

Solving the Riddle of Activity-Stability Trade-Off

Shengwen Liu, Qiurong Shi and Gang Wu*

Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York, Buffalo 14260, New York, United States

*E-mail: gangwu@buffalo.edu

Atomically dispersed and nitrogen coordinated single iron site (i.e., FeN₄) catalysts hold great promise to replace platinum for proton-exchange membrane fuel cells (PEMFCs). However, the possible demetallation of FeN₄ active sites is primarily responsible for the rapid degradation. The higher the catalyst activity, the faster the decay at the initial stage. Now, solving the conundrum to distinguish durable and non-durable FeN₄ active sites can guide the rational design of high-performance catalysts for PEMFCs.

Developing platinum group metal (PGM)-free catalysts for proton exchange membrane fuel cells (PEMFCs) represents a high-risk but high reward solution to implement PEMFCs for broad applications.^{1,2} Atomically dispersed and nitrogen coordinated FeN₄ sites embedded in carbon planes (Fe-N-C) have exhibited encouraging oxygen reduction reaction (ORR) activity approaching Pt in challenging acidic media.^{3,4} However, current Fe-N-C catalysts suffer from significant performance loss in PEMFCs, which are not viable yet to replace Pt. Active site demetallation, carbon corrosion, and possible H₂O₂ attack are considered key factors affecting the catalyst stability.^{5,6} However, many questions remain unanswered. Why are highly active catalysts often degraded rapidly, especially at the initial stage? Also, how do different atmospheres, potentials, temperatures, and pH values affect catalyst degradation?

Therefore, before addressing the challenging durability issue, the primary research task should be excavating the underlying science toward the FeN₄ site evolution during the ORR process, especially in practical H₂-air cells. Insightful understanding of the FeN₄ active site degradation involving their electronic spin state and local atomic configuration is critical for designing durable Fe-N-C catalysts. However, previous studies of unveiling degradation mechanisms focused on *ex-situ* and less-sensitive characterization,⁷ which cannot clearly distinguish the chemical and structural changes of active sites during the degradation and correlate to measured activity degradation. The *in situ*/operando characterization is powerful and informative to provide real-time and dynamic changes of each active site in a real Nafion[®]-rich electrode during fuel cell operation.

Now, writing in this issue of Nature Catalysis,⁸ Jaouen and co-workers provide an insightful understanding of FeN₄ site degradation by combining operando ⁵⁷Fe Mössbauer spectroscopy and X-ray absorption spectroscopy (XAS) for studying Fe-N-C catalysts in a house-made-fuel cell (**Fig. 1a**). There are two types of FeN₄ sites identified in the catalyst, including high-spin FeN₄C₁₂ moiety (denoted as S1) and a low-or intermediate-spin FeN₄C₁₀ moiety (denoted as S2). The S1 site is more intrinsically active for the ORR with reduced activation energy to break O-O bonds. A significant fraction of S1 is stable under

an O₂-free atmosphere. Applied potentials can drive the reversible change between Fe(III) and Fe(II) in the S1 site (**Fig. 1b**). However, S1 sites are irreversibly converted to inactive ferric oxides rapidly during the ORR, especially at low potentials. In contrast, the S2 site embedded in a compact carbon plane has relatively low intrinsic activity but is more stable against demetallation and insensitive to local carbon's surface oxidation. The S2 site has no redox transition, which is independent of O₂ presence. Its electronic state remains stable at different potentials during the ORR. The operando analysis verified that the rapid initial activity decline is due to the loss of S1 sites and the ferric oxide formation. The number of the S2 sites remains unchanged, critical for maintaining stable performance after the initial degradation. Therefore, the critical knowledge solves the conundrum that the active Fe-N-C catalyst, containing significant S1 sites, always suffers from rapid degradation during fuel cell operation.

This paper's most significant implication provides a new direction for designing durable Fe-N-C catalysts rationally. Increasing the density of stable S2 sites would improve catalyst activity and durability. A pathway is to deposit a thin layer of nitrogen-doped carbon on the top of Fe-N-C catalysts for the possible transformation of S1 into S2 site. Alternatively, stabilizing active S1 sites could be realized by adding co-catalysts (*e.g.*, CeO₂) to scavenge H₂O₂ or reactive oxygen species (ROS) formed⁹ or integrating S1 sites in a more graphitic carbon support.¹⁰ Removing S1 sites from Fe-N-C catalysts before incorporated into fuel cell cathodes was suggested, which could avoid ferric oxide formation, likely generating harmful ROS in the presence of H₂O₂.

