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High performance Fe–N–C oxygen reduction electrocatalysts by solid-phase preparation of metal–organic frameworks

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Abstract

Iron-nitrogen-carbon (Fe–N–C) compounds have been regarded as efficient and non-precious metal electrocatalysts for oxygen reduction reaction (ORR). The environmentally friendly preparation of Fe–N–C electrocatalysts is desirable but still challenging. Here, several Fe–N–C catalysts incorporated by ZIF-8 has been simply prepared by solid state reaction method. Fe–N–C containing 2% mole percentage Fe electrocatalysts fired at 900 °C exhibited superior intrinsic activities in oxygen saturated-0.1 M KOH for ORR with half wave potential of 0.831 V (versus RHE), comparable with Pt/C from JM (0.838 V). It also exhibited higher stability than those of Pt–C in alkaline condition. The higher intrinsic ORR activity and remarkable stability can be due to the more dispersed Fe–Nx active sites, which indicate that Fe–N–C by 2% mole percentage Fe electrocatalyst is an excellent alternative electrocatalyst for energy applications.

1. Introduction

Oxygen reduction reaction (ORR) is a very complicated reaction and kinetically sluggish, which is almost five orders magnitude slower due to using Pt electrocatalysts [1]. However, ORR is playing a pivotal role in the field of energy storage as well as conversion devices including proton exchange membrane fuel cells. Platinum (Pt) is regarded as one of the most efficient catalysts for ORR and can account for 40% of the total cell cost [2]. It is being paid much more attention to develop cost-effective, abundant and highly-active alternatives to Pt-based catalysts like non precious group metal catalysts (NPMCs) like metal oxides [3–5], perovskite oxides [5–9], sulphides [10], carbides [11, 12], metal-doped into carbon materials M–N–C (M = Fe, Co etc) [13–17]. Among NPMCs mentioned above, iron-nitrogen-carbon (Fe–N–C) based materials are regarded as one of the most suitable alternatives [18–21].

The parameters of Fe–N–C electrocatalysts mostly depended on preparation process, which involved the annealing of C, N and Fe precursors to get porous carbon with more active sites. Gang Wu et al [22] firstly reported that highly active Fe–N–C catalyst by uniform Fe distribution with an atomic level. Fe was doped into zeolitic imidazolate framework (ZIF-8) by replacing Zn ions partially. Fe–N–C catalyst showed excellent ORR activity with half wave potential (0.82 V versus RHE) and good potential cycling stability under acidic condition. They also found oxygen free environment was critical for obtaining highly porous nitrogen doped carbon with uniform Fe distribution. Yuanjun Chen et al [23] reported a way to prepare catalysts composed of single Fe sites supported on nitrogen, phosphorus and sulfur doped hollow carbon from a ZIF-8@polymer composite. The obtained catalyst exhibited excellent ORR performance under alkaline condition with positive half wave potential (0.912 V), and it also exhibited good performance in acidic media with half wave potential (0.791 V).

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Recently, Jianglan Shui et al. [24] reported a series of single atom Fe–N–C catalysts with good external surface area and mesoporosity. It can meet the DOE target of PGM-free catalysts, and a current density of 0.047 A cm⁻² at 0.88 Vₚt–free. One of the main reasons was due to the increased utilization of Fe-N₄ and the enhancing of catalyst layer mass transport. Despite extensive efforts mentioned above regarding to the synthetic method, they still need to consider the use of some organic solvents and surfactants during precursor preparation, which could lead to the numerous waste and environmental pollution.

In this paper, Fe doped zeolitic imidazolate frameworks (ZIF-8) was simply prepared by solid state reaction method in argon atmosphere. For comparison, it was also prepared under the ambient atmosphere to study the effect of synthesis atmosphere on the Fe distribution level. The results showed that with 2% mole percentage Fe doped metal, Fe–N–C catalyst fired at 900 °C in argon exhibited superior oxygen reduction reaction performance with half wave potential of 0.831 V (versus RHE) in 0.1 M KOH, comparable with commercial Pt/C from JM (0.838 V). Fe–N–C electrocatalysts fired at 900 °C suggested the excellent properties for ORR with remarkable activity and durability. The PEMFC performance was also tested initially in our study.

