

3D Porous Nitrogen-rich Octahedral Carbon as advanced Oxygen Reduction Reaction catalyst

Pengyu Tao, Wenjing Pu, Bo Shi, Hui Zhang, Desheng Cheng, Xiaomin Ma, Junli Qi, Lingling Huang

Basic Department, Army Academy of Artillery and Air Defense, Hefei, China

*Corresponding author e-mail: 18009481269@163.com

Abstract. A Metal-organic-frameworks (MOFs) derived 3D porous nitrogen-rich octahedral carbon (PNOC) catalyst is successfully fabricated via carbonization of MIL-101(Fe) precursor process. As-obtained PNOC combines the advantages of high surface area, well permeable pore and rich nitrogen content in one catalyst, which shows excellent catalytic activity and stability for oxygen reduction reaction (ORR). This work would offer some new insights to advanced ORR electrocatalyst material designed in fuel cells.

Keywords: Metal-Organic-Frameworks derived; Electrocatalyst; 3D Porous Nitrogen-rich Octahedral Carbon; Oxygen Reduction Reaction.

1. Introduction

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On account of high efficiency and zero pollution, great attentions have been paid to the proton exchange membrane fuel cells (PEMFCs). Nevertheless, its commercialization is much impeded due to sluggish oxygen reduction reaction (ORR) kinetics in cathode. And state-of-the-art Pt-based catalysts have the property of high-cost, poor stability and methanol intolerance, making it difficult to wide practical application. One promising strategy to solve these is to reduce noble metal using. Over the years, great efforts have been devoted to the size-, composition-, shape- and/or architecture-controlled syntheses of noble metal via different controlling approach [1]. Another strategy is to fabricate advanced carbon-based materials. They have been considered as promising candidates for developing excellent catalysts, contributing to their pronounced electrocatalytic activities, long-term stability, relatively low costs and brilliant tolerance against effects. Recently, much of doped heteroatom (B, N, S, P and F) can tailor its electronic structures and induce a positive synergistic effects to increase activity [2]. However, owing to the relatively limited amount of active sites induced by doping, its unsatisfactory performance still needs improvement [3].

And now, building unique structure by interface atomic or molecular engineering, can induce novel physicochemical properties and strong synergistic effects, providing an efficient strategy to enhance the catalytic activity of electrocatalysts [4, 5]. The simple 1D/2D unique structure based catalysts, such as N-doped carbon nanospheres, nanofibers and nanosheets, have been used as good ORR electrocatalysts [6-11]. However, the lower surface area and less pore structures still limit the developing of their ORR performance. Apparently, 3D unique structure based catalysts usually have abundant pore structure with high BET surface area. With more 3D geometric morphologies and pore structures, many honeycomb-like nanostructures, nanopolyhedrons, nanocubes and other unique structured catalysts have drawn great attention in ORR study [12-16]. Normally, the main features of reported excellent ORR catalysts possess large surface area, complex pore structures and high N content with 3D unique structure. Meanwhile, it is worth mentioning that Metal-organic-frameworks (MOFs) making by linking metal ions and organic moieties have the

advantages of controllable morphology and pore structure with multiple 3D unique structure, which makes it an ideal candidate as a 3D unique structured precursor.

In this study, a MOFs (MIL-101(Fe)) derived 3D porous nitrogen-rich octahedral carbon (PNOC) was developed and used as an advanced ORR electrocatalytic material. Some favorable N-rich, permeably porous and high surface area features combined in as-prepared PNOC, resulting in it possesses a brilliant activity, high stability, good methanol-tolerance, low HO_2^- yield and pseudo four-electron transfer pathway towards ORR. This work would offer some new insights to advanced ORR electrocatalytic material design in fuel cells.

2. Experimental

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.35 g, 5 mmol) and 1, 4-benzene dicarboxylic acid (H_2bdc) (0.415 g, 2.5 mmol) were dissolved in N, N-dimethylformamide (DMF, 30 mL). And then the solution was put in a Teflon-lined autoclave and heated at 110 °C of 24 h. The powders which we got were washed by DMF and ethanol for several times. Then, the MIL-101 (Fe) was obtained.

