</sup>-N-C possessed a FeN<sub>4</sub>O<sub>2</sub> configuration, *i.e.*, near square planar FeN<sub>4</sub> moieties with two axial oxygen atoms. Recent studies underscore the significance of gas- and proton-accessible FeN<sub>4</sub>O<sub>2</sub> sites for enhanced ORR activity, alongside the FeN<sub>4</sub> sites whose oxidation and spin states remain unaltered at varying electrochemical potentials.<sup>24</sup> The cyclic voltammetry (CV) curve in O<sub>2</sub>/



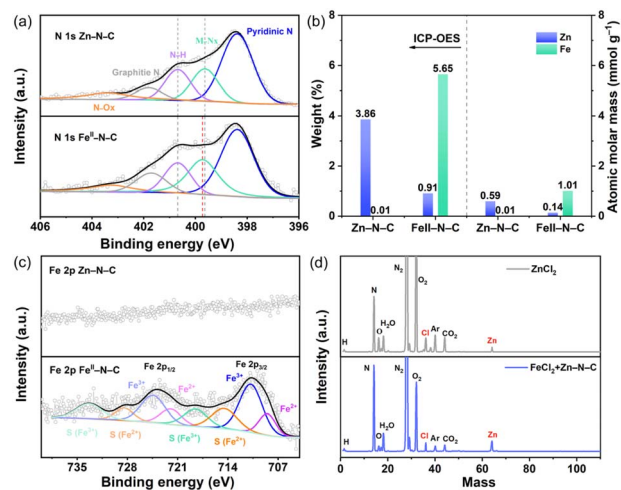


Fig. 4 (a) High-resolution N 1s XPS spectra of Zn-N-C and Fe<sup>II</sup>-N-C. (b) The histogram reveals the weight fraction (wt%) of Zn and Fe for Zn-N-C and Fe<sup>II</sup>-N-C detected by ICP-OES (left) and the corresponding values converted to atomic number per gram of the sample (mmol g<sup>-1</sup>) (right). (c) High-resolution Fe 2p XPS spectra of Zn-N-C and Fe<sup>II</sup>-N-C. (d) Mass spectrum analysis of the reaction process (FeCl<sub>2</sub> and ZnN<sub>4</sub>).

N<sub>2</sub>-saturated electrolyte demonstrates that Fe<sup>II</sup>-N-C undergoes a reversible Fe<sup>III</sup>/Fe<sup>II</sup> redox transition at ~0.66 V, predominantly attributable to the redox-active Fe sites (Fig. S8†).

### Catalyst activity and stability

The ORR activity of the Fe<sup>II</sup>-N-C, Fe<sup>III</sup>-N-C, Zn-N-C, and Pt/C catalysts was evaluated in 0.1 M HClO<sub>4</sub> electrolyte. As depicted in Fig. 6a, the Fe<sup>II</sup>-N-C catalyst exhibits a half-wave potential ( $E_{1/2}$ )

