Atomically dispersed Pt and Fe sites and Pt–Fe nanoparticles for durable proton exchange membrane fuel cells

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Proton exchange membrane fuel cells convert hydrogen and oxygen into electricity without emissions. The high cost and low durability of Pt-based electrocatalysts for the oxygen reduction reaction hinder their wide application, and the development of non-precious metal electrocatalysts is limited by their low performance. Here we design a hybrid electrocatalyst that consists of atomically dispersed Pt and Fe single atoms and Pt–Fe alloy nanoparticles. Its Pt mass activity is 3.7 times higher than that of commercial Pt/C in a fuel cell. More importantly, the fuel cell with a low Pt loading in the cathode (0.015 mgPt cm⁻²) shows an excellent durability, with a 97% activity retention after 100,000 cycles and no noticeable current drop at 0.6 V for over 200 hours. These results highlight the importance of the synergistic effects among active sites in hybrid electrocatalysts and provide an alternative way to design more active and durable low-Pt electrocatalysts for electrochemical devices.

Despite great efforts in the development of advanced Pt-based catalysts to improve the Pt utilization and mass activity (MA) of Pt-based nanocatalysts for the cathodic oxygen reduction reaction (ORR) hinder the wide adoption of this technology. According to the ultimate cost target of US$30 kW⁻¹ for the fuel cell stack, the Pt loading in the catalyst layers must be below 0.125 mg cm⁻² (ref. 1). However, as the Pt loading decreases, the oxygen transfer resistance increases because of the limited accessible active sites, which results in a lower durability. Thus, the ambition to develop low-Pt-loading cathodes poses great challenges in the areas of Pt utilization and the intrinsic durability of Pt-based electrocatalysts.

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**Results**

**Structure and composition of Pt–Fe–N–C**. Figure 1a shows a typical transmission electron microscopy (TEM) image of the as-synthesized Pt–Fe–N–C catalyst, which clearly reveals nanoparticles with a main size distribution of 2–3 nm (Supplementary Fig. 1) dispersed on a carbon substrate with a Brunauer–Emmett–Teller surface area of 750 m² g⁻¹ and mesopores (Supplementary Fig. 2). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image (Fig. 1b) of the as-synthesized Pt–Fe–N–C catalyst reveals the presence of atomically dispersed Pt and Fe sites in a nitrogen-doped carbon support. The high-resolution transmission electron microscopy (HRTEM) images (Fig. 1c) of Pt–Fe–N–C show the Pt–Fe alloy nanoparticles supported on a nitrogen-doped carbon support with a high Pt mass activity (1.77 A mgPt⁻¹ at 0.9 V, ohne without pressure correction) (ref. 1). This result indicates that even small amounts of Pt could contribute to a high activity enhancement of the hybrid electrocatalyst. Despite the excellent Pt MA of this hybrid ORR catalyst, it still suffered notable activity losses during potential cycling (83% after 30,000 cycles between 0.6 and 0.95 V) and potential hold (45% after 22 hours at 0.75 V) (ref. 1). Jaouen and co-workers (ref. 1) found that the stability of Fe–N–C could be improved by adding a small amount of Pt (1–2 wt%), although the activity did not change.

Here we report a hybrid electrocatalyst (denoted as Pt–Fe–N–C) that consists of Pt–Fe alloy nanoparticles on highly dispersed Pt and Fe single atoms in a nitrogen-doped carbon support. The multiple types of active sites result not only in a 3.7 times higher Pt MA, but also in an excellent durability. The performance loss is negligible even after 100,000 potential cycles, and no current drop is observed at 0.6 V in a fuel cell test with an ultralow Pt loading (0.015 mgPt cm⁻²) in the cathode.
microscopy (HAADF-STEM) images of Pt-Fe-N-C at a relatively low magnification (Fig. 1b and Supplementary Fig. 3) clearly indicate a high density of isolated atoms anchored on the carbon substrate in addition to the nanoparticles. The set of peaks from intermetallic PtFe was well-assigned in the X-ray diffraction pattern of Pt-Fe-N-C (Supplementary Fig. 4). An additional peak at 42.5° could be attributed to disordered PtFe$_x$ (1 < x < 3) based on Vegard’s law$^{[14-15]}$. The characterized alternating bright and dim atomic column as well as the lattice distance of 3.78 Å (001) revealed an ordered structure (Fig. 1c) for the smaller nanoparticle in Fig. 1b, which is consistent with the atomic model and simulated STEM image of a face-centred-tetragonal PtFe structure. It is worth noting that the ordered structure can be clearly identified in almost all the small nanoparticles (the characteristically alternating bright and dim lattice is also observed in Supplementary Fig. 3), which indicates the high order degree of the nanoparticles$^{[16]}$. No super-lattice atom contrast was observed for the bigger nanoparticle (Supplementary Fig. 5), which indicates its disordered structure. Its
The Pt-Fe-N-C catalyst mainly consists of small intermetallic PtFe nanoparticles and a small number of PtFe$_{1-x}$ (1 < x < 3) bigger disordered nanoparticles.