After that, both MIL-101(Fe) (0.80 g) and melamine (0.40 g) were dispersed in ethanol (20 mL) with ultrasonic for 2 h, put them statics for 12 h, it is separated and dried at 50 °C for 6 h. Then, the powders were treated at 900 °C for 4 h with a heating ramp of 10 °C min^{-1} from room temperature with N_2 current of 10 mL min^{-1} . Finally, we put the powders into 3 M HCl (30 mL) for 12 h, used water washing to pH 7 and dry at 60 °C for 12 h.

3. Results and discussion

Based on porosity and unique carbon frameworks, in this study, MIL-101(Fe) has been used as the precursor for preparing the 3D porous carbon frameworks. With great adsorption capacities of this precursor, melamine could be adsorbed into its structure as small molecule nitrogen source [4, 17]. At high temperature, the nitrogen could be doped on the surface and inner of carbon frameworks as ORR active species.

The structure and morphology were examined by scanning electron microscopy (SEM). To figure out the effect of before and after heat treatment, the SEM of PNOC and its precursor was observed. In Fig. 1a and 1b, it shows that PNOC precursor possesses a regular octahedral structure with the average size of 1 to 1.5 μm . While, remarkably, PNOC still keeps the shape of octahedral with clear edge and shrinks less in Fig. 1c. Concretely, the magnified SEM image of PNOC discloses that the rough surfaces of PNOC are comprised of numerous nanopores in Fig. 1d. These structure features would be favorable to the accessibility of oxygen molecular, thus facilitating to ORR kinetics.

And then, the inner structure of PNOC was explored by transmission electron microscope (TEM) (Fig. 1e and Fig. 1f). In Fig. 1e, it can be further proved that PNOC is consisted by 3D carbon frameworks with many pores and clear boundaries. Additionally, the inner pore structures are well-connected in the magnified images (Fig. 1f), where it is endowed by MOFs precursor. These permeable pore structures may play an important role in solid-liquid-gas three phases of ORR process. Due to channels of these cross-linked permeable pores providing low-resistant diffusion for mass transfer, the well-connected permeable porous morphology would ensure fast mass exchanges of electrolyte and/or O_2 . It is worth mentioning that, the permeable porous structure forms in organic molecules pyrolyzed at high temperature and etching of HCl solution processes. And this complex inner pore structure may provide much active sites and easily approach reaction substrate. In Fig. 1e and Fig. 1f, no obvious Fe and/or Fe compounds nanoparticles were found on the carbon frameworks, which suggest that major Fe and/or Fe compounds were etched. To explore the distribution of each element, the high-angle annular dark-field scanning TEM (HAADF-STEM) and the EDX line-scanning profile (Fig. 1 h, i) were performed. As can be seen in the HAADF-STEM and the EDX line-scanning profile, the C element counts suggest that PNOC is porous carbon

frameworks. Compared to the C and N elements, the content of Fe is obviously less. However, the signal of Fe always appears at the dense area of the C and N elements. This suggests that Fe is doped in the layer of PNOC, may affect the performance for ORR.

In the high-resolution TEM (HRTEM), the lattice spacing of 0.316 nm consistent matches the (002) plane of graphitic carbon (Fig. 1g). To explore the distribution of each element, the high-angle annular dark-field scanning TEM (HAADF-STEM) and the energy-dispersive X-ray (EDX) line-scanning profile (Fig. 1h, i) were performed. As can be seen in the HAADF-STEM and the EDX line-scanning profile, the C element counts suggest that PNOC is porous carbon frameworks. It shows that the thickness has been thickened gradually from the edge to the middle. Meanwhile, N element counts increased with the increase of C element counts, it proves that N element is evenly doped. As we all know, MIL-101(Fe) can be decomposed above 300 °C, comparing the reported works, as-prepared PNOC keeps the unique structure maximally [18, 19]. It can be explained by reason that, maybe the method of N doped into structure of the precursor by ultrasonic dispersion not simple mixed avoid destroying the total structure of precursor at high heat temperature with N₂ current of 10 mL min⁻¹. Above all, colligating the SEM, TEM and EDX line-scanning profile, it can be concluded that PNOC is a highly graphitic 3D porous nitrogen-rich permeable octahedral carbon frameworks.