of 0.86 V and a kinetic current density ( $j_k$ ) of 60.8 mA cm<sup>-2</sup> at 0.8 V, and significantly outperforms the Zn-N-C precursor. The calculated turnover frequency (TOF) values for Fe<sup>II</sup>-N-C at 0.80 and 0.85 V were 0.84 and 7.7 e per site per s, respectively (Fig. S9†). The *in situ* nitrite stripping technique was employed to quantify the active site density (SD).<sup>37,38</sup> LSV curves were recorded in oxygen-saturated solutions under three conditions: pre-poisoning, poisoned, and recovered states. The stripping process involves cyclic voltammetry in argon-saturated solution, where a reduction peak appears due to NO reduction to ammonia, linking the stripping charge to the NO molecule quantity and consequently to Fe-N<sub>x</sub> site density in the catalyst. A pronounced nitrite reduction peak emerged in Fe<sup>II</sup>-N-C in the poisoned CV cycles, implying that the active sites synthesized by high-temperature active-site imprinting are accessible to gas and protons. The total amount of charge associated with the NO stripping peak of Fe<sup>II</sup>-N-C was quantified as 20.49 C g<sup>-1</sup> (Fig. 6b), corresponding to an SD value of  $4.27 \times 10^{19}$  sites per g. The TOF value for the Fe<sup>II</sup>-N-C catalyst at 0.85 V was evaluated to be 0.84 e per site per s. These values are comparable to those of the state-of-the-art Fe-N-C catalysts in Table S3,† indicating the high loading and intrinsic activity of the Fe sites in Fe<sup>II</sup>-N-C. The Tafel slope of the ORR over the Fe<sup>II</sup>-N-C catalyst is 87 mV dec<sup>-1</sup>, indicating favorable ORR kinetics (Fig. S10†). Evaluated by the rotating ring-disc electrode (RRDE) technique, the average electron transfer number of Fe<sup>II</sup>-N-C is 3.94 (Fig. S11†) with an H<sub>2</sub>O<sub>2</sub> yield below 4%, which is consistent with the linear fitting result from the K-L equation (Fig. S12†). After 5000 potential cycles, no ORR activity loss was observed (Fig. S13†), and chronoamperometric measurements at 0.4 V demonstrated 84% current retention after a 40000 s test (Fig. S14†), indicating good ORR stability of the Fe<sup>II</sup>-N-C catalyst in aqueous acidic electrolytes.

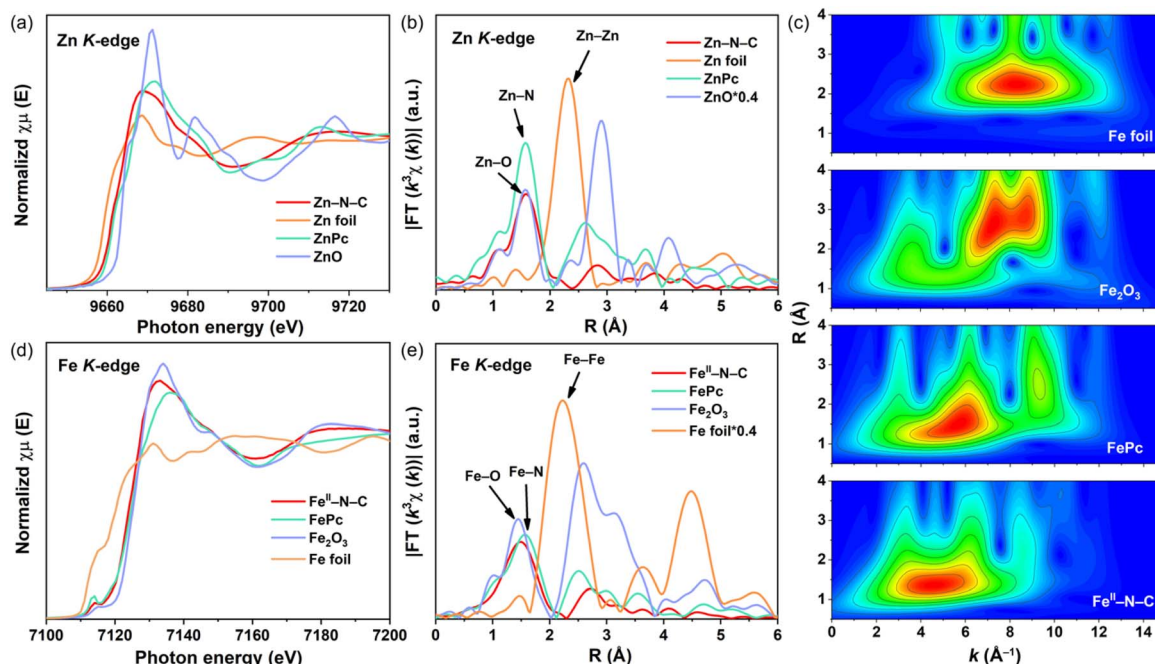


Fig. 5 (a) Zn K-edge XANES spectra, and (b) FT-EXAFS spectra of Zn-N-C and corresponding control samples (Zn foil, ZnPc, and ZnO). (d) Fe K-edge XANES spectra, (e) FT-EXAFS spectra, and (c) WT-EXAFS images of Fe<sup>II</sup>-N-C and corresponding control samples (FePc, Fe<sub>2</sub>O<sub>3</sub>, and Fe foil).