Two sets of bright isolated spots, distinguished by their contrast differences in HAADF-STEM$^{17}$. The identification of these different isolated spots was further confirmed by local electron energy loss spectroscopy (EELS) analysis (Fig. 1e and Supplementary Fig. 6). The EELS profile of the nanoparticle shows strong Fe and O signals, and the Pt signal could not be detected owing to the high energy loss (around 2,200 eV) of the Pt major peak$^{18}$. The profile of the single atom in a blue dashed circle shows weak Fe and N signals, which suggests that the weaker spot is an Fe–N moiety. In contrast, the profile of the single atom in a red dashed circle only shows a weak N signal, which indicates the brighter spot to be a Pt–N moiety. These results are in good agreement with their contrast differences in the STEM images. The microscopic characterizations clearly demonstrate the co-existence of abundant Pt and Fe single atoms and Pt–Fe nanoparticles in the hybrid material.

According to the inductively coupled plasma mass spectrometry results, the metal loadings in Pt-Fe-N-C are 2.0 wt%Fe and 1.7 wt%Pt. The Fe 2p spectrum was resolved into doublet peaks of Fe$^{2+}$ and triplet peaks of Fe$^{3+}$ (Supplementary Fig. 7b). Meanwhile, the deconvoluted N 1s spectrum (Supplementary Fig. 7c) includes a dominant graphitic N along with pyridinic, metal and oxidized N. The decreased intensity of pyridinic N in the Pt-Fe-N-C catalyst in comparison with that in Fe-N-C (Supplementary Fig. 8) is due to the two-step high-temperature pyrolysis of the former. The structures of Pt-Fe-N-C and Fe-N-C (Supplementary Fig. 9) were further characterized by X-ray absorption spectroscopy (XAS). Figure 1f$^{19}$ compare the Pt L$_3$-edge and Fe K-edge, respectively, X-ray absorption near-edge structure spectra of Pt-Fe-N-C with various standards. There was no obvious difference in the Pt L$_3$ edge (Fig. 1f) in the pre-edge region in comparison with that of a metallic Pt foil. The stronger intensity of the white line for Pt-Fe-N-C, which results from the electron transfer from the Pt 5d to the Fe K 3d orbitals, suggests that Pt is in the oxidized form in Pt-Fe-N-C (ref. 19). The negative shift of the main peak from 2.42 Å for the Pt foil to 2.23 Å for Pt-Fe-N-C in the Fourier transforms of the extended X-ray absorption fine structure data (Supplementary Fig. 10a) affirmed unambiguously the formation of Pt–Fe bonds, whereas the weak peak at 1.5 Å may be contributed by the Pt–N configuration. For the Fe K edge in Fig. 1g, the intensity of the pre-edge peak is the highest for the Pt-Fe-N-C sample, whereas the white-line intensity decreased dramatically compared with those of Fe–N–C and Fe oxides. The loss of the pre-edge characteristic of Fe in Pt-Fe-N-C in comparison with that in Fe–N–C (Supplementary Fig. 9) indicates that most of the Fe metal centres in the former lost the octahedral...
symmetry\textsuperscript{23}. The strong Fourier transform peak at 2.06 Å was due to the scattering from the Pt–Fe alloy, whereas the shoulder at 1.50 Å arose from scattering by the Fe–C/N/O bonds in the carbon support (Supplementary Fig. 10b). The coordination information of the Pt and Fe elements were further supported by the relative fitting results (Supplementary Fig. 11 and Supplementary Table 1).

