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F127 Assisted Synthesis of Tri-(Fe/F/N)-doped Porous Carbons with a High Density of Fe₃C and Fe-N₄ Catalytic Sites as Efficient Electrocatalysts for ORR

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Because of the slow reaction rate of the oxygen reduction reaction (ORR), high-performance catalysts are needed to accelerate the reaction. However, platinum (Pt)-based electrocatalysts have the shortcomings of high cost and poor stability. The development of low-cost, high catalytic activity and long-term durability non-precious metal electrocatalysts has become a research hotspot. In this study, we successfully prepared tri(Fe/N/F)-doped FeNF-F127C catalyst featuring mesoporous carbon via polyacrylonitrile/polyvinylidene fluoride/F127 (PAN/PVDF/F127) tricomponent polymers and iron(III) nitrate nonahydrate (Fe(NO₃)₃.9H₂O) followed by thermal carbonization. Compared with commercial Pt/C catalysts, FeNF-F127C showed excellent long-term durability and considerably better methanol tolerance as well as a high electrocatalytic activity (E_{onset} : 0.956 V vs RHE, $E_{1/2}$: 0.823 vs RHE, and electron transfer number: 4.0) in alkaline media. The improved ORR performance could be explained by larger specific surface area with a well-ordered mesoporous structure, high density of Fe₃C sites and Fe-N₄ sites.

Keywords: Tri-(Fe/N/F)-doped mesoporous carbons; Non-precious metal electrocatalysts; Oxygen reduction reaction

1. INTRODUCTION

Fuel cells are considered as one of the most promising power sources due to their high energy density, excellent energy conversion efficiency and clean products. However, the slow reaction rate of

the oxygen reduction reaction (ORR) has become a key factor restricting the development of fuel cells[1-5]. Therefore, there is an urgent need to develop high-performance ORR catalysts. To date, Pt-based catalysts are effective ORR catalysts, but Pt-based catalysts have the shortcomings of poor durability, high cost, and limited reserves. Additionally, improvements of Pt-based catalysts such as alloying, cannot completely eliminate the abovementioned disadvantages[6-8]. Recently, researchers have attracted intense interest to low-cost, high catalytic activity and long-term durability non-precious metal electrocatalysts. Metal-free heteroatom-doped carbon (nitrogen (N) [9-11], sulfur (S) [12, 13], phosphorus (P) [14-16], fluorine (F) [17, 18]and their multiple-doped carbon) and transition metal complexes (such as their metal carbon, nitrogen, oxygen compounds) have been studied as promising candidates.

Among the promising candidates, M/N-C (M = Fe[19-22], Co[23, 24], Ni[25, 26], Cu[27, 28], etc.) catalysts formed by transition metal and nitrogen doping have attracted great interest because of their excellent ORR activity. The Fe/N-C catalyst is one of the most promising non-precious metal catalysts because of its high ORR activity Fe₃C and Fe-N_x sites[29-33]. To improve the ORR activity of Fe/N-C catalysts, numerous studies have sought to dope them with the second or more heteroatoms. These results showed that heteroatoms and nitrogen co-doped carbon exhibited excellent ability to adsorb O₂ through the synergistic effect between heteroatoms and nitrogen, thus improving the ORR activity[34, 35]. The fluorine atom has the largest electronegativity (4.0), which may have greatly improved the ORR performance of the Fe/N-C catalyst, but there are relatively few studies on the preparation of tri(Fe/N/F)-doped catalysts at present. Lee et al. proposed the strategy of preparing tri(Fe/N/F)-doped catalyst for the first time in 2019, and synthesized tri(Fe/N/F)-doped mesoporous carbon nanofibers (MCNFs) followed by electrospinning and thermal treatment as ORR catalysts[36]. Although the half-wave potential of the MCNFs was 10 mV lower than that of commercial Pt/C catalysts, its long-term durability and methanol tolerance were better. Diao et al. used the structural advantage of metal-organic framework (MOF) to evenly distribute Fe-N_x active sites and developed tri(Fe/N/F)-doped porous carbon (FeFNC) as an efficient ORR catalyst, which had an excellent ORR performance in alkaline and acidic media. These studies showed that doping with nitrogen, fluorine and iron had a synergistic effect. The fluorine sources selected in the above studies were fluoride salts such as ammonium fluoride (NH₄F), however, the facile decomposition property of NH₄F increased the difficulty of synthesizing F-doped carbons [37] [38]. The use of fluoropolymer materials as fluorine sources has become an effective method of F-doping. Gong et al. applied polyvinylidene fluoride (PVDF) as fluorine source in ORR catalysis for the first time. N, F-codoped carbon nanofiber (N,F-MCFs) exhibited high catalytic activity with a fluorine content of 2.81 wt%[39]. PVDF, as a typical fluoropolymer, is a green and efficient fluorine source with the advantages of a high level of fluorine residue after carbonization, non-toxic and so on.