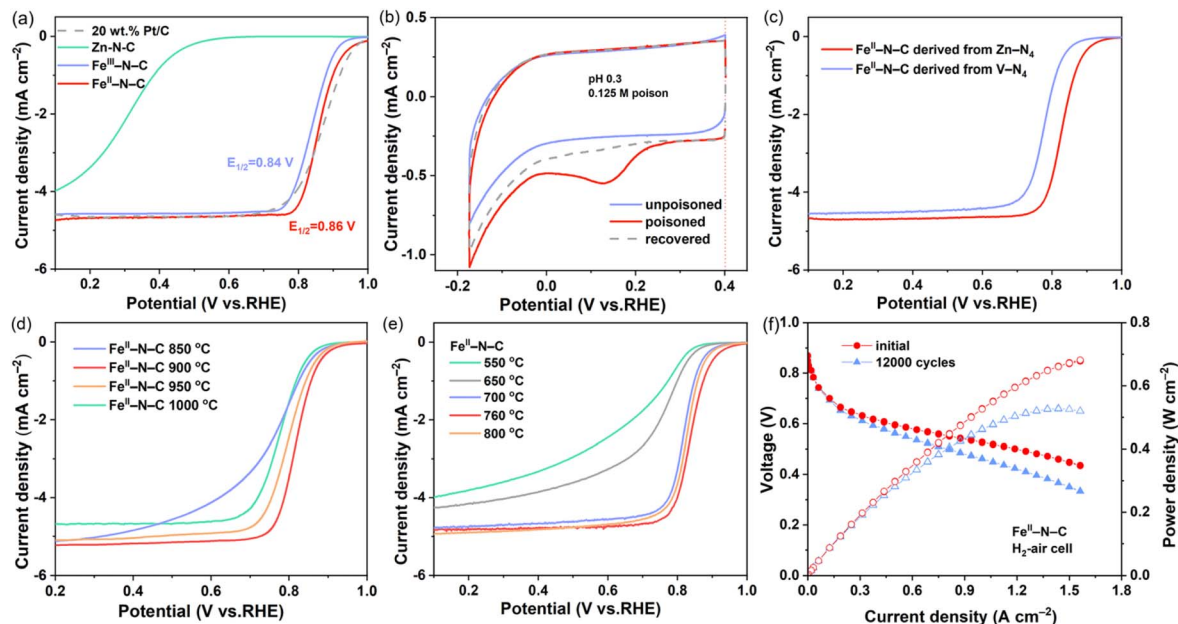


Fig. 6 (a) ORR polarization curves of  $\text{Fe}^{\text{II}}\text{-N-C}$ ,  $\text{Fe}^{\text{III}}\text{-N-C}$ ,  $\text{Zn-N-C}$ , and  $\text{Pt/C}$  catalysts in 0.1 M  $\text{HClO}_4$  electrolyte. (b) CV curves of  $\text{Fe}^{\text{II}}\text{-N-C}$  before and after nitrite adsorption in the nitrite reductive stripping region. (c) ORR polarization curves of  $\text{Fe}^{\text{II}}\text{-N-C}$  from  $\text{Zn-N-C}$  and  $\text{V-N-C}$  precursors at 0.1 M  $\text{HClO}_4$ . (d) ORR polarization curves of  $\text{Fe}^{\text{II}}\text{-N-C}$  derived from  $\text{Zn-N-C}$  precursors at various pyrolytic temperatures. (e) ORR polarization curves of  $\text{Fe}^{\text{II}}\text{-N-C}$  synthesized at different active-site imprinting temperatures. (f) Polarization and power density curves of the optimal  $\text{Fe}^{\text{II}}\text{-N-C}$  catalyst before and after 12 000 cycles under  $\text{H}_2\text{-Air}$  conditions. Test conditions: the anode loading is  $0.1 \text{ mg cm}^{-2}$ , the cathode loading is  $4.0 \text{ mg cm}^{-2}$ , the relative humidity is 100%, and the battery temperature is  $80^\circ\text{C}$ .

