Challenging the Activity-Durability Tradeoff of Fe-N-C Fuel Cell Catalysts via Controlling thermal Activation Atmosphere

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Abstract. Fe-N-C catalysts, the most promising platinum group metal (PGM)-free oxygen-reduction catalysts, often simultaneously contain pyrrolic N- (S1) and pyridinic N (S2) -coordinated FeN4 sites. These two types of active sites show significantly different intrinsic activity and stability. S1 sites are more active but less stable compared to S2 sites. Designing a Fe-N-C catalyst, which exclusively contains active S1 sites with enhanced intrinsic stability, is highly desirable to break the activity-stability trade-off. Herein, we report a Fe-N-C model catalyst that solely comprises S1 sites prepared by adding H2 in the pyrolysis atmosphere (i.e., 10% H2/Ar). A membrane electrode assembly (MEA) with the Fe-N-C cathode demonstrated compelling activity and generated a current density of 50.8 mA cm−2 at 0.9 VR-free (H2-O2) and 211 mA cm−2 at 0.8 V (H2-air), which have significantly exceeded the U.S. DOE 2025 targets. The highly active Fe-N-C catalyst also demonstrated improved stability during life tests and accelerated stability tests (ASTs).
The knowledge obtained from experimental and theoretical results elucidates that the FeN₄ site formation process can be controlled by thermal activation atmospheres, which is essential to breaking activity-stability trade-off and design viable Fe-N-C catalysts with adequate activity and stability for proton exchange membrane fuel cells.

**Keywords:** PGM-free catalysts; Fe-N-C catalysts; oxygen reduction reaction; proton-exchange membrane fuel cells

### 1. Introduction

The deployment of platinum-group-metal (PGM)-free catalysts for hydrogen proton-exchange membrane fuel cells (PEMFCs) will significantly reduce the cost for their large-scale applications. The atomically-dispersed and nitrogen-coordinated FeN₄ sites hosted in carbon (Fe-N-C) have exhibited either encouraging activity or stability for the challenging oxygen reduction reaction (ORR) cathode in acidic media. However, further simultaneous improvements in catalytic performance for current Fe-N-C catalysts has been limited by this activity-stability trade-off.

Like Pt active sites, the adsorption strength of O₂ and ORR intermediates on FeN₄ active sites is too strong. The activation barrier to cleave O-O bond is too high for the preferred 4e⁻ transfer pathway. Regulating the electronic and geometric structures of FeN₄ active sites to modulate adsorption energies and reduce activation energies is critical for improving the intrinsic activity and stability of FeN₄ sites. Recently, two different FeN₄ sites were identified in Fe-N-C catalysts: an FeN₄C₁₂ moiety containing pyrrolic N ligations (denoted as S₁ site) and an FeN₄C₁₀ moiety with pyridinic N environments (S₂ site). Based on operando Mössbauer experiments, S₁ sites are more intrinsically active but are irreversibly and rapidly converted to inactive ferric oxides, causing dramatic activity loss. The S₂ site is more stable against demetallation but less active due to stronger adsorption of oxygen and intermediates. Generally, it is challenging to synthesize catalysts exclusively containing either highly active S₁ sites or highly stable S₂ sites as model systems.

In our previous work, we developed a synthesis approach to controlling the geometry of the metal center and its local coordination structure of FeN₄ moieties. The catalyst treated with NH₄Cl salts contained primarily S₁ sites with significantly improved intrinsic activity. The in-situ produced NH₃ and HCl could create local carbon defects and remove residual Fe aggregates in catalysts. However, the NH₄Cl-treated catalyst suffered from a significant activity loss in a running fuel cell. We further discovered a post-treatment to convert unstable S₁ to highly stable S₂ sites by depositing a nitrogen-doped porous carbon thin film (<< 1 nm) at high temperatures to overcome the grand stability challenge of Fe-N-C catalysts. The conversion of unstable FeN₄ sites (FeN₄C₁₂, S₁) to stable FeN₄ (FeN₄C₁₀, S₂) sites in the surface of the catalyst was directly evidenced by ⁵⁷Fe Mössbauer spectroscopy. The compelling stability enhancement was further verified by standard stability ASTs and a fuel cell life test for >300 hours at a practical voltage of 0.67 V.

Motivated by the compelling performance improvements and fundamental understanding of the structural evolution of active sites, herein we explore innovative methods to regulate local carbon structures by using an H₂/Ar mixture atmosphere (i.e., forming gas) during the catalyst synthesis. The resulting Fe-N-C catalysts dominate with highly active S₁ sites with enhanced intrinsic stability, thus leading to exceptional activity and improved stability. The MEA made from
the Fe-N-C cathode reaches 50.8 mA cm\(^{-2}\) under 1.0 bar O\(_2\), exceeding the U.S. DOE target set for 2025 (44.0 mA cm\(^{-2}\)). Under practical operation conditions (1.0 bar air), the Fe-N-C-FG cathode in an MEA generated current densities of 211 and 784 mA cm\(^{-2}\) at 0.80 and 0.67 V, respectively, which outperforms a typical Pt/C cathode (TEC10V20E. 0.1 mgPt cm\(^{-2}\)) in the kinetic voltage range (0.95 to 0.75 V). Under an optimal relative humidity (RH) of 75 %, the MEA can achieve a power density of 501.0 mW cm\(^{-2}\) at 0.67 V, competing with many state-of-the-art PtCo catalyst for PEMFCs. Compared to previously reported NH\(_4\)Cl-treated catalysts, the degradation in MEA is also significantly mitigated, likely due to more graphitized local carbon structures enhancing the intrinsic stability of pyrrolic-N coordinated Fe sites.

Results and Discussion

Catalyst synthesis, activity and stability

Pyrolyzing precursors under an inert atmosphere (e.g., N\(_2\) or Ar) has long been the prevailing approach for constructing FeN\(_4\) active sites in Fe-N-C catalysts.\(^{16-18}\) Later on, Dodelet et al. found that a post-treatment in NH\(_3\)/N\(_2\) can efficiently promote the ORR activity due to the formation of substantial micropores to host increased numbers of active sites.\(^{19,20}\) Here, we found that controlling H\(_2\) content in the forming gas (FG) (H\(_2\)/Ar mixture) can efficiently promote the activity by exclusively generating active S1 sites (\textbf{Figure 1a}).

