

Iron-Based Atomically Dispersed Fe-N-C Catalysts for the Oxygen Reduction Reaction Within PEMFCs

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Abstract. Since the cathode oxygen reduction reaction (ORR) of proton-exchange membrane fuel cells (PEMFC) depends on sluggish reaction kinetics and is greatly dependent on costly Pt-based catalysts, it hinders the large-scale commercialization. As a result, atomically isolated Fe-N-C materials are highly promising non-precious-metal ORR catalysts for PEMFCs because of their low cost, high atomic efficiency and intrinsic catalytic activity coming from Fe-N₄ binding sites. However, Fe-N-C systems also have some shortcomings compared to Pt-based systems in terms of intrinsic activity, active site concentration and long term stability in acidic environment. Taking these aforementioned constraints into account, this review thoroughly introduces two types of enhancement tactics, namely, coordination environment adjustment and dual atom site assembly. Coordination-environment modification is achieved by heteroatom doping, axial coordination and spin-state regulation to change the electronic framework of Fe centers. Synergistic interaction between the homonuclear or heteronuclear metal active sites in dual atom catalyst promotes the O-O bond dissociation and 4-electron transfer selectivity. In this survey, the progress of these approaches in investigations is systematically analyzed. Future research needs to include operando characterization and theory-based design, along with testing of membrane-electrode-assemblies.

Keywords: Iron-based atomically dispersed catalysts, Oxygen reduction reaction, coordination environment modulation, Dual-atom catalysts, PEMFCs

1. Introduction

PEMFCs represent electrochemical apparatuses which immediately transform the chemical potential of hydrogen into electrical power. PEMFCs are key technology for the transition towards green energy because of its better energy conversion effectiveness and localized output emissions. However, the sluggish ORR at the cathode side and the high cost of Pt catalysts limit the industrial applications of industrialization [1].

Among the various non-precious metal catalyst systems, atomically dispersed Fe-N-C materials are considered to be a very promising alternative because of the large amount of Fe resources and low price. The Fe-N-C catalysts consist of highly dispersed Fe atoms in the form of isolated atoms on nitrogen-rich carbon frameworks. These atoms make up structurally specific and very homogeneous reactive sites, which is why catalysts can in principle be 100% atom efficient, but in

practice the density of actually electrocatalytically active sites is limited by the preparation parameters and the structure of the carbon support, and is usually well below these limits. However, the binding strength of Fe-N₄ centers to intermediates is not ideal, and the large distance between the isolated atoms makes the O-O bond cooperative activation difficult, resulting in the durability and performance of the Fe-based catalysts are inferior to the Pt-based catalysts [1, 2].

To overcome the challenges mentioned above, two approaches at the micro scale have been suggested to evolve. One is changing the coordination environment of individual atoms: Fe – Refine the electronic configuration of Fe (change the adsorption spectra of the oxygen-related intermediates by incorporation of heteroatoms (e.g., Fe-N₃S₁), by addition of axial ligands or by manipulation of spin state). The other involves the creation of neighbouring dual-atom catalytic centres (homonuclear Fe-Fe or heteronuclear Fe-M) which reduce the energy barriers of O-O bond dissociation by bidentate uptake and counterbalance the limitation of the synergy of isolated atoms. Both of these methods are a synergistic methodology under the "atomically dispersed" architecture and represent a complete set of methods to enhance the efficiency of the system [1, 3].

This survey covers the recent developments in atomically isolated Fe-N-C materials for ORR, highlighting the strategies of single-atom coordination tuning and dual-atom site engineering nearby single atoms.

2. Fundamentals and synthesis of Fe-N-C catalysts

2.1. Overview of ORR

The catalyst site at the anode serves as the primary electrochemical mechanism for PEMFC to sustain steady power delivery. Its intricate multi-stage proton-electron exchange procedures directly dictate the energy efficiency of the entire device [4]. Concerning reaction mechanisms, the oxygen reduction process primarily advances via two distinct pathways:

Reaction Pathway I:



Reaction Pathway II:



Equation (1) is called direct 4-electron reaction pathway: O₂ directly received four electrons and was reduced to H₂O.: Equation (2) is called Indirect 2-electron pathway: Before O₂ is reduced to H₂O, there is an intermediate product that first accepts two electrons to form H₂O₂. As shown in Equation (1), the direct 4e⁻ pathway involves the complete reduction of O₂ to H₂O, with a standard electrode potential of $E^\theta = 1.23$ V vs. RHE. Equation (2) represents the indirect 2e⁻ pathway, where O₂ is first reduced to H₂O₂ with $E^\theta = 0.69$ V vs. RHE, before further reduction to H₂O.

