



Atomically dispersed iron sites with a nitrogen-carbon coating as highly active and durable oxygen reduction catalysts for fuel cells

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Nitrogen-coordinated single atom iron sites (FeN₄) embedded in carbon (Fe–N–C) are the most active platinum group metal-free oxygen reduction catalysts for proton-exchange membrane fuel cells. However, current Fe–N–C catalysts lack sufficient long-term durability and are not yet viable for practical applications. Here we report a highly durable and active Fe–N–C catalyst synthesized using heat treatment with ammonia chloride followed by high-temperature deposition of a thin layer of nitrogen-doped carbon on the catalyst surface. We propose that catalyst stability is improved by converting defect-rich pyrrolic N-coordinated FeN₄ sites into highly stable pyridinic N-coordinated FeN₄ sites. The stability enhancement is demonstrated in membrane electrode assemblies using accelerated stress testing and a long-term steady-state test (>300 h at 0.67 V), approaching a typical Pt/C cathode (0.1 mg_{Pt} cm^{−2}). The encouraging stability improvement represents a critical step in developing viable Fe–N–C catalysts to overcome the cost barriers of hydrogen fuel cells for numerous applications.

The development of platinum group metal (PGM)-free catalysts to replace Pt is a critical step towards significantly reducing the cost for proton-exchange membrane fuel cells (PEMFCs)^{1–4}. Catalysts with atomically dispersed, nitrogen-coordinated iron sites (FeN₄) hosted in carbon (denoted as Fe–N–C) have exhibited encouraging activity for the oxygen reduction reaction (ORR) in challenging acidic electrolytes⁵. Since Dodelet and his coworkers identified zinc-based zeolite imidazole framework (ZIF-8) precursors for Fe–N–C catalysts⁶, many researchers have developed various approaches to introducing active Fe species into ZIF-8 nanocrystals to significantly improve atomic Fe site dispersion with increased density in catalysts^{7–12}. The inexpensive ZIF-8s with adequate N ligation have become the most effective precursors to facilitate the formation of FeN₄ sites in partially graphitized and microporous carbon during controlled thermal activation^{13,14}. Despite the encouraging catalytic activity that is steadily approaching that of Pt, the stability of Fe–N–C catalysts remains a critical hurdle for viable applications⁵.

Further improving Fe–N–C catalyst performance faces a grand challenge of the activity–stability trade-off¹⁵. Small carbon planes with local defects facilitate the O–O bond-breaking¹⁶. However, oxidation of such defect-rich carbon domains probably triggers the demetallation of FeN₄ sites from catalysts during the ORR¹⁷.

Graphitized carbon structures have higher corrosion/oxidation resistance to stabilize FeN₄ active sites^{18,19}. However, they lack sufficient defects and nitrogen dopants to host adequate FeN₄ site densities. Therefore, coordination environments and local carbon structures of FeN₄ sites are critical to their intrinsic activity and stability²⁰.

Generally, FeN₄ sites embedded in carbon planes in Fe–N–C catalysts are like molecular macrocyclic compounds containing Fe–N coordination. The molecular Fe sites are hosted in two types of ligation environment containing pyrrolic and pyridinic N, respectively. Conventional Fe phthalocyanine (FePc) contains pyrrolic N ligands to coordinate Fe sites. Surendranath et al.²¹ synthesized a molecular Fe catalyst containing FeN₄ sites with defined pyridinic N ligation and corresponding electronic/geometric structures. In contrast, Fe–N–C catalysts are synthesized through high-temperature pyrolysis, leading to less controlled iron environments with a wide diversity²¹. This long-standing uncertainty presents a grand challenge to correlate ORR performance with the local structures of the Fe sites in Fe–N–C catalysts. Recently, Jaouen et al.²² identified two key FeN₄ site structures in Fe–N–C catalysts based on operando Mössbauer experiments. One is an FeN₄C₁₂ moiety featuring a pyrrolic N ligation environment (denoted as S1), such as Fe(Pc). The other is an FeN₄C₁₀ moiety with four pyridinic N ligands (S2)

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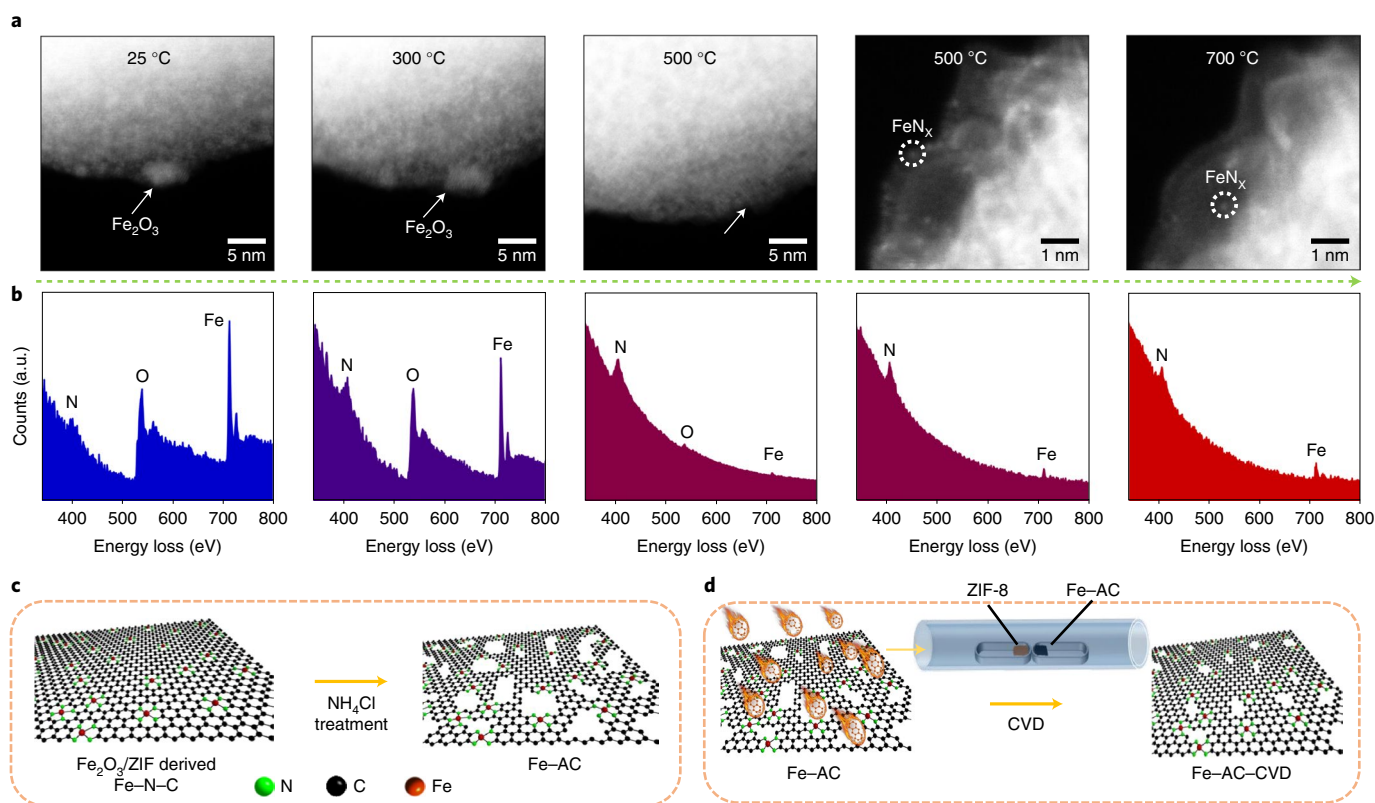


Fig. 1 | Catalyst synthesis principles. **a, b**, ADF-STEM images (**a**) and corresponding EEL point spectra (**b**) captured during in situ heating of the Fe₂O₃@ZIF-8 precursor at 25 °C, 300 °C, 500 °C and 700 °C. White arrows mark initial location of an Fe₂O₃ nanoparticle, while white circles mark FeN_x sites. The dashed green arrow presents the temperature-dependent structural changes from Fe₂O₃ nanoparticles to atomic FeN₄ sites. **c**, The Fe₂O₃@ZIF-8-derived Fe-N-C catalyst was treated with NH₄Cl salts at high temperatures (for example, 1,100 °C), denoted as Fe-AC. **d**, A CVD process using ZIF-8 as the carbon and nitrogen sources to deposit a thin layer of N-doped carbon onto the NH₄Cl-treated Fe-AC catalysts, denoted as Fe-AC-CVD. The orange dashed borders are to highlight these two critical post-treatment steps during the synthesis.

close to the molecular catalyst synthesized by Surendranath et al.²¹. S1 sites are more intrinsically active but are irreversibly and rapidly converted to inactive ferric oxides during the ORR. S2 sites are more stable against demetallation but relatively less active. Therefore, simultaneously realizing high activity and stability for an Fe-N-C catalyst is challenging^{15,23}. The rational catalyst design is essential to increasing the density of stable FeN₄ sites (that is, S2 sites)⁵.

Herein, we developed an Fe-N-C catalyst that achieved excellent stability while maintaining adequate activity through engineering the carbon structures and ligation environments of FeN₄ sites. A critical NH₄Cl treatment at high temperature produced abundant defects in the carbon structure of the Fe-N-C catalyst derived from ZIF-8 precursors that encapsulates Fe₂O₃ nanoparticles. The resulting catalyst attained high activity but is poorly stable due to the dominant S1 sites. Next, a chemical vapour deposition (CVD) was designed to deposit nitrogen-doped carbon thin layers on the NH₄Cl-treated Fe-N-C catalyst, achieving improved stability because of the formation of a substantial proportion of S2 sites. Despite the relatively lower initial activity, the CVD-coated catalyst in membrane electrode assemblies (MEA) retained comparable performance to a Pt/C catalyst after identical accelerated stress tests (ASTs).