In this research, Fe\(_2\)O\(_3\)-doped ZIFs was used as the precursor. When the H\(_2\) content in the forming gas increases from 0 (i.e., Ar atmosphere) to 2 mol.% (denoted as Fe-N-C-2\(\%\)FG), the ORR activity of the catalyst was greatly promoted (\textbf{Figure 1b}), evidenced by an increase of half-wave-potential (\(E_{1/2}\)) from 0.843 to 0.884 V vs. RHE under established test conditions (600 \(\mu\)g cm\(^{-2}\), 25 \(^\circ\)C, 900 r.p.m., and O\(_2\)-saturated 0.5 M H\(_2\)SO\(_4\)). When the H\(_2\) content increases to 5 mol. %, the catalyst exhibited an \(E_{1/2}\) up to 0.922 V\(_{\text{RHE}}\), outperforming a Pt/C baseline catalyst (60 \(\mu\)gPt cm\(^{-2}\)). Further increasing H\(_2\) content to 10 mol.% only led to a minor improvement in ORR activity, achieving a reproducible \(E_{1/2}\) of 0.925 V\(_{\text{RHE}}\) (\textbf{Supplementary Figure 1}). The active sites density (SD), as determined by using electrochemical stripping of nitrite\(^{21}\), was increased with an increase of H\(_2\) content in the pyrolysis atmosphere (\textbf{Figure 1c, Supplementary Figure 2}). In addition, the turnover frequency (TOF) of Fe-N-C-10\(\%\)FG is 3.3 site\(^{-1}\) s\(^{-1}\) at 0.9 V, significantly higher than Fe-N-C-Ar (0.56 site\(^{-1}\) s\(^{-1}\)), suggesting enhanced intrinsic activity.

The activity, 4e\(^-\)-selectivity, and stability of the Fe-N-C catalysts prepared from different atmospheres were also compared following standard accelerated stress tests (ASTs) (0.60 to 0.95 V for 30,000 cycles) in O\(_2\)-saturated 0.5 M H\(_2\)SO\(_4\) using rotary ring-disk electrode (RRDE) (\textbf{Supplementary Figure 3}). The stability of Fe-N-C catalysts was decreased with increasing H\(_2\) content in the atmosphere during the pyrolysis, i.e., 52 mV loss in \(E_{1/2}\) for the Fe-N-C-Ar, 72 mV for the Fe-N-C-2\(\%\)FG, and 92 mV for the Fe-N-C-10\(\%\)FG catalyst. Notably, the \(E_{1/2}\) of Fe-N-C-10\(\%\)FG at the end of test dropped to 0.833 V\(_{\text{RHE}}\), which is close to the initial performance of Fe-N-C-Ar. The Fe-N-C-Ar and the Fe-NC-10\(\%\)FG catalyst presented different degradation modes in RDE stability tests (\textbf{Supplementary Figure 3}). The ORR activity of the Fe-NC-10\(\%\)FG catalyst was stabilized after 5,000 cycles AST, while the activity of the Fe-N-C-Ar kept decreasing during the AST. \textbf{Figure 1d} further summarizes the correlations of the activity and stability of Fe-N-C catalysts with pyrolysis atmospheres (i.e., H\(_2\) content), in which the \(E_{1/2}\) and kinetic current density
at 0.9 \( V_{\text{RHE}} \) (\( j_{\text{k}}@0.9 \) V) are identified as indicators for activity and their changes during the AST for evaluating stability. The strategy of construction of highly active Fe-N-C catalysts via the forming gas atmosphere has also been applied to the conventional Fe ion-doped ZIF precursors. As shown in Supplementary Figure 4a, the catalyst prepared in forming gas (Fe-ZIF-NC-FG) exhibited improved ORR activity (\( E_{1/2} = 0.896 \) \( V_{\text{RHE}} \)), higher than the catalyst from traditional Ar. In addition to the high activity, the forming gas treatment also has a higher selectivity towards 4e\(^-\) process (Supplementary Figure 4b). The determined active site densities of these Fe-ZIF-NC-Ar and Fe-ZIF-NC-FG are 2.33\( \times 10^{19} \) and 3.16\( \times 10^{19} \) site g\(^{-1}\), respectively. The similar tendency to promote activity and selectivity for both Fe\(_2\)O\(_3\)-doped ZIF and Fe-ion-doped ZIF precursors further verifies the effectiveness of the forming gas during the formation of active sites and their local structures.

\(^{57}\)Fe Mössbauer spectroscopy, highly sensitive to the oxidation state, electron configuration, and atomic coordination environment of Fe nuclei, was performed to study the impact of pyrolysis atmosphere on coordinating environments and local structures of FeN\(_4\) sites (Figure 1e-g, Supplementary Table 1). The Mössbauer spectra of the Fe-N-C catalysts were fitted with two doublets, in addition to a singlet and a sextet assigned to \( \gamma \)-Fe. D1 doublets with lower isomer shifts (IS) and quadrupole splitting (QS) values are assigned to the high-spin S1 moiety (S1 site, Figure 1a), in which Fe nucleus coordinates with four porphyrinic (i.e., pyrrolic) nitrogen atoms. The D2 doublets featuring larger QS values were assigned to low- or intermediate-spin S2 moiety (Figure 1a), in which the Fe nucleus coordinates with four pyridinic nitrogen atoms. The ratio of S2/S1 decreased from 0.78 for the Fe-N-C-Ar catalyst to nearly zero for the Fe-N-C-10\%FG, indicating the exclusive existence of S1 sites in the highly active catalyst. The correlation between catalyst activity/stability and the \(^{57}\)Fe Mössbauer spectroscopy illuminates that the pyrolysis atmosphere can regulate the nature of FeN\(_4\) active sites. \(^{57}\)Fe Mössbauer spectra suggest minor differences in the atomic configurations of S1 sites in the Fe-N-C-Ar and the Fe-N-C-10\%FG catalysts, which could contribute to their stability behaviors. For example, the isomer shift (IS) of the Fe-N-C-10\%FG catalyst (0.396 mm s\(^{-1}\)) is higher than the Fe-N-C-Ar catalyst (0.338 mm s\(^{-1}\)), indicating strengthened Fe-N bonds due to the \( \sigma \)-donation of p-electrons from nitrogen atoms to Fe 4s orbitals. A higher quadrupole splitting (1.43 vs. 1.22 mm s\(^{-1}\)) also suggested shortened Fe-N bonds in the Fe-N-C-10\%FG catalyst.