The pore structure of the ORR catalyst is also a key factor affecting its performance. Macropores and mesopores are conducive to the transport of reactants and products (O_2 and H_2O , etc.), and the high micropore ratio enables the catalyst to accommodate a large number of electrocatalytic active sites[40-42]. In the construction of porous structures, the hard template method usually requires hydrofluoric acid (HF) etching and other post-treatment methods, which makes the preparation of catalysts quite complicated and dangerous [1, 39]. The soft template method (such as block copolymer F127) is a

popular method to synthesize porous carbon materials because it can decompose the materials to form pores after carbonization, which makes the tedious post-treatment process simple and maintains the porous structure [43, 44]. In this study, block copolymer F127 was used as a soft template. PAN was used as a carbon and nitrogen source. PVDF was used as a carbon source and fluorine source. Iron(III) nitrate nonahydrate was used as an iron source. Tri(Fe/N/F)-doped FeNF-F127C catalyst featuring mesoporous carbon was prepared via PAN/PVDF/F127 tricomponent polymers and iron(III) nitrate nonahydrate followed by thermal carbonization. The as-synthesized FeNF-F127C was characterized systematically, and its ORR performance and long-term durability were investigated. With the benefit of its large specific surface area with a mesoporous structure, multiple heteroatom-doped elements, a high density of Fe₃C sites and Fe-N_x sites, FeNF-F127C exhibited a remarkable ORR activity in alkaline media. Compared to commercial Pt/C catalysts, the obtained catalyst showed higher long-term durability and methanol tolerance.

2. EXPERIMENTAL DETAIL

2.1 Materials and Chemicals

PAN ($M_w = 150,000 \text{ g/mol}$) and *N*, *N*-dimethylformamide (DMF, 99.8%) were obtained from J&K Scientific Ltd. PVDF (Solef 5130) was purchased from Solvay. F127 ($M_w = 10,000 \text{ g/mol}$) was purchased from Beijing Innochem Science & Technology Co., Ltd. 5% Nafion[®] solution (Nafion 117) was obtained from E. I. DuPont Company. The commercial 20 wt% Pt/C catalyst was purchased from Johnson Matthey (UK) Company. Other chemicals, such as iron(III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O), potassium hydroxide (KOH), ethanol and methanol were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received.

2.2 Materials preparation

PAN (0.25 g), PVDF (0.25 g), F127 (0.5 g) and Fe(NO₃)₃·9H₂O (0.135 g) were mixed in DMF (24 g) and stirred for 12 h. The mixed solution was transferred to a watch glass, and the watch glass was put in a blast oven and kept at 80 °C for 12 h, and then dried at 60°C for 6 h under vacuum, and a redbrown transparent membrane was obtained. Then, the membrane was stabilized in the air under 220 °C for 2 h, heated at a rate of 5 °C min⁻¹ in an electrically heated tube furnace and carbonized at 800 °C for 2 h under a nitrogen flow at a heating rate of 5 °C min⁻¹. The final tri(Fe/N/F)-doped porous carbon was named as FeNF-F127C. For comparison, N-F127C without PVDF and Fe(NO₃)₃·9H₂O, NF-F127C without Fe(NO₃)₃·9H₂O and FeN-F127C without Fe(NO₃)₃·9H₂O were prepared by the same procedures.

2.3 Physical and Electrochemical Characterization

The morphologies of the samples were observed by scanning electron microscopy (SEM, Nova NanoSEM 450) and transmission electron microscopy (TEM, TALOS F200X). Powder X-ray

diffraction (XRD) patterns were obtained on a D8 Advance diffractometer (Bruker, German) operating at 40 kV and 40 mA current with Cu K α radiation sources. The graphitization degree and defect degree of all the samples were analyzed by Raman spectroscopy (DXR). The Brunauer-Emmett-Teller (BET) measurements were performed on an ASAP 2460 surface area and porosimetry analyzer (Micromeritics Instrument Corp., USA). The chemical properties were obtained via X-ray photoelectron analyses (XPS, AXIS UltraDLD) equipped with Al K α sources.