To investigate the impact of the  $\text{ZnN}_4$  sites within the  $\text{Zn-N-C}$  precursor on the ORR activity of  $\text{Fe}^{\text{II}}\text{-N-C}$ , the  $\text{ZnN}_4$  sites were converted into  $\text{V-N}_4$  through an intense acidic washing treatment. Under identical active site imprinting conditions, the  $E_{1/2}$  of the control sample decreased obviously by 50 mV (Fig. 6c), implying that trans-metalation facilitates the formation of more  $\text{FeN}_4$  sites than metalation. We further synthesized  $\text{Zn-N-C}$  precursors with varying Zn contents by pyrolyzing ZIF-8 at different temperatures. As depicted in Fig. 6d, the ORR activity of  $\text{Fe}^{\text{II}}\text{-N-C}$  ( $T$ ) catalysts, where  $T$  represents the pyrolysis temperature of the  $\text{Zn-N-C}$  catalyst *via* high-temperature active-site imprinting, follows the order  $\text{Fe}^{\text{II}}\text{-N-C}$  ( $900^\circ\text{C}$ ) >  $\text{Fe}^{\text{II}}\text{-N-C}$  ( $950^\circ\text{C}$ ) >  $\text{Fe}^{\text{II}}\text{-N-C}$  ( $1000^\circ\text{C}$ ) >  $\text{Fe}^{\text{II}}\text{-N-C}$  ( $850^\circ\text{C}$ ). This result reveals that the Zn content is closely related to the ORR activity, as the trans-metalation pathway has a lower reaction barrier than the metallization pathway. Meanwhile, pyrolysis temperatures lower than  $900^\circ\text{C}$  lead to higher Zn content but a significant decrease in conductivity. Conversely, exceeding  $900^\circ\text{C}$  results in the loss of N content, leading to fewer  $\text{ZnN}_4$  sites. Both extreme heating temperatures lead to a decrease in  $\text{FeN}_4$  density. To determine the optimal Fe loading, we conducted a series of comparative experiments using different mass ratios of the Fe source to  $\text{Zn-N-C}$  precursor, corresponding to  $\text{Fe}^{\text{II}}\text{-N-C}$  catalysts with 5%, 15%, 25%, and 35% Fe contents. The ORR activity initially improves with increasing Fe content, reaching an optimum at 15%, and then declines with further increases (Fig. S15†).

We further investigate the impact of reaction temperatures of the active-site imprinting process on the ORR performance of the  $\text{Fe}^{\text{II}}\text{-N-C}$  ( $900^\circ\text{C}$ ) catalyst. As shown in Fig. 6e, a reaction

temperature around the boiling point of  $\text{ZnCl}_2$  ( $760^\circ\text{C}$ ) leads to the best ORR activity, and the temperature gradient facilitates the activity enhancement (Fig. S16†).

Since  $\text{FeCl}_3$  has a lower boiling point than  $\text{FeCl}_2$ , we further explored using  $\text{FeCl}_3$  as a Fe resource (denoted as  $\text{Fe}^{\text{III}}\text{-N-C}$ ) for high-temperature active-site imprinting. Interestingly, the  $\text{Fe}^{\text{III}}\text{-N-C}$  catalyst exhibited relatively lower ORR activity than the  $\text{Fe}^{\text{II}}\text{-N-C}$  catalyst (Fig. 6a), despite the easier volatilization of  $\text{FeCl}_3$  compared to  $\text{FeCl}_2$ . This result is consistent with the DFT conclusions, indicating that  $\text{FeCl}_2$  has a lower reaction barrier for both metalation and trans-metalation. Moreover,  $\text{FeCl}_2$  is more stable, whereas  $\text{FeCl}_3$  is prone to decomposition, forming chlorine (Cl) to poison the  $\text{FeN}_4$  sites by forming  $\text{Fe-Cl}$  coordination. Besides, even at temperatures lower than the boiling point of  $\text{FeCl}_2$ , the reaction can still proceed because the closed vacuum system can reduce the vapor pressure, and the temperature gradient also promotes the gaseous reaction.