In practical electrochemical operation, hydrogen peroxide and active oxygen species (ROS) derived from the indirect 2-electron pathway feature strong oxidation capacity. These substances induce destructive radical oxidative degradation of carbon supports and proton exchange membranes, bringing about premature failure of the system [2]. Therefore, the ideal high-efficiency ORR catalyst must have high selective catalytic activity, which can accurately regulate the reaction front along the 4-electron transfer pathway, and comprehensively improve the energy efficiency and long-range safety of the system while minimizing the generation of H₂O₂ [5].

2.2. Definition and characteristics of atomically dispersed catalysts

Atomically isolated catalysts consist of distinct metal ions or well-defined neighboring metal dimers anchored on a substrate, encompassing mononuclear catalysts and binary atom catalysts. Specifically, single-atom catalysts denote a framework where metal atoms are separated from one another and no metal-metal linkage exists.

Furthermore, owing to the extremely consistent and transparent local cooperative framework of individual-atom functional sites, the catalytic interaction mechanism is significantly streamlined, enabling the investigation of the performance-correlation of the material at the microscopic and electronic configuration level, and offering a perfect conceptual and practical foundation for the systematic construction of advanced electrochemical catalysts [2].

2.3. Synthetic strategies of Fe-N-C catalysts

The preparation of Fe-N-C catalysts usually relies on high-temperature pyrolysis. The precursors consisting of iron salts, nitrogen sources and carbon sources are carbonized at high temperatures under an inert atmosphere. Widely used iron sources contain ferric nitrate and ferric chloride. Nitrogen and carbon sources can originate from nitrogen-containing organic ligands, metal-organic frameworks or nitrogen-rich polymers. To avoid the agglomeration of iron atoms, researchers have developed strategies such as spatial confinement and template-assisted methods [2, 5, 6]. Even with identical confinement-template precursors, the subsequent pyrolysis atmosphere as a synthetic parameter can still significantly tune the final microstructure and ORR performance (Figure 1).

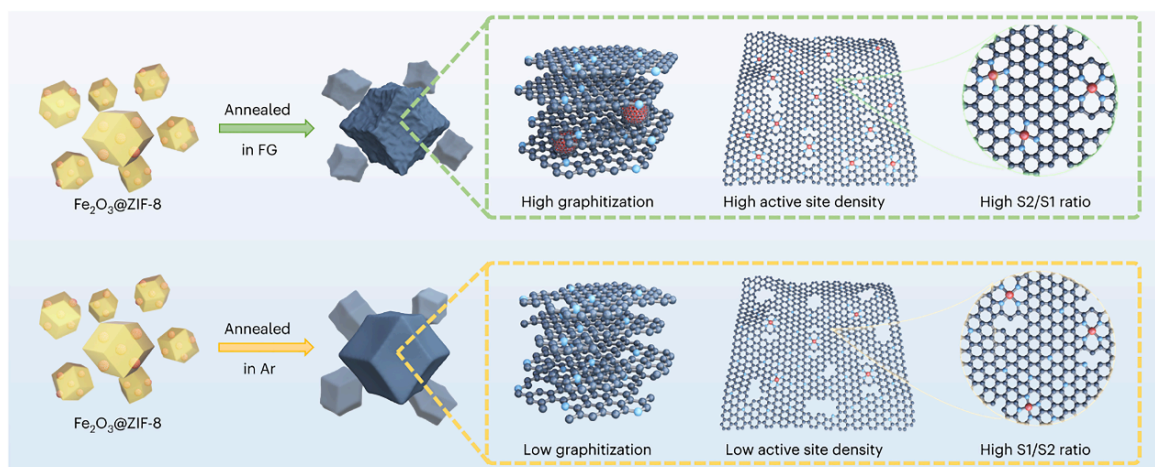


Figure 1. Low-temperature thermal condensation of Fe–organic precursors followed by high-temperature pyrolysis to produce Fe-N-C electrocatalysts [based on: advancing Fe-N-C catalysts: synthesis strategies and performance enhancements for fuel cell applications] adapted from [2]

The empirical analysis verified that the peak pyrolysis temperature, heating velocity and the specific composition of reaction atmosphere exerted a significant impact on the phase purity of Fe-N_x coordination structures, carbon substrate graphitization and the ultimate ORR performance [2].

3. Precise regulation of single-atom active sites

This section focuses on increasing the efficiency of the single-atom functional active centres of Fe-series atomically isolated Fe-N-C electrocatalysts, and reveals the subtle control strategies that can

be used on the single Fe atoms on three hierarchical levels: ligand atom substitution, extended-range coordination tuning and magnetic spin state adjustment.