\textsuperscript{57}Fe Mössbauer spectroscopy was applied to identify the local structure of the Fe species. As shown in Supplementary Fig. 12 and Supplementary Table 2, the Mössbauer spectrum of Fe–N–C was fitted with two dominated doublets and a small amount of singlet assigned to γ-Fe. The doublet D1 and D2 are assigned to square-planar Fe(II)N\textsubscript{4} coordinated with Fe(II) in the low- and medium-spin state, respectively\textsuperscript{21,22}. After the Pt addition and a two-step heat treatment, the areas of doublets and singlets decrease and increase, respectively. \textsuperscript{57}Fe Mössbauer studies of Fe alloys, such as Pt–Fe (ref. \textsuperscript{23}), Ru–Fe (ref. \textsuperscript{24}) and Pd–Fe (refs. \textsuperscript{25,26}) suggested that Fe was zero valent in the alloys. Bartholomew and Boudart\textsuperscript{23} observed that the Mössbauer absorption probability of surface Fe atoms in the alloy was substantially the same as those in the bulk, especially for nanosize Pt–Fe particles. Thus, the singlet component in Pt–Fe-N–C is largely due to Pt–Fe alloys, whereas the D1 and D2 doublets are from nitrogen-coordinated Fe single atoms.

**Performance evaluation of Pt-Fe-N-C.** A cyclic voltamogram curve of Pt-Fe-N-C in an Ar-saturated 0.1 M HClO\textsubscript{4} electrolyte did not present profound hydrogen adsorption and/or desorption peaks characteristic of Pt because of the ultralow Pt loading (Supplementary Fig. 13). The ORR performance of the Pt-Fe-N-C catalyst was evaluated by a rotating-ring disk electrode in an O\textsubscript{2}-saturated 0.1 M HClO\textsubscript{4} electrolyte with a Pt loading of 4.25 µg cm\textsuperscript{-2}, without background or iR correction. Supplementary Fig. 14 shows that Pt-Fe-N-C had a significantly improved ORR
activity over Fe–N–C, as the half-wave potential shifted from 0.765 to 0.909 V. The corresponding Pt MA of Pt–Fe–N–C at 0.9 V reached 1.74 A mgPt⁻¹, which was around ten times higher than that of Pt/C (0.18 A mgPt⁻¹). In addition, the ring current of Pt–Fe–N–C was much lower than that of Fe–N–C in a broad potential window (Supplementary Fig. 14). The calculated maximum hydrogen peroxide yield (H₂O₂%) and the electron transfer number were 2.4% and 4, respectively, which suggests a complete four-electron transfer reaction.

The durability of the Pt–Fe–N–C catalyst was evaluated in an O₂-saturated 0.1 M HClO₄ electrolyte during potential cycling from 0.6 to 1.0 V. The half-wave potential of Pt–Fe–N–C (Supplementary Fig. 15) showed a drop of only 14 mV after 40,000 cycles between 0.6 and 1.0 V, much better than those of Fe–N–C (16 mV) (ref. 27) and Pt/C (10 mV) after only 10,000 cycles (Supplementary Fig. 16). No particle aggregation was observed, and the uniform distribution of Fe and Pt single atoms was well-preserved according to the HAADF-STEM image taken after testing (Supplementary Figs. 17 and 18). Energy-dispersive X-ray spectroscopy (EDX) mapping and the corresponding elemental line (Supplementary Fig. 18) further confirmed the retention of the highly stable ordered structure and Pt-shell formation of the Pt–Fe nanoparticles after 40,000 cycles.

The fuel cell performances of the Fe–N–C, Pt–N–C, Pt/C and Pt–Fe–N–C catalysts were evaluated in an H₂/O₂ environment and are compared in Fig. 2a. The cutoff current density was 2 A cm⁻² for all the testing. The Pt loadings at the anode were 0.1 mg cm⁻² in all the measurements; the Pt loadings at the cathode were 0.015 mg cm⁻² for Pt–Fe–N–C, and 0.1 mg cm⁻² for Pt–N–C and Pt/C. The fuel cells with Pt–N–C and Fe–N–C reached peak power densities of 0.32 and 0.66 W cm⁻², respectively, which are comparable to values reported in the literature. Although the MA of Pt–Fe–N–C achieved a high MA at 0.9 V, it still cannot compete with Pt-based electrocatalysts in the high current density region due to a much lower Pt loading.

