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Unraveling the Nature of Sites Active toward Hydrogen Peroxide Reduction in Fe-N-C Catalysts

Chang Hyuck Choi,* Won Seok Choi, Olga Kasian, Anna K. Mechler, Moulay Tahar Sougrati, Sebastian Brüller, Kara Strickland, Qingying Jia, Sanjeev Mukerjee, Karl J. J. Mayrhofer, and Frédéric Jaouen*

Abstract: Fe-N-C catalysts with high O_2 reduction performance are crucial for displacing Pt in low-temperature fuel cells. However, insufficient understanding of which reaction steps are catalyzed by what sites limits their progress. The nature of sites were investigated that are active toward H_2O_2 reduction, a key intermediate during indirect O_2 reduction and a source of deactivation in fuel cells. Catalysts comprising different relative contents of FeNC moieties and Fe particles encapsulated in N-doped carbon layers (0–100%) show that both types of sites are active, although moderately, toward H_2O_2 reduction. In contrast, N-doped carbons free of Fe and Fe particles exposed to the electrolyte are inactive. When catalyzing the ORR, FeNC moieties are more selective than Fe particles encapsulated in N-doped carbon. These novel insights offer rational approaches for more selective and therefore more durable Fe-N-C catalysts.

The oxygen reduction reaction (ORR), a key reaction for acidic fuel cells, is today most efficiently catalyzed by Pt materials.[1] However, the large-scale deployment of acidic fuel cells will be confronted with the grand challenge of developing inexpensive catalysts with high activity and stability.[2] While metal–nitrogen–carbon catalysts (M-N-C, especially M = Fe or Co) are promising,[3] further advances and fundamental insights into the factors governing their catalysis and durability are needed to meet the stringent industrial requirements.

The nature of active sites in pyrolyzed Fe-N-C catalysts is a highly complex and debated topic.[4] The simultaneous presence of multiple Fe species in most catalysts investigated hitherto has obscured the interpretation of their ORR behaviors, especially since multiple sites may lead to unexpected synergies. In particular, several types of active sites may be necessary to catalyze the multielectronic ORR, which may proceed either through a direct 4e^- pathway on a single site (O_2–H_2O), or through indirect pathways involving a desorbed H_2O_2 intermediate (O_2–H_2O_2–H_2O) on two sites. These may be identical in nature (consequential 2e^- × 2e^- mechanism), or different (bifunctional 2e^- + 2e^- mechanism). If the ORR proceeds via the bifunctional mechanism, one type of site (S1) reduces O_2 to H_2O_2 and another (S2) catalyzes the peroxyde reduction reaction (PRR). Under this hypothesis, only Fe-N-C catalysts comprising a high density of sites S1 and S2 may catalyze the ORR with an apparent low % H_2O_2. PRR catalysis is also highly desirable for improved durability of Fe-N-C catalysts because even low H_2O_2 production can lead to significant degradation during fuel cell operation.[5]

From advanced spectroscopy (Mössbauer[6] and X-ray absorption spectroscopy (XAS)[7] and mass spectrometry[8]) or molecular-probe approaches,[9] there is a growing consensus that FeNC moieties or N-C species encapsulating Fe particles (Fe@N-C) catalyze the transfer of the first 2e^- during ORR (S1).[10] Then, if the ORR mostly follows the 2e^- + 2e^- pathway, highly selective Fe-N-C catalysts should be characterized by a high number of sites S2.[11] It has been recently suggested that Fe particles or pyridinic-N groups might be the site S2.[12] However, improved understanding on...
the nature of the sites active toward PRR is still pivotal for improved durability. To determine whether Fe-N-C materials catalyze the ORR via a direct, consequential, or bifunctional mechanism, we have investigated the PRR activity on a set of catalysts, including model catalysts only comprising either FeNₓCᵧ moieties or Fe particles.