2. Experimental

2.1. Raw chemicals
Zinc oxide (ZnO), 2-methylimidazole(2-mim) were order from Sigma-Aldrich, and ferrous oxalate (FeC₂O₄·2H₂O) was purchased from Aldrich. KOH was ordered from Beijing Chemical Reagent Company with all analytical grade. Naﬁon solution (5%) was purchased from Alfa company. Ultrapure water was used. For comparison, Pt/C electrocatalyst (20 wt%, Johnson Matthey) was used.

2.2. Catalysts preparation
Firstly, the calculated optimum amounts of 2-mim, ZnO, and FeC₂O₄·2H₂O were mixed and sealed in a clave in the presence of argon atmosphere and heated to 220 °C to form Fe-doped ZIF-8 composited by solid state reaction process. The mole percentage of Fe was 2% and 10%, respectively to investigate the effect of Fe amounts on the electrocatalytic performance of the electrocatalysts. The doped ZIF-8 was set as Fe2-Z8-Ar and Fe10-Z8-Ar, respectively. For comparison, instead of being prepared in the presence of argon atmosphere, the calculated optimum amounts of 2-mim, ZnO, and FeC₂O₄·2H₂O were mixed and sealed in the ambient air, and then Fe10-Z8-air and Fe10-Z8-air were prepared as well, respectively.

Subsequently, Fe2-Z8 and Fe10-Z8 composites were ball milled into powders and washed in a polyvinyl pyrrolidone (PVP) solution, which inhibited particles from agglomeration. Modiﬁed Fe2-Z8 and Fe10-Z8 powders were calcined for carbonization at 1000 °C for 3 h in argon to get C-Fe2-Z8-Ar and C-Fe10-Z8-Ar electrocatalysts without any further treatment. Fe2-Z8 and Fe10-Z8 powders were also calcined in the ambient air atmosphere under the same situation. They were denoted as C-Fe2-Z8-air and C-Fe10-Z8-air, respectively.

2.3. Catalysts characterizations
The phase of prepared samples was characterized by XRD (Bruker D8 Advances) using Cu-Kα radiation in step scan mode of 5°–80° (2θ) at intervals for 0.02°. XPS was tested using ESCALAB 250Xi instrument from Thermo Fisher company. The spectrums were calibrated by C 1s. Transmission electron microscopy (TEM) and element mapping analysis were tested on Titan G2 60–300 microscope from Thermo Fisher company. BET speciﬁc surface areas were obtained using adsorption data by Micromeritics TriStar II instrument.

Electrochemical performances were tested with three-electrode cell through Ivium work station. 5 mg electrocatalysts were mixed in 1 mL ethanol/naﬁon solution (naﬁon; ethanol = 1:9) to make uniform inks, which were put on glassy carbon disc electrode (diameter 3 mm). Pt wire and Hg/HgO were used as counter electrode and reference electrode, respectively.

Oxygen reduction reaction activities of electrodes were tested by linear scan voltammetry (LSVs) in oxygen saturated-0.1 M KOH with 50 mV s⁻¹ scan rate when catalysts loadings were 0.38 mg cm⁻². Oxygen gas was purged for 30 min to make electrolyte saturated with oxygen. Linear scan voltammetry was tested at 10 mV s⁻¹ in oxygen saturated 0.1 M KOH from 400 rpm to 2500 rpm with same catalysts’ loadings. Chronopotentiometry curves were obtained at constant potential (0.75 V) as well.

IR correction as well as related curves including LSVs were already done, which were shown in the previous paper. Pt/C from Johnson Matthey (Pt/C-JM) was studied for ORR under the same condition. Potentials were given versus RHE reference electrode (E_RHE = E(Hg/HgO) + E_Hg/HgO + 0.059 × pH, where E_Hg/HgO = 0.165 V versus RHE at 20°C).
Transferred electron number (n) was acquired by Koutechy-Levich (K-L) equation shown:

\[
\frac{1}{j} = \frac{1}{jk} + \frac{1}{jl}
\]

\[
jl = B w^{0.5}
\]

\[j_k\] and \[jl\] w were kinetic current and diffusion-limiting current, and \(w\) was the rotating rate, respectively. \(B\) was acquired from K-L slope:

\[B = 0.2nF(D_{O_2})^{3/2}v^{-1/6}C_{O_2}\]

\(N\) indicates electron number, \(F\) is Faraday constant of 96485 C mol\(^{-1}\), \(D_{O_2}\) is \(O_2\) diffusion coefficient under 0.1 M KOH of \(1.9 \times 10^{-5}\) cm\(^2\) s\(^{-1}\), \(v\) is kinetic viscosity of 0.01 cm\(^2\) s\(^{-1}\), and \(C_{O_2}\) is bulk concentration of \(O_2\) \((1.2 \times 10^{-6}\) mol cm\(^{-3}\)), 0.2 was used when rotation speed was expressed.