The cells assembled with Pt–Fe–N–C, Pt/C and Fe–N–C cathodes were further subjected to an accelerated durability testing under repeated square-wave cycles at 0.6 and 0.95 V by holding at each potential for 3 s, following the DOE testing protocol. As shown in Fig. 2b, the fuel cell polarization curves with the Pt–Fe–N–C cathode showed a negligible change after 100,000 cycles. The MA at 0.9 V, i.e., 40% MA loss after 30,000 cycles. In comparison, the Pt/C (Supplementary Fig. 20a) and Fe–N–C (Supplementary Fig. 20b) cathodes showed a substantial performance loss after 30,000 cycles. The Pt MA of Pt/C dropped from 0.21 to 0.10 A mgPt⁻¹ and the peak power density of Fe–N–C decreased noticeably from 0.66 to 0.56 W cm⁻².

The morphology and structure of the Pt–Fe–N–C catalyst after 100,000 cycles in a fuel cell were further analysed by STEM-EELS. Abundant single atoms were still uniformly distributed on the carbon support (Fig. 3a,b). The EELS analysis (Fig. 3b) verified the preservation of Pt and Fe single atoms with the N-coordinated configuration, which is similar to that of the pristine sample (Fig. 1d). No noticeable aggregation of the Pt–Fe nanoparticles was observed (Supplementary Fig. 21). The structure and composition of the nanoparticles did change during the potential cycling. In general, the structural evolution of the Pt–Fe nanoparticles followed two pathways. When the particle size was smaller than ~4 nm, a solid PtFe@Pt core–shell structure was formed (Fig. 3c), indicated by the lattice spacing of 0.191 nm for PtFe(002) in the core and 0.204 nm for Pt(111) in the shell, which originated from the pristine PtFe core–shell structure. This conclusion was further supported by the line intensity profile (Fig. 3d). Periodic oscillations of intensity in the centre and monotonicity in the shell were observed, which can be attributed to the contrast differences between Pt and Fe in an ordered lattice. At the outermost three layers, the intensity oscillation disappeared, and the lattice expanded, which confirmed the formation of a Pt shell.
to form a percolated structure due to its unstable disordered structure (Fig. 3c) with a lattice spacing of 0.204 nm, which is close to the spacing of Pt(002). The EDX line profile of Pt in Fig. 3f shows a clear concavity in the middle of the particle, which indicates the formation of a pit in the nanoparticle. Relative EDX mapping (Supplementary Fig. 22) also showed that the atomic ratio of Fe to Pt was around 1:4, which implies that most of the Fe leached during the potential cycling to leave a Pt-rich percolated structure. Similar phenomena were observed in Pt–Ni alloy nanoparticles during potential cycling. It is worth noting that most of Pt–Fe nanoparticles were transformed into a more stable core–shell structure and maintained their intermetallic structure in the core, which played an important role in achieving the good durability of Pt–Fe–N–C, and a high durability of intermetallic nanoparticles was reported by other groups.

Only ∼7% of nanoparticles formed a percolated structure, as indicated with yellow hexagons in Supplementary Fig. 21. The preservation of the carbon support was also confirmed by the negligible change of the intensity of D–Raman peak and G–Raman peak (I_D/I_G) in the micro-Raman results (Supplementary Fig. 23).

A chronoamperometric test at a voltage of 0.6 V was also conducted at 1 bar absolute pressure for both the anode and cathode to further evaluate the long-term durability of different cathode catalysts. As shown in Fig. 2c (red line), the fuel cell with a Pt–Fe–N–C cathode (Pt loading of 0.015 mgPt cm⁻²) showed a nearly constant current density over 206 hours in the H₂/air environment. In contrast, the current density of the Pt/C cell (Pt loading of 0.1 mgPt cm⁻²) dropped by 8% in 120 hours (Supplementary Fig. 24a). The Pt MA of Pt–Fe–N–C at 0.9 V, as normalized to 1 bar absolute pressure slightly increased from 0.72 to 0.75 A mgPt⁻¹ h⁻¹. This enhancement may be due to the structural evolution of the Pt–Fe nanoparticles (a more desired core–shell structure). For Fe–N–C (Supplementary Fig. 24b), the current density drop was even faster, with a 73% loss after 49.3 hours, similar to results reported in the literature. A similar testing was also conducted in a H₂/O₂ environment. After 210 hours of potential hold at 0.6 V, the current density of the Pt/C cell (Pt loading of 0.015 mgPt cm⁻²) dropped by 8% in 120 hours (Supplementary Fig. 24a). The Pt MA of Pt–Fe–N–C at 0.9 V, as normalized to 1 bar absolute pressure slightly increased from 0.72 to 0.75 A mgPt⁻¹ h⁻¹. This enhancement may be due to the structural evolution of the Pt–Fe nanoparticles (a more desired core–shell structure). For Fe–N–C (Supplementary Fig. 24b), the current density drop was even faster, with a 73% loss after 49.3 hours, similar to results reported in the literature.