The morphologies of the Fe-N-C-Ar and the Fe- N-C-10\%FG were compared concerning carbon particles, carbon structures, and atomic single-site dispersion in a carbon matrix (Figures 2, Supplementary Figure 5). Unlike the Fe-N-C-Ar catalyst with well-defined polyhedral particles of clear edges and faces, Deformation and collapse of particle surface and highly curved carbon structures are apparent in the Fe-N-C-10\%FG catalyst (Figures 2a and e). Comparing with Fe-N-C-Ar, the surface of the Fe-N-C-10\%FG catalyst is composed of microporosity as indicated by the arrows in Figures 2g, Supplementary Figure 5 compared the morphologies of the catalyst prepared in the different atmosphere, from which an increase in the H\(_2\) concentration in the pyrolysis atmosphere leads to deformed catalyst particles with concaved facets. Unlike Fe-N-C-Ar catalyst with a homogeneous porosity distribution, hollow structures can be occasionally found in the Fe-N-C-10\%FG catalyst (Figures 2f). Fe nanoparticles can be also found in the Fe-N-C-
10%FG catalysts, corresponding to the presence of singlet and sextet in the $^{57}$Fe Mössbauer spectrum. The Fe nanoparticles were encapsulated within the compact carbon shells up to 14 layers (Figures 2i), some of which can even catalyze the growth of nitrogen-doped multiwall carbon nanotube (MWCNT, Figures 2j-k). ADF-STEM further confirmed that atomically dispersed metal sites were hosted in the nitrogen-doped MWCNT (Figures 2i).

The edges of both Fe-N-C-Ar and Fe-N-C-10%FG have crumpled few-layer thick graphitic structure, except that the graphitic structure in Fe-N-C-10%FG is more distinct (Figure 3a-f). Both Ar- and forming gas-treated catalysts present the atomically dispersed nature of the iron species as observed by aberration-corrected annular-dark-field scanning transmission electron microscopy (ADF-STEM, Figure 2c and g). The STEM-EDS quantification indicates that the Fe-N-C-FG catalyst contains significantly reduced Zn content relative to the Fe-N-C-Ar after the identical high-temperature treatment (Supplementary Table 2). X-ray absorption spectroscopy analysis indicates that the absorption edge positions of both Fe-N-C catalysts were located between those of Fe foil and Fe$_2$O$_3$ references (Figure 2c), suggesting that the valence state of these Fe atoms resides between 0 and $+3$.27,28 Notably, the XANES analysis confirms that the Fe-N-C-FG catalyst has a similar oxidation state and local structure to the FePc, likely containing a similar pyrrolic N coordination environment (Figure 2i). The best-fitting result indicated a coordination number (C/N) of 4.0 (±1) in the first shell of Fe atoms in these Fe−N−C catalysts (Supplementary Table 3).29 EXAFS fitting suggested a decreased Fe-N bond length induced by the pyrolysis atmosphere, reducing from 2.02 Å in the Fe-N-C-Ar to 1.95 Å in the Fe-N-C-10%FG catalyst. The shortened Fe-N bond in Fe-N-C-10%FG could be vital for the enhanced intrinsic stability of its FeN$_4$-S$^1$ sites towards demetallation in an acid medium.

As the microporosity is crucial to anchor active sites,30,31 Brunauer – Emmett – Teller (BET) and pore analysis were performed to assess the impact of pyrolysis atmosphere on the porosities of the catalysts. The BET surface area of the Fe-N-C catalysts increased from 824.4 (Fe-N-C-Ar) to 1187.3 m$^2$ g$^{-1}$ (Fe-N-C-10%FG) (Supplementary Figure 6, Supplementary Table 4), corresponding significantly increased micropore surface areas from 753.0 to 1047.0 m$^2$ g$^{-1}$ (Supplementary Figure 7d). Notably, the external surface areas, which are comprised of meso- and macro-porosity, are increased monotonically with the H$_2$ concentration, likely due to the graphitic carbon shells formed in the forming gas cause thermal stress and uneven shrinkage of carbon particles.32,33 The presence of graphitic carbon shells was evidenced by the appearance of 2D peak in the Raman spectrum of the Fe-N-C-10%FG catalyst (Figure 2i), which relates to the stack of multilayered graphitic structures in the catalyst (Supplementary Figure 7).34 Notably, there is no apparent 2D peak for the Fe-N-C-Ar catalyst, indicating a less graphitized carbon structure. It has been found that the 2D peak appears when the H$_2$ concentration is above 2 mol.%, indicating the stack of multilayered graphitic structures. The thermal stress leads to a highly concaved surface, contributing to the high specific surface area in Fe-N-C-FG catalysts.35