The electrochemical measurements of all the samples were performed on an Autolab PGSTAT302 (Metrohm, Netherland) electrochemical workstation with a standard three-electrode system. A glassy carbon electrode, Ag/AgCl (3 M KCl solution) and Pt wire served as the working electrode, the reference electrode and counter electrode, respectively. The catalyst ink was prepared as fellows. 1 mg sample was mixed with 10 μ L 5% Nafion 117 solution and 1 ml hydroalcoholic solution (volume ratio of water: ethanol=4:1). After ultrasonic homogenization for 30 min, 14 μ L catalyst ink was coated on the working electrode and dried under infrared light. The loading of the sample was approximately 0.19 mg cm⁻². Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) measurements were performed in O₂-saturated and N₂-saturated 0.1 M KOH solution with a sweep rate of 10 mV s⁻¹, and the LSV test was performed using rotating disk electrode (RDE) scanned at various rotating speeds from 400 to 2000 rpm. The Koutecky–Levich (K–L) equations (Eqs. 1, 2) were used to calculate the electron transfer number (n).

$$J^{-1} = J_k^{-1} + (0.62nFD_{0_2}^{2/3}C_{0_2}^b v^{-1/6}\omega^{1/2})^{-1}$$
(1)
$$|J_k| = nFk_f C_{0_2}^b$$
(2)

where *J* is the measured disk current density and J_k is the kinetic current density; n is the electron transfer number; *F* is the Faraday constant; $C_{O_2}^b$ and D_{O_2} are the bulk concentration and diffusion coefficient of O₂ in the electrolytes, respectively; *v* is the kinematic viscosity of the electrolyte; ω is the disk rotation rate; and k_f is the electron transfer rate constant.

Durability testing used the chronoamperometric technique and was measured at 0.62 V (vs. RHE) for 10000 s in an 0.1 M KOH solution (rotation rate = 1600 rpm).

3. RESULTS AND DISCUSSION

The morphology of FeNF-F127C for the whole preparation process was characterized by SEM. From FeNF-F127C precursor SEM images (Fig. 1a, b), due to the presence of F127 triblock copolymer, small bumps were observed on the surface of the film sample, but no pores were observed on the surface of FeNF-F127C. After pyrolysis, because of the removal of F127, FeNF-F127C had distinct porous structures on the surface (Fig. 1c, d).



Figure 1. SEM images of FeNF-F127C precursor (a, b) and FeNF-F127C (c, d).

To further demonstrate the structural characteristics of FeNF-F127C, TEM observations were performed. As shown in Fig. 2a, Fe nanoparticles were well-dispersed and appeared as relatively dark spots, approximately 10~40 nm in size. According to the HRTEM images (Fig. 2b, c), Fe nanoparticles were well wrapped in the graphitized carbon lattice. The enclosed Fe nanoparticles could activate the surrounding graphite layer, which could lead to excellent ORR activity. To further investigate the content distribution of various elements in the catalyst, a TEM-EDS mapping test was performed (Fig. 2d). The test results showed the presence of iron, nitrogen and fluorine, which proved the successful preparation of the tri-(Fe/N/F) doped catalyst. As a whole, each element was well distributed in the FeNF-F127C catalyst.



Figure 2. TEM (a), HRTEM images (b, c) and the corresponding elemental mapping images (d) of FeNF-F127C.

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The crystal structure of the samples was characterized by XRD analysis. From the XRD patterns (Fig. 3a), four samples displayed peaks at around 25° and 44° , corresponding to the diffraction peaks of the (002) and (101) crystal planes of carbon (JCPDS card No. 41-1487), respectively. The difference among the samples was that N-F127C and NF-F127C samples displayed broad peaks at approximately 25° , while the FeN-F127C and FeNF-F127C samples displayed sharp diffraction peaks at 26.1°. The increase in the peak intensity and the shift of the peak position to higher diffraction angles indicated that the doping of Fe can catalyze the formation of graphitized carbon. Peaks at 37.6°, 42.8°, 43.7° and 49.1° were detected in the FeN-F127C and FeNF-F127C samples, corresponding to the (121), (211), (121), and (221) crystal planes of Fe, respectively. This result showed that a nitrogen atmosphere and high-temperature conditions can reduce Fe³⁺ to Fe during the preparation process.