### Fuel cell testing

To evaluate the  $\text{Fe}^{\text{II}}\text{-N-C}$  catalyst in a practical PEMFC, the catalyst was incorporated into membrane electrode assemblies (MEAs) and investigated under fuel cell operating conditions. As shown in Fig. S17,† the  $\text{Fe}^{\text{II}}\text{-N-C}$  cathode exhibited an open-circuit voltage (OCV) of 0.92 V and a peak power density of  $1.29 \text{ W cm}^{-2}$  under 1.8 bar  $\text{H}_2\text{-O}_2$  conditions. Under more practical  $\text{H}_2\text{-air}$  conditions, the peak power density is still around  $0.68 \text{ W cm}^{-2}$  (Fig. 6f). After an accelerated stress test (AST) using 12 000 voltage cycles, the  $\text{Fe}^{\text{II}}\text{-N-C}$  cathode only lost about 29% and 24% under  $\text{H}_2\text{-O}_2$  and  $\text{H}_2\text{-air}$  conditions,



respectively, comparable to most reported Fe–N–C catalysts due to the possible demetallation in harsh fuel cell environments.<sup>39,40</sup> Significant efforts are still needed to simultaneously improve fuel cell performance and durability, which remains a grand challenge in the field.

## Conclusions

In summary, we have developed a high-temperature active-site imprinting method to effectively synthesize Fe–N–C catalysts with significantly increased atomic FeN<sub>4</sub> site loading. Theoretical and experimental research elucidates that the reaction mechanism involves the trans-metalation between FeCl<sub>2</sub> and ZnN<sub>4</sub> and the direct metalation between FeCl<sub>2</sub> and V–N<sub>4</sub>. The reaction barrier for trans-metalation is lower than that for direct metalation, suggesting that more ZnN<sub>4</sub> in the Zn–N–C precursor is essential for achieving high loading of FeN<sub>4</sub> sites. FeCl<sub>2</sub> is a more suitable Fe resource for this process than FeCl<sub>3</sub> due to the reduced energy barrier during the imprinting process. In particular, the vacuum-sealed reaction system enables the use of high boiling point FeCl<sub>2</sub> as a precursor to trigger the active-site imprinting reaction. Only a stoichiometric amount of Fe precursor is required, preventing the deactivation of the Fe–N–C catalyst due to the formation of Fe agglomeration. As the gasified FeCl<sub>2</sub> and ZnCl<sub>2</sub> may open the channels of the carbon support, the FeN<sub>4</sub> sites are easily accessible to both gas and protons during the ORR. The optimal Fe–N–C catalyst achieved a high FeN<sub>4</sub> loading of 5.65 wt%, exhibiting high ORR performance under acidic conditions, as evidenced by the RDE technique in acidic solution and MEA tests under PEMFC conditions. This study provides insight into the formation mechanism of high-loading FeN<sub>4</sub> sites *via* the ZnN<sub>4</sub>-rich Zn–N–C precursor using effective high-temperature imprinting.

## Experimental

### Preparation of Zn–N–C precursors

4.7 g of zinc nitrate hexahydrate was mixed with 100 mL of methanol and 100 mL of water. Simultaneously, 10.02 g of 2-methylimidazole was dissolved in 100 mL of methanol. The methanol solution containing zinc nitrate hexahydrate was then poured into the methanol solution containing 2-methylimidazole and mixed thoroughly, followed by stirring for three hours.<sup>41</sup> After ceasing stirring, the mixture was allowed to stand for 3 hours, and then centrifuged, and the resultant white product was washed several times with methanol. The obtained ZIF-8 powder was then heat-treated in a tube furnace at a heating rate of 3 °C per minute up to 900 °C for 3 hours. The pyrolyzed product underwent treatment in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at 80 °C for 8 hours to remove excess Zn nanoparticles, followed by repeated washing with water and ethanol, and then drying.