The function of the pyrolysis atmosphere in governing the formation of S1 and S2 sites has been investigated by in-situ X-ray photon electron spectroscopy (XPS), as shown in Figure 3 and Supplementary Figure 8. Below 200 °C, the nitrogen atoms are mostly coordinating with carbon in ZIF-8 precursors.36 As the temperature increased above 400 °C, the formation of pyridinic and
pyrrolic nitrogen species became apparent. Five peaks for Fe-N-C catalysts were observed in N 1s spectra, including 398.8 eV for pyridinic N, 399.8 eV for Fe-N, 400.7 eV for pyrrolic N, 402.3 eV for graphitic N, and 403.3 eV for oxidized N.\textsuperscript{14,37,38} Figure 3a illustrates that, at the same temperature, more pyrrolic nitrogen was produced in the forming gas compared to Ar. The difference becomes more apparent when the temperatures are above 700 °C, from which the percentage of pyrrolic nitrogen formed in the forming gas becomes dominant relative to pyridinic nitrogen. The relevant scheme of S1 sites under forming gas atmosphere is depicted in Figure 3b, in which the Fe-N bonds start to form at 200 °C in forming gas, significantly lower than in Ar (400 °C, Supplementary Figure 8).\textsuperscript{28} Unlike the Fe-N-C-FG, iron oxides still exist until 900 °C and can only be partially converted to FeN\textsubscript{4} active sites under Ar atmosphere. Metallic Fe was detected in forming gas at a lower temperature than Ar (Supplementary Figure 8).\textsuperscript{28} These metallic Fe nanoparticles could catalyze the graphitization of the carbon matrix,\textsuperscript{39} as evidenced by the Raman spectra recorded at different temperatures (Supplementary Figure 10). They can then be thermally decomposed and removed during the high temperature treatment. The relatively high percentage of pyrrolic nitrogen in the Fe-N-C-FG was maintained even after thermal annealing at 1100 °C (Figure 3c and Supplementary Table 6), indicating the formation of pyrrolic nitrogen is more favorable in the forming gas. Figure 3d correlates the Zn contents and M-N contents in the Fe-N-C-Ar and Fe-N-C-FG catalysts. Above 600 °C, a sharp decrease of Zn was observed in the forming gas. The content of Zn in Fe-N-C-10%FG approaches to zero above 800 °C, while considerable Zn still exists in the Fe-N-C-Ar catalyst. In a wide temperature range, the M-N contents in the catalysts prepared in forming gas are higher than those prepared in Ar atmosphere. Correlating with the lower Zn content in Fe-N-C-FG, the pyrolysis in forming gas is more efficient in removing Zn, leaving the cavities for the constructing of FeNx sites. The critical temperature for the active site construction in the forming gas was examined by using two differently combined temperatures (Figure 3e). A second heat treatment at 1100 °C in Ar is necessary to accomplish a full carbonization and removal of Zn in the Fe-N-C catalysts, which is critical to the actual ORR performance (Supplementary Figure 9). We found that 700 °C is the critical temperature for the formation of highly active sites under the forming gas atmosphere. Above which, the indicators for ORR, including $E_{1/2}$, kinetic current densities at 0.9 V_{RHE} and Tafel slope, were improved dramatically, indicating a significant enhancement in the ORR activity. The electrochemical performance is consistent with the in-situ N 1s XPS analysis, showing the dominant formation of pyrrolic N at 700 °C. A further increase in the temperatures beyond 800 °C will trigger the evaporation of Zn, making more pyrrolic Zn-imprinted N4 cavities available.\textsuperscript{15}

**Fuel cell MEA performance**

The ORR performance of the best-performing Fe-N-C-FG catalyst was further studied in H\textsubscript{2}-fuel cells and direct methanol fuel cells (DMFCs). As for the H\textsubscript{2} cell, the MEA with the Fe-N-C-10%FG cathode reaches 50.8 mA cm\textsuperscript{-2} at 0.9 V_{RHE-free} under 1.0 bar O\textsubscript{2} (Figure 5a), significantly exceeding the U.S. DOE target set for 2025 (44.0 mA cm\textsuperscript{-2}). Under practical air conditions (1.0 bar air), the same MEA generated 211 and 784 mA cm\textsuperscript{-2} at 0.80 and 0.67 V, respectively, which outperforms a typical Pt/C cathode (TEC10V20E. 0.1 mgPt cm\textsuperscript{-2}) in the kinetic voltage range (0.95 to 0.75 V).
Due to the water flooding within the thick PGM-free cathode, an optimal RH of 75 % can achieve a maximum power density of 501.0 mW cm\(^{-2}\) at 0.67 V (Supplementary Table 9).

During the durability AST using a square-wave voltage cycling protocol, the current density of Fe-N-C-10%FG cathode at 0.8 V was decreased from 162 to 67 mA cm\(^{-2}\) after 30,000 cycles corresponding to a loss of 58.7 % (Figure 5c).\(^{40}\) The voltage loss at 0.8 A cm\(^{-2}\) is 76 mV (Supplementary Table 11). Relative to the Fe-NC-10%FG cathode, the performance loss of the Fe-N-C-Ar cathode in a MEA is more significant, showing a current density loss of ca. 90 % at 0.8 V (Supplementary Table 11). Similar to the catalyst degradation in RRDE, Fe-N-C-Ar catalyst decayed in a continuous pattern, while Fe-N-C-10%FG tended to be stabilized after 5000 cycles of AST in the H\(_2\)-air fuel cell. Notably, ASTs performed under H\(_2\)/N\(_2\) atmosphere for the Fe-NC-10%FG catalyst exhibited comparable performance loss relative to the H\(_2\)/air conditions (Supplementary Figure 12), suggesting that the demetallation is primarily driven by voltage/potential cycling. Compared to a Pt/C (TEC10V20E) cathode, the Fe-NC-10%FG cathode-based MEA demonstrated similar durability (Figure 5e), since significant performance loss was also observed with the Pt/C cathode after the identical AST. In addition to voltage cycling AST stability evaluation, we also carried out a long-term life test for these Fe-N-C cathodes by holding them at a constant voltage of 0.67 V (Figure 5g). Compared with the Fe-AC cathode,\(^{6}\) the Fe-NC-10%FG cathode showed much high retention of current density during the test. In particular, the Fe-N-C-FG cathode showed an exponential decay in the initial stage, followed by a linear decay with a slow rate.\(^{41}\) The much-enhanced MEA durability is mainly contributed by the new S1 site in the robust carbon matrix with enhanced intrinsic stability.

As Fe-N-C catalysts are highly methanol-tolerant,\(^{42}\) such PGM-free catalysts are highly desirable for DMFCs with reduced cost and mitigated catalyst poisoning. Thus, the Fe-NC-10%FG has been utilized as a cathode catalyst in DMFCs, which exhibited a peak power density of 275 mW cm\(^{-2}\) at a loading of 3.0 mg\(_{\text{PGM}}\) cm\(^{-2}\), significantly exceeding Pt/C cathode (80 mW/cm\(^{2}\)) under the similar conditions (Figure 5f). Like the behavior in the H\(_2\)-fuel cell, the performance of the Fe-N-C-FG cathode decayed after 10,000 cycles of AST and then stabilized until 30,000 cycles. Moreover, a 20-h steady-state test at 0.5 V was performed to verify its stability under DMFC conditions. As shown in Figure 5h, the 20h stability test practically maintained the current density at 250 mA cm\(^{-2}\) at 0.5 V.

