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Correlating Fe source with Fe-N-C active site construction: Guidance for rational design of high-performance ORR catalyst[☆]

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ABSTRACT

Pyrolyzed Fe-N_x/C materials derived from Fe-doped ZIF-8 are recently emerged as promising alternatives to noble metal platinum-based catalysts towards oxygen reduction reaction (ORR) and elucidating the dependence of Fe source on the active site structure and final ORR performance is highly desirable for further development of these materials. Here, we designed and synthesized a series of Fe-N-C catalysts using ZIF-8 and various iron salts (Fe(acac)₃, FeCl₃, Fe(NO₃)₃) as precursors. We found that the iron precursors, mainly the molecular size, hydrolysis extent, do play a major role in determining the final morphology of Fe, namely forming the Fe-N_x coordination or Fe₃C nanoparticles, as well as the site density, therefore, significantly affecting the ORR activity. Among the three iron sources, Fe(acac)₃ is most advantageous to the preferential formation of single-atom Fe-N_x active sites and the derived catalyst demonstrated best ORR performance.

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1. Introduction

Fuel cell is regarded as one of the most promising clean energy conversion devices due to its higher energy efficiency and lower emissions than internal combustion engines [1–4]. However, the high cost, which is mainly originated from the noble metal platinum-based cathode catalysts, seriously limits the practical application of PEM fuel cells [5]. To overcome this obstacle, developing high-performance nonprecious metal catalysts (NPMCs) for oxygen reduction reaction (ORR) has been considered as the most effective solution and captured intensive attention in recent years [6–9]. A variety of NPMCs have been reported catalytically active to ORR, among which, carbon-supported transition metal-nitrogen co-

ordinations (M-N_x/C, M = Fe, Co) have been generally recognized as the most promising candidates, ascribable to their superior activity and stability in acidic electrolyte [10–12]. As the active sites M-N_x are more inclined to be formed in certain specific pore structures of the carbon substrate [13,14], and various microporous carbon materials are developed to promote the formation of the desired active sites [15–17], such as Ketjenblack [18], BP 2000 carbons [19] and some microporous metal-organic frameworks [13,20,21]. Especially, zeolite imidazole framework-8 (ZIF-8) is demonstrated as an ideal host for the synthesis of M-N_x/C due to its exceptionally abundant micropores [14,22], inherent presence of coordinated M-N species and tunable structure at molecular level [23,24].

Notably, the catalytic performance of the ZIF-8 derived Fe-N-C catalysts differs greatly in the reported literatures [1,18,23,25–28], which may be caused by different synthetic parameters; however, such effect is rarely studied. Elucidating the origins of the performance difference is significant for further designing the highly efficient catalysts. As is known to all, the metal content [18,29], the precursor concentration [18], and the pyrolytic temperature [26] will all affect the final chemical composition and structure of the resulted material, thus leading to the difference in their catalytic property. Lai et al. demonstrate that the increase in iron content results in decrease of ORR activity, due to fact that inactive iron species dominate at high iron content [25]. Wu's group investigates the dependence of particle size of Fe-doped-ZIF-8 and

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Table 1. The mass addition of iron source and the mass percentage of iron in the final catalyst by ICP-OES.

Sample	mFe(acac) ₃ -added (mM)	Fe (wt%)	Sample	mFeCl ₃ -added (mM)	Fe (wt%)	Sample	mFe(NO ₃) ₃ -added (mM)	Fe (wt%)
Czif-Fe(acac) ₃ -1	0.623	0.1644	Czif-FeCl ₃ -1	0.155	1.202	Czif-Fe(NO ₃) ₃ -1	0.156	0.6117
Czif-Fe(acac) ₃ -2	1.245	0.3798	Czif-FeCl ₃ -2	0.192	2.410	Czif-Fe(NO ₃) ₃ -2	0.233	2.949
Czif-Fe(acac) ₃ -3	1.868	0.5568	Czif-FeCl ₃ -3	0.233	3.179	Czif-Fe(NO ₃) ₃ -3	0.312	3.759
Czif-Fe(acac) ₃ -4	2.491	0.7576	Czif-FeCl ₃ -4	0.310	5.628	Czif-Fe(NO ₃) ₃ -4	0.468	4.640
Czif-Fe(acac) ₃ -5	3.114	0.9718	Czif-FeCl ₃ -5	0.621	2.657*	Czif-Fe(NO ₃) ₃ -5	0.624	5.377
Czif-Fe(acac) ₃ -6	3.737	1.466	Czif-FeCl ₃ -6	0.777	3.113*			
Czif-Fe(acac) ₃ -7	4.983	1.629						
Czif-Fe(acac) ₃ -8	7.475	1.680						

* The imperfectly carbon-coated Fe₃C particles would be form due to adding too much FeCl₃ in precursor then be etched after pickling. It can be proved by TEM as shown in Fig. S5(c, d).

38 pyrolytic temperature on the performance of the catalysts via controlling the precursors' concentration [26]. Previous study showed that iron–ligand coordination influences the fuel-cell performance [1,29,30], however, the effect of iron precursor, which is closely related with coordination nature and the final catalytic activity, is yet to be studied to date.