Figure 3. XRD patterns (a) and Raman spectra (b) of different samples

The degree of graphitization of the samples was characterized by Raman spectroscopy. Raman spectrum in Fig. 3b exhibited typical D and G bands of carbon at approximately 1346 cm⁻¹ and 1587 cm⁻¹, respectively. In addition, the peak area value ratio of the D-band and G-band (I_D/I_G) could be used to evaluate the doping effect and the degree of defects in the catalysts[45, 46]. The I_D/I_G ratio of N-F127C, NF-F127C, FeN-F127C and FeNF-F127C was 2.93, 3.12, 2.25 and 2.27, respectively. This result showed that the doping of iron obviously led to a reduction of the I_D/I_G ratio, which induced graphitization of the surrounding carbon. An increase in the degree of graphitization could increase the conductivity of the catalyst. The doping of fluorine caused an increase in the I_D/I_G ratio. The increased I_D/I_G ratio indicated that the doping of fluorine could induce structural defects, which was beneficial to the formation of more ORR active sites.

The specific surface areas and porous structures of the samples were investigated by N_2 adsorption-desorption measurements. The N_2 adsorption-desorption isotherms of four samples (Fig. 4a) displayed a striking feature of a type IV profile with an H2 hysteresis loop following IUPAC classification, which revealed that all samples possessed mesoporous features. The existence of

mesopores was beneficial to the penetration of the electrolyte and the transportation of reactant products, thereby effectively improving the ORR activity of the catalyst. The BET surface areas of N-F127C, NF-F127C, FeN-F127C and FeNF-F127C were 41.5, 71.5, 166.8 and 312.5 m² g⁻¹, respectively. The corresponding pore size distributions were calculated by Barrett–Joyner–Halenda (BJH) desorption analysis, and the results were shown in Table 1. By comparing these results, the doping of fluorine increased the specific surface area and pore size of the catalyst, which was more conducive to the exposure of ORR active sites and ion transport. During the process of carbonization, fluorine easily volatilized by forming hydrogen fluoride and other gases, leaving pores and large specific surface area. The doping of iron increased the specific surface area of the samples while decreased the pore size of the catalyst. Based on the above factors, the FeNF-F127C sample had the largest specific surface area (312.5 m² g⁻¹) and a relatively regular mesoporous structure with an average pore diameter of 3.6 nm, which might have led to its excellent ORR activity.



Figure 4. N₂ adsorption-desorption isotherms (a) and pore size distributions (b) of different samples

Samples	Sbet (m ² g ⁻¹)	D (nm)	IG/ID
N-F127C	41.5	5.1	2.93
NF-F127C	71.5	7.2	3.12
FeN-F127C	166.8	3.3	2.25
FeNF-F127C	312.5	3.6	2.27

Table 1. Summary of the structural parameters of different samples

The elemental composition and the contents of each element on the catalysts surface were characterized by XPS measurements. The XPS quantitative results (Table 2) demonstrated that the mass ratios of N, F and Fe were 7.12, 0.85, and 2.48 in FeNF-F127C, which proved the successful preparation

of the tri-(Fe/N/F) doped catalyst. The peaks resulting from the doped N could be further deconvoluted into several peaks centered at 398.2±0.2 eV, 398.8±0.2 eV, 400.0±0.2 eV, 401.1±0.2 eV and 403.0±0.2 eV, corresponding to pyridinic-N, metal-N, pyrrolic-N, graphitic-N, and oxidized-N, respectively (Fig. 5b-e and Table 3)[8,17]. The doping of fluorine significantly increased the contents of pyridinic-N and pyrrolic-N, leading to the improvement of the ORR activity. This result indicated that the fluorine atoms could break the graphitic bonds and induce structural defects, which was consistent with the result of the Raman test. In addition, Fe-N_x macrocycles could be observed in the iron-doped samples: FeN-F127C and FeNF-F127C. Previous studies indicated that the four pyridinic-N atoms in the porphyrin planar structure could form the Por-N₄ sites, and Por-N₄ could anchor and stabilize the active Fe atoms during the carbonization process to form the Fe-N₄ sites. The Fe-N₄ sites could effectively deduct electrons, causing carbon to become positively charged, which enabled it to effectively adsorb oxygen, thereby improving ORR activity. The proportion of Fe-N₄ in FeNF-F127C reached 17.80%, indicating that the sample contained a large amount of Fe-N₄ active sites. The peaks attributed to the doped F could be further deconvoluted into two peaks centered at 685.5 eV and 687.2 eV, corresponding to ionic F and semi-ionic F, respectively [47]. The doping of fluorine made the carbon have a positive charge on the carbon atoms, improving the activity of π -electrons in carbon, which in turn improved the oxygen adsorption and ORR activity of the catalyst [48]. Previous studies indicated that the ORR activity order of different types of F bonds was: ionic F> semi-ionic F> covalent F[49]. The fraction of ionic F in FeNF-F127C reached 74.87%, indicating that the sample might have a high ORR activity.