In the continuation of our recent studies,[10b,13] the catalysts were synthesized by pyrolysis of Fe¹⁺ acetate, 1,10-phenanthroline (Phen), and a Zn¹⁺ zeolitic imidazolate framework (ZIF-8). Three catalysts were first prepared, named FeNC-wet-1, FeNC-dry-1, and FeNC-dry-0.5, the labeling referring to homogenization conditions and Fe content before pyrolysis (see Methods in the Supporting Information). A catalyst pyrolyzed without Fe¹⁺ acetate was also prepared (“NC”). FeNC-wet-1, FeNC-dry-1, and FeNC-dry-0.5 showed Fe content of ca. 3.4, 3.0, and 1.5 wt% after pyrolysis, respectively, while about 100 ppm Fe was detected with inductively coupled plasma mass spectrometry (ICP-MS) for NC.[14] X-ray diffraction (XRD) and Raman spectroscopy revealed carbonization of ZIF-8 and Phen after pyrolysis (Supporting Information, Figure S1). X-ray photoelectron spectroscopy (XPS) shows similar N-doping level and N-components for all catalysts (Supporting Information, Figure S2, Table S1).

To identify the Fe structures in the catalysts, we examined their morphology with transmission electron microscopy (TEM), which revealed a larger number of Fe particles in FeNC-wet-1 than in FeNC-dry-1, with most Fe particles embedded in N-doped carbon layers (Supporting Information, Figure S3). ⁵⁷Fe Mössbauer spectroscopy showed that the crystalline Fe particles seen in TEM images correspond to α-Fe, Fe carbide, or γ-Fe (Figure 1a–c; Supporting Information, Table S2). The relative absorption area owing to Fe particles was 47% for FeNC-wet-1 and 8% for FeNC-dry-1. No signal assigned to Fe particles was detected for FeNC-dry-0.5, the Mössbauer spectrum of which shows only the doublets D1 and D2 (FeNₓCᵧ moieties). These observations were confirmed by extended X-ray absorption fine structure (EXAFS), with a lower intensity of the Fe-Fe backscattering signal for FeNC-dry-1 vs. FeNC-wet-1 (Figure 1d). As previously reported,[10b] a strong Fe-N(O) interaction without Fe-Fe interaction for FeNC-dry-0.5 confirms the sole presence of FeNₓCᵧ moieties. Quantification of the absolute content of each Fe component was derived from the Mössbauer spectra fittings (Figure 1e).[6c] Thus, Fe-N-C catalysts with high (FeNC-wet-1) and low content (FeNC-dry-1) of Fe particles are identified, along with those devoid of Fe particles (FeNC-dry-0.5) and nearly devoid of Fe altogether (NC). Furthermore, a catalyst labeled FePhen@MOF-ArNH₃ exclusively comprising Fe particles was investigated.[10a] Its Fe content was 3.1 wt% (Figure 1e), with Fe being present as metallic, carbide, and nitride particles.

The electrochemical properties were then measured using a rotating disk electrode (RDE) in 0.1 M HClO₄ electrolyte.

![Figure 1.](image-url)
All four of the Fe-N-C catalysts showed high ORR activity (Figure 2a), comparable to that of other high-performing Fe-N-C catalysts.[14] The NC catalyst showed poor ORR kinetics, as expected in acidic medium.[4,10a,b] Rotating ring disk electrode (RRDE) measurements at 800 μg cm⁻² loading showed low H₂O₂ production (<6%) during ORR for the four Fe-N-C catalysts (Figure 2b and S4). However, at 100 μg cm⁻², up to 32% H₂O₂ production was measured. This indicates that H₂O₂ produced at a given catalytic site may be consecutively reduced to H₂O. This suggests that, on some Fe sites at least, H₂O₂ may desorb and then re-adsorb on the same type or on another type of Fe sites having a higher affinity for H₂O₂. Furthermore, the positive correlation between % H₂O₂ and absolute content of Fe particles at low loading (Supporting Information, Figure S4, right) suggests FeN₅ moieties catalyze the ORR to H₂O more selectively than Fe@NC sites. Owing to 15–30% H₂O₂ produced during ORR at low loading, investigating the PRR activity of different sites in Fe-N-C catalysts is important to rationally improve their selectivity.