### 3. Results and discussion

#### 3.1. Structural and morphology characterization of the catalysts

Figure 1 show that x-ray powder diffraction (XRD) of ZIF-8, and Fe2-Z8-air, Fe2-Z8-Ar, Fe10-Z8-air and Fe10-Z8-Ar before firing. It can be clearly seen that ZIF-8, Fe2-Z8-air, Fe2-Z8-Ar, Fe10-Z8-air and Fe10-Z8-Ar all exhibited well defined diffraction peaks that were corresponded to MOF (JCPDS No. 15-0806) (figure 1(a)).
peaks didn’t change with synthesis condition, and results can indicate that the effect of synthesis atmosphere had little influence on the formation of ZIF-8, which was in accordance with previous published papers [22]. Figure 1 (b) clearly shows SEM image of ZIF-8 and it exhibited uniform dodecahedral shapes with average size of 300–400 nm. The structural similarity was found for C-Fe2-Z8-Ar, C-Fe10-Z8-Ar, and C-Fe10-Z8-Air. In figures 2(a)–(d), four samples only showed two broad peaks centred at 25° and 43°, which were corresponded to graphitized carbon.
Figure 3 shows SEM images of the catalysts for C-Fe2-Z8-air, C-Fe2-Z8-Ar, C-Fe10-Z8-air and C-Fe10-Z8-Ar, it can be clearly seen that there was an obvious morphology difference for these samples, especially for the samples after treated in Ar and air. For C-Fe2-Z8-Ar and C-Fe10-Z8-Ar as shown figures 3(a)–(d), an amorphous structure can be seen, however, obvious carbon nanotube structures in C-Fe2-Z8-air and C-Fe10-Z8-air appeared in figures 3(e)–(h). The formation of carbon nanotubes was probably due to generated metallic Fe in catalysts. It is commonly known that the formation of nanocarbon like carbon tube structures benefited active site and was correlated with enhanced ORR activity and stability [25, 26]. However, dominant amorphous distribution of N and Fe were found in C-Fe2-Z8-Ar catalyst exhibiting better ORR activity and stability that were relevant to nanocarbon–rich Fe–N–C catalysts. Su et al [27] also observed that carbon nanotubes was observed in the pyrolysis of Fe doped ZIF-8 exhibiting bad ORR activity. Fe-doped ZIF-8 was prepared by solvothermal reaction without firing in the air, which was the same to Fe2-Z8-air in our study. It can be seen in table 1, the BET surface area of C-Fe2-Z8 air was smaller (1235.4 m² g⁻¹) than that of C-Fe2-Z8-Ar (1038.2 m² g⁻¹). As for C-Fe2-Z8-Ar electrocatalysts with enough surface areas can exhibit excellent ORR activity. It is critical to control catalyst morphology with big surface areas to enhance the catalytic performance.

Figure S1-(a) is available online at stacks.iop.org/MRX/7/025506/mmedia shows selected survey scan of the catalysts for C-Fe2-Z8-air, C-Fe2-Z8-Ar, C-Fe10-Z8-air and C-Fe10-Z8-Ar, indicating the presence of O, N, C and Fe elements. XPS analysis (figure S1-(b)) indicates Fe was exclusively found in C-Fe-Z8-Ar with single peak at 710 eV. It suggests strong interaction between Fe and nitrogen doped carbon. This result agrees well with porous carbon morphology observed in the TEM images. In MOF precursor, Fe2-ZIF8-Ar and Fe10-ZIF8-Ar, Fe was coordinated by four N atoms from 2-mim, which was desirable for forming FeNx sites into porous carbon matrix by simple thermal conversion.

As shown in the TEM images (figure 4), the C-Fe2-Z8-Ar was comprised of small and well-dispersed nanoparticles, which were like that of ZIF-8 prepared under the identical conditions. Moreover, homogeneity features were found in C-Fe2-Z8-Ar, which can suggest the distributing of particle sizes in TEM. C, N, and Fe element were overlapped well according to the element mapping result in figure 4.