### Preparation of Fe<sup>II</sup>–N–C

A specific ratio (15 wt%) of the Zn–N–C material and ferrous chloride were enclosed in a quartz tube under vacuum conditions, ensuring that the ferrous chloride powder did not directly

come into contact with the Zn–N–C powder. The tube was then subjected to pyrolysis at 760 °C in the high-temperature zone and 730 °C in the low-temperature zone for 10 hours. The high-temperature zone is set at 760 °C because this temperature is slightly higher than the vaporization temperature of ZnCl<sub>2</sub> (732 °C), ensuring that the formed ZnCl<sub>2</sub> will not deposit on the Fe–N–C surface. Meanwhile, the temperature in the low-temperature zone is 730 °C, which facilitates the deposition of ZnCl<sub>2</sub>, thus enabling its separation from Fe–N–C. After the active-site imprinting reaction, the resulting sample was washed with ethanol and deionized water to yield the Fe<sup>II</sup>–N–C catalyst. Similarly, FeCl<sub>3</sub> precursors were also used for the high-temperature imprinting synthesis under identical procedures and conditions.

### XAS characterization

X-ray Absorption Spectroscopy (XAS) was conducted at the Zn K-edge (9659 eV) and Fe K-edge (7112 eV) at the 1W1B beamline of the Beijing Synchrotron Radiation Facility (BSRF). Using a Si (111) double-crystal monochromator, the Zn SAC and Fe SAC data were acquired in the transmission mode and fluorescence mode using a Lytle detector under ambient conditions, respectively.<sup>42</sup> For energy calibration, Zn and Fe foil were tested, and the energy of the most substantial peak of the first-order derivative of its X-ray absorption near edge structure (XANES) was found to be 9659 and 7112 eV, respectively.

The raw data were processed and analyzed using the Demeter software package (including Athena and Artemis software).<sup>43</sup> A linear function was subtracted from the pre-edge region. Then, the edge jump was normalized using Athena software. The  $\chi(k)$  data were isolated by subtracting a smooth, third-order polynomial approximating the absorption background of an isolated atom. The  $k^3$ -weighted and  $k^2$ -weighted  $\chi(k)$  data were Fourier-transformed after applying a Hanning window function ( $\Delta k = 1$ ) to extract the EXAFS for Zn and Fe elements, respectively. The global amplitude reduction factor ( $S_0^2$ ), coordination numbers ( $N$ ), distances to the scattering atoms ( $R$ ), and the Debye–Waller factor ( $\sigma^2$ ) were obtained by non-linear least-squares refinement of the EXAFS equation of the Fourier-transformed data in  $R$ -space, using Artemis software. The detailed fitting parameters are shown in Table S1.†

### Electrochemical evaluations

The catalyst ink was prepared by uniformly dispersing 5 mg of catalyst in 1000  $\mu$ L mixed solvent (volume ratio of ethanol to 5 wt% perfluorosulfonic acid resin is 99 : 1), and the test equipment was a rotating disk electrode. The ink prepared by using 20  $\mu$ L catalyst was dropped onto the disk electrode dried in air, and the thin film electrode was evaluated by using an electrochemical workstation. A Pt mesh electrode and Ag/AgCl electrode were used as counter and reference electrodes, respectively. All potentials are related to the reversible hydrogen electrode (RHE). In an Ar-saturated 0.1 M HClO<sub>4</sub> solution, 20 cycles of CV cleaning were performed in the potential range of 0 to 1.2 V at 100 mV s<sup>−1</sup>, and then a stable CV curve was obtained in the same potential range at 50 mV s<sup>−1</sup>. The ORR



performance was measured at 1600 rpm in an O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> solution. Linear sweep voltammetry was performed on Zn–N–C and Fe<sup>II</sup>–N–C in the potential range of –0.2 V to 0.9 V at a 5 mV s<sup>–1</sup> scan rate. To test the durability of Fe<sup>II</sup>–N–C, the steady-state current of 5000 CV cycles was recorded in the voltage range of 0.33–0.73 V. The LSV curves before and after the cycle were compared.