Brunauer-Emmet-Teller (BET) test was used to study the porous structure of PNOC. Fig. 2a shows that it is a typical IV isotherm with an obvious distinct hysteresis loop and its surface area is 897.81 m² g⁻¹ with 3.7 nm pore size (BJH). Compared to its precursor (3200-3900 m²g⁻¹) [20], BET surface area of PNOC shrunk remarkably. It would be caused by pyrolyzed organic molecules at high temperature destroying most of microporous in precursor. Even though, the PNOC still keeps a high surface area with multitudinous mesoporous. The PNOC was also characterized by XRD and Raman. In Fig. 2b, XRD of PNOC peak appears at 22.5 °, corresponding to (002) planes of graphite. In Fig. 2c, the Raman result shows that the intensity ratio of D (1345 cm⁻¹) to G (1575 cm⁻¹) band (ID/IG) is determined to be 0.99 for NPOC. By the way, in a typical Raman spectrum, the D band is expressed as a series of structural defects, whereas the G band stands for the graphitic structure. This also suggests that the organic part of precursor has carbonized to be inorganic 3D carbon frameworks.

X-ray photoelectron spectroscopic (XPS) was also performed to study the PNOC. In Fig. 2d, it reveals the presence of C, O, N and Fe in the PNOC. And the surface contents of C, O, N and Fe are calculated to be 88.60, 5.62, 5.33 and 0.45 at %, respectively. Additionally, in Fig. 2e, the main surface components are C=C, C=N and C-N species, suggesting PNOC is a typical carbon material and N element has already been doped in 3D carbon frameworks [21]. The precursor adsorbed melamine could result in the high N counts in PNOC at high temperature. As can be seen in Fig. 2f, the four peaks at 398.4, 399.6, 401.2 and 403.0 eV in the N 1s spectrum can be assigned to pyridinic N (32.7 %), pyrrolic N (0.9 %), graphitic N (52.3 %) and N-O (14.1 %), respectively. To get better ORR performance, the crucial factors are not only the nitrogen contents, but also the nitrogen types in carbon-based materials. Anterior literature has demonstrated that the pyridinic N and graphitic N can provide active sites to facilitate oxygen reduction [14]. More concretely, pyridinic N can reduce the energy barrier for O₂ adsorption on adjacent carbon atoms during the ORR process [22]. While, graphitic N can facilitate O₂ adsorption and subsequent disassociation/weakening of O=O bonds through inducing a non-uniform electron distribution and short C-N bonds, comparable to O-O bonds. Both graphitic N and pyridinic N (> 80 %) in PNOC perform a favourable synergistic effect, which would promote the rate-limiting first-electron transfer process [23]. It is mentionable that there are some minute quantity of Fe element is detected in PNOC. However, the result of XRD test suggested the obvious existence of Fe₃C. Moreover, the Fe₃C is known as an excellent ORR catalyst. Coordinating with carbon frameworks, trace amounts of Fe₃C would benefit the adsorption and activation of O₂ molecules, thus boosting the ORR activity [24].

Electrochemical measurements are the most important tests to evaluate its ORR performance. In Fig. 4c, the CV curves of PNOC shows well-defined cathodic peaks in N₂ saturated solution and appears a pronounced cathodic peak at -0.17 V in O₂ saturated solution. Moreover, from Fig. 3a, the linear sweep voltammetry (LSV) curves of PNOC exhibits more positive half potential (E_{1/2}) than the sample of PNOC without N, which is even 10 mV positive than that of the Pt/C (-0.12 V). And the heating temperature (700, 800, 900, 1000 °C) at 900 °C is most appropriate of this series catalyst. (Fig. 4b) Also, the Tafel slope of PNOC is 56.5 mV dec⁻¹, greatly smaller than that of Pt/C (74.5 mV dec⁻¹) (Fig. 4d). Clearly, PNOC exhibits more brilliant ORR performance than the sample of PNOC without N, suggesting that N-doping in PNOC has a favorable effect. Both pyridinic N and graphitic N provide active species which can improve the ORR performance. As be reported, the graphitic N provides a good electronic conductivity which could improve the limited current densities with reducing ORR kinetic limitations. And the pyridinic N could adsorb O₂ molecules by well-connected mesoporous structure in PNOC, which can make for transferring O₂ molecules and the electrolyte easily, thus, enhancing the mass transport of ORR [23].