Figure 5. XPS spectra of different samples (a) and high-resolution XPS spectra of different samples: N1s XPS spectra (b-e) and F1s XPS spectra (f)

Samples	C (wt. %)	O (wt. %)	N (wt. %)	F (wt. %)	Fe (wt. %)
N-F127C	84.16	8.12	7.72	_	—
NF-F127C	84.57	7.65	6.95	0.83	_
FeN-F127C	81.64	8.22	7.82	_	2.32
FeNF-F127C	82.30	7.25	7.12	0.85	2.48

Table 2. Elemental content of different samples

Table 3. Fractions of N species present in different samples

Samples	Oxidized-N (%)	Graphitic-N (%)	Pyrrolic-N (%)	Metal-N (%)	Pyridinic-N (%)
N-F127C	19.05	49.24	11.50	_	20.21
NF-F127C	17.90	46.11	12.46	_	23.52
FeN-F127C	21.90	39.54	14.00	13.41	11.97
FeNF-F127C	20.47	22.86	16.52	17.81	22.34

The ORR activities of all the samples were first evaluated by CV measurements in O₂-saturated 0.1 M KOH solution. As shown in Fig. 6a and Table 4, the oxygen reduction peak potentials of N-F127C, NF-F127C, FeN-F127C and FeNF-F127C were 0.681, 0.684, 0.798 and 0.830 V, respectively, indicating that both iron doping and fluorine doping resulted in higher electrocatalytic activity [36]. Tri(Fe/N/F)-doped sample FeNF-F127C indicated the highest ORR activity.



Figure 6. CV curves of different samples in O₂-saturated 0.1 M KOH with a scan rate of 10 mV s⁻¹ (a); LSV curves of different samples and 20% Pt/C in O₂-saturated 0.1 M KOH with a scan rate of 10 mV s⁻¹ at a rotation speed of 1600 rpm (b)

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To further investigate the electrochemical performance of the samples, LSV measurements on the RDE were measured at the rotating speed of 1600 rpm. As depicted in Fig. 6b and Table 4, these results demonstrated that both iron doping and fluorine doping the samples led to enhanced ORR activity, and FeNF-F127C presented an improved on-set potential $E_0 = 0.956$ V (vs RHE), half-wave potential $E_{1/2} = 0.823$ V (vs RHE) and limiting-current density of 5.30 mA cm⁻². Moreover, these values were extremely close to those of the commercial Pt/C ($E_0 = 0.968$ V, $E_{1/2} = 0.825$ V and limiting-current density of 5.48 mA cm⁻²), indicating that FeNF-F127C had an excellent electrocatalytic ORR activity. These results may be due to several factors: (i) the doping of fluorine, due to its strong electronegativity, made carbon have a positive charge and improved the activity of π electrons in the carbon, thereby improving oxygen adsorption, and fluorine doping destroyed the graphite bond, resulting in a high proportion of pyridinic-N and pyrrolic-N, which promoted the production of ORR active sites [36, 48]; (ii) Fe atoms were reduced at high temperature, forming Fe₃C and Fe-N₄ ORR active sites with carbon matrix and Por-N₄ sites, respectively; (iii) after the F127 template was removed, the tri(Fe/N/F)-doped precursor formed a large specific surface area and a regular mesoporous structure [43].