Despite these valuable insights into identifying durable active sites in Fe-N-C catalysts, a few fundamental questions remain unresolved. For example, what is the underlying driving force to breaking Fe-N bonds and causing the demetallation of the S1 site? Are there any other more active and stable FeN_x sites for the ORR? How are these FeN₄ sites formed during the necessary thermal activation process? How different FeN₄ sites behave differently in terms of adsorption of O₂ and intermediates and subsequent O-O bond breaking, electron transfer, and protonation during the ORR? Also, Jaouen *et al.* indicated that the local carbon surface oxidation likely triggers the degradation of S1 sites to inactive ferric oxides, while the local graphitic structure stabilizes the durable S2 site. Hence, one question remains that can we eventually achieve a perfect Fe-N-C catalyst with superior activity and stability by regulating the local carbon structure of FeN₄ sites? Or, activity and stability always are contradictory? These puzzles remaining in this paper will continue to be essential topics for exploring advanced Fe-N-C catalysts.

The work opens new directions to elucidate the degradation mechanism of FeN₄ active site and develop highly durable Fe-N-C catalysts, including (i) investigation kinetic behavior of active sites' demetallation under various conditions, (ii) understanding the interaction between FeN₄ active site and its local carbon structure during the degradation, and (iii) exploring innovative synthetic chemistry to engineer local carbon structure, which can stabilize and activate the surrounding FeN₄ active sites. Finally, the developing research methods in this paper to identify the durable and non-durable FeN₄ active sites can benefit the understanding of other single metal site catalysts such as CoN₄, MnN₄, and NiN₄ sites.^{11,12}

References

- 1 Wang, X. X., Swihart, M. T. & Wu, G. *Nat. Catal.* **2**, 578-589 (2019).
- 2 Wu, G. et al. *Science* **332**, 443-447 (2011).
- 3 Zhang, H. et al. *Energy Environ. Sci.* **12**, 2548-2558 (2019).
- 4 Zhang, H. et al. *J. Am. Chem. Soc.* **139**, 14143-14149 (2017).
- 5 He, Y. et al. *Chem. Soc. Rev.* **49**, 3484-3524, (2020).
- 6 Shao, Y. et al. *Adv. Mater.* **31**, 1807615, (2019).
- 7 Jia, Q. et al. *Adv. Mater.* **31**, 1805157, (2019).
- 8 Li, J. et al. *Nat. Catal.* **4**, doi xxxxxxxxxx: (2021).
- 9 Wang, X. X. et al. *Adv. Mater.* **31**, 1805126, (2019).
- 10 He, Y. et al. *Adv. Mater.* **32**, 2003577 (2020).
- 11 Shi, Q. et al. *Mater. Today* **37**, 93-111 (2020).
- 12 Zhu, Y. et al. *Adv. Energy Mater.* **10**, 1902844 (2020).

Competing Interests

The authors declare no competing financial interests.

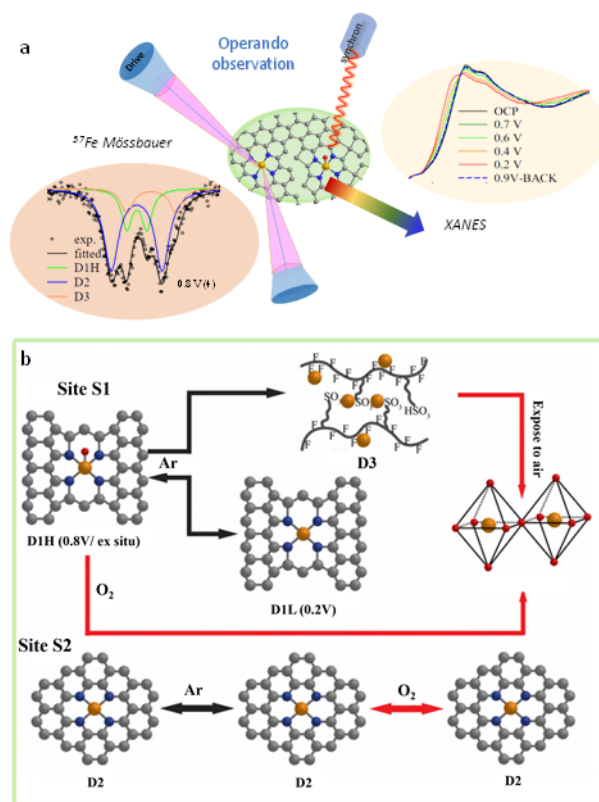


Fig 1. | In-situ identification of active sites in Fe-N-C catalysts. a, Operando X-ray absorption spectroscopy and ^{57}Fe Mössbauer spectroscopy to study structural and chemical changes of active sites in a Fe-N-C catalyst during the fuel cell operation. **b**, Two types of active sites identified: highly active S1 sites are not durable and quickly converted to inactive ferric oxide. In contrast, less active S1 sites are durable and maintain fuel cell performance after the initial degradation (adapted from ref.⁸, Springer Nature Ltd).