Theoretical study. Density functional theory (DFT) calculations were performed to explore the origins of the high activity and durability of the hybrid electrocatalyst. Several simulation models were constructed to represent the possible types of active sites (Supplementary Fig. 26), which include a single atom (Pt–N₁C₃, Pt–N₃C₆, and Fe–N₁C₃ based on the extended X-ray absorption fine structure fitting result in Supplementary Table 1), Fe–Pt dual metal and the Ptma/Fe(111) core–shell structure (a one-monolayer (ML) Pt skin on the PtFe(111) substrate). Pure Pt(111) was also included for comparison. Among these models, Pt–N₃C₆ and Fe–Pt dual metal were carefully designed and selected on the basis of structure optimizations and energy calculations (Supplementary Figs. 27 and 28 and Supplementary Table 5). To evaluate the ORR pathway for various simulation models, the key intermediates *OOH, *O and *OH (‘ denotes the adsorbed state) were optimized. The corresponding adsorption structures of the reaction intermediates on carbon-based models (Pt–N₁C₃, Pt–N₃C₆, Fe–N₁C₃ and Fe–Pt dual metal) are shown in Supplementary Fig. 29, and those on Ptma/Fe(111) are shown in Supplementary Fig. 30. The Gibbs free energy diagrams of the ORR for the 4e⁻ pathway on various possible active sites were constructed at U_RHE = 0.9 V (RHE, reversible hydrogen electrode), which corresponds to the potential for activity evaluation in the experiment. As shown in Fig. 4a and Supplementary Table 6, the single Pt metal site in Pt–N₁C₃ (green curve) exhibited the best ORR activity, with a downhills trend across all of the elementary reactions, except for the final *OH protonation step, and the energy barrier during the ORR was only 0.17 eV, much smaller than that on a single Fe site in Fe–N₁C₃ (0.53 eV, black curve in Fig. 4a). For another two carbon-based models, Pt–N₃C₆ showed a very high energy barrier for *OOH formation (0.54 eV) as the potential limiting step (red curve), as did the Fe–Pt dual metal (blue curve) which was not expected to be very active because of the very strong OH binding energy that made *OH removal very difficult (0.75 eV). The Ptma/Fe(111) was also predicted to be very active for ORR because of a low energy barrier of 0.18 eV in the final *OH protonation step (purple curve in Fig. 4a), which was close to that for Pt–N₁C₃ (0.17 eV). Note that the energy barrier here is only the thermodynamic energy barrier, and the desorption of *OH is endothermic except for that on Pt–N₃C₆. Such a core–shell structure with a 1 ML Pt skin shows a better ORR activity than that of Pt(111) (yellow curve in Fig. 4b) because of the weaker bindings to the reaction intermediates, especially for *O and *OH. The thickness of the Pt shell in the PtFe@Pt nanoparticles may vary from one to three atomic layers after the potential cycling. Hence, simulations were also conducted on 2Ptma/Fe(111) and 3Ptma/Fe(111). As shown in Supplementary Fig. 31, all the Pt skins showed better ORR activities than that of pure Pt. Among these, Ptma/Fe(111) was the best, with the lowest barrier for the *OH-to-H₂O step. On the basis of our calculations, Pt–N₁C₃ and the core–shell nanoparticles formed after leaching Fe in the surface and subsurfaces are proposed to be the most active sites in Pt–Fe–N–C.