The PRR activity was measured in Ar-saturated 0.1m HClO₄ electrolyte containing 1.3 or 10 mM H₂O₂ (Figure 2c). The NC catalyst showed no PRR activity, indicating that surface N-groups unpromoted by Fe cannot be a site S2. In contrast, high PRR current on FeNC-dry-0.5 demonstrates that FeN₅ moieties are PRR-active. This is a first major finding of the present study, enabled by the synthesis of Fe-N-C catalysts free of Fe particles.[10a,15]

Previous work hypothesized that Fe-N-C catalysts catalyze the ORR via a bifunctional 2e⁻ + 2e⁻ mechanism in acidic medium; the site S1 for 2e⁻ ORR being FeN₅ moieties and site S2 for PRR being Fe particles.[12a] However, the turnover frequency of FeN₅ moieties for PRR is much lower than that for ORR (FeNC-dry-0.5: lower PRR than ORR current at 0.8 V_RHE for the same reactant concentration of 1.3 mM, Figure 2a,c). This suggests that ORR on FeN₅ moieties predominantly occurs via the direct 4e⁻ pathway. This is also supported by the low H₂O₂ production measured for FeNC-dry-0.5 at low loading (Figure 2b).

At this stage, however, we do not know yet whether Fe particles present in other Fe-N-C catalysts are PRR active. If such particles are PRR inactive, the PRR activity should be linearly correlated with the absolute FeN₅ content. However, no linear correlation between FeN₅ content and PRR activity is observed (Figure 2d, center). This suggests that FeN₅ sites are not the sole active site for PRR but that Fe particles should also be considered. Some correlation is observed between PRR activity and content of Fe particles (Figure 2d, right), but a better correlation is observed between PRR activity and the total Fe content (Figure 2d, left). Significant PRR activity of FePhen@MOF-ArNH₂ also demonstrates that Fe particles are PRR active, with an activity commensurate to those of FeN₅ moieties (Figure 2c,d).

While Fe particles are PRR-active, it is still unclear whether they need to be directly exposed to the electrolyte for catalyzing the PRR. Fe particles in direct contact with electrolyte have previously been suggested to be a site S2.[12a,14] Recently, we showed that electrolyte-exposed Fe particles can survive in acidic environments at >0.7 V_RHE, which is due to stabilization of ferric hydroxide species.[13] The presence of Fe particles exposed to acidic electrolyte during short RDE studies is thus possible.

To elucidate whether Fe particles must be directly exposed to the electrolyte to catalyze the PRR, the PRR activity of FeNC-wet-1 and FeNC-dry-1 was measured before and after dissolution (electrochemical dissolution[13b]) of electrolyte-exposed particles (Figure 3). Operando analysis using a scanning flow cell (SFC) connected with ICP-MS (Supporting Information, Figure S5) showed that a significant fraction of electrolyte-exposed Fe particles in FeNC-wet-1 were removed during 100 cyclic voltamograms (CV) between 0 and 1 V_RHE (Figure 3a). The dissolved Fe reaches 9% of the total content of Fe particles present in pristine FeNC-wet-1. FeN₅ moieties are highly stable during this treatment, as previously demonstrated by negligible Fe leaching from FeNC-dry-0.5.[13b]

The PRR activity of FeNC-dry-1 and FeNC-wet-1 were however unmodified, even after extended dissolution up to 1000 CVs (Figure 3b and c). An extrapolation predicts that the vast majority of electrolyte-exposed Fe particles are removed after 1000 CVs (Supporting Information, Figure S6). As previously reported,[13] the dissolution of exposed Fe particles did not decrease the ORR activity (Supporting Information, Figure S7). Therefore, it is concluded that electrolyte-exposed Fe particles in pristine FeNC-wet-1 are inactive toward PRR and ORR. It demonstrates that Fe@N-C sites are therefore PRR active and can be a site S2, as previously hypothesized.[13a]

In conclusion, we elucidated the PRR and ORR reactivity of four different structures existing in Fe-N-C catalysts, that is, metal-free N-C groups, electrolyte-exposed Fe particles, FeN₅ moieties and Fe@N-C. The ORR pathways on Fe-
N-C catalysts could consequently be established (Figure 4). Contrary to previous hypotheses, N-C groups and electrolyte-exposed Fe particles were shown to be inactive toward PRR in acidic medium. We also demonstrated that FeNₓ moieties and Fe@N-C species are moderately active toward PRR, proving their possible roles in both direct (major path) and indirect 4e⁻ ORR pathways. Since the synthesis of Fe-N-C catalysts with only FeNₓ moieties [10,15] or only Fe@N-C particles [104] or their combination [3b,14,17] is now controllable, the understanding of the nature of active sites for PRR provided herein offers new insights for the rational design of advanced Fe-N-C catalysts with high selectivity and expectedly improved durability in polymer electrolyte fuel cells.

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**Conflict of interest**

The authors declare no conflict of interest.

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