3.1. First coordination shell modulation

The first coordination sphere (atoms directly bonded to Fe) plays a crucial role in determining the electronic structure of Fe d-bands and the binding energies of the oxygenated species [3]. Based on the typical Fe-N₄ framework, because of the high symmetry, the adsorption forces of Fe towards the *OH intermediates are more robust, and the ORR theoretical overpotential is about 0.78V. The specific coordination environment (e.g., Fe-N₃S₁ or Fe-N₃P₁) formed after the incorporation of atoms with a higher N electronegativity is able to effectively regulate charge redistribution and adjust the adsorption free energy of oxygen-containing intermediates (*OOH, *O, and *OH), therefore reducing the reaction d-band center overpotential of Fe from -1.12 eV to -1.28 eV, and the desorption barrier of *OH from 0.85 eV to 0.62 eV [7]. Taking the case of the Fe-N₃S₁ structure with S replacing the N atoms for an example, the half wave potential is 0.89V in alkaline media, which is about 70 mV more positive than the conventional Fe-N₄, and the Tafel slope is reduced from 78 mV dec⁻¹ to 62 mV dec⁻¹. The maximum power density of the experiments in H₂O₂ fuel cell (H₂O₂ FC) increased from 0.41 W cm⁻² to 0.92 W cm⁻² [8]. The heteroatom substitution method in the first coordination shell can in general increase the half-wave potential by 60-90 mV, significantly improving ORR catalytic activity (Figure 2) [3].

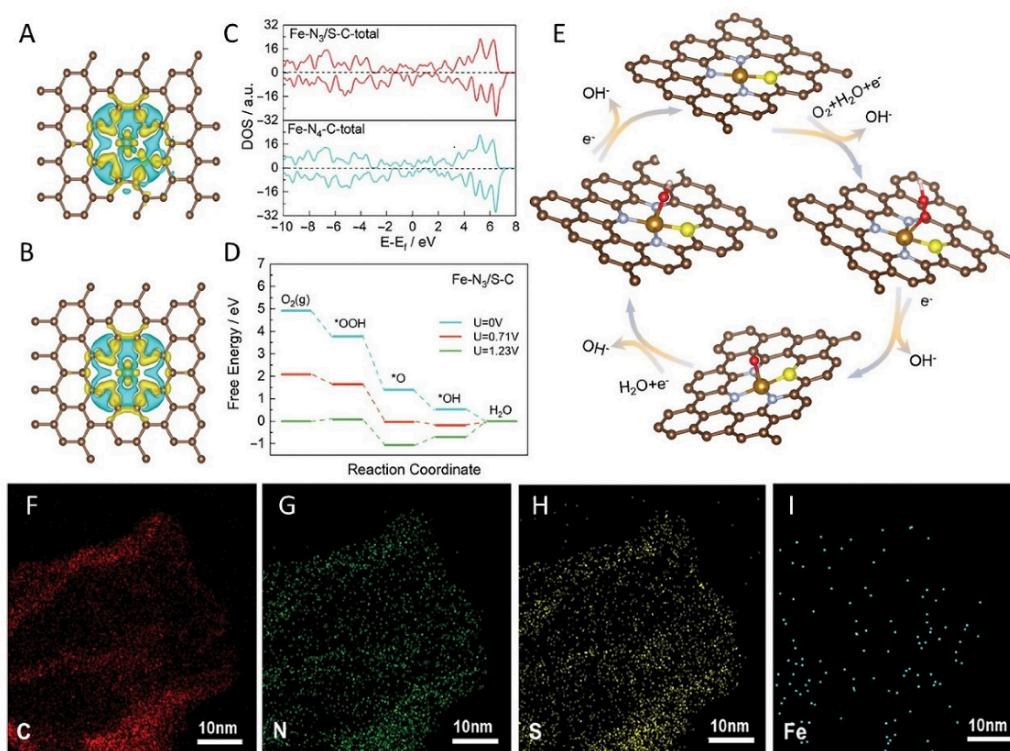


Figure 2. The charge density profiles for (a) Fe-N₃/S-C plus (b) Fe-N₄-C. (c) DOS curves for Fe-N₃/S-C and Fe-N₄-C. (d) Free energy profile, (e) reaction mechanism of Fe-N₃/S-C; Fe (brown), N (grey), S (yellow). (f-i) STEM images and elemental mapping; C (red), N (green), S (yellow), Fe (blue) [based on research progress on atomically dispersed Fe-N-C catalysts for the oxygen reduction reaction] reproduced from [9]

3.2. Second/long-range coordination modulation

Beyond the immediate first coordination layer, the influence of the secondary coordination environment and further remote microscales on Fe catalytic performance remains significant [9]. Even though the second coordination regulation does not alter the specific bonded atoms within the Fe core, subtle modifications to the electronic framework can be realized primarily via the following mechanisms [9, 10].

Incorporation of axial ligands (like OH, Cl or axial N/O bonding) into the vertical orientation of the planar Fe-N₄ framework can cause minor out-of-plane motion of the Fe center, disrupt planar symmetry and rearrange its dz₂ orbital electronic structure [10].

