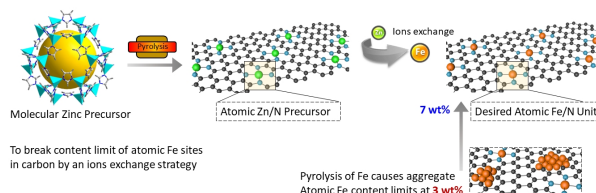


To Break the Limit of Catalytic Site Density of Fe-NCs

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ABSTRACT Rational design of Fe and N co-doped carbon catalysts (Fe-NCs), one promising non-precious cathode catalyst, is critical to commercialization of proton exchange membrane fuel cells. The atomic Fe site density of Fe-NCs is critical to improve catalytic currents approaching industrial levels. One recent research proposes a template-guided strategy to break the limit of Fe site density, and greatly promotes the fuel cell performance.

Keywords: Fe-NC catalysts, site density, oxygen reduction reaction



Low temperature proton exchange membrane fuel cells (PEMFCs) offer a potential technology for clean energy output with high efficiency. For commercial viability of PEMFCs, one major task is seeking for appropriate catalysts to promote the sluggish kinetics of oxygen reduction reaction (ORR) emerging at the cell cathode. The catalysts must be made of low-cost elements, intrinsically active and structurally durable at moderate potentials. In this context, one of the most promising ORR catalysts has been known as the non-precious Fe and N co-doped carbon catalysts (Fe-NCs).^[1]

The typical Fe-NCs contain atomically sized Fe/N coordination units serving as the ORR active sites and embedding within carbon supports. Their performance mainly relates to the coordination spheres of Fe sites and their site density (SD_{Fe}) over carbon. The Fe-NCs are normally derived from the pyrolysis of Fe complexes with carbon, or within metal/covalent organic frameworks (MOFs/COFs). Versatile Fe/N sphere structures have been discovered and optimized. However, progress is limited in increasing SD_{Fe} , because those precursors of Fe complexes can be easily reduced into large particles by carbon at high temperature. The atomic characters of Fe sites thus disappear, substantially decreasing the catalytic turnover frequencies (TOFs). Now, writing in *Nature Catalysis*, Anthony Kucernak and colleagues explore a straightforward template-guided strategy to break the current SD_{Fe} limit of Fe-NCs, and its influence on ORR performance is quantitatively analyzed.^[2]

First, the authors depict the correlation among SD_{Fe} , TOFs and specific surface areas of Fe-NCs based on the US Department of Energy targets. Considering an upper TOF limit of $2\text{ e site}^{-1}\text{ s}^{-1}$ referring to benchmark Pt/C catalysts, SD_{Fe} needs to reach around $10^{20}\text{ sites g}^{-1}$. In the meantime, the catalyst loading needs to be less than 10 mg cm^{-2} to avoid slow mass transport near the electrode surfaces. Currently, the atomic Fe contents of state-of-the-art Fe-NCs are limited at 3 wt%, which cannot satisfy such a target. Thus, the authors used Zn based MOFs (i.e., ZIF-8) to derive a Zn-NC precursor, because Zn can maintain atomic size in pyrolysis with 25 wt% contents and serve as a solid template (Figure 1a, b). By using template-guided strategy, the nitrogen-doped carbon scaffold, which contained a high concentration of Zn/N sites, was then converted into \square/N sites. This method improves the atomic Fe dispersion and avoids Fe clustering as metallic nanoparticles,

iron carbide, iron nitride and so on during pyrolysis. Then following coordination and pyrolysis, Fe ions are filled into Zn positions to result in an Fe-NC with atomic Fe content up to 7 wt%. During these processes, the authors also applied a blowing agent of cyandiamide to improve the specific surface area of Fe-NC. For the same purpose, Shui and colleagues rationally designed Fe-NCs through silica coating of MOF precursor to avoid materials aggregating, and it achieved high specific surface area that made high SD_{Fe} .^[3]

