


On the Nature of Durable Active Sites in Fe–N–C Fuel Cell Catalysts

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Abstract

Fe–N–C catalysts have the potential to replace the costly platinum catalysts in fuel cells but face the challenge of instability. It is of vital importance to identify the chemical nature of durable active sites in Fe–N–C. In this perspective, we analyze the geometric and electronic factors that affect the intrinsic durability of the FeN_xC_y moieties and propose that iron–oxygen binding energy is most relevant. A weak Fe–O binding is beneficial to mitigate the oxidation attack to the iron center by reaction intermediates thus enhancing its resistance to demetalation. We then propose the iron oxidation (valence) state as an apparent descriptor of the Fe–O binding strength. A valence state of +2 indicates a high anti-oxidation ability and promises superior stability. Our proposal will deepen the understanding of the activity–stability trade-off for Fe–N–C catalysts and guide future active site optimization.

Key words: Stability; Binding strength; Demetalation; Anti-oxidation; Trade-off

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The widespread use of proton exchange membrane fuel cells is hampered by the scarcity and high cost of platinum catalysts that catalyze the cathode oxygen reduction reaction (ORR). Developing low-cost Pt-free catalysts is a highly beneficial solution.^[1] Fe–N–C catalysts featuring nitrogen-coordinated iron active sites (Fe–N_x) are the most promising candidates due to their highest activity in acid media among Pt-free catalysts.^[2–5] However, the application of Fe–N–C catalysts in realistic fuel cells is still hindered by their insufficient stability.^[6–9] A major degradation pathway is the demetalation of active sites.^[10,11] Fe–N–C catalysts typically lose more than half of their initial performance after 100 hours of fuel cell testing, which is far from meeting the durability target for light-duty vehicle applications set by the U.S. Department of Energy (<10% performance loss in 8000 hours).^[12]

The decay of Fe–N–C was often characterized by two-stage kinetics: rapid initial decay lasting about a dozen hours accounts for the major performance loss, followed by retarded decay that continues until the end of the test. This phenomenon suggests that the seemingly identical Fe–N_x sites may have distinct fates during fuel cell operation. In other words, there should be sub-families of Fe–N_x sites with distinct intrinsic durability. Then, it is promising to solve the instability conundrum if we could find out the durable active sites and selectively prepare such sites. Now, a key question arises: what is the chemical nature of the durable active sites?

Mössbauer spectroscopy is highly sensitive to the electronic states of iron species, albeit in similar coordination environments.^[13] Even for an iron single-atom catalyst, at least two distinct doublets (D1/D2) are required to fit its Mössbauer

spectrum, indicating the co-existence of sub-families of FeN_xC_y moieties. Jaouen et al. identified D1 to be $\text{Fe(III)N}_4\text{C}_{12}$ moiety in high-spin state and D2 to be $\text{Fe(II)N}_4\text{C}_{10}$ moiety in low and medium spin.^[14] The spin states depend on the energy levels of the five 3d orbitals and thus affect the adsorption free energies of adsorbates.^[15] As a result, the adsorption characters of the sub-families to oxygen and other small molecules are distinct. Choi et al. showed that D1 bound CN^- moderately relative to O_2 , while D2 bound CN^- much more strongly than O_2 .^[16] Our temperature-programmed desorption results revealed two kinds of O_2 adsorption strength in an Fe–N–C single-atom catalyst.^[17] Further, Jaouen et al. followed the structural changes of D1 and D2 in fuel cells by in situ ^{57}Fe Mössbauer spectroscopy.^[18] As shown in Fig. 1, in the potential range of 0–1 V, D1 underwent an Fe(III)/Fe(II) redox transition (D1H/D1L) with the reversible axial OH adsorbate, while D2 bound O_2 weakly and its oxidation state kept +2 regardless of the potential. After a 50-h operation, D1 was nondurable and quickly transformed to inactive ferric oxides, while D2 survived. The durability of D2 was believed to be associated with a more graphitic local structure.