The major concern for Me–N–C catalysts in fuel cells is the formation of a large amount of H₂O₂ as the final product, which is detrimental to the membrane and ionomers. It was found that mixing Pt (refs. 12,13), Pt–Co alloy11 and/or CeO₂ (ref. 8) particles as the peroxide/radical scavenger with Me–N–C could alleviate H₂O₂ accumulation. Thus, in our hybrid catalyst, H₂O₂ generated at the Fe–N–C (Supplementary Fig. 32) or even Pt–N–C sites (Supplementary Fig. 33) may also be further reduced to H₂O on nearby Pt–Fe nanoparticles. To validate this hypothesis, H₂O₂ reduction on Ptma/Fe(111) and Pt(111) surfaces was compared (Fig. 4b and Supplementary Table 7). It turned out that Ptma/Fe(111) contributed to the fast H₂O₂-to-2OH conversion and the final *OH-to-H₂O step was also facile, with an energy barrier of 0.18 eV lower than that on Pt(111) (0.34 eV). Thus, we expect that all three active sites, namely, Pt–N₁C₃, Fe–N₁C₃, and Ptma/Fe(111), contribute to the high performance of the ORR in Pt–Fe–N–C. The formation of a Pt dual skin on PtFe@Pt during the fuel cell operation and the further reduction of H₂O₂ on PtFe@Pt produced by single-atom active sites are the main reasons for the exceptional durability.

Conclusions

In summary, a hybrid ORR electrocatalyst with an ultralow Pt loading (1.7 wt%) that consisted of atomically dispersed Pt and Fe single atoms and Pt–Fe alloy nanoparticles was successfully synthesized. A good performance, which included 0.77 A mgPt⁻¹ at absolute H₂
O2 pressures of 1 bar at 0.9 V_{cell} and a 1.08 W cm−2 power density at 2.0 A cm−2, was achieved in the fuel cell. More importantly, this hybrid electrocatalyst demonstrated an excellent durability, with 97% activity retention after 100,000 cycles at 0.6 and 0.95 V, and no noticeable current drop at 0.6 V over 200 hours. Theoretical simulations suggested that Pt–N–C, Fe–N–C, and PtFe@Pt were all active sites for the Pt. The enhanced durability of the hybrid electrocatalyst may result from a reduced H2O2 formation and consequent alleviation of the membrane and ionomer degradation. Our results highlight the importance of the synergistic effects among different active sites in hybrid electrocatalysts and provide an alternative way to design more active and durable low-Pt-group metal electrocatalysts for fuel cells and other chemical processes.

**Methods**

**Chemicals and reagents.** Zinc nitrate hexahydrate (Zn(NO3)2·6H2O, Aladdin, 99.99% metals basis), ferrous sulfate heptahydrate (FeSO4·7H2O, Aladdin, 99.95% metals basis), 2-methylimidazole (C5H7N, Aladdin, 98%), 1,10-phenanthroline monohydrate (C12H8N2, Aladdin, 99%), potassium ferricyanide (K3Fe(CN)6, Aladdin, 99.95% metals basis), potassium hydroxide (KOH, Aladdin, 99.99% metals basis), platinum(II) acetylacetonate (Pt(C5H7O2)2, Sigma-Aldrich, 99.95% metals basis), ferrous sulfate heptahydrate (FeSO4·7H2O, Aladdin, 99.95% metals basis), potassium ferricyanide (K3Fe(CN)6, Aladdin, 99.95% metals basis), sodium hydroxide (NaOH, Aladdin, 99.98% metals basis), solution that contained isopropanol (C3H8O, Fisher, 99.8%), Nafion 117 (Sigma-Aldrich, 5 wt% in a mixture of lower aliphatic alcohols and water), methanol (CH3OH, Scharlau, 99.8%) and ethanol absolute (C2H6O, Scharlau, 99.9%), dichloromethane (CH2Cl2, Aladdin, 99%), chloroform (CHCl3, Aladdin, 99.8%), acetonitrile (CH3CN, Scharlau, 99%), tetrahydrofuran (THF, Aladdin, 99.998% metals basis), methanol (CH3OH, Scharlau, 99.8%) and ethanol absolute (C2H6O, Scharlau, 99.9%) and ethanol absolute (C2H6O, Scharlau, 99.9%).

**Synthesis of Fe-doped ZIF-8.** As a reference electrocatalyst, Pt–N–C was prepared from a ZIF-8 support, which was formed by mixing 1 mM Zn(NO3)2·6H2O and 8.21 g of 2-methylimidazole in a methanol solvent and following the same collecting and drying protocols as for Fe-doped ZIF-8. Similarly, 10 mg of platinum(II) acetylacetonate was homogeneously dispersed in 3 ml of ethanol via ultrasonication until the solvent became transparent. In the meantime, 110 mg of 1,10-phenanthroline monohydrate dissolved in 10 ml of ethanol was added to the Pt solution to provide a sufficient nitrogen source for Pt coordination. Around 400 mg of Fe-doped ZIF-8 was added to this solution to form a uniform suspension. After drying at 60 °C in a vacuum oven overnight, the solid was collected and ball milled (ZrO2 ball, 350 r.p.m., 4 h) to uniformly distribute Fe and ZIF-8 sources on the ZIF-8 support. The mixed precursors were also initially treated in NH3 gas at 900 °C for 15 min and then transferred into an Ar atmosphere at 1,000 °C for 1 h. The final catalyst, Pt–N–C, had a Pt loading of 2.3 wt%.