Mechanistic insights into the activity and stability enhancement

To further understand the observed superior ORR activity and improved durability of the Fe-N-C-FG catalyst, we performed the first-principles density functional theory (DFT) calculations to predict the effect of thermal activation atmosphere and electrochemical stability of FeN\(_4\) sites embedded in carbon. Considering that the forming gas environment used in our synthesis process could introduce additional hydrogen adsorbed on the carbon surface, we constructed both S1-4H and S2-4H sites (Figure 6a) containing four hydrogen atoms bound with the carbon atoms directly adjacent to the FeN\(_4\) moiety, to model the FeN\(_4\) active site formation mechanisms under a forming gas environment.
We predicted the Fe-N bond length to be 2.09 Å in S1 type FeN₄ whereas 2.05 Å in the S1-4H site, respectively, consistent with the experimental observations of Fe-N bond shrinking in the Fe-N-C-FG catalyst from R-values of Fe-N in X-ray absorption. Moreover, we calculated the enthalpy change ($\Delta E$) for the transition of a single Fe atom from the S2 type N₄ moiety to the S1 type N₄ moiety to gauge the thermal stability of two types of FeN₄ sites under the forming gas environment. As shown in Figure 6 b₁-b₂, we predicted that the value of $\Delta E$ would decrease from 0.34 to 0.10 eV if the carbon atoms directly adjacent to the FeN₄ moiety were hydrogenated. This result suggests that introducing hydrogen could enhance the formation of the S1 FeN₄ site, relative to the S2 site. This can explain that the Fe-N-C-FG catalyst was found to show a lower S2/S1 ratio than the Fe-N-C-Ar catalyst (Figure 1g). The higher concentration of S1 FeN₄ site modified by 4H is believed to lead to the observed ORR activity in the Fe-N-C-FG catalyst. The electronic structure analysis was conducted to evaluate the charge transfer between FeN₄ moiety and carbon matrix. The charge density difference of the S1 site (Figure 6c) shows electron accumulation near FeN₄ moiety. This finding agrees well with our Bader charge analysis result that the FeN₄ moiety gained 1.91 |e| from the graphene layer in the S1 site, lower than that of 2.09 |e| in the S1-4H site. This result indicates the introduction of hydrogen in S1 type FeN₄ sites could enhance the interaction between FeN₄ moiety and the graphene layer, underlying the improved thermal stability of the S1 FeN₄ site.

In addition, the DFT calculations were performed to study the stability of these possible active sites against demetallation in an electrochemical environment. The proposed demetallation process of Fe is presented in Figure 6d, which shows that the Fe, together with adsorbed O₂ moves away from an N₄-coordinated state into an N₂-coordinated state. At the same time, the other two N atoms form N-H bonds with protons from the electrolyte. The Gibbs free energy for the demetallation process was predicted to be 0.05 eV for the S1 type FeN₄ site, lower than that of 0.35 eV on the S1-4H site. This result indicates that the electrochemical stability against demetallation of the S1 FeN₄ site could be improved via hydrogenating those carbon atoms immediately adjacent to N atoms of FeN₄ moiety along with shortened Fe-N bond caused by H₂ adsorption during the thermal activation. Therefore, the DFT calculations elucidate the experimental observations, predicting that the Fe-N-C-FG catalyst has higher intrinsic stability than traditional Fe-N-C catalyst containing regular pyrrolic N-coordinated sites (Figure 4g).

Conclusions
Simultaneously enhancing the activity and stability for current Fe-N-C catalysts faces grand challenges due to the co-existence of active/unstable S1 sites and durable/less active S2 sites. Traditional synthesis methods cannot well control the ratios of S1 to S2, generating catalysts that are either active but not stable or more stable but less active. In this work, we developed effective approaches that begin to break the activity-stability trade-off by preparing a highly active S1 site-rich catalyst with enhanced stability. Using H₂/Ar forming gas, instead of pure Ar, leads to exclusive S1 sites in the corresponding catalyst, which exhibited high ORR activity in MEAs (50.8 mA cm⁻² at 0.9 Vₚₐₜ-free under 1.0 bar O₂ and 211 mA cm⁻² at 0.8 V under 1.0 bar air, significantly exceeding DOE 2025 targets), outperforming a typical Pt/C catalyst in both RDE and MEA. Due
to the shortened Fe-N bond and graphitized local carbon structure, the catalyst containing a new type of S1 sites exhibited improved catalyst stability. Although the catalyst still degraded during the stability ASTs (162 to 67 mA cm\(^{-2}\) at 0.8 V under 1.0 bar air), it behaved better than traditional Pt/C cathode. \(^{57}\)Fe Mössbauer spectroscopy and other critical techniques, along with DFT calculations, have been combined to elucidate the origin of improved activity and stability. A robust coordinating environment of the S1 site, which includes shortened Fe-N bonds and graphitized carbon basal, will contribute to the high retention of activity and stability.

**Methods**

**Synthesis of Fe-N-C-n\%FG.** In a typical procedure, 10 mg Fe\(_2\)O\(_3\) nanoparticles (Alfa-Aesar, 5 nm APS Powder) and 6.78 g zinc nitrate hexahydrate were dispersed and dissolved into 150 mL methanol solution. The other 150 mL methanol solution contained 7.88 g 2-methylimidazole. Then both solutions were mixed and heated at 60 °C for 24 h, the precipitant was collected and washed with ethanol, and dried at 60 °C in a vacuum oven to obtain Fe\(_2\)O\(_3\)@ZIF-8 composite. The Fe\(_2\)O\(_3\)@ZIF-8 composite was pyrolyzed at 1100 °C for one h under forming gas (10 mol.% H\(_2\) in Ar) to obtain Fe-N-C-FG. For comparison, the Fe\(_2\)O\(_3\)@ZIF-8 composite was pyrolyzed at 1100 °C for one h in Ar and forming gas with lower H\(_2\) concentrations (2-5 mol. % H\(_2\)).