### Fuel-cell testing

The homogeneous suspension of the Fe<sup>II</sup>–N–C catalyst was prepared in a solvent mixture consisting of isopropanol, water, and a 5 wt% Nafion dispersion. The volumetric ratio of alcohol to water was adjusted to 1:1, with the mass of the perfluorosulfonic acid resin solution constituting 50% of the total catalyst mass. After a 20 minute wet milling process with isopropanol solution, water, additional isopropanol, and a 5 wt% Nafion<sup>TM</sup> solution were added in accordance with the pre-determined blending ratio. The resulting mixture was then uniformly dispersed *via* ultrasonication and sprayed onto a Gas Diffusion Layer (GDL) until a cathode catalyst loading of 4.0 mg cm<sup>–2</sup> was achieved. For the anode, a Pt/C-coated GDL with a Pt loading of 0.1 mg cm<sup>–2</sup> was used. To create the Membrane Electrode Assembly (MEA), two Gas Diffusion Layers (GDLs) were aligned on either side of a Nafion membrane and thermally pressed for 120 s at 130 °C under a pressure of 3.0 bar.

The performance of the MEA, which had an active area of 4 cm<sup>2</sup>, was rigorously evaluated in a fuel cell setup. The operational conditions during the test maintained the battery temperature and Relative Humidity (RH) at 100%, respectively. Before the performance evaluation, the Fe<sup>II</sup>–N–C cathode underwent an activation phase at a fixed voltage of 0.5 V in an H<sub>2</sub>/O<sub>2</sub> environment for 20 minutes. The current density progressively increased during this time until it stabilized at a maximum value. The cathode and anode were supplied with H<sub>2</sub> and O<sub>2</sub> at flow rates of 300 and 800 mL min<sup>–1</sup>, respectively, both under a back pressure of 1.8 bar. Polarization curves were recorded under these specified conditions. The Fe<sup>II</sup>–N–C cathode was subjected to durability testing, square-wave potential cycling at 0.6 and 0.92 V with each potential applied for 3 s, following the DOE protocol for evaluating the dura-

The rotating ring disk electrode (RRDE) test was applied to measure the hydrogen peroxide yield (H<sub>2</sub>O<sub>2</sub>%) and the electron transfer number (*n*). During the test, polarization curves were recorded by scanning the disk electrode with a rate of 1 mV s<sup>–1</sup> in the voltage range of 1.0–0.125 V, where the ring electrode voltage was 1.20 V. H<sub>2</sub>O<sub>2</sub> yields are determined by using the following equations:<sup>45</sup>

$$\text{H}_2\text{O}_2\% = \frac{200I_r}{I_dN + I_r}$$

$$n = \frac{4I_dN}{I_dN + I_r}$$

The currents associated with both the disk (denoted as *I<sub>d</sub>*) and the ring (denoted as *I<sub>r</sub>*) electrodes can be directly extracted from the polarization curves obtained during the experiments. The collection efficiency, symbolized as *N*, is established to have a value of 0.37. All the electrochemical measurements were performed at room temperature.