Figure 7. LSV curves (a) and K-L plots (b) of FeNF-F127

 Table 4. Comparison of electrocatalytic performance of different samples and commercial 20 wt.% Pt/C catalyst.

Samples	Onset potential (V vs. RHE)	Half-wave potential (V vs. RHE)	Limiting current density (mA cm ⁻²)
N-F127	0.813	0.601	2.55
NF-F127	0.865	0.649	2.80
FeN-F127	0.918	0.773	4.91
FeNF-F127	0.956	0.823	5.30
20 wt.% Pt/C	0.968	0.825	5.48

To further clarify the ORR reaction kinetics of FeNF-F127C, LSV tests were performed on FeNF-F127C at various rotation speeds from 400 rpm to 2000 rpm in an O₂-saturated 0.1 M KOH system. As shown in Fig. 7a, the limiting current density of the catalyst gradually increased with increasing rotation speed [2, 8]. The electron transfer number (n) was calculated using the Koutecky-Levich (K-L) equations. The K–L plots were shown in Fig. 7b. The K–L plots of FeNF-F127C showed an excellent linear relationship in the potential range of 0.2 to 0.7 V (vs RHE), and the average number of n was 4.0, indicating FeNF-F127C had a complete four-electron pathway for an effective ORR [6, 50].



Figure 8. CV curves of FeNF-F127 (a) and 20% Pt/C (b) with and without 3 wt.% CH₃OH in 0.1 M KOH; Current-time (i-t) chronoamperometric response of and 20% Pt/C in O₂-saturated 0.1 M KOH at a rotating rate of 1600 rpm for 10000 s (c).

Table 5. Comparison	of electrocatalytic j	performance of d	lifferent samples	and commercial	20 wt.% Pt/C
catalyst.					

References	Catalyst	Onset potential (V vs. RHE)	Half-wave potential (V vs. RHE)
This work	FeNF-F127	0.956	0.823
[36]	Fe/N/F-MCNF	0.90	0.82
[48]	FeFNC-5	0.976	0.872
[50]	Fe@EY-NH ₃	0.9	0.81
[51]	Fe/N/S-PCNT	0.96	0.84
[52]	Fe ₇ C ₃ @FeNC	0.96	0.83
[53]	Fe-N-CC	0.94	0.83
[54]	HDCA-800	0.94	0.79
[55]	Fe-N/MCS-181	0.95	0.82
[56]	FBC-Fe	0.92	0.81
[57]	Fe ₃ C@Fe,N,S- GCM	0.980	0.779

In addition, FeNF-F127C also exhibited excellent tolerance to methanol oxidation, as shown in Figures 8a and 8b. After methanol was added, the CV curves of commercial Pt/C changed significantly, and a characteristic peak appeared which represented methanol oxidation [39]. However, methanol had almost no effect on FeNF-F127C. Thus, FeNF-F127C was a practical non-precious metal ORR catalyst in fuel cells with high durability and methanol tolerance.

Furthermore, the durability of FeNF-F127C was also investigated. As shown in Fig. 8c, the current-time (i-t) chronoamperpmetric of FeNF-F127C and commercial Pt/C was performed in O₂-saturated 0.1 M KOH under 0.62 V (vs RHE) at a rotating rate of 1600 rpm. The current density of the Fe/N-PCNs decreased by only 5.0% after 10000 s, compared with 17.6% for Pt/C catalyst. This high stability of FeNF-F127C may be due to the presence of Fe active sites surrounded by graphitized carbon [4, 58].

4. CONCLUSION

In conclusion, we demonstrated a facile approach to synthesize tri(Fe/N/F)-doped FeNF-F127C catalyst featuring mesoporous carbon via PAN/PVDF/F127 tricomponent polymers followed by thermal carbonization. Because of its large specific surface area with well-ordered mesoporous structure and high density of Fe₃C sites and Fe-N₄ sites, FeNF-F127C exhibited a remarkable ORR activity in alkaline media with high onset potential of 0.956 V (vs RHE), half-wave potential $E_{1/2}$ of 0.823 V (vs RHE), the limiting-current density of 5.30 mA cm⁻², and electron transfer number (4.0). In addition, in comparison with commercial Pt/C, FeNF-F127C exhibited excellent long-term stability (95.0%) and superior tolerance to methanol. To conclude, this work provided an effective pathway to synthesize a high-performance non-precious-metal ORR electrocatalyst for use in fuel cells.

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