**Morphology and Structure Characterizations.**

\(^{57}\)Fe Mössbauer spectra were acquired at room temperature and without applying an external magnetic field using a \(^{57}\)Co/Pd source in constant acceleration modes. \(^{57}\)Fe-N-C catalysts were prepared with \(^{57}\)Fe\(_2\)O\(_3\) nanoparticles (\(^{57}\)Fe enrichment >95 %, American Elements) with the identical method mentioned above. The spectra were analyzed using the WinNormos program, a commercial package provided by WissEl – Wissenschaftliche Elektronik GmbH (Starnberg, Germany). Mössbauer doublets were fit using the Lorentzian mode of WinNormos.

Secondary electron microscopy images were obtained on Focused Ion Beam Scanning Electron Microscope (FIB-SEM, Carl Zeiss AURIGA CrossBeam). STEM images were acquired on a proper-corrected JEOL NEOARM operated at 80 kV in the Center for Nanophase Materials Sciences at Oak Ridge National Laboratory. Fe K-edge X-ray absorption spectroscopy was measured at beamline 11-2 at the Stanford Synchrotron Radiation Light source (SSRL). Data reduction, data analysis, and EXAFS fitting were performed with the Athena, Artemis, and IFEFFIT software packages.

In-situ X-ray photoelectron spectroscopy (XPS) analysis was performed with a Kratos AXIS Ultra DLD XPS (Kratos Analytical). The XPS system is equipped with a monochromatic Al K\(_\alpha\) source operated at 15 keV and 150 W, a hemispherical analyzer, a charge neutralizer, a catalysis cell, and a load lock chamber for the rapid introduction of samples without breaking the vacuum. X-rays were incident at an angle of 45 °, with respect to the surface. The in-situ reduction of the materials was performed in an in-situ catalyst treatment cell directly attached to the XPS chamber, which allows the sample to be treated under gas flow conditions. The samples were transferred between the reaction cell and the analysis chamber without exposure to the atmosphere. The in-situ treatments were performed under the flow of 10% H\(_2\)/Ar and Ar for one hour at various temperatures. Limited to the hardware, the highest temperature for in-situ XPS was terminated at
Micromeritics TriStar II measured the N\textsubscript{2} isothermal adsorption/desorption for the catalysts at 77 K. The BET surface areas were derived with a correlation coefficient higher than 99.99% and with positive constants. The distribution of porosity was obtained with the classic cylinder model calculated by the DFT method (Halsey thickness curve). The micropore surface area was obtained by t-Plot.

**Electrochemical measurements.** At room temperature, an electrochemical workstation (CHI 760E) equipped with Pine AFMSRCE 3005 in a three-electrode cell was employed to take all rotation disk electrode (RDE) measurements. The Hg/Hg\textsubscript{2}SO\textsubscript{4} (saturated K\textsubscript{2}SO\textsubscript{4} electrolyte) electrode and a graphite rod were used as the reference and counter electrodes, respectively. A glassy carbon rotating-disk electrode (RDE) coated with the catalyst ink as the working electrode with a controlled loading of 0.6 mg cm\textsuperscript{-2} at 900 rpm for all measurements. Before each test, the reference electrode was calibrated to a reversible hydrogen electrode (RHE) in the same electrolyte. The catalyst ink for the RRDE tests was prepared by mixing 5.0 mg catalyst with the diluted Nafion solution under ultrasonic conditions for 30 min. Steady-state polarization curves were recorded in O\textsubscript{2}-saturated 0.5 M H\textsubscript{2}SO\textsubscript{4} to determine the ORR activity, using a potential staircase at a step of 0.05 V at an interval of 30 seconds from 1.0 to 0 V versus RHE. Four-electron selectivity and H\textsubscript{2}O\textsubscript{2} yield during the ORR were determined by applying a high potential (1.10 V vs. RHE) on the ring electrode, leading to H\textsubscript{2}O\textsubscript{2} electrooxidation during the ORR process.

**In-situ nitrite stripping for the determination of FeN\textsubscript{x} site density (SD)**

The active site density was determined according to an in-situ nitrite adsorption/stripping method reported by Kucernak et al.\textsuperscript{21} The catalyst ink for nitrite adsorption/stripping was prepared by dispersing 1 wt. % catalyst in a mixture of isopropanol (IPA), H\textsubscript{2}O (MilliQ 18.2 M \(\Omega\) cm), and Nafion (D521). The volume ratio of IPA to water is 1:1. The weight ratio of catalyst to Nafion dispersion is 1:1. The homogeneous catalyst ink was drop-casted onto a glassy carbon electrode (0.247 cm\textsuperscript{2}) to yield a catalyst loading of 0.20 mg cm\textsuperscript{-2} for all experiments. 0.5 M acetate buffer (pH 5.2) was utilized as an electrolyte and prepared from sodium acetate (99.0 %) and glacial acetic acid for nitrite adsorption/stripping. 125 mM NaNO\textsubscript{2} solution was used as a probing electrolyte. A graphitic rod and Hg/Hg\textsubscript{2}SO\textsubscript{4} (saturated K\textsubscript{2}SO\textsubscript{4} solution) electrode were used as counter and reference electrodes, respectively. The testing protocol, including electrode cleaning, ORR performance measurement, poisoning, and stripping (recovery), was summarized as follows: (1) the working electrode was subjected to potential cycling between −0.4 and 1.0 V with a scan rate of 50 and 10 mV s\textsuperscript{-1} in Ar-saturated electrolyte until a steady-state CV profile was obtained. (2) Evaluate the ORR performance of Fe-N-C catalyst (un-poisoned) in O\textsubscript{2}-saturated electrolyte at a rotation speed of 1600 r.p.m and scan rate of 10 mV s\textsuperscript{-1}. The background current density was recorded by cyclovoltammetry between −0.35 and 0.35 V in Ar-saturated electrolyte at a scan rate of 10 mV s\textsuperscript{-1}. (3) The working electrode was immersed in 125 mM NaNO\textsubscript{2} solution and conditioned at open circuit potential for 5 minutes. The rotation speed of the working electrode is 300 r.p.m. The working electrode was then cleaned in deionized water (5 min), electrolyte (5 min) and deionized water (5 min) at a rotating rate of 300 r.p.m. (4) The ORR performance of the
working electrode (poisoned) was measured in O2-saturated electrolyte with the same parameters in Step (2). (5) The nitrite stripping was performed in Ar-saturated electrolyte with identical parameters in Step (2). Step (2) was repeated to record the ORR performance after recovery.