Rotating ring-disk electrode (RRDE) measurement was conducted from -0.8 to 0.2 V to explore the oxygen reduction selectivity and peroxide yields in Fig. 3 d. The corresponding electron transfer number (n) and the HO₂⁻ yields (%) during the ORR process can be determined via the formulas in supporting information. In RRDE measurement of PNOC, the electron transfer number (n) is 3.9 to 3.8, and the HO₂⁻ yield is 2.6 % to 6.7 % on the edge of -0.3 V to -0.5 V (Fig. 4e). Because the electron transfer number n is near to the 4, suggesting a pseudo four-electron transfer ORR pathway of PNOC. Meanwhile, the HO₂⁻ yield (%HO₂⁻) of PNOC is below 10 %, implying their domination of the less two-electron pathway with peroxide as the final product [24].

As shown in Fig. 3c and Fig. 4f of methanol tolerance study, LSV curves of PNOC in 0.1 M KOH + 0.5 M CH₃OH solution shift much smaller than that of Pt/C with a huge oxidation peak. Moreover, continuous chronoamperometric measurements were used to test the stability of the catalysts in Fig. 3d. It is finding that the PNOC (83.4 %) keeps a higher stability than Pt/C (69.9 %). Generally, the same result can be proved by the durability of PNOC after 1000 cycles. After 1000 cycles (In Fig. 3e and Fig. 3f), the half potential (E_{1/2}) of PNOC negatively shifts 19.8 mV which is smaller than that of Pt/C (about 23.2 mV). Obviously, Pt/C has a relatively poor stability. As everyone knows, the non-metal materials are ensured that they have doughty tolerance in harsh conditions [3]. Generally, 1D and 2D carbon materials have serious aggregation problems. While, 3D carbon materials with unique structure could avoid this problem [4]. Thus, due to the unique 3D octahedral carbon frameworks of PNOC, it could avoid active species blocking/covering and promise the mass transfer of electrolyte and O₂. Consequently, the 3D porous carbon framework of PNOC possesses better catalytic stability and tolerance to methanol crossover effects than Pt/C catalyst for ORR.

Overall, this unique 3D frameworks structure of PNOC is expected to be an ideal design for ORR due to the following advantages: i) The well-distributed N element and much N active species in 3D carbon frameworks would be favorable to synergistic effects in ORR process; ii) The 3D graphited carbon frameworks of PNOC can facilitate electron transfer in ORR; iii) The well-connected and permeable porous morphology offers high BET surface area, which can easily achieve with a low-resistant diffusion channels for O₂ and electrolyte thus enhancing the fast mass exchanges during the ORR process.