Dodelet et al. explained the difference in durability from the perspective of spatial location.^[19] They proposed that the Fe–N_4 sites hosted in micropores easily leached out. The driving force of demetalation was the quick water flux running through the micropores, which shifted the thermodynamic equilibrium between Fe ions and Fe–N_4 sites towards the direction of demetalation according to Le Chatelier principle. For Fe–N_4 sites located in the mesopores, the dynamic equilibrium could be established because Nafion penetrated the

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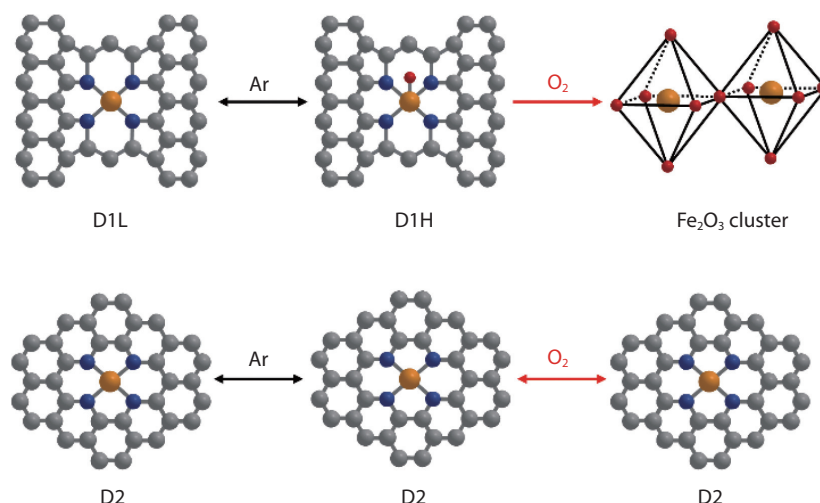


Fig. 1 Coordination or structural changes of D1 and D2 under in situ (Ar) or operando (O_2) conditions.^[18] Copyright 2020, Springer Nature.

mesopores and retained some leached Fe ions. Therefore, the mesopore-hosted $Fe-N_4$ sites should have better stability.

It is reasonable for D1 hosted in micropores and D2 hosted in mesopores, because micropores are made of randomly oriented, disordered carbon domains, where graphene-based D2 cannot be easily integrated. Hence, a model catalyst of graphene-enclosed single iron atoms would bridge the above two site-specific demetalation mechanisms. This kind of catalyst is expected to possess mesopore-hosted FeN_4C_{10} moieties. Huang et al. prepared such catalyst using graphene oxide as carbon substrate, however, the X-ray absorption spectroscopy (XAS) identified an $Fe(III)N_4C_{10}$ moiety with one axial O_2 molecule.^[20] Cao et al. tested a similar catalyst in fuel cells but obtained rather poor stability.^[21] Therefore, graphene substrate and FeN_4C_{10} coordination structure do not guarantee a D2-like electronic structure. Unlike metal macrocycles, the FeN_xC_y moieties are embedded in a conductive long-range carbon matrix, which also affects the electron density at the Fe center. Therefore, instead of coordination structure, electronic structure is the direct influencing factor for stability.

A key feature of the durable D2 site is the weak O_2 binding and stable oxidation state of +2. The $Fe(III)/Fe(II)$ redox potential for D2 might be higher than the open circuit potential so that it is stabilized as $Fe(II)$ when exposed to air and during the ORR process. Therefore, we can conclude that D2 has a higher anti-oxidation ability than D1. Shao et al. calculated the Gibbs free energy change (ΔG) for demetalation and found that axial adsorbates (such as O_2 and OH^*) exacerbated the metal leaching.^[22] Compared with other transition metal centers (such as Co), the iron center is thus suffered from its high affinity to O_2 and the OH^* coverage at high reaction potential. It is likely that the axial adsorbates break the planar symmetry of the active site and pull the iron center out of the plane. Wei et al. found that at high reaction potential the oxygen reduction and the oxidation attack of the iron center by reaction intermediates were competitive.^[23] When the same side of $Fe-N_4$ was adsorbed by two OH ligands, the $Fe-N$ bond would be significantly elongated and weakened. Then, subsequent N protonation became possible on the