Catalyst synthesis, structures and catalytic properties

The scheme using the two-stage approach to prepare highly stable and active Fe-N-C catalysts is described in Supplementary Fig. 1. First, an Fe-N-C catalyst was prepared via thermal activation from an Fe₂O₃@ZIF-8 composite precursor (Supplementary Fig. 2).

In situ scanning transmission electron microscope (STEM) heating experiments were performed to elucidate the structural evolution of Fe₂O₃ nanoparticles to atomically dispersed FeN₄ sites. Atomic resolution images were recorded as the temperature was ramped up to 700 °C. Representative annular dark-field (ADF)-STEM images and electron energy-loss (EEL) point spectra in this temperature range are shown in Fig. 1a,b, respectively. The Fe₂O₃@ZIF-8 composite precursor presented several Fe₂O₃ nanoparticles anchored on the ZIF-8 nanocrystals (Supplementary Figs. 2 and 4). EEL point spectra confirmed that the observed nanoparticles (~5 nm) were iron oxide. The nanoparticles remained intact up to 300 °C but were no longer visible upon further heating to 500 °C. The Fe₂O₃ was transformed into atomically dispersed individual Fe sites, while, simultaneously, the ZIF-8 nanocrystals began to carbonize and converted to nitrogen-doped carbon nanoparticles. At 500 °C, EEL point spectra acquired with the electron probe positioned on an isolated bright atom simultaneously detected Fe and N, suggesting the initial formation of FeN₄ sites²⁴. Similar EEL point spectra at 700 °C further confirmed these atomically dispersed and nitrogen-coordinated Fe sites. The possible formation of Fe-N coordination in FeN₄ sites is responsible for ORR activities, agreeing with our previous work showing that the ORR occurs at thermal temperatures of 400–500 °C and becomes optimal at 700 °C (ref. 9).

The catalyst was further treated with ammonium chloride (AC) salt (NH₄Cl) under an Ar atmosphere at 1,100 °C (Fig. 1c); the resulting catalyst is denoted as Fe-AC. Abundant carbon defects and micro/mesopores were created during the NH₄Cl treatment (Supplementary Figs. 5 and 6 and Supplementary Tables 1 and 2).

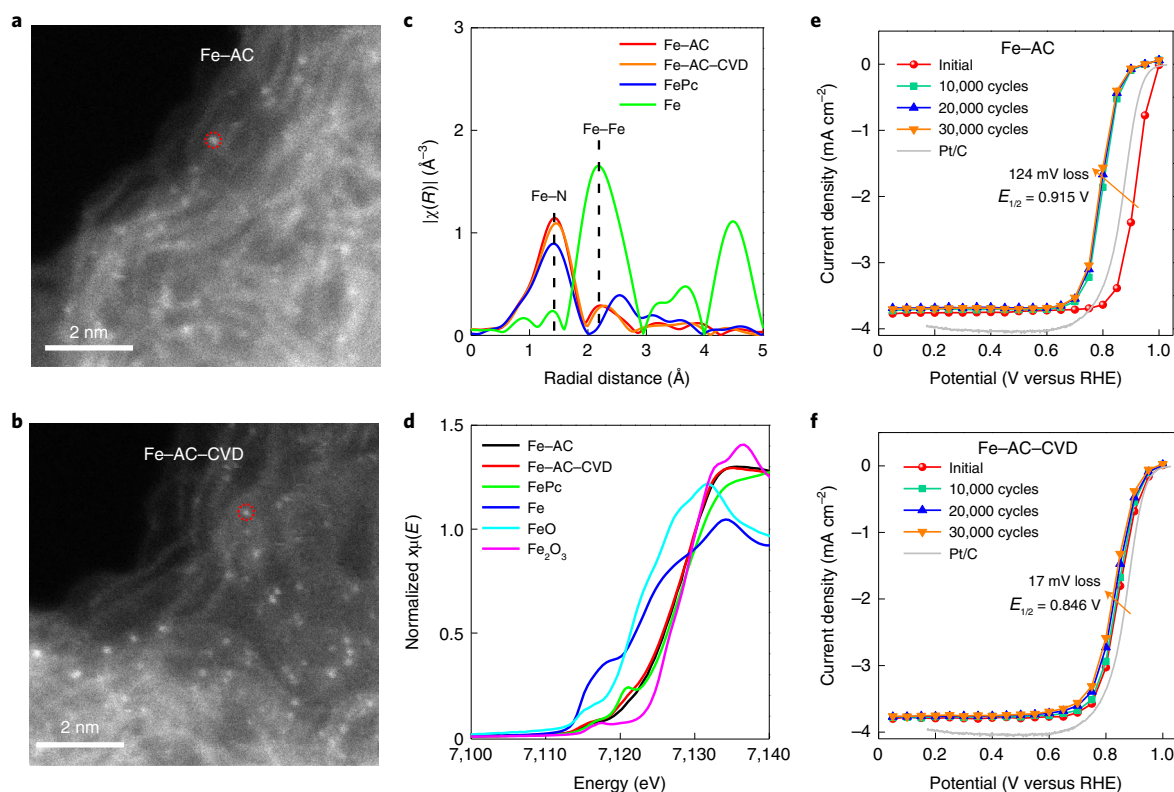


Fig. 2 | Catalyst structures and catalytic properties. **a,b**, Aberration-corrected ADF-STEM images of the Fe-AC and Fe-AC-CVD catalysts. Red circles indicate examples of the types of location where EEL point spectra shown in Supplementary Fig. 7 were acquired. **c,d**, X-ray absorption spectroscopy (XAS) analysis for these two catalysts: Fourier-transformed EXAFS in *R*-space (**c**) and Fe K-edge XANES spectra (**d**). $\chi(R)$ is the magnitude of the Fourier transform of the extended X-ray absorption fine structure. X , μ and E are the absorption length, the absorption coefficient, and the energy of the X-rays, respectively. **e,f**, Initial activity and stability results of these two catalysts from the AST by cycling the potentials (0.6–1.0 V, 30 000 cycles) in O_2 -saturated 0.5 M H_2SO_4 . The orange arrows indicate the activity loss concerning the negative shifts of half-wave potentials.

Next, a CVD process with ZIF-8 nanocrystal powder as carbon and nitrogen sources is used for depositing a thin layer of nitrogen-doped carbon species on the Fe-AC catalyst at 1,100 °C (Fig. 1d); the resulting catalyst is denoted as Fe-AC-CVD. The catalyst has a slightly reduced surface area ($668.6 \text{ m}^2 \text{ g}^{-1}$) than the Fe-AC catalyst ($809.1 \text{ m}^2 \text{ g}^{-1}$). Still, it retains significant porosity across multiple length scales (Supplementary Fig. 5 and Supplementary Table 1).

Figure 2a,b displays ADF-STEM images for the Fe-AC and Fe-AC-CVD catalysts, respectively, showing well-dispersed atomic Fe sites (bright dots) in both catalysts. These Fe sites are probably coordinated with N, as the EEL point spectra showed both N and Fe edges when the electron probe was placed on the transition metal sites that appear as bright dots in the images (Supplementary Fig. 7). The Fourier transform of the extended X-ray absorption fine structure (EXAFS) of these catalysts verifies that both are substantially free of Fe aggregates due to the absence of an Fe-Fe scattering path (Fig. 2c). The Fourier transform is dominated by a scattering path at $\sim 1.4 \text{ \AA}$, attributed to single Fe sites coordinated with low atomic number elements (for example, N, C and O). This scattering path length agrees well with an FeN_4 -containing Fe(Pc). Therefore, this scattering path in the EXAFS Fourier transform can probably be attributed to Fe-N (Fig. 2c), consistent with the electron energy loss spectroscopy (EELS) data that show N co-located with Fe at the atomic level. Model-based EXAFS fitting was carried out to elucidate the local Fe bonding environment, confirming that an Fe site coordinates with four N atoms (Supplementary Fig. 8 and Supplementary Tables 3 and 4) and that the first shell Fe coordination was not changed by the CVD process. A comparison of the energies of the Fe K-edges in X-ray spectra for both catalysts with ferrous and ferric standards,

Fe(II) oxide and Fe(III) phthalocyanine- O_{22} , indicates that the Fe in both catalysts is predominantly in the 3+ oxidation state (Fig. 2d).