The number of FeNx active sites was quantified by the stripping charge of nitrite anions:

$$\text{SD} = \frac{Q_{\text{strip}}[\text{C g}^{-1}]N_A[\text{atom mol}^{-1}]}{n_{\text{strip}}F[\text{C mol}^{-1}]}$$

Where $Q_{\text{strip}}$ is the coulometric charge associated with the stripping of nitrite; $N_A$ is Avogadro’s constant; $n_{\text{strip}}$ ($= 5$) is the number of electrons associated with the reduction of one adsorbed nitrite anion per site, $F$ is Faraday’s constant. The TOF (site$^{-1}$ s$^{-1}$, at 0.9 V) can be calculated from the kinetic current density $i_k$ at 0.9 V and SD via:

$$\text{TOF}(@0.9 \text{ V versus RHE}) [\text{s}^{-1}] = \frac{i_k[\text{A g}^{-1}]N_A[\text{mol}^{-1}]}{\text{SD [sites g}^{-1}F[\text{A s mol}^{-1}]}}$$

**H2-air fuel cell tests.** Both anodic and cathodic electrode was prepared by the catalyst-coated membrane (CCM) method. For the anodic electrode, the catalyst ink was prepared by mixing 20 wt. % Pt/XC-72 catalyst and ionomer dispersion (25 wt. %, Aquivion D79–25BS), the ionomer to carbon ratio is 0.6, the solvent is a mixture of n-propanol and deionized-water (DI-water) with 1:6 ratio. The prepared ink was firstly sonicated for 30 minutes in a water bath with a temperature under 30 °C followed by sonicating for 4 minutes using a sonic dismembrator (Fisher Scientific Model 120, Waltham, MA). The prepared ink was then sprayed onto a 5 cm$^2$ square Gore membrane by Exacta Coat spray machine (Sono-Tek, NY), and the Pt loading at the anode was controlled as 0.1 mg Pt cm$^{-2}$. Preparing cathode to follow a similar protocol, but the ionomer to carbon ratio was controlled to 0.6. The solvent mixture was replaced by a mixture of 2-propanol and DI-water with a 1:1 volume ratio. The prepared ink was sprayed on the opposite side of the anode, aligning with the anode, and the loading was controlled between 4.0 and 4.5 mg catalyst cm$^{-2}$. Two pieces of SGL–22BB served as the gas diffusion layer in an MEA. MEAs were measured by a fuel cell test station (Fuel Cell technology, Inc., Albuquerque, NM, USA). First, the cell was heated to 80 °C without flow, then 200 mL min$^{-1}$ of N2 in the anode and cathode for 2 hours to hydrate the membrane and ionomer. Air/oxygen flowing at 500 mL min$^{-1}$ and H2 (purity 99.999%) flowing at 300 mL min$^{-1}$ was supplied to the cathode and anode, respectively. The back pressures during the fuel cell tests are 150 kPa abs. The Dew points of anodic flow and cathodic flow are 80 °C. The cell temperature was maintained at 80 °C during the recording of I-V curves. MEA performance under H2-O2 and H2-air conditions were measured by following the latest U.S. ElectroCat Consortium protocols.$^{46}$ Especially the polarization curves were measured using the scan voltage method: in a range of 0.96 to 0.84 V, the scan rate is 20 mV per step and hold 45 s for each step, in a range of 0.84 to 0.72 V, the scan rate is 40 mV per step with 45 s holding for each step. MEA durability was evaluated by applying trapezoid potential on the cathode. The cathode was held at 0.96 V and 0.6 V for 2.5 seconds, the rising time from 0.6 to 0.96 V is 0.25 seconds, and the reverse is the same. Flow rates are 200 and 400 sccm of H2 and air in the anode and cathode at 100 % RH, respectively. The backup pressure is 150 kPa abs, and the cell temperature is 80 °C.
All fuel cell cathodes: catalyst loading 4.0 mg cm\(^{-2}\) for Fe-N-C and 0.1 mg cm\(^{-2}\) Pt for Pt/C (20 \%, JM); 100 \% RH; 0.6 I/C; 150 kPa\(_{\text{abs}}\) total pressure. Membrane: Gore membrane. Temperature: 80 \(^\circ\) C. MEA area: 5.0 cm\(^2\). MEA tests were performed in a differential cell with 14 parallel flow channels. The polarization curves were separately recorded at 5,000, 10,000, 20,000, and 30,000 cycles.\(^{40}\)

**Direct methanol fuel cell tests.** The MEA was prepared by a CCM method, in which catalyst ink was deposited onto Nafion 212 membrane through the air-spraying coating. The anode catalyst ink was made with PtRu/C (75 wt. \%, JM), 2-propanol, and 5 wt. \% Nafion dispersion (D521), the I/C ratio was 0.8. The mixture was dispersed in an ultrasonication bath for 2 hours. Then the ink was deposited onto Nafion 212 membrane. The loading of PtRu was controlled to be 3.0 mg cm\(^{-2}\). The cathode electrode was prepared by a blade coating technique. Carbon fiber paper with a microporous layer (Sigracet 22BB) was used as anode GDL. The cathode catalyst ink was prepared by dispersing 40.0 mg Fe-N-C-FG, 640 mg 5 wt. \% Nafion dispersion (D521) in the solvent. Then the homogeneous slurry was applied onto GDL (Sigracet 22BB) with a blade, and the loading of the Fe-N-C-10\%FG was controlled to be 4.5 mg cm\(^{-2}\). During the DMFC testing, the anode and cathode were purged with 1 M methanol aqueous solution and dry air. The flow rates were 0.5 and 1000 sccm, respectively. The cell temperature was 94 \(^\circ\) C, the backpressure was 250 kPa\(_{\text{abs}}\). The I-V curves in the DMFC were recorded by scanning voltages from the O.C.V to 0.2 V with a staircase of 25 mV, each potential held for 60 seconds. The MEA durability in DMFC was evaluated by square wave AST, in which potential was cycled between 0.8 and 0.4 V, and each potential was held for 2.5 seconds. The transient time between 0.8 and 0.4 V was 0.25 seconds.