**Physical characterization.** The TEM results were collected with a double Cs-corrected FEI Themis G2 operating at 300 kV equipped with a Gatan Enfina EELS detector, with the performance of the Pt on a TEM (111) monocrystal. XAS data were processed with the ATHENA and ARTEMIS software packages. The FE Mössbauer spectra of Fe–N–C and Pt–Fe–N–C were recorded on a SEI Co W304 Mössbauer spectrometer using a 5CoRh source in transmission geometry. The data were fitted by using the MOSSWINN 4.0 software. Micro-Raman spectroscopy (Renishaw, InVia) was used to probe the change in the carbon support before and after durability testing. Efficient water samples collected from the cathode gas outlet were analysed by ion chromatography (Metrohm 881 with an ultraviolet and conductivity detector) to evaluate the fluoride emissions.

**Electrochemical measurement.** To prepare the catalyst ink, 2.5 mg of catalyst was uniformly dispersed in 500 μl of a mixed solvent (water and isopropanol in a 4:1 volume ratio) and 10 μl of a 5 wt% Nafion 117 solution. The rotating-ring disk electrode (5.5 mm in diameter) was then immersed in a 0.1 M HClO4 electrolyte with a Pt foil and Ag/AgCl used as the counter and reference electrodes, respectively. All potentials are referred to the RHE. The potential of the Ag/AgCl electrode with reference to the RHE was calibrated before every activity test. During the calibration process, the Ag/AgCl electrode and a Pt foil were put into a H2-saturated 0.1 M HClO4 solution, and the voltage difference between these two electrodes was then recorded. The value of Ag/AgCl measured in this way was around 0.26–0.27 V_{SHE}.

**Cyclic voltammograms (20 cycles) in the potential range 0–1.2 V at 100 mV s−1 were applied to clean the thin film in an Ar-saturated 0.1 M HClO4 solution, followed by taking a stable cyclic voltammogram curve in the same potential range at 50 mV s−1. The ORR performance was measured in an O2-saturated 0.1 M HClO4 solution with a 1,600 rpm rotation rate at 5 mV s−1. A linear sweep voltammometry curve was applied during the activity evaluation and the polarization curves were all recorded from 0.125 to 1.0 V. In the durability testing, Pt–Fe–N–C and Pt/C were subjected to potential cycling between 0.6 and 1.0 V at 50 mV s−1 in an O2-saturated 1 M HClO4 electrolyte.

The collection efficiency of the rotating-ring disk electrode was first determined in an Ar-saturated 10 mM KFe(CN)6·3 H2O solution, which corresponded to the current efficiency applied during the measurement and the amperometric i–t measurements were performed by setting the ring and disk voltages to 1.5 and 0.1 V, respectively.

**Disk: Fe(CN)6^{3−} + e− → Fe(CN)6^{4−} (1)**

**Ring: Fe(CN)6^{4−} → Fe(CN)6^{3−} + e− (2)**

The disk (I_d) and ring (I_r) currents were recorded. The measurement was repeated once with a disconnected disk to obtain another ring current (I_0), which included all the currents (not from Fe(CN)6^{3−}) reduced on the disk. The collection efficiency could be calculated from:

\[ N = \frac{I_d - I_0}{I_d} \] (3)