$*Fe(OH)_2-N_4$ intermediate, which finally led to the demetalation of the active site in the form of $Fe(OH)_2$. Therefore, an enhanced anti-oxidation ability means the facile desorption of OH , thus eliminating the formation of the fragile intermediate of $*Fe(OH)_2$ and enhancing the resistance to demetalation.

At present, we have several descriptors to define the geometric and electronic structure of the FeN_xC_y moieties, including coordination structure, spin state, spatial location, graphitic degree, oxidation state, and so on. So, what are the key factors in determining the intrinsic durability of the active sites? Based on the above discussion and analyses, we here propose that the oxidation state (valence) of iron centers is most relevant because it directly reflects the anti-oxidation ability (Fig. 2). A valence state of or close to +2 promises superior stability. For example, Li et al. reported that an $Fe-N-C$ catalyst with a much lower iron oxidation state than its counterpart showed significantly improved fuel cell stability.^[7] Valence can be easily characterized by X-ray photoelectron spectroscopy (XPS).^[24] XAS is also a good choice if available. The absorption threshold position of a desired catalyst should closely resemble that of iron phthalocyanine. The effect of valence on stability can also be reasonably explained by ionic radius: the oxidation of the iron center shortens its ionic radius thus reducing its stability.^[25]

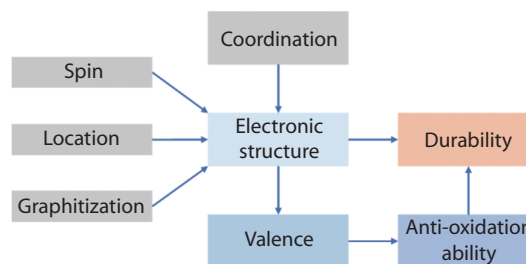


Fig. 2 Factors that affect the durability of active sites.

The high intrinsic activity of FeN_xC_y moieties originates from a moderate $Fe-O$ binding energy, whereas D2 sites bind

O₂ very weak. This discrepancy seems to lead to an activity–stability trade-off in Fe–N_x sites.^[26] However, Jaouen et al. claimed that the intrinsic activity of D2 was no less than D1 based on the linear correlation between the activity and the number of (D1 + D2).^[18] The stronger Fe–O binding of D1 locates the Fe(III)/Fe(II) redox in the ORR potential range, which decreases the active site availability and limits the activity as a result of the site-blocking effect.^[27] The lack of Fe(III)/Fe(II) redox for D2 is not incompatible with its ORR activity. For example, Co–N_x sites are known not to spontaneously bind O₂ but show decent ORR activity in acid.^[28,29] A properly weak M–O binding leads to similar high intrinsic activity and also suppresses the site-blocking effect. Ideally, D2 is of both high activity and durability.

In summary, iron–oxygen binding energy determines not only the activity but also the stability of the FeN_xC_y moieties. For the active sites with strong Fe–O binding, ORR activity is limited by the desorption of oxygen adsorbates as well as the site-blocking effect arising from the Fe(III)/Fe(II) redox. An overly strong Fe–O binding also makes the iron center more vulnerable to oxidation attack by reaction intermediates, leading to increased demetalation tendency. For the active sites with weak Fe–O binding, ORR activity is solely limited by the adsorption of the oxygen while the oxidation attack by reaction intermediates is largely suppressed. Hence, the focus of continued research may turn to optimizing the electronic structure of active sites with weak Fe–O binding.

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Conflict of interest

The authors declare no conflict of interest.

Author contributions

X. Wan and J. Shui co-wrote this paper. All authors had approved the final version.

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