**Computational methods.** The first-principles density functional theory (DFT) calculations\(^{47,48}\) were performed using the Vienna ab initio simulation package (VASP) code\(^{49,50}\). The generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) functionals was used to describe the electronic exchange and correlation energy\(^{51}\). The energy cutoff was set as 400 eV to expand the wave function. The Brillouin zone was sampled using the Monkhorst-Pack\(^{52}\) scheme with a \(2 \times 3 \times 1\) k-points grid for all modeled FeN\(_4\) sites. A vacuum region of 14 Å thick was added in the direction normal to the carbon layer to ensure negligible interaction between the slab and its images. The optimized structures were obtained until the forces on each ion fell below 0.01 eV/Å. The computational hydrogen electrode method developed by Norskov et al\(^{53}\), was used to calculate the free energy change for the demetallation process. Zero-point energy (ZPE) corrections were included in all the energies reported in this work. ZPE corrections were calculated as \(\text{ZPE} = \frac{1}{2} \sum v_i h\), where \(h\) is Planck’s constant and \(v_i\) is the frequency of the vibrational mode of binding molecules.

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References


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Figure 1. (a) Schematic illustration of the construction of highly active S1 site (FeN₄C₁₂) via the control of the pyrolysis atmosphere. (b) Comparison of ORR performance of the Fe-N-C catalysts prepared in Ar and forming gas, in which commercial Pt/C (60 µgPt cm⁻²) served as baseline. The loadings for Fe-N-C catalysts are 0.6 mg cm⁻², the electrolyte is O₂-saturated 0.5 M H₂SO₄. (c) Tendency of the site density of the Fe-N-C catalysts prepared in the different atmosphere. (d) Evolution of activity and stability of Fe-N-C catalysts prepared in the different atmospheres before and after 30,000 cycles of accelerated degradation test. (e-g) The $^{57}$Fe Mössbauer spectra of the Fe-N-C-Ar and Fe-N-C-FG (2 and 10 mol. % H₂) catalysts, in which the ratios of D1 to D2 have been shown.
Figure 2. (a-h) ADF-STEM and TEM images of Fe-N-C-Ar (a-c) and Fe-N-C-FG (e-h) catalysts prepared at 1100 °C, in which the red arrow indicates the micropore in the surface of the Fe-N-C-FG (g). (i-l) Fe nanoparticles and multiwall carbon nanotubes in the Fe-N-C-FG, in which the Fe nanoparticle was encapsulated in the compact carbon shells.
Figure 3. (a-f) ADF-STEM images of Fe-N-C-Ar (a-c), and Fe-N-C-FG (d-f). (g-i) Fe K-edge XANES spectra (g) and Fourier-transformed EXAFS in R-space (h) and FT-EXAFS fitting curves in R spaces and q spaces (i) for Fe-N-C-Ar, Fe-N-C-FG and FePc without O\textsubscript{2} adsorption for the Fe-N-C-Ar and Fe-N-C-FG catalysts.
Figure 4. (a) In-situ N 1s XPS during the preparation of Fe-N-C catalysts in forming gas (10 mol. %) and Ar. (b) Schematic illustration of the transition of FeNₓ active site during the pyrolysis in forming gas at different temperatures. (c) Comparison of N 1s ex-situ XPS of Fe-N-C-Ar and Fe-N-C-FG prepared at 1100 °C. (d) Correlation of Zn content and M-N percentage at different temperatures in the pyrolysis in forming gas and Ar. (e) Determination of the critical temperature for boosting ORR activity of Fe-N-C during the pyrolysis in the forming gas, a secondary annealing at 1100 °C in Ar was performed to achieve a full carbonization of the catalysts.
Figure 5. (a) Determination of the catalysts’ activities at 0.9 V_{IR-free} under 150 kPa_{abs} backpressure for both anodic and cathodic sides, the green star denotes the U.S. DOE target for 2025. (b) Comparison of H_{2}-air fuel cell performance of Fe-N-C-10%FG and commercial Pt/C performances under 150 kPa_{abs} of air pressure with the flow rates of 700/1700 sccm (H_{2}/air). (c) Impact of relative humidity on single cell performance. The performance was recorded by increasing RH from 50 to 100 %. (d, e) H_{2}-air fuel cell polarization plots of (d) Fe-N-C-Ar, and (e) Fe-N-C-FG catalyst cathodes recorded at different cycles during the 30,000 cycles of AST. (f) Comparison of I-V curves of Fe-N-C-FG, and Pt/C before and after 30,000 cycles of AST in H_{2}-air fuel cells. (g) Long-term fuel cell life test under H_{2}-air conditions at a constant potential of 0.67 V (150 kPa_{abs} pressure and flow rates of air 200 sccm and H_{2} 200 sccm). (h) Direct methanol fuel cell (DMFC) performance of Fe-N-C-FG as cathode catalyst during the AST. The anode catalyst is 75% PtRu/C (JM) with a loading of 3.0 mgPtRu cm^{-2}. The anode was purged with 1.0 M methanol solution with a flow rate of 0.5 sccm, the cathode was purged with dry air with a flow rate of 1000 sccm, the cell temperature was 94 °C, the back pressure in the cathode is 250 kPa_{abs}. 
Figure 6. (a) Atomistic structure of proposed S1 FeN4 site, S2 FeN4 site, S1-4H FeN4 site, and S2-4H FeN4 site. (b1, b2) Atomistic model for the transition of a single Fe atom from the S2 type N4 moiety to the S1 type N4 moiety in the Ar (b1) and the S2-4H FeN4 site to the S1-4H FeN4 site (b2). (c) Charge density difference for the S1-4H site, which is calculated as $\rho(\text{FeN}_4+4\text{H}^+)-\rho(\text{FeN}_4)-\rho(4\text{H})$. Cyan and yellow represent charge accumulation and depletion in the region; the isosurface value is 0.002 e Å⁻³. (d) Atomistic structures of the simulation model for demetallation of central Fe from S1-4H site. In the figure, the black, blue, orange, red, and white balls represent C, N, Fe, O, and H atoms, respectively.