The ORR $4e^-$ selectivities and activities of the Fe-AC and Fe-AC-CVD catalysts were evaluated using a rotating ring-disk electrode (RRDE) in an O_2 -saturated 0.5 M H_2SO_4 electrolyte. All the studied Fe-N-C catalysts produced a low H_2O_2 yield of $<2\%$ (Supplementary Fig. 9), suggesting a nearly complete $4e^-$ ORR pathway. The Fe-AC catalyst showed activity with an half-wave potential ($E_{1/2}$) of 0.915 V versus reversible hydrogen electrode (RHE) ($0.6 \text{ mg}_{\text{cat}} \text{ cm}^{-2}$, mg_{cat} denoted as catalyst mass; 900 r.p.m.) and a kinetic current density of $10.3 \text{ mA mg}_{\text{cat}}^{-1}$ at 0.9 V (Fig. 2e), outperforming the catalyst without the NH_4Cl treatment (Supplementary Fig. 10) and, to the best of our knowledge, all previously reported Fe-N-C catalysts (Supplementary Fig. 11 and Supplementary Table 5). The crucial role of NH_4Cl treatment in boosting ORR activity was further verified by using an Fe-N-C catalyst from typical Fe^{3+} doping (Supplementary Fig. 12). X-ray photoelectron spectroscopy (XPS), energy-dispersive X-ray spectroscopy (EDS) and inductively coupled plasma-optical emission spectroscopy analyses indicated that the NH_4Cl treatment slightly reduces Fe content (Supplementary Tables 6–8). Electrochemical stripping of a probe molecule²⁵ (Supplementary Fig. 13) also indicated the slight reduction of Fe site density, suggesting enhanced intrinsic activity concerning turnover frequency (TOF) of $2.75 e^-$ per site per s at 0.9 V. Notably, the Fe-AC catalyst still has a higher FeN_4 active site density (site density = $3.95 \times 10^{-5} \text{ mol g}^{-1}$) than the catalyst from typical Fe^{3+} ion precursors (Supplementary Fig. 14), highlighting the importance of using Fe_2O_3 precursors to increase active site density. The NH_4Cl treatment also dramatically reduced the Zn content

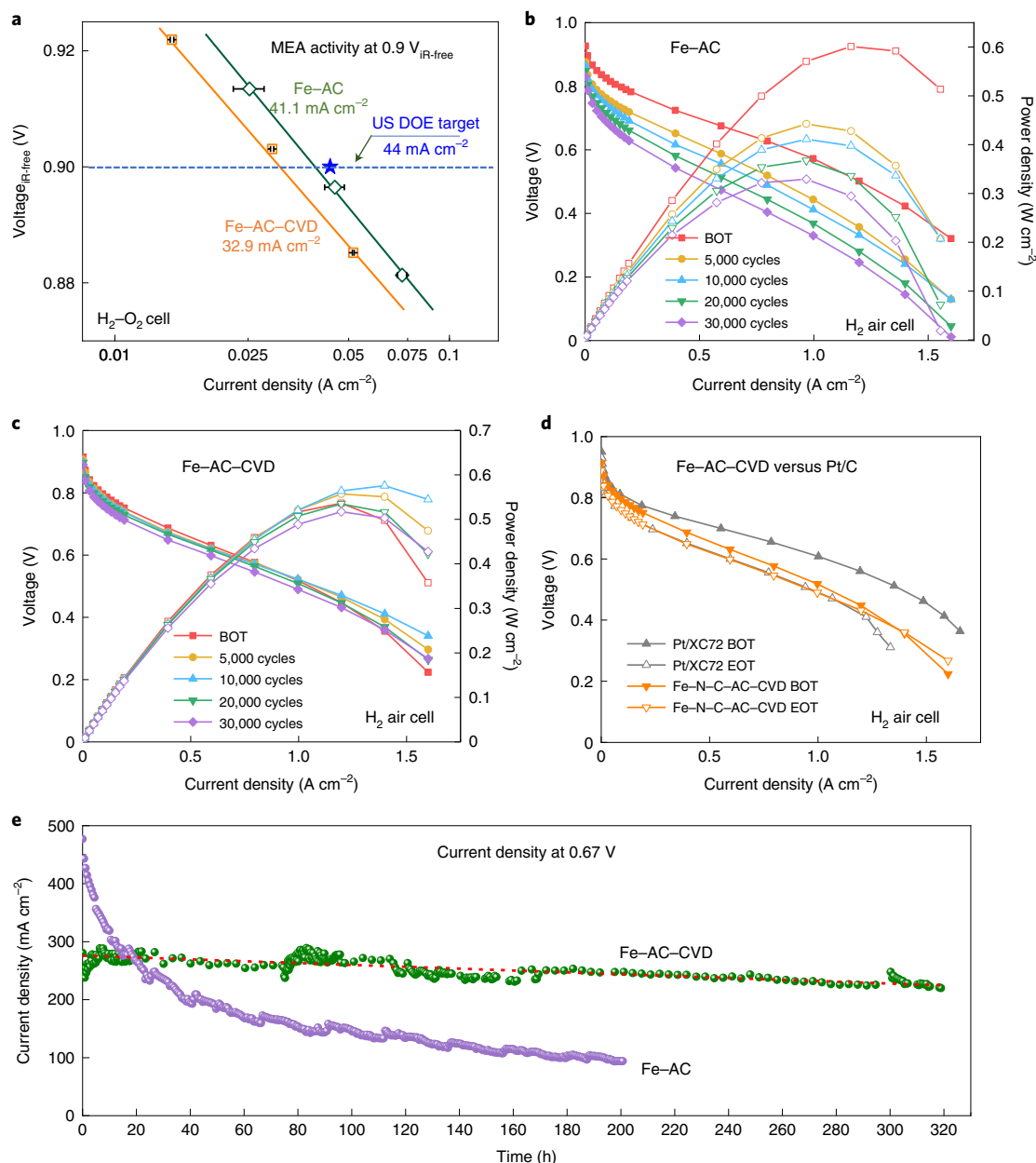


Fig. 3 | MEA performance of the Fe-AC and Fe-AC-CVD cathode catalysts. **a**, Determination of the activities at 0.9 V_{ir-free} in MEA at 100 kPa absolute O₂ pressure; the blue star denotes the US DOE 2025 target (44 mA cm⁻²). **b,c**, H₂ air fuel cell polarization plots of the Fe-AC (**b**) and Fe-AC-CVD (**c**) cathode recorded under 100 kPa absolute air pressure at air and H₂ flow rates of 500 sccm and 300 sccm, respectively, after various numbers of square wave AST cycles (0.6 V to OCV, ~0.92 V) at H₂ and air flows and under ambient pressure. The sccm represents standard cubic centimeter per minute; the BOT stands for the beginning-of-test. **d**, Comparison of H₂ air fuel cell polarization plots of the Fe-AC-CVD and a commercial Pt/XC-72 catalyst recorded at BOT and after the 30,000 cycle stability AST (EOT: end-of-test). **e**, Long-term fuel cell life tests for both Fe-N-C catalysts under H₂ air conditions at a constant potential of 0.67 V (100 kPa air pressure and flow rates of air 200 sccm and H₂ 200 sccm). Anodes: Pt/C, 0.20 mg_{Pt} cm⁻², 100% RH, and 100 kPa absolute H₂ pressure. Membrane: Nafion 212. Temperature: 80 °C. MEA area: 5.0 cm². Error bars represent the standard deviation for three separate measurements.

and mitigated the negative impacts of Zn on catalyst performance²⁶ (Supplementary Fig. 15). Despite the high ORR activity in acids, unfortunately, the Fe-AC catalyst suffered from significant activity loss (124 mV in $E_{1/2}$) after a standard stability AST (30,000 cycles from 0.6 V to 1.0 V in O₂-saturated 0.5 M H₂SO₄) (Fig. 2e), much larger than the catalyst before the NH₄Cl treatment (34 mV loss) (Supplementary Fig. 11).

In contrast, the Fe-AC-CVD catalyst exhibited both high activity ($E_{1/2}$ of 0.846 V) and remarkable durability (only 17 mV loss in

$E_{1/2}$ after the AST) (Fig. 2f). We also found that the ZIF-8 precursor used for the CVD is essential for achieving an optimal balance of activity and stability, compared with other N-containing and N-free hydrocarbon compound precursors (Supplementary Figs. 16 and 17 and Supplementary Table 9). The CVD process also improved stability for the less active Fe-N-C catalyst without the NH₄Cl treatment but resulted in much lower initial activity ($E_{1/2}$ = 0.773 V) (Supplementary Fig. 18). Therefore, the two-stage approach through combining an NH₄Cl treatment and a nitrogen-doped carbon