44 Here, we designed and synthesized a series of Fe-N-C catalysts derived from ZIF-8 and various iron salts (Fe(acac)₃, FeCl₃, Fe(NO₃)₃). The structural and performance differences between the different samples were studied in-depth by combination of varied physical characterization techniques coupled with electrochemical measurements. From the study, it is found that although ZIF-8 is featured with high capability in synthesizing highly dispersed Fe-Nx type of catalysts, the iron precursors do play a major role in determining the final forms of Fe, namely forming the Fe-Nx coordination or Fe₃C nanoparticles. Specifically, two properties of the Fe precursors, i.e., the molecular size and the hydrolysis feature of the iron source, are found crucial. Meanwhile, the ORR catalytic behavior dependency on the Fe precursor sources and content were studied in detail.

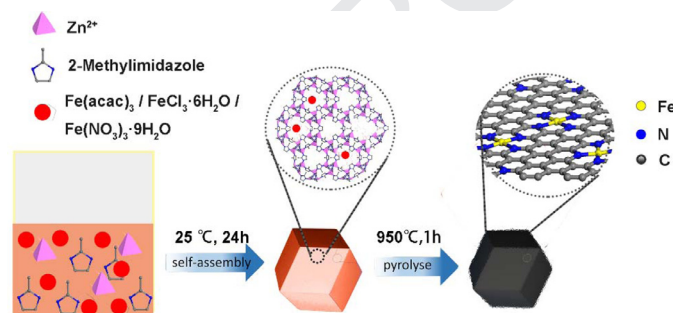
58 2. Experimental

59 2.1. Material synthesis

60 Typically, ZIF-8-FeX (FeX indicates a variety of iron sources) is made by rapidly adding a 40 mL 0.1 M Zn(NO₃)₃ solution into the solution of 80 mL 0.2 M dimethylimidazole in methanol a specific iron source pre-added (list in Table 1) and stirring 24h in room temperature. The obtained product was separated by centrifugation and washed with methanol and finally dried at 60°C under vacuum for overnight, which was marked as ZIF-Fe-X-Y. The power of ZIF-Fe-X was then transferred into a ceramic boat and placed in a tube furnace. The sample was heated to 950°C with a heating rate of 5°C·min⁻¹, kept at 950°C for 1 h under 10% H₂/Ar mix gas, naturally cooled to room temperature, and then preleached in 1 M HNO₃ to remove unstable species. The resultant was denoted as Czif-Fe-X-Y.

73 2.2. Electrochemical measurement

74 All electrochemical measurements were conducted in a conventional three-electrode cell at room temperature (~25°C) using the 750E Bipotentiostat (CH Instruments). Non-noble metal catalyst ink was prepared by ultrasonically dispersing 5 mg catalyst in a suspension containing 25 μL Nafion (5 wt%) solution and 475 μL ethanol; the catalyst film coated electrode was obtained by dispersing the catalyst ink on a glassy carbon rotating ring-disk electrode followed by drying in air. The catalyst loading on RRDE was 0.6 mg cm⁻² for Non-noble metal catalysts. And the comparison platinum was adopted as 20% Pt on Vulcan carbon with an electrode Pt loading of 20 μg·cm⁻². The ink was



Scheme 1. Schematic illustration of the preparation of the Czif-Fe(acac)₃/FeCl₃/Fe(NO₃)₃.

85 prepared by ultrasonically dispersing 5 mg catalyst in a suspension containing 500 μL isopropanol, 5 μL Nafion (5 wt%) solution and 1.995 mL H₂O. And the catalyst film coated electrode was obtained by dispersing the catalyst ink on a glassy carbon rotating ring-disk electrode followed by drying in air with 500 rpm rotating. The ORR stability was investigated by continuous potential cycling in oxygen-saturated 0.1 M HClO₄ solution between 0.6 V and 1.2 V with the scan rate at 0.2 V·s⁻¹. And after 5000/10,000 cycles, the ORR steady-state polarization measurements were conducted in O₂-saturated 0.1 M HClO₄ solution with scanning rates of 5 mV·s⁻¹ and rotation rate at 1600 rpm. The ORR catalytic activity can be further investigated based on the Kouteckye–Levich equations:

$$\frac{1}{J} = \frac{1}{J_K} + \frac{1}{J_L} = \frac{1}{J_K} + \frac{1}{B\omega^{1/2}}$$

$$B = 0.62nFC_0(D_0)^{2/3}\nu^{-1/6}$$

99 Where J is the measured current density, J_K is the kinetic current density, J_L is the diffusion-limited current density, ω is the electrode rotation rate, F is the Faraday constant (96,485 C/mol), C_0 is the bulk concentration of O₂ (1.3×10^{-3} mol/L), D_0 is the diffusion coefficient of O₂ (1.9×10^{-5} cm²/s) in acidic solution and ν is the kinetic viscosity of the electrolyte (1.0×10^{-2} cm²/s).

105 2.3. Materials characterization

106 The products were characterized using the below methods: transmission electron microscopy (TEM) on a JEM-2100 transmission electron microscope (JEOL, Japan) operating at 120 kV; X-ray diffraction (XRD) on a TD-3500 powder diffractometer (Tongda, China) operating at 30 kV and 20 mA, using Cu K α radiation sources; Nitrogen adsorption on ASIQUF60U-5 (Quantachrome instruments, USA) at 77 K, scanning electron microscopy (SEM) on a Merlin field emission SEM (Carl Zeiss); X-ray photoelectron spectroscopy (XPS) on a VG ESCALAB MK2 X-ray photoelectron spectrometer (VG corporation, UK), using an Al K α X-ray source. Fe

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