Second, the SD_{Fe} of Fe-NCs needs to be measured by precise quantitative methods. This might be challenging at atomic levels, while is prerequisite to have deep insights into the SD_{Fe} effects. Both in situ NO electrochemical stripping and ex situ CO cyro chemisorption are applied, showing that the 7 wt% atomic Fe content of Fe-NC corresponds to SD_{Fe} of $4.67/7.83 \times 10^{19}\text{ site g}^{-1}$. This is increased by 3- to 18-fold compared to those of reported Fe-NCs, and approaches the target SD_{Fe} . The TOF toward ORR is derived as $5.4\text{ e sites}^{-1}\text{ s}^{-1}$ @ $0.8\text{ V}_{\text{vs RHE}}$. By combining these two factors, such a novel Fe-NC affords a high current density of 145 mA cm^{-2} in the H_2 -air condition at $0.8\text{ V}_{\text{cell}}$ voltage, which is increased by 130%-190% compared to the previous levels. At various TOFs (or potentials), the ORR kinetic current densities are fitted to linearly increased with SD_{Fe} (i.e., $j_{\text{kinetic}} \propto k(SD_{Fe} - SD_0)$). Interestingly, the linear curves all point to above zero SD (i.e., $SD_0 > 0$) at the zero intercepts, suggesting a minimum requirement of SD_{Fe} value which needs to be exceeded (Figure 1c). This might be ascribed to the inhomogeneity of Fe-NC that parts of Fe sites are intrinsically ORR inactive. Long-term durability is also a critical parameter to evaluate the performance of PEMFCs for practical use. However, in the continuous cell running, the Fe-NC exhibits some catalytic degradation. This is a common issue in this research field, which is attributed to the electrooxidation of carbon supports and de-coordination of Fe sites at relatively high potentials. Further studies are potentially required to improve the particle sizes and graphitization degree of Fe-NCs, as well as the cathode layer structures.

We notice that TOFs vary in previously reported Fe-NCs and are moderate in the current work. This links to tunable coordination spheres of Fe sites, and should be further structurally investigated at atomic scales. It remains to require more advances in

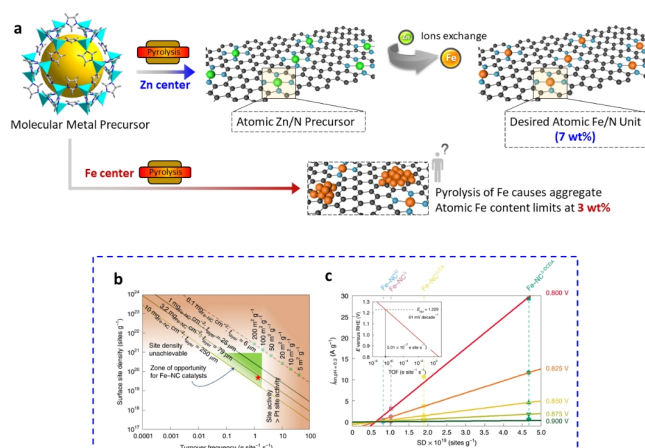


Figure 1. The synthesis of a novel Fe-NC based on a Zn template-guided strategy to avoid aggregate of atomic Fe into particles. The atomic Fe content of such an Fe-NC is increased to 7 wt% approaching the practical demands. (b, c) The correlation among SD-Fe, specific surface areas and ORR activity of Fe-NCs. Figure 1b, c are reprinted from Nature Publishing Group, copyright 2022.

the optimization of TOFs and SD_{Fe} (i.e., approaching Pt activity and 10^{20} site g^{-1} levels). Perhaps, it is another routine to prepare novel Fe-NCs based on covalent organic frameworks (COFs) or metal organic frameworks (MOFs) that possess high specific surface areas and SD_{Fe} with continuously tunable structures. Yaghi and colleagues have reported an analogous Co/N sites embedded in COF which exhibited high TOFs (e.g., $2.6 s^{-1}$ @ $-0.55 V_{vs RHE}$) toward CO_2 electroreduction with only 4% Co sites involved in the electrochemical process.^[4] Thus, once the critical issue of interfacial electron transfer inside COFs or MOFs are overcome, such materials might turn to be advantageous. For instance, recently, Zhang and colleagues have used a highly conductive, self-doping PEDOT:PSS matrix to enhance electron transfer between electrodes and MOF particles, significantly improving the electrocatalytic activities.^[5]

In summary, in the field of developing classical Fe-NCs, to improve SD_{Fe} is critical to make ORR currents of PEMFCs meet the practical demands, which is however limited by the Fe aggregating issue in synthetic process. The authors propose a simple Zn template-guided strategy to break the limit of atomic Fe content

increasing from 3 wt% to 7 wt%, and quantitatively linking SD_{Fe} , TOFs with specific surface area of Fe-NCs. These results provide a deep insight into the SD_{Fe} effects on ORR catalysis, and would stimulate rational design of Fe-NCs for PEMFCs application.

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COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

Full paper can be accessed via
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