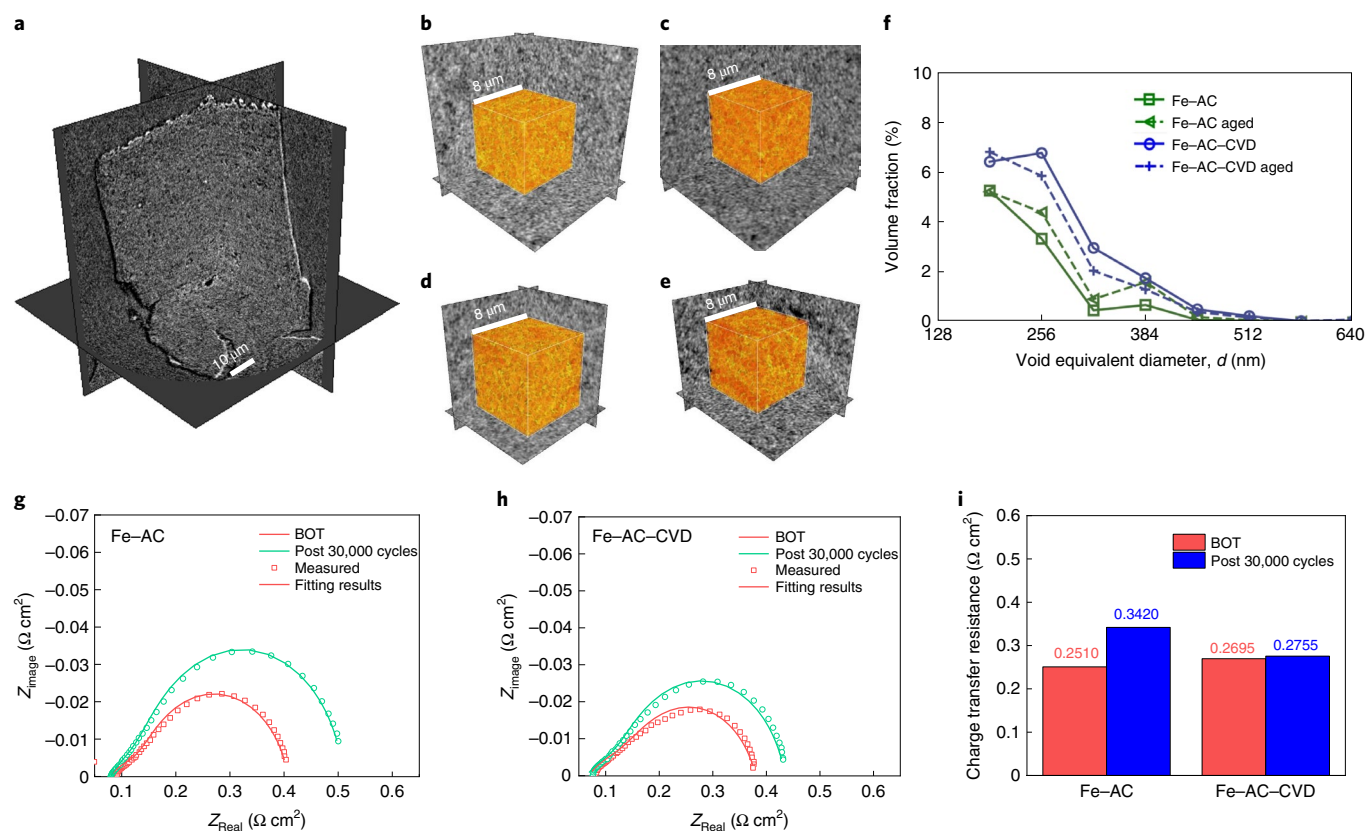


Fig. 4 | Nano-CT tomography and EIS analysis of PGM-free cathode. **a–e**, Phase-contrast renderings of the full laser-milled pillar from the stable Fe-AC-CVD sample (**a**) and extracted sub-volumes of Fe-AC (**b**), Fe-AC aged (**c**), Fe-AC-CVD (**d**) and Fe-AC-CVD aged samples (**e**). **f**, Macroscopic void feature distributions from sub-volumes shown in **b–e**. Note that the bright pixels in the phase-contrast renderings (**a–e**) correspond to solids, and dark pixels correspond to voids. **g,h**, Comparison of measured and simulated EIS at the BOT and after 30,000 cycles during the AST at the current density of 0.8 A cm^{-2} for MEAs from the Fe-AC (**g**) and the Fe-AC-CVD (**h**) cathode in MEAs. Z_{real} represents the real impedance in Nyquist plots. **i**, Comparison of the charge transfer resistance of the ORR under fuel cell operating conditions for these two cathodes simulated from EIS.

deposition is crucial for simultaneously achieving enhanced stability and adequate activity.

The $E_{1/2}$ loss during the stability ASTs was proportionally consistent with the determined loss of FeN_4 sites through the electrochemical probe²⁵ for both catalysts (Supplementary Fig. 19). The unstable Fe-AC catalyst suffered a more significant and faster FeN_4 site loss (20%) after 10,000 AST cycles, relative to the stable Fe-AC-CVD catalyst (2.6% loss) in good agreement with STEM-EDS analysis for fresh and aged catalysts (Supplementary Table 8). We also investigated the demetallation during ASTs in $0.5 \text{ M H}_2\text{SO}_4$ electrolytes with different atmospheres (N_2 versus O_2). Similar $E_{1/2}$ losses occurred in both electrolytes for these catalysts (Supplementary Fig. 20), suggesting that, unlike the previous reports^{17,27,28}, O_2 or H_2O_2 is probably not the main culprit causing the degradation of these highly active Fe-N-C catalysts derived from $\text{Fe}_2\text{O}_3/\text{ZIF-8}$ precursors. Instead, the electrochemically driven demetallation of FeN_4 active sites is a primary degradation mechanism.

Fuel cell performance and durability

Both catalysts were incorporated into MEAs as the cathode to evaluate their performance and durability under fuel cell operating conditions. The Fe-AC cathode generated an initial current density of 44.2 mA cm^{-2} at $0.9 V_{\text{IR-free}}$, O_2 partial pressure of $100 \text{ kPa}_{\text{abs}}$ and an average of 41.1 mA cm^{-2} from three consecutive polarization curves (Fig. 3a and Supplementary Fig. 21), approaching the US Department of Energy (DOE) 2025 target (44 mA cm^{-2}) (ref. 3). Under practical H_2 air conditions, the cathode generated

151 mA cm^{-2} at 0.80 V , comparable to a typical Pt/C cathode ($0.1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$) (Supplementary Fig. 22). The peak power density reached 601 mW cm^{-2} , significantly improved than other Fe-N-C catalysts^{5,29,30}. However, similar to rotating disk electrode (RDE) stability tests in $0.5 \text{ M H}_2\text{SO}_4$ electrolytes, the Fe-AC-cathode in Nafion-based MEAs suffered a significant and rapid performance loss during the stability AST voltage cycling, losing 94% of its current density at 0.8 V after 30,000 cycles under H_2 air (Fig. 3b and Supplementary Table 10).

An MEA with the Fe-AC-CVD cathode exhibited a promising activity of 33 mA cm^{-2} at $0.9 V_{\text{IR-free}}$ under O_2 (Fig. 3a), which was stable during the three consecutive tests (Supplementary Fig. 21b). The Fe-AC-CVD cathode also achieved decent H_2 air performance of 85 mA cm^{-2} at 0.8 V ($>60 \text{ mA cm}^{-2}$ DOE 2021 milestone) and 430 mA cm^{-2} at 0.675 V ($\geq 300 \text{ mA cm}^{-2}$) at the beginning of test (BOT). The stable cathode further demonstrated promising MEA durability, only losing 30 mV (5.1%) at a current density of 0.8 A cm^{-2} after the 30,000 voltage cycling AST (Fig. 3c), which met the US DOE 2025 target ($\leq 30 \text{ mV}$ loss at 0.8 A cm^{-2}) (ref. 31). The peak power density was reduced by only 3.9% from 535 (BOT) to 514 mW cm^{-2} (EOT: end-of-test), which is even higher than BOT peak power densities for most Fe-N-C catalysts (Supplementary Fig. 23). The EOT performance of the Fe-AC-CVD cathode is comparable to a typical Pt/C cathode ($0.1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$) after the identical stability AST (Fig. 3d). Unlike the Fe-AC, the Fe-AC-CVD cathode can maintain the same open-circuit voltages (OCVs) during the AST, suggesting FeN_4 sites in the catalyst are intrinsically stable.

We further carried out long-term MEA stability tests for both cathodes under H_2 air at 0.67 V, a practical voltage to achieve high energy efficiency³² (Fig. 3e). A fast degradation occurred on the Fe-AC cathode (80% loss after 200 h). In contrast, 87% of the original performance was retained after the 319 h life test for the Fe-AC-CVD cathode, showing a low current density decay rate of $0.132 \text{ mA cm}^{-2} \text{ h}^{-1}$. The corresponding polarization curves recorded at different time intervals are shown in Supplementary Fig. 24. The possible reasons for the slow decay were discussed in Supplementary Note 1.

X-ray nano-computed tomography (nano-CT) analysis (Fig. 4a–f and Supplementary Fig. 25) is consistent with the electron microscopy analysis (Supplementary Fig. 26 and Supplementary Table 11), showing no statistically significant changes in primary catalyst particles, microporosity or void distribution shape between the fresh and aged cathodes. The charge transfer resistance (R_{ct}) at 0.8 A cm^{-2} determined by electrochemical impedance spectroscopy (EIS) is significantly increased for the Fe-AC cathode from $0.251 \Omega \text{ cm}^2$ to $0.342 \Omega \text{ cm}^2$ after the AST, relative to the Fe-AC-CVD cathode from $0.270 \Omega \text{ cm}^2$ to $0.276 \Omega \text{ cm}^2$ (Fig. 4g–i). An equivalent circuit used for analysing these impedance spectra is shown in Supplementary Fig. 27, and Supplementary Note 2 provides a detailed discussion.

We further carried out MEA stability ASTs under H_2/N_2 conditions to elucidate possible degradation mechanisms (Supplementary Fig. 28). In agreement with RDE stability studies in both O_2 - and N_2 -saturated $0.5 \text{ M H}_2\text{SO}_4$ electrolytes, similar performance losses were observed during the AST under air and N_2 (Supplementary Table 12), suggesting that the primary degradation mechanism is electrochemically driven demetallation. The Fe-AC-CVD cathode exhibited higher resistance against electrochemical oxidation in high voltage regions under O_2 -free environments (Supplementary Fig. 29), consistent with improved stability. The extensive stability evaluation and analysis verified the effectiveness of the CVD approach to stabilizing the active FeN_4 sites against electrochemically driven demetallation under fuel cell environments.

Mechanistic insights into the stability enhancement

Extensive characterization techniques were employed to study the change in coordination environments and local carbon structures of the FeN_4 sites in the highly stable Fe-AC-CVD catalyst, aiming to elucidate stability enhancement mechanisms. The carbon sp^2/sp^3 ratio of these two catalysts before and after the CVD was compared using the Auger electron spectroscopy D parameter, that is, the distance between the peak maximum and minimum of the first derivative of the C KLL (the K shell represents the $1s$ orbital and the L shell represents the $2s$ and $2p$ orbitals). (Supplementary Fig. 30). For pure sp^3 carbon (for example, diamond), the D parameter equals $\sim 13 \text{ eV}$, while, for pure sp^2 (for example, highly ordered pyrolytic graphite), it is $\sim 21 \text{ eV}$. The Fe-AC-CVD (18.45 eV) catalyst has a slightly higher average D parameter, that is, a larger sp^2 content, than the Fe-AC (17.40 eV) catalyst. The increased sp^2 content and chemical state of the carbon structures in these catalysts were also determined from the high-resolution XPS C $1s$ spectra (Supplementary Fig. 31 and Supplementary Table 13) and Raman spectroscopy analysis (Supplementary Fig. 32). The change in local carbon structure may be responsible for the significantly enhanced stability of the Fe-AC-CVD catalyst due to the more graphitized and stable carbon structures adjacent to FeN_4 sites.