The measured collection efficiency (N) was 0.42 at 1,600 rpm. The H2O2% yield and electron transfer number (n) of the electrocatalysts were further determined in an O2-saturated 0.1 M HClO4 solution at 1,600 rpm. A linear sweep voltammometry technique was applied to the disk to record the performance of the Fe–N–C and Pt–Fe–N–C electrodes at a scanning rate of 5 mV s−1 from 0.125 to 1.0 V, while keeping the ring voltage at 1.2 V. Four-electrode and two-electron ORRs were then performed on the disk to confirm this finding. After drying at 60 °C in a vacuum oven overnight, the solid was collected and ball milled (ZrO2 ball, 350 r.p.m., 4 h) to uniformly distribute Pt and N sources on the ZIF-8 support. The mixed precursors were also initially treated in NH3 gas at 900 °C for 15 min and then transferred into an Ar atmosphere at 1,000 °C for 1 h. The final catalyst, Pt–N–C, had a Pt loading of 2.3 wt%.
**Theoretical calculations.** DFT calculations were performed to explore the ORR mechanisms of Pt-Fe-N-C hybrid electrocatalysts by using the VASP (Vienna Ab-Initio Simulation Package) code\(^{(20)}\). The projector augmented wave method\(^{(20)}\) pseudopotentials with the revised Perdew–Burke–Ernzerhof generalized gradient approximation (GGA-RPBE)\(^{(20)}\) functional, which were provided in the VASP database, were used to describe the electron–ion interactions. The plane-wave cutoff energy was set to be 400 eV. The Gaussian smearing scheme was used with a width of 0.1 eV. For structure optimizations, the total energy convergence was set to be smaller than 1 × 10^{-5} eV and the force convergence was set to be lower than 0.01 eV Å^{-1} on the atoms. Dipole corrections were applied in all the slab simulations. Spin polarization was considered in our calculations. The DFT-D3 method of Grimme with zero damping\(^{(20)}\) was used to include the van der Waals corrections. A vacuum slab of 16 Å was added in the z direction to avoid spurious periodic interactions. For carbon-based models, the lattice parameters were 14.79 Å × 14.79 Å × 20 Å with a 6 × 6 supercell. For core–shell nanoparticles, a four-atomic-layer (2 × 2) surface unit cell was built with a Pt skin on top of PtFe(111) at the substrate’s lattice constants (5.39 Å × 5.39 Å × 22.63 Å). During the geometry optimizations, the carbon-based models were fully relaxed, and the top two layers with adsorbates on metal slabs were optimized. For the Brillouin zone integrations, the Monkhorst–Pack\(^{(20)}\) grids of 3 × 3 × 1 and 5 × 5 × 1 were sampled for carbon-based models and core–shell slab models, respectively. The GGA+U (U = 3.29 eV) was used to describe the localized 3d orbital electrons for Fe atoms, considering the magnetic moment of Fe correctly\(^{(20)}\).

The calculation of Gibbs free energy for each elementary step was based on the computational hydrogen electrode scheme proposed by Norskov et al.\(^{(20)}\), which is calculated at 298 K and 1 atmosphere according to the equation

\[
\Delta G_i = E_{\text{red}}^{\ast} + ZPE_i + TS_i + U_i + U_e + \text{corr} + \text{corr}^{\ast} - H_i^{\ast} (\text{versus RHE}) + nF \Delta \mu \text{H}_2
\]

Therefore, at \(U = 0\) (versus RHE) and standard conditions, the free energy of the elementary steps can be calculated as:

\[
\Delta G_i = E_i^{\ast} + ZPE_i + TS_i + U_i + U_e + \text{corr} + \text{corr}^{\ast} - H_i^{\ast} (\text{versus RHE}) + nF \Delta \mu \text{H}_2
\]

The bias effect is considered by shifting the energy state by \(\Delta G_i = -neU\), where \(U\) is the electrode applied potential relative to the RHE, \(e\) is the transferred charge and \(n\) is the number of the transferred proton–electron pairs. The detailed results are summarized in Supplementary Table 6.

**Data availability**

The data that support findings of this study are available within the article and its Supplementary Information files or from the corresponding author upon reasonable request. The atomic coordinates of the optimized models are provided in Supplementary Data 1. Source data are provided with this paper.

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Author contributions
M.S. supervised the whole project. E.X. and M.S. conceived the idea and designed the experiments. E.X. performed the catalyst development and performance evaluation. M.G., Q.W., Y.Z. and D.W. carried out electron microscopy characterization. K.A., G.-L.X., I.H. and C.-I.S. performed the XAS spectroscopy characterization and relative data analysis. X.Q. carried out the DFT simulation. M.L. performed the Fe Mössbauer spectroscopy and relative data analysis. E.X., H.W., S.Z., J.-C.L, W.H., J.G.W. and Z.W. performed the material preparation and general characterizations. F.X., G.-L.X., Q.W., X.Q., M.S. and K.A. and M.G. analysed the data and wrote the manuscript. All the authors discussed the results and commented on the manuscript.
Competing interests
The authors declare no competing interests.

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