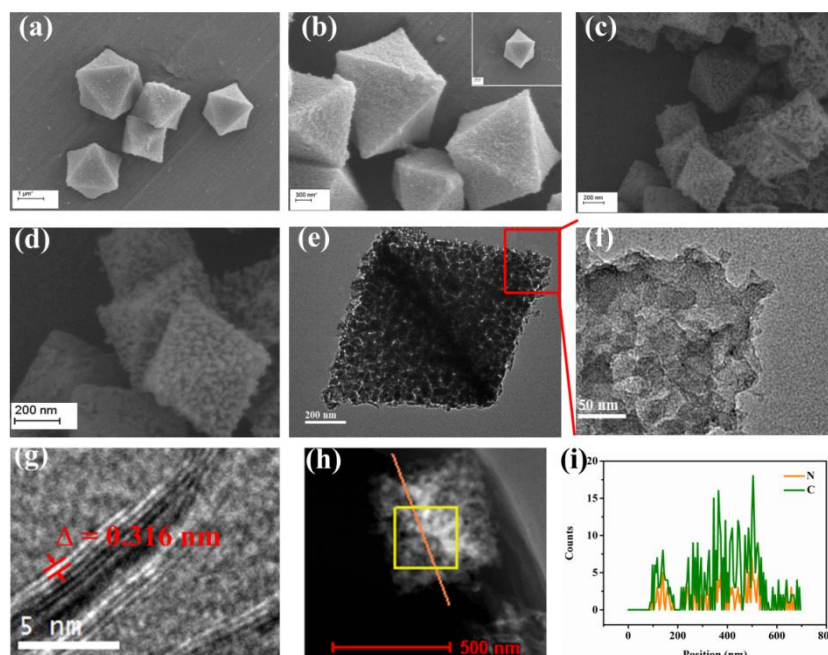


Fig. 1 Low-magnification and b) High-magnification SEM images of precursor, c) Low-magnification and d) High-magnification SEM images of PNOC, e) TEM image of PNOC, f) Magnified TEM image of PNOC as detached, g) HRTEM images of graphene layers in the PNOC, h) and i) HAAD-STEM for PNOC.

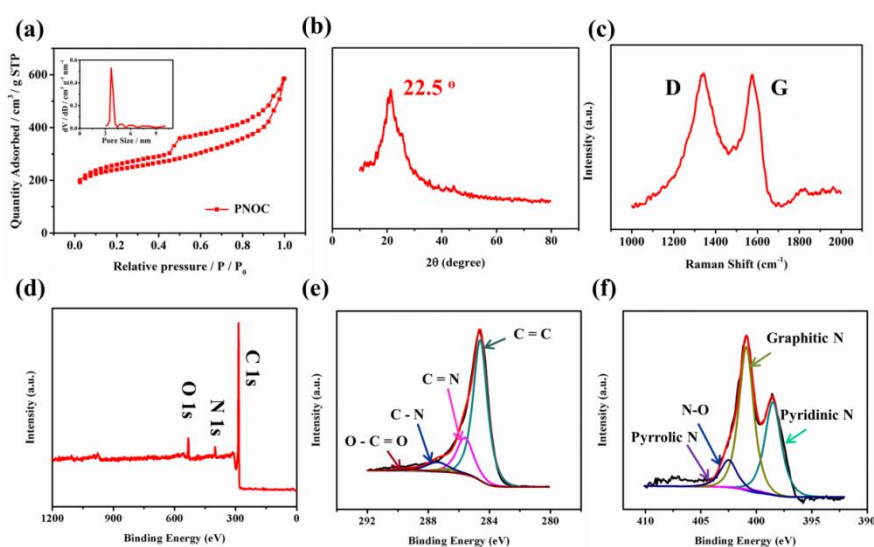


Fig. 2 BET test of PNOC N2 sorption isotherms at 77 K, b) XRD test of PNOC, c) Raman spectrum of PNOC, d) XPS survey of PNOC, e) C 1s XPS spectra of PNOC, f) N 1s XPS spectra of PNOC.