Both catalysts compose crumpled few-layer graphitic structures, showing no significant differences according to ADF and bright-field STEM images (Supplementary Fig. 33). To elucidate the subtle changes in the carbon morphology and structure, an identical location (IL)-STEM experiment was designed and carried out with the Fe-AC catalyst supported on a porous SiN grid. For this experiment, ADF-STEM imaging and EELS were performed on the same regions of the catalyst before and after the CVD

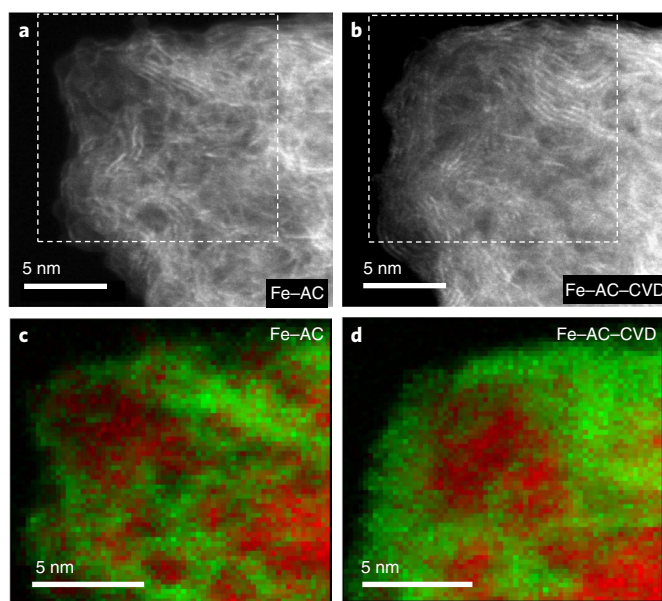


Fig. 5 | Carbon structure changes in catalysts after nitrogen-doped carbon layer deposition. a–d, Annular dark-field IL-STEM images (a,b) and carbon K-edge EELS orientational maps (c,d) generated by MCR from the same region of an Fe-AC catalyst before and after the CVD process. In c and d, red indicates domains where graphitic sheets are oriented perpendicularly to the beam direction, while green indicates domains with sheets parallel to the beam. The increase in green on the surface of the catalyst between c and d confirms the deposition of graphitic carbon layers in a shell-like structure due to the CVD process. White boxes mark typical catalyst's surface coated with nitrogen-carbon layers. Maps in c and d were taken from the dashed regions in a and b, respectively.

treatment at $1,100^\circ \text{C}$ in a tube furnace (Fig. 5a,b and Supplementary Figs. 34–38). Additional thin graphitic layers were observed on the particle surface after the CVD, forming a shell-like structure. In contrast, the interior features of the catalyst particles remained relatively unchanged.

The shell-like nature of these additional graphitic layers was further confirmed by EELS mapping (Fig. 5c,d). Multivariate curve resolution (MCR) analysis of the EELS data, which allows regions of the sample containing distinct spectra to be identified and separated, enabled mapping of the graphitic layer orientations before and after the CVD process (Supplementary Fig. 37) (ref. 33). The additional graphitic layers deposited during the CVD formed a shell-like structure at the particle surface, as indicated by the more pronounced green regions. Relevant discussions are in Supplementary Note 3. The emergence of similar shell-like structures was observed in other catalyst regions after the CVD as well. The dashed line in Supplementary Fig. 36 denotes the change of a particle surface resulting from the CVD process, gaining approximately 1 nm of additional material in these specific deposition conditions. STEM-EDS analysis (Supplementary Fig. 38) indicates that, after the CVD treatment, the deposited layers on the particle surfaces showed slightly higher N content than the particle interiors (Supplementary Table 14). IL-STEM annular dark-field (ADF) images also showed individual Fe sites at the edges of the carbon support (arrows in Supplementary Fig. 36), indicating that the deposited thin carbon layers do not block active Fe sites.

The local structures of FeN_4 sites in both catalysts were further investigated using room-temperature ^{57}Fe Mössbauer spectroscopy (Fig. 6a,b). Two doublets, labelled D1 and D2, were identified in both catalysts, corresponding to two types of FeN_4 site with different local structures: highly active and less stable $\text{FeN}_4\text{C}_{12}$ S1 site and

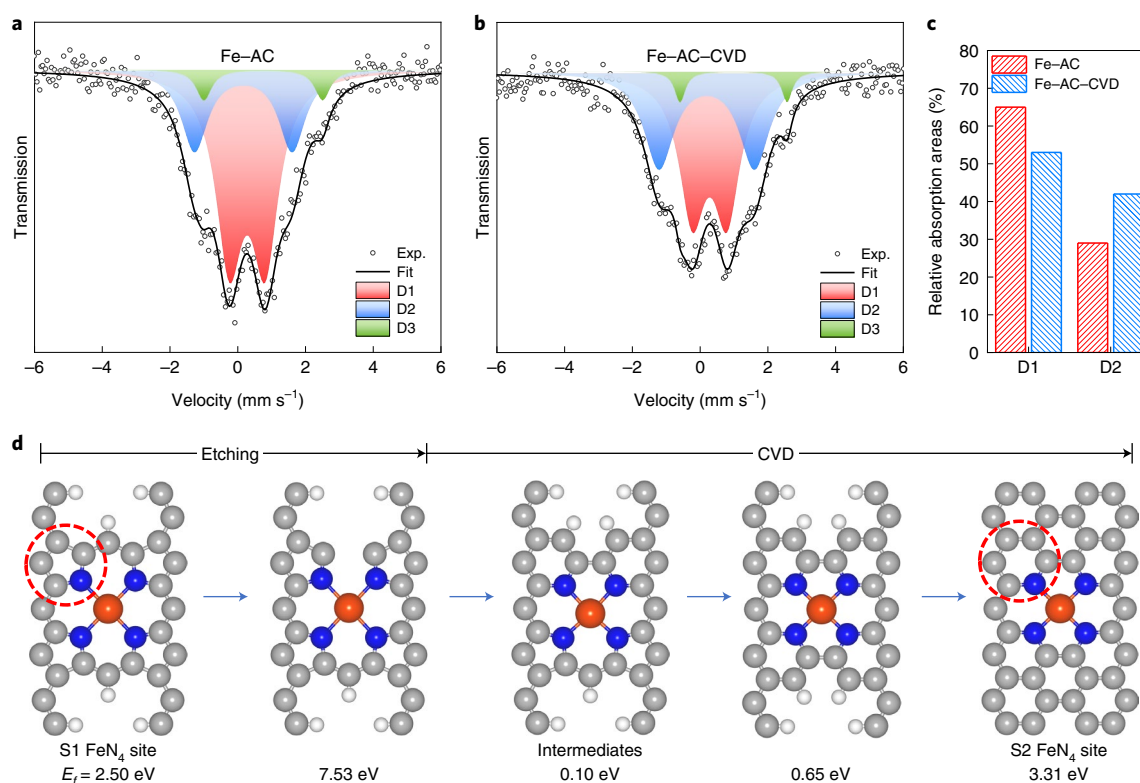


Fig. 6 | Possible FeN_4 site conversion during the CVD process. **a, b**, The ^{57}Fe Mössbauer spectra of the Fe-AC and Fe-AC-CVD catalysts. Exp., experimental. **c**, Comparison of D1 (65%) and D2 (29%) contents for the Fe-AC with D1 (53%) and D2 (42%) contents for the Fe-AC-CVD catalysts. Red dash circles mark pyrrolic N and pyridinic N in FeN_4 sites. **d**, Possible structural evolution pathway from an S1 to an S2 site. The grey, blue, white and orange balls represent C, N, H and Fe atoms, respectively. E_f denotes free energy. Blue arrows represent possible structural evolution pathway.

highly stable and less active $\text{FeN}_4\text{C}_{10}$ S2 site (Supplementary Fig. 39 and Supplementary Note 4) (refs. ^{22,34–36}). Quantitative analysis indicates that the Fe-AC catalyst contains 65% S1 and 29% S2 of the absorption area, while the stable Fe-AC-CVD catalyst comprises 53% S1 and 42% S2 FeN_4 sites (Fig. 6c and Supplementary Table 15). The CVD process probably increases the stable S2 site content, compared with either the unstable Fe-AC or other catalysts typified by Mössbauer results^{37–39}. Considering Mössbauer is a bulk technique, the relatively higher S2 content in the Fe-AC-CVD catalyst is due to the possible changes in coordination ligation and local structures of FeN_4 sites during the high-temperature CVD process. Thus, the deposition of a thin layer of N-doped carbon at high temperatures probably led to a transition from S1 to S2 sites in the surface layers of the catalyst, primarily responsible for dramatically enhanced catalyst stability. Density-functional theory (DFT) calculations were further conducted to shed light on the possible S1 to S2 transformation from the thermodynamic point of view and also propose a kinetically favourable pathway (Fig. 6d). At first, the calculated formation energy of the S2 site is more negative than the S1 site, suggesting that this conversion is thermodynamically favourable (Supplementary Note 5). The defect-rich S1 site could undergo a structural change during the CVD process at high temperatures (for example, 1,100 °C) such that a transformation of pyrrolic nitrogen into pyridinic nitrogen by deposition of carbon atoms into vacant sites. The activation energy for a pyrrolic N transitioning to a pyridinic N was predicted to be 2.87 eV (Supplementary Fig. 40 and Supplementary Note 6), which is surmountable at 1,100 °C during the CVD process⁴⁰. The proposed models do not elaborate all the possible pathways for such a transformation process. For example, the conversion of S1 sites without local defects⁴¹ to S2 sites could be kinetically sluggish. This highlights the importance of the NH_4Cl

treatment during the synthesis to create sufficient carbon defects for favourable S1 to S2 site conversion via the CVD.