Figure 5 shows high resolution deconvoluted N 1s peaks for C-Fe2-Z8-air, C-Fe2-Z8-Ar, C-Fe10-Z8-air and C-Fe10-Z8-Ar. For two samples including C-Fe2-Z8-air and C-Fe10-Z8-air, pyridinic, oxidized and graphitic N with binding energy 398.7 eV–398.8 eV, 403.3 eV–403.6 eV and 401.2 eV–401.9 eV were clearly deconvoluted. While for two samples including C-Fe2-Z8-Ar and C-Fe10-Z8-Ar, only pyridinic and graphitic N with binding energy 398.7 eV–398.8 eV, and 401.2 eV–401.9 eV were deconvoluted.
The N content of C-Fe10-ZIF8-Ar (3.35 wt%) was also more than that of C-Fe10-ZIF8-Air (2.22 wt%, table 2). Moreover, the N content of C-Fe2-ZIF8-Ar (2.62 wt%) was also slightly more than that of C-Fe2-ZIF8-Air (2.6 wt%). Importantly, C-Fe2-ZIF8-Ar and C-Fe10-ZIF8-Ar samples contained higher pyridinic N compared to C-Fe2-ZIF8-Air and C-Fe10-ZIF8-Air. In addition, considering much higher Fe dispersion by divalent state, the higher pyridinic N amount in the C-Fe2-ZIF8-Ar was indicative of more Fe–N bonding in the catalysts. The nature of the N dopant was crucial for ORR activity of Fe–N–C type catalysts. The high pyridinic N and graphitic N content was desirable due to imparting higher positive charge density on carbon atoms and increasing limiting current density by benefiting O\textsubscript{12} adsorption and weakening of O=O bonds.

3.2. The electrochemical performance of Fe–N–C catalysts

ORR activity of C-Fe2-ZIF8-Ar, C-Fe10-ZIF8-Ar, C-Fe2-ZIF8-Air and C-Fe10-ZIF8-Air electrodes were investigated by LSV measurements on rotating ring disk electrode (RRDE) measurements under O\textsubscript{2} saturated-0.1 M KOH with 10 mV s\textsuperscript{−1} with rotation rate from 400 rpm to 2500 rpm (as shown in figure 6). Half-wave potential of C-Fe2-ZIF8-Ar and C-Fe10-ZIF8-Ar were 0.831 V and 0.791 V, respectively. However, C-Fe2-ZIF8-Air and C-Fe10-ZIF8-Air exhibited worse ORR performance, which were 0.73 V and 0.61 V for half-wave potential, respectively. For C-Fe2-ZIF8-Air, it was 61 mV more negative than C-Fe2-ZIF8-Ar, which can indicate the obvious effect of the atmosphere on the electrochemical performance of catalysts. Noticeably, half-wave potential of C-Fe2-ZIF8-Ar was 40 mV more positive than C-Fe10-ZIF8-Ar (0.791 V) when loading was 0.38 mg cm\textsuperscript{−2}. It can be identified that C-Fe2-ZIF8-Ar exhibited excellent ORR performance under this testing condition. Half-wave potential value of 0.831 V was comparable with commercialized Pt/C catalyst (half-wave potential 0.838 V). Table listed the reported value of typical NPMC catalyst. For instance, Chen et al.\cite{28} developed Fe–N–C and showed an onset potential of 0.95 V and half-wave potential of 0.85 V when catalyst loading was 0.6 mg cm\textsuperscript{−2}. C-Fe2-ZIF8-Ar also exhibited competitive ORR performance among these reported catalysts.

Four electron selectivity is an important standard for ORR catalysts. The linearity of K–L curves (figure 7) could indicate first order reaction kinetics towards concentrations for dissolved oxygen. The superior ORR
performance of C-Fe2-ZIF8-Ar was also supported by cathodic current density obtained at 0.75 V (figure 8). Cathodic current density of C-Fe2-ZIF8-Ar was 4.2 mA cm$^{-2}$, which was 93% for C-Fe10-ZIF8-Ar. ORR activity was better than that of C-Fe2-ZIF8-Air and C-Fe10-ZIF8-Air, which was 8.2 times and 2.6 times,

Table 1. Comparison of total N content and pyridinic N, oxidized N, graphitic N for C-Fe2-Z8-air, C-Fe2-Z8-Ar, C-Fe10-Z8-air and C-Fe10-Z8-Ar catalysts after deconvolution, BET surface area for C-Fe2-Z8-air, C-Fe2-Z8-Ar, C-Fe10-Z8-air and C-Fe10-Z8-Ar catalysts.