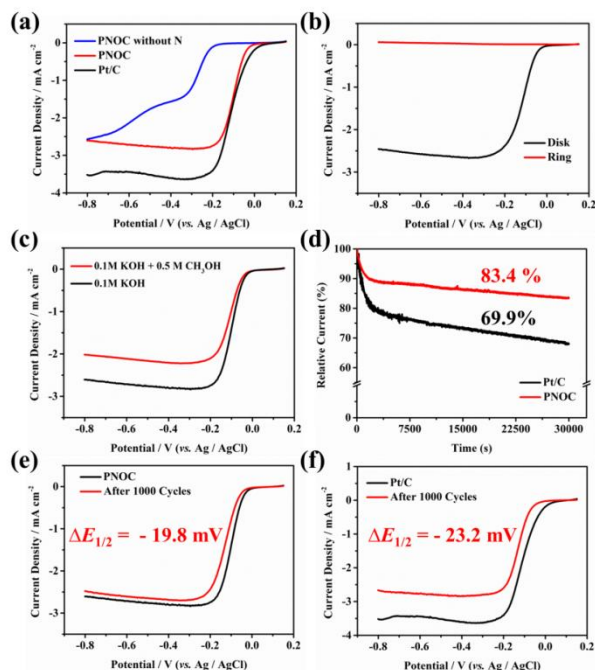


Fig. 3 Linear sweep voltammogram (LSV) curves of PNOC, PNOC without N and Pt/C (20 wt%) in 0.1 M KOH at 5 mV s⁻¹ and a rotating speed of 1600 rpm, b) Rotating ring-disk electrode measurement for PNOC in 0.1 M KOH at 5 mV s⁻¹ and a rotating speed of 1600 rpm, c) LSV curves of PNOC in O₂-saturated 0.1 M KOH and O₂-saturated 0.1 M KOH + 0.5 M CH₃OH solution, d) Chronoamperometric of PNOC and Pt/C (20 wt%) response at -0.3 V for 30000 s in 0.1 M KOH and a rotating speed of 1600 rpm, e) LSV curves of PNOC before and after cycling for 1000 cycles in 0.1 M KOH, f) LSV curves of Pt/C (20 wt%) before and after cycling for 1000 cycles in 0.1 M KOH.

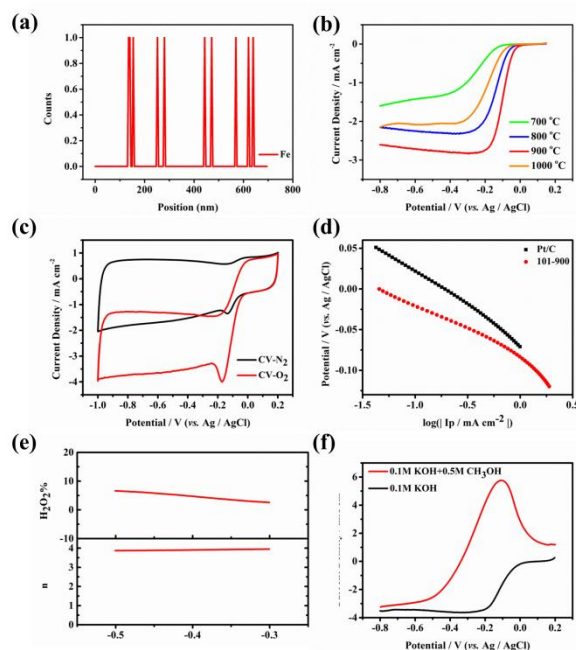


Fig. 4 HAAD-STEM for PNOC about Fe, b) LSV curves of PNOC at different temperatures(700, 800, 900, 1000 oC) in O₂-saturated 0.1 M KOH and O₂-saturated 0.1 M KOH solution at 5 mV s⁻¹ and a rotating speed of 1600 rpm, c) Cyclic voltammogram (CV) of PNOC in (red line) O₂ and (black line) N₂ -saturated 0.1 M KOH at 50 mV s⁻¹ , d) Tafel slopes of PNOC without N, PNOC and Pt/C, e) Calculated H₂O₂% and electron transfer number n are from RRDE (Fig. 3b), f) LSV

curves of Pt/C (20 wt%) in O₂-saturated 0.1 M KOH and O₂-saturated 0.1 M KOH + 0.5 M CH₃OH solution at 5 mV s⁻¹ and a rotating speed of 1600 rpm.

4. Conclusion

In summary, in this work, a 3D porous octahedral carbon frameworks PNOC derived from MOFs has been successfully produced as ORR electrocatalyst. As-obtained PNOC has a large surface area (897.81 m²g⁻¹), well-connected and permeable porous structure and high graphitic- and pyridinic- N content. And it exhibits high ORR catalytic activity comparable to the commercial Pt/C with good tolerance and stability. This work would provide a simple and low-cost way on preparing advanced 3D unique structure catalyst for ORR in fuel cells.

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