DFT calculations were further performed to elucidate the effect of coordination ligation and local structure on the electronic and catalytic properties of S1 and S2 FeN_4 sites. The predicted quadrupole values of Fe in our DFT modelled FeN_4 sites are consistent with those observed in Mössbauer spectroscopy (Supplementary Table 16 and Supplementary Note 7). The corresponding electronic structures and oxidation states of Fe ions in the two FeN_4 sites were also theoretically compared (Supplementary Fig. 41, Supplementary Table 17 and Supplementary Note 8). Like previous Fe-N-C catalysts^{22,42} the DFT-predicted quadrupole splitting (QS) values of Fe (at 0 K) are similar to those measured at 300 K in this study. These results reveal that the atomistic models of S1 and S2 FeN_4 sites in this study are consistent with those identified in the experiment.

The intrinsic catalytic activity of the two FeN_4 sites towards the 4e[−] associative ORR pathway was predicted (Fig. 7a,c), concerning both the adsorption energies (Supplementary Table 18) and the kinetic O–O bond dissociation process (Supplementary Figs. 42 and 43). The ORR on the S1 site becomes an exothermic reaction when the electrode potential is lower than a limiting potential of 0.73 V, higher than that on the S2 site (0.65 V). Climbing image nudged elastic band⁴³ calculations suggest that OOH dissociation is kinetically feasible on both sites. The calculated electron distribution indicates more charge depletion along the direction perpendicular to the catalyst surface on the S2 site (Fig. 7b) than that on the S1 site (Fig. 7d), unveiling that the central Fe in the S2 site has more unoccupied *d* orbital to bind with O_2 much stronger, that is, relatively lower intrinsic activity than the S1 sites.

DFT calculations were further performed to theoretically study the stability of both FeN_4 sites against the demetallation (Fig. 8a,b).

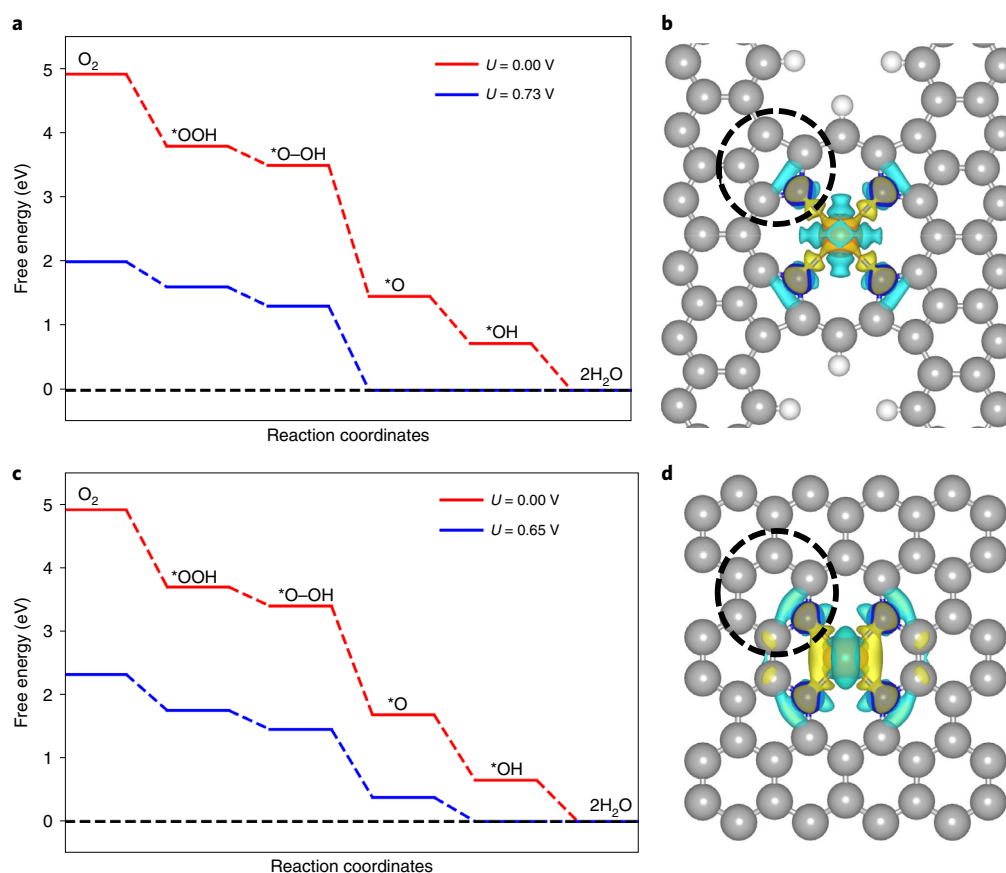


Fig. 7 | DFT calculations to elucidate the activity of two types of FeN_4 site. **a, c**, Predicted free energy evolution for ORR through $4e^-$ associative pathway on S1 site (**a**) and S2 site (**c**) under electrode potentials of $U = 0.00$ V and their corresponding limiting potential, respectively. Asterisk denotes the adsorption site. **b, d**, The charge density difference of the central part of S1-type FeN_4 site (**b**) and S2-type FeN_4 site (**d**) in Fe-AC and Fe-AC-CVD catalysts. The charge density difference is calculated as $\rho(Fe - N_4/C) - \rho(Fe) - \rho(N_4/C)$. Cyan and yellow represent charge accumulation and depletion in the region, respectively; the iso-surface value is $0.005 e \text{ \AA}^{-3}$. Black dash circles mark pyrrolic N and pyridinic N in FeN_4 sites.

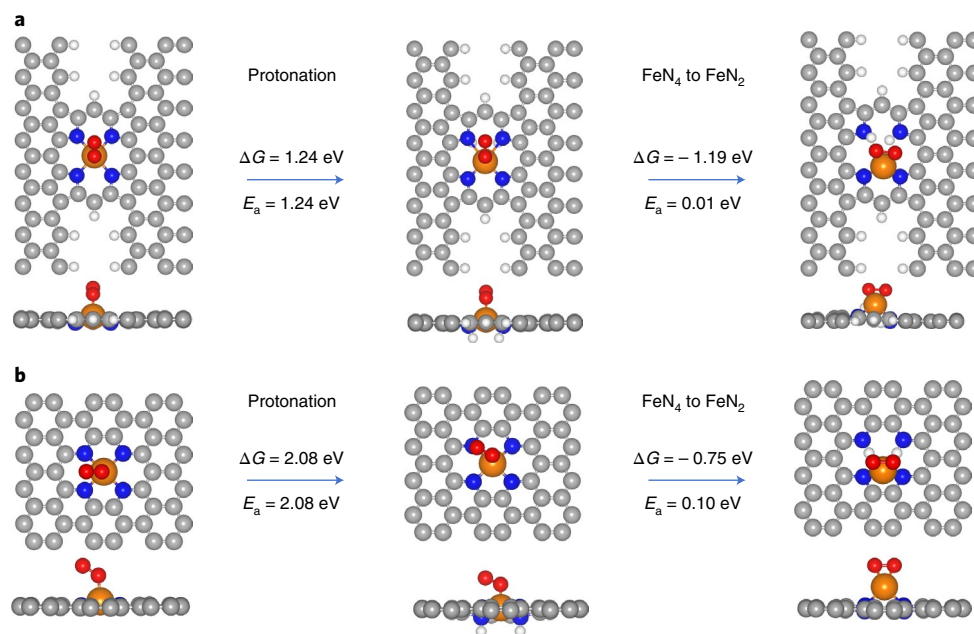


Fig. 8 | DFT calculations to study the stability of two types of FeN_4 site. **a, b**, Structural evolution during the demetallation of central Fe from an S1-type FeN_4 site (**a**) and an S2-type FeN_4 site (**b**). In these figures, the grey, blue, orange, red and white balls represent C, N, Fe, O and H atoms, respectively. E_a and ΔG represent the activation energy and free energy change for the corresponding reaction, respectively.

We proposed that the demetallation process of FeN_4 sites consists of three sequential steps. First, two N atoms in an FeN_4 moiety are protonated to form two N–H bonds. Then the central Fe ion, together with adsorbed O_2 , moves away from the N_4 coordination into an inactive N_2 coordination. Finally, the Fe–O_2 desorbs from catalysts (Supplementary Note 9). Compared with the N_4 to N_2 coordination transition and the desorption of Fe–O_2 (ref. 44), the nitrogen protonation step with the highest activation energy is the rate-determining step during the demetallation kinetic process. The activation energy for the nitrogen protonation step was predicted to be 1.24 eV and 2.08 eV for S1 and S2 sites, respectively, indicating better intrinsic stability of the S2 site against the demetallation kinetically.