### Nitrite stripping technique for determining active site density<sup>46</sup>

The nitric oxide (NO) stripping technique employs a classical three-electrode setup, utilizing 0.5 M H<sub>2</sub>SO<sub>4</sub> as the electrolyte. The selection of this medium was based on the proposer's rationale that it represents an optimal compromise, emulating the conditions of an acidic measurement while simultaneously providing an adequate potential window to facilitate the observation of NO stripping devoid of interference from hydrogen evolution.<sup>47</sup> LSVs are recorded in an oxygen-saturated solution before poisoning, after poisoning, and after stripping. The stripping procedure is simple cyclic voltammetry (in an oxygen-free solution) where a reductive peak appears because of the reduction of NO to ammonia, which makes the stripping charge linked to the amount of NO molecules and so to the number of Fe<sup>II</sup>–N–C sites in the material according to the formula:

$$\begin{aligned} \text{MSD} \text{ [mol per sites per g]} &= \frac{Q_{\text{strip}} [\text{C g}^{-1}]}{n_{\text{strip}} F [\text{C mol}^{-1}]} \\ &= \frac{\text{SD} [\text{site per g}]}{N_A [\text{mol}^{-1}]} \end{aligned}$$

where *n<sub>strip</sub>* is the number of electrons associated with the reduction of one adsorbed nitrosyl per site to NH<sub>3</sub> (or more precisely to NH<sub>4</sub><sup>+</sup>), which is quantitatively defined as 5.<sup>48</sup> By extracting the difference in kinetic current *J<sub>k</sub>* at 0.8 V/0.85 V *versus* RHE, the mean TOF of all different nitrite sensitive active sites with respect to electrons can be obtained *via*:<sup>49w</sup>

$$\text{TOF} = \frac{J_k A}{\left(\frac{m_{\text{Fe}}}{M_{\text{Fe}}}\right) N_A} = \frac{J_k A}{\left(\frac{L A W_{\text{Fe}}}{M_{\text{Fe}}}\right) N_A} = \frac{J_k M_{\text{Fe}}}{L N_A W_{\text{Fe}}}$$

here *J<sub>k</sub>* is the mass transfer corrected kinetic current density at 0.8 V/0.85 V. *A* is the electrode area. *m<sub>Fe</sub>* is the mass loading of

### Electron transfer number and hydrogen peroxide yield

The electron transfer number from the RDE test was calculated from the Koutecky–Levich equation:<sup>10,44</sup>

$$\frac{1}{J} = \frac{1}{J_k} + \frac{1}{J_L} = \frac{1}{B\omega^{\frac{1}{2}}} + \frac{1}{J_k}$$

where *ω* is the rotation rate applied in the test. Current density (*J*) and kinetic current density (*J<sub>k</sub>*) were determined from the steady-state polarization curves. The constant *B* was calculated from the above equation (diffusion coefficient of O<sub>2</sub> is 1.93 × 10<sup>–5</sup> cm<sup>2</sup> s<sup>–1</sup>; the kinetic viscosity *ν* equals 1.009 × 10<sup>–2</sup> cm<sup>2</sup> s<sup>–1</sup>; the concentration of O<sub>2</sub> in the electrolyte is 1.26 × 10<sup>–3</sup> mol L<sup>–1</sup>; and *F* and *A* are the Faraday constant and the electrode's geometric area (0.19625 cm<sup>2</sup>), respectively).





Fe on the electrode.  $M_{\text{Fe}}$  is the molar mass of Fe ( $M_{\text{Fe}} = 55.85 \text{ g mol}^{-1}$ ).  $N$  is Avogadro's number ( $N = 6.02 \times 10^{23} \text{ mol}^{-1}$ ).  $L$  is the catalyst loading on the electrode ( $L = 0.27 \text{ mg cm}^{-2}$ ).  $W_{\text{Fe}}$  is the mass fraction of Fe in the catalyst from ICP-OES analysis ( $W_{\text{Fe}} = 5.65 \text{ wt\%}$ ).

## Data availability

All experimental and characterization data are available in the ESI.†

## Author contributions

Xinhong Liang and Pengwei Zhao completed the experimental and theoretical calculation work of this study. Zhiyuan Gao, Jiashun Liang, Xiaoxuan Yang, Kai Ao and Jianwen Zhu contributed to the experimental design and investigation. Yi Mei contributed to the experimental design. Yuanzhi Zhu and Gang Wu were responsible for experimental design, supervision and writing, while Yuanzhi Zhu was responsible for reviewing, editing, and funding acquisition.

## Conflicts of interest

There are no conflicts to declare.

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