Distant electronic influence from supports: regional imperfections in carbon substrates or remote heteroatom impregnation could produce extended-range electron transport via connected π electron frameworks, and fluctuatingly regulate the regional charge distribution and oxidation level of Fe nodes [9, 11].

The downward shift of the d-band center of Fe as a result of the axial B coordination, combined with the better absorption spectra of the oxygen containing species, enhances the absorption spectra of oxygen containing species. Thus, the half-wave potential will reach 0.915 V, which is higher than that of commercial Pt/C [3]. The modulation of charge density of the Fe site by the long-range electronic influence of the carrier doping also improves the adsorption kinetics of ORR intermediates and greatly improves the catalytic performance [3].

3.3. Spin state modulation

The magnetic spin configuration of an Fe ion is a crucial fundamental electronic structural parameter that could be used to characterize its ORR catalytic activity. Fe site in octahedral or planar tetragonal environment has low, intermediate or high spin depending on the gap between the energy levels of the d-orbitals and the pattern of filling of electrons in those d-orbitals. Taking the case of axial coordination field regulation by Cl, this method is able to regulate the spin state of Fe centers precisely by varying the intensity of the coordination field (by changing the type and geometric symmetry of the coordinating atoms), which can increase the half-wave potential to 0.91V and significantly reduce the desorption energy of *OH. The Fe-II Fe-N₄ sites with singly occupied dz₂ orbital are known to be intermediate spin. The adsorption free energies of these sites are the most favorable for the ORR intermediates and are the Sabatier optimal value. Hence, these centers show a better intrinsic catalytic activity [12]. The upper limit of the efficiency of Fe-N-C catalysts is currently hit [12] and can be overcome by the novel physicochemical perspective of spin state engineering.

4. Synergistic construction of adjacent dual-atom sites

4.1. Synergistic limitations of isolated single-atom sites

Single-site catalysts for ORR are still mostly limited by the issue of an extremely large spatial gap of individual-atom catalysts. The O-O bond is difficult to break and O₂ is unable to attack two Fe nuclei at once. Thus, it is possible that neighbouring dual-atomic sites would be able to provide synergistic adsorption and O-O linkage activation.

4.2. Homonuclear dual-atom catalysts

The principle method is Fe-Fe bonding. This strategy is able to compensate for the lack of isolated single-atom synergy. In the vicinity of Fe, the local point density is increased by neighbouring Fe positions [3]. Taking the Fe-N-C catalyst synthesized by sublimation conversion as an example, its Fe-Fe distance is as large as 0.3nm, the half-wave potential is 0.90V, and it is better than commercial Pt/C and Fe single atom catalysts. DFT calculations show that the longer the Fe-Fe distance the easier it is for the O₂ to bind, and then go through protonation steps that are important for optimizing efficiency [3]. Results showed that such bimetallic cooperative mechanism greatly reduced the energy barrier of dissociation of O–O bond and thus enhanced the catalytic efficiency of ORR.

4.3. Heteronuclear dual-atom catalysts

However, the catalytic performance of Fe combined with other metal (e.g. Cu, Co or Ni) is usually better than that of homonuclear diatomic species. The difference in electronegativity between these two elements causes the redistribution of charge, resulting in better adsorption affinity of ORR intermediates [3]. The electronic configuration of Fe is changed by addition of Cu, resulting in a 15 mV shift in half wave potential with the Fe-Cu bimetallic catalyst as an example. The maximum power density achieved by this catalyst in the PEMFC single cell tests is close to the commercialized Pt/C (0.912 W cm⁻²) [13]. The power density of zinc-air batteries reaches maximum of 165 mW cm⁻², which is higher than the Fe single-atom catalyst (138 mW cm⁻²) [6].

The above results indicate that the presence of heteronuclear diatomic centers may facilitate the activation energy required through electronic cooperative mechanisms and be able to maintain better ORR performance under the acidic functional environment in PEMFCs (proton exchange membrane fuel cells).

5. Conclusions

This survey concentrates on iron-based atomically dispersed catalysts, and consolidates their adjustment techniques and investigative advancements for the ORR. To address the restricted inherent activity of Fe-N₄ centers, this article categorizes current investigations into two perspectives: single-atom coordination-environment tuning and collaborative building of diatomic centers. At the single-atom level, heteroatom impregnation, axial-ligand incorporation and spin-state alteration are able to adjust Fe electronic structure, reaching half-wave potentials of 0.89–0.92 V. For diatomic frameworks, homonuclear Fe-Fe and heteronuclear Fe-M sites increase site concentration and trigger electronic synergy respectively, advancing the half-wave potential past 0.90 V. Such approaches show that atomic-scale local coordination adjustment functions as a viable method to enhance the ORR efficiency of Fe-N-C catalysts, providing direction for developing non-precious-metal catalysts in subsequent research.

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