Conclusions

In summary, we demonstrated a highly stable and active Fe–N–C oxygen-reduction cathode catalyst for PEMFCs, representing a critical step towards replacing Pt and making PEMFCs viable for numerous applications. We explored how the intrinsic stability of FeN_4 active sites in the catalyst can be dramatically enhanced by regulating the catalyst's local carbon structure and converting unstable pyrrolic N-coordinated S1 ($\text{FeN}_4\text{C}_{12}$) to stable pyridinic N-coordinated S2 sites ($\text{FeN}_4\text{C}_{10}$). The combination of an NH_4Cl treatment to create a high density of carbon defects with a subsequent CVD process to deposit a thin layer of nitrogen-doped carbon at the catalyst surface was found to be crucial for achieving high Fe–N–C catalyst stability, while maintaining adequate activity.

The catalyst with only NH_4Cl treatment showed high ORR activity ($E_{1/2}=0.915\text{ V}$) and MEA performance (44.2 mA cm^{-2} at $0.9\text{ V}_{\text{ir-free O}_2}$) but suffered significant and rapid performance loss. The stability issue of this highly active catalyst was addressed by subsequently depositing a thin layer of nitrogen-doped carbon on the catalyst using CVD with a modest impact on activity (32.9 mA cm^{-2} at $0.9\text{ V}_{\text{ir-free O}_2}$, 26% decrease). Its long-term stability was demonstrated in an MEA using a standard voltage cycling AST (30,000 voltage cycles under H_2 air conditions) and a fuel cell life test (>300 h) at 0.67 V under H_2 air conditions. The MEA lost only 30 mV at 0.8 A cm^{-2} and 21 mW cm^{-2} (3.9%) of peak power density after the AST, meeting the challenging DOE stability target for PEMFC cathode catalysts. The MEA retains sufficient performance and its EOT performance is comparable to a typical Pt/C cathode ($0.1\text{ mg}_{\text{Pt}}\text{ cm}^{-2}$) after applying identical ASTs. Therefore, simultaneously achieving promising activity and stability in a single PGM-free catalyst reported here demonstrated a great promise towards replacing Pt catalysts in PEMFCs and ultimately addressing the cost barrier for current PEMFCs.

Methods

Catalyst synthesis. During the synthesis, an Fe–N–C catalyst with a high FeN_4 active site density was prepared via pyrolysis of an $\text{Fe}_2\text{O}_3@\text{ZIF-8}$ composite precursor consisting of ultra-fine Fe_2O_3 nanoparticles encapsulated in ZIF-8 nanocrystals. In a typical procedure to synthesize $\text{Fe}_2\text{O}_3@\text{ZIF-8}$ composite precursors, Fe_2O_3 nanoparticles (Alfa-Aesar) with a size of $\sim 5\text{ nm}$ (10 mg) and zinc nitrate hexahydrate (6.78 g) were dispersed and dissolved into a methanol solution (150 ml). The other methanol solution (150 ml) containing 2-methylimidazole (7.92 g) was prepared. Then both solutions were mixed and heated at 60°C for 24 h. The resulting precipitant was collected and washed with ethanol, then dried at 60°C in a vacuum oven to obtain $\text{Fe}_2\text{O}_3@\text{ZIF-8}$ composite precursor. In the first step to synthesize Fe–N–C catalysts, the composite precursors were subjected to a heating treatment at 800°C for 30 min under flowing Ar gas to obtain a sample denoted as Fe–N–C-800. We found that Fe_2O_3 nanoparticles can gradually release Fe contents during thermal activation, which are captured by surrounding defected nitrogen ligands from ZIF-8s, increasing atomically dispersed FeN_4 site density⁷, superior to the typically used Fe^{3+} ion precursors such as FeCl_3 and $\text{Fe}(\text{NO}_3)_3$.

Then the Fe–N–C-800 (100 mg) were ground with NH_4Cl salts (300 mg) thoroughly, followed by a heating treatment at $1,100^\circ\text{C}$ (taking 30 mins to rapidly increase the temperature to $1,100^\circ\text{C}$) under Ar flow for 1 h to obtain the first catalyst, denoted as Fe–AC (AC: ammonia chloride) catalyst. NH_4Cl decomposes to NH_3 and HCl gas at high temperatures, which produce substantial internal stress and etch the carbon, thus creating a multitude of micropores and carbon defects⁴⁵, similar to previously reported Fe–N–C catalysts with NH_3 gas treatments^{6,46}.

The HCl probably further dissociates at high temperatures to form H_2 and Cl_2 gases, and according to Gewirth et al.⁴⁷, the Cl_2 gas reacts with residual Fe aggregates in catalysts and facilitates the formation of atomically dispersed Fe sites.

In the second step, the Fe–AC catalyst was subjected to deposition of a thin layer of nitrogen-doped carbon via a CVD approach. ZIF-8 nanocrystals were discovered as optimal carbon and nitrogen sources to release N/C species at high temperatures and gradually deposit them onto the Fe–AC catalyst located downstream of the tube furnace. In a typical procedure, 150 mg pristine ZIF-8 nanocrystals and 50 mg Fe–AC were separately placed on two high-temperature alumina combustion boats located at the up- and downstream places in a tube furnace, respectively. The tube furnace was heated to $1,100^\circ\text{C}$ under an optimal Ar flow rate of 10 ml min^{-1} for 1 h. The CVD conditions, such as the amount of ZIF-8 precursors, flow rates, temperatures and duration, were carefully optimized. The resulting catalyst was denoted as Fe–AC–CVD.

Physical characterization. XPS was performed using a Thermo Scientific Model K-Alpha XPS instrument. The instrument utilizes monochromated, micro-focused, Al K_{α} X-rays (1,486.6 eV) with a variable spot size (that is, 30–400 μm). Analyses of the sample were performed with the 400 μm X-ray spot size for maximum signal and to obtain an average surface composition over the largest possible area. The instrument has a hemispherical electron energy analyser equipped with a 128-channel detector system. Base pressure in the analysis chamber is typically 2×10^{-9} mbar or lower. Samples were prepared for analysis by dispersing the powder material onto double-sided tape fixed to clean glass slides. Sufficient material was used to prevent any interfering signals from the tape. After transferring the sample into the analysis chamber, a survey spectrum (step size 1 eV, pass energy = 200 eV) was acquired to determine all elements present. Next, high-resolution core-level spectra (step size 0.1 eV, pass energy = 50 eV) were acquired for detailed chemical state analysis. C KLL (Auger) spectra were acquired using a step size of 2 eV and a pass energy of 100 eV. All spectra were acquired with the charge neutralization flood gun (combination of low-energy electrons and argon ions) turned on to maintain a stable analysis condition. The typical pressure in the analysis chamber with the flood gun operating is 2×10^{-7} mbar. Data were collected and processed using the Thermo Scientific Avantage XPS software package (v.5.96).

Micromeritics TriStar II measured the N_2 isothermal adsorption/desorption for the catalysts at 77 K. Aberration-corrected STEM imaging and EELS were performed on a Nion UltraSTEM equipped with a Gatan Enfina and operated at 60 kV. The in situ heating experiments were performed on micro-electromechanical systems (MEMS)-based heating chips using a specialized Protochips heating platform designed for Nion instruments. IL-STEM was performed on a JEOL NEOARM operated at 80 kV. MCR analysis of the carbon K-edge fine structure was performed in Python using the 'pyMCR' package⁴⁸. The red regions in Fig. 5c,d corresponds to graphitic layers oriented perpendicularly to the electron beam (that is, parallel to the page), and green regions correspond to graphitic layers parallel to the electron beam (that is, into the page). The CVD process was performed after the catalyst powder was dispersed on the TEM grid. It is expected that the exposed surfaces of the catalyst, that is, those areas imaged, experienced a much higher flux of the CVD material than the majority of the material under normal synthesis conditions, thus exaggerating the amount of deposited material observed. Additional STEM–EDS analysis was performed on a FEI Talos operated at 200 kV with data processing performed in the Bruker Esprit software.

Fe K-edge X-ray absorption spectra were measured at beam line 10BM, The Materials Research Collaborative Access Team (MRCAT), Advanced Photon Source, Argonne National Laboratory. Data reduction, data analysis and EXAFS fitting were performed with the Athena, Artemis and IFEFFIT software packages. Mössbauer data were acquired for 21 days with the samples at room temperature and without the application of an external magnetic field using a $^{57}\text{Co}/\text{Pd}$ source in constant acceleration modes. The spectra were analysed using WinNormos programme, a commercial package provided by WissEl—Wissenschaftliche Elektronik. Mössbauer doublets were fit using the Lorentzian mode of WinNormos.

Nanoscale X-ray computed tomography (nano-CT) (XRadia UltraXRM-L200, Carl Zeiss X-ray Microscopy) was employed to study Fe–N–C cathode before and after stability tests to determine whether performance degradation in MEAs occurred on a scale smaller than the 150 nm resolution. The cathode samples were submerged in saturated aqueous caesium (Cs) sulfate solution for at least one day to exchange the protons in the ionomer with Cs cations for improved ionomer attenuation and contrast with the iron and nitrogen-doped carbon support. The samples were rinsed with deionized water and allowed to dry in the nano-CT chamber before imaging. We used the nano-CT's large field of view optics, which have a resolution of 150 nm and a field of view of 65 μm . We performed imaging in both traditional absorption contrast and Zernike phase-contrast modes for the ionomer distributions and solid/void characterizations, respectively. The radiograph sets were aligned and reconstructed using Zeiss' proprietary reconstruction software, which uses the filtered back-projection algorithm, yielding solid volumes of intensity data corresponding to density and atomic number in the absorption scans and solid/void interfaces in the phase-contrast scans.