| Material         | Total atomic N % | Pyridinic N | Graphitic N | Oxidized N | BET surface area (m$^2$ g$^{-1}$) |
|------------------|------------------|-------------|-------------|------------|----------------------------------|
| C-Fe10-Z8-Ar     | 3.35             | 33.0%       | 67.0%       | 0          | 921.3                            |
| C-Fe10-Z8-air    | 2.22             | 26.7%       | 54.0%       | 19.3%      | 832.3                            |
| C-Fe2-Z8-Ar      | 2.62             | 49.4%       | 50.6%       | 0          | 1235.4                           |
| C-Fe2-Z8-air     | 2.6              | 27.5%       | 43.0%       | 29.5%      | 1038.2                           |

Table 2. Comparison of oxygen reduction reaction activity of NPMCs electrocatalysts under alkaline condition reported in literature.

| Materials               | Testing condition | ORR | References |
|-------------------------|-------------------|-----|------------|
| FePc/rGO               | 0.1 M             | E$_{onset}$ 0.53 | 0.940 0.855 | [29] |
| Co/N-C                 | 0.1 M             | E$_{onset}$ 0.25 | 0.834 0.75  | [30] |
| Atomically Dispersed Fe–N–C | 0.1 M | E$_{onset}$ 0.6  | 0.95 0.85  | [28] |
| Co–N/C                 | 0.1 M             | E$_{onset}$ 0.6  | 0.95 0.85  | [31] |
| Fe–N–C                 | 0.1 M             | E$_{onset}$ 0.38 | 0.98 0.831 | In this paper |

E$_{onset}$ and E$_{half-wave}$ is obtained based on the linear scan voltammetry results from literature.
respectively. Using equation (1), electron transfer numbers were 3.98 and 3.98 for C-Fe2-ZIF8-Ar and C-Fe10-ZIF8-Ar from 0.2 to 0.8 V. Importantly, there is no monotonic variation trend of H2O2 yield, indicating a real direct 4-electron reduction. Thus, a more advantage of the catalyst is extremely low H2O2 yield (<1%) without loading dependence. H2O2 was undesirable for Fe–N–C catalyst due to famous Fenton reaction, which could damage Nafion membrane in proton exchange membrane fuel cells. For C-Fe2-ZIF8-air and C-Fe10-ZIF8-air, electron transfer numbers were between 3.35 and 3.81 from 0.2 to 0.8 V.

Chronopotentiometry stability for C-Fe2-ZIF8-Ar was studied at a constant current density of 3 mA cm⁻² (figure 9) with catalyst loading of 0.38 mg cm⁻². C-Fe2-ZIF8-Ar exhibited remarkable ORR stability, achieving potential at 0.75 V of 5.1 mA cm⁻² during start point then obtained to 4.9 mA cm⁻² after 10000 s, which can
indicate that current slightly decreased. Our results demonstrate that C-Fe2-ZIF8-Ar (0.38 mg cm\(^{-2}\)) showed excellent performance. These results showed the remarkable performance of C-Fe2-ZIF8-Ar electrodes as nonprecious metal catalysts with excellent ORR activity and stability.

To validate the catalysts for practical systems, it is necessary to investigate the catalyst performance under practical H\(_2\)–air conditions. PEMFC activities of PGM-free catalysts measured under 1 bar H\(_2\)–air was initially shown in figure S2. The \(P_{\text{max}}\) reached 55 mW cm\(^{-2}\) when the fuel pressure was 2.5 bar. Although the power density was not high enough, it can still show that Fe–N–C catalyst had the potential to be used in the fields of PEMFC. There are a lot to be done to optimize the fuel cell performance when using Fe–N–C electrocatalysts in the next step.

4. Conclusions

In summary, we reported solid synthesis of into Fe–N–C electrocatalyst from Fe-doped metal–organic frameworks. Fe–N–C electrocatalysts have been regarded as one of best non precious metal oxygen catalysts, obtaining an onset potential and half-wave potential of 0.98 V and 0.831 V, which was comparable with that of Pt/C catalysts. The as-prepared C-Fe2-ZIF8-Ar delivered the initial power density of 55 mW cm\(^{-2}\) in acidic PEMFCs. This work achieved the rational design and precise preparation of Fe-based NPMC catalyst, and it also makes a step forward toward the better fabrication of highly pure and active NPMCs for PEMFC applications.

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Figure 9. Current-time chronoamperometric response of for C-Fe2-ZIF8-Ar under 1600 rpm in O\(_2\) saturated 0.1 M KOH at 0.75V.
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