Electrochemical measurements. An electrochemical workstation (CHI760b) equipped with Pine AFMSRCE 3005 in a three-electrode cell at room temperature was employed to carry out all RDE and RRDE measurements. A $\text{Hg}/\text{Hg}_2\text{SO}_4$ (K_2SO_4 -saturated) electrode and a graphite rod were used as the reference and counter electrodes, respectively. A glassy carbon RRDE coated with PGM-free catalyst ink was the working electrode with a controlled loading of 0.6 mg cm^{-2} at 900 r.p.m. and room temperature in $0.5 \text{ M H}_2\text{SO}_4$ electrolyte for all ORR tests. A commercial TKK (Tanaka Kikinzoku Kogyo, Co., Ltd) 20 wt% Pt/C catalyst was employed as a reference and tested in 0.1 M HClO_4 electrolyte with a loading of $60 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$. Before each test, the reference electrode was calibrated to a RHE in the same electrolyte. The catalyst ink for the RDE and RRDE tests was prepared by mixing 5 mg catalyst with the diluted Nafion solution under ultrasonic conditions for 30 min. Steady-state polarization curves of PGM-free catalysts were recorded using a potential staircase at a step of 0.05 V at an interval of 30 s from 1.0 V to 0 V versus RHE. As for Pt/C catalyst, linear scanning voltammetry plots were recorded from 0 V to 1.0 V at a scanning rate of 10 mV s^{-1} . Four-electron selectivity and H_2O_2 yield during the ORR were determined by using RRDE with a constant Pt ring potential (1.20 V versus RHE) to measure H_2O_2 electrooxidation current density during the ORR.

Before and after stability ASTs, MEAs were studied by using EIS at 0.8 A cm^{-2} under H_2/O_2 conditions at 80°C . During the test, a direct current amplitude of 5% was applied. The MEA was held at 0.8 A cm^{-2} for 10 min before measurement. The flow rate at the anode and cathode were 300 sccm and 500 sccm, respectively. The pressure was $150 \text{ kPa}_{\text{abs}}$ and the relative humidity was 100%. The frequency was then swept from 10,000 Hz to 0.1 Hz in 10 step per decade. The acquired data were fitted using Zview software.

Fuel cell MEA tests. Anodes and cathodes were prepared by the catalyst coated membrane (CCM) method to fabricate MEAs. For the anode, a 20 wt% Pt/XC-72 catalyst and ionomer dispersion (25 wt%, Aquivon D-79-25BS) with a 0.45 ionomer to carbon ratio, were added to 1-propanol and deionized water mixed solvent with 1:6 volume ratio to form an ink. The prepared ink was then sprayed onto a 5 cm^2 square Nafion 212 membrane using an Exacta Coat spray machine (Sono-Tek), and the Pt loading at the anode was controlled at $0.2 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$. The PGM-free cathode was mixed with the similar ionomer in a mixed solvent of 2-propanol and deionized water with a 1:1 volume ratio. The ionomer/carbon ratio was optimized at 0.6. The prepared ink was sprayed on the other side of the membrane, aligning with the anode, to achieve a loading of $\sim 4.0 \text{ mg}_{\text{cat}} \text{ cm}^{-2}$. The gas diffusion layers were SGL-22BB. Polarization curves were measured using a fuel cell test station (Fuel Cell Technology). First, the cell was heated to 80°C without flow, then 200 sccm of humidified N_2 was flowed on the cathode and anode for 2 h to hydrate the membrane and ionomer. Air/oxygen flowing at 500 sccm and H_2 (purity 99.999%) flowing at 300 sccm were supplied to the cathode and anode, respectively. The absolute pressures during the fuel cell tests were 100 kPa for reactant gases. The cathode and anode gas dew points and the cell temperature were maintained at 80°C during the measurement of the polarization curves. The protocol for measuring the MEA performance under H_2 - O_2 and H_2 air conditions followed those proposed by the US ElectroCat Consortium. Especially, the holding time at each voltage is 45 s to achieve steady-state current density.

MEA stability was first evaluated using square wave voltage cycling from 0.6 V and OCV ($\sim 0.92 \text{ V}$), 2.5 s hold at each potential with a rise time of 0.5 s (that is, six seconds per cycle). Flow rates were 200 sccm and 400 sccm of H_2 and air, 100% RH, in the anode and cathode, respectively. The polarization curves were recorded after 5,000, 10,000, 20,000 and 30,000 voltage cycles. Second, H_2 air cell durability tests were performed at a constant cell voltage of 0.67 V for 319 h with flow rates of air and H_2 at 200 sccm. Polarization curves were recorded at different times during the 319 h durability test using 100% RH air and H_2 at flow rates of 500 sccm and 300 sccm, respectively.

Computational methods. The first-principles DFT calculations^{49,50} were performed using the Vienna ab initio simulation package (VASP) code^{51,52}. The generalized gradient approximation of Perdew, Burke, and Ernzerhof functionals was used to describe the electronic exchange and correlation energy⁵³. The energy cut-off of plane wave basis was set as 400 eV for plane wave expansion. A $17.28 \text{ \AA} \times 12.82 \text{ \AA}$ supercell of a graphene layer was used to model S1-type FeN_4 site and the supercell contains 62 carbon atoms, 4 nitrogen atoms, 8 hydrogen atoms and 1 iron atom. A $9.84 \text{ \AA} \times 12.79 \text{ \AA}$ supercell of a graphene layer was used to model S2-type FeN_4 site, and the supercell contains 42 carbon atoms, 4 nitrogen atoms and 1 iron atom. In the supercells, a vacuum region with a thickness of $14 \text{ \AA}$ was added in the direction normal to the carbon layer to ensure negligible interaction between periodic images. The Brillouin zone was sampled using the Monkhorst-Pack⁵⁴ scheme with a $2 \times 3 \times 1$ k-points grid for the supercell containing an S1-type FeN_4 site and a $4 \times 3 \times 1$ k-points grid for the supercell containing an S2-type FeN_4 site. The optimized structures were obtained until the forces on each ion fell below $0.01 \text{ eV \AA}^{-1}$.

The climbing image nudged elastic band method⁴³ with six intermediate images between the initial and the final states was used to identify the minimum-energy paths and locate the transition states of structural transformation processes. A convergence criteria of $0.05 \text{ eV \AA}^{-1}$, $0.05 \text{ eV \AA}^{-1}$ and $0.10 \text{ eV \AA}^{-1}$ for the force

components both along and perpendicular to the tangent of the minimum-energy path was used in the climbing image nudged elastic band calculations for OOH dissociation, Fe demetallation and structural transition from a pyrrolic nitrogen to a pyridinic nitrogen, respectively.

The computational hydrogen electrode method developed by Norskov et al.⁵⁵ was used to calculate the free energy change for all elementary steps of the ORR on FeN_4 sites. Zero-point energy (ZPE) corrections were included in all the energies reported in this work. ZPE corrections were calculated as:

$$\text{ZPE} = \frac{1}{2} \sum h\nu_i$$

where h is Planck's constant and ν_i is the frequency of the vibrational mode of binding molecules.

Moreover, the quadrupole splitting (QS) value of Fe in FeN_4 sites was calculated using the following equation:²²

$$\Delta E_Q = \frac{1}{2} eQV_{zz} \sqrt{1 + \frac{\eta^2}{3}}$$

where ΔE_Q is the QS value measured in ^{57}Fe Mössbauer, e is the charge of the electron, Q is the nuclear quadrupole moment ($Q = 0.16 \text{ barn}$ for $J = 3/2$ in this work), and the asymmetry parameter η is computed as:

$$\eta = (V_{xx} - V_{yy})/V_{zz}$$

where $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$. The electric field gradient tensor V_{ij} is calculated using the following equation:

$$V_{ij} = \Psi_0 \left| \frac{3ij - r^2}{r^5} \right| \Psi_0$$

where Ψ_0 is the electronic ground state and x, y, z refer to the components of the electron radius vector r . The values of V_{ij} can be directly computed from the DFT calculations.

Data availability

The authors declare that all data supporting the findings of this study are available within the paper and Supplementary Information files. Source data are provided with this paper.

Code availability

All the DFT calculations were performed using the commercial software VASP. All the input and output files of the calculations are available from Guofeng Wang per request.

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Author contributions

G. Wu and S. Liu were the primary writers of the manuscript. S. Liu, Y.Z., Q.S. and G. Wu designed catalyst synthesis and performed the electrochemical experiments, characterized the catalyst and analysed the data. C.L., Q.G. and J.X. carried out fuel cell tests and data analysis. H.X. assisted with MEA design and fabrication. H.M.M. conducted XPS and Auger experiments and data analysis. D.A.C., M.J.Z. and H.Y. together performed electron microscopy imaging and further characterizations. B.L. and G. Wang designed and performed DFT calculations. M.W., M.L., A.J.K., Z.F. and D.J.M. together designed and performed X-ray absorption spectroscopy and data analysis. E.E.A. and D.J.M. designed and performed Mössbauer spectroscopy experiments and data analysis. J.B., J.L. and S. Litster acquired and analysed X-ray nano-CT imaging. G. Wu supervised the execution of the overall project.

Competing interests

G. Wu, S. Liu and H. Xu have filed joint patent applications through the University at Buffalo and Giner Inc. (US Patent application number 17/531,461 and PCT application number PCT/US21/60195) on technology related to the Fe_2O_3 precursor, the NH_4Cl treatment and the CVD process. H. Xu is an employee at Giner Inc., who assisted with MEA design and fabrication. The remaining authors declare no competing interests.

Additional information

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