Accepted Article

Title: Rational Design of N- S- Fe- Doped Nanoporous Carbon Catalysts from Covalent Triazine Framework for High Efficient ORR

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemSusChem 10.1002/cssc.201800855

Link to VoR: http://dx.doi.org/10.1002/cssc.201800855
Rational Design of N- S- Fe- Doped Nanoporous Carbon Catalysts from Covalent Triazine Framework for High Efficient ORR


Abstract: Porous organic polymers (POFs) are promising precursors for developing high performance transition metal-nitrogen-carbon (M-N/C) catalysts towards ORR. But the rational design of POFs precursors remain a great challenge, because of the elusive structural association between the sacrificial POFs and the final M-N/C catalysts. Based on covalent triazine frameworks (CTFs), we developed a series of sulfur-doped Fe-N/C catalysts by selecting six different aromatic nitriles as building blocks. A new mixed solvent of molten FeCl₃ and S was used for CTF polymerization, which benefit the formation of Fe-N₅ sites and make the subsequent pyrolysis process more convenient. Comprehensive study on these CTF-derived catalysts shows their ORR activities are not directly dependent on the theoretical N/C ratio of the building block, but closely correlated to the ratios of the nitrile group to benzene ring (N nitride/NC benzene) and geometries of the building blocks. The high ratios of the N nitride/NC benzene are crucial for ORR activity of the final catalysts due to the formation of more N-doped microporous and Fe-N₅ sites in pyrolysis possess. The optimized catalyst shows high ORR performances in acid and superior ORR activity to the Pt/C catalysts under alkaline conditions.

Introduction

Oxygen reduction reaction (ORR) is of paramount importance for a variety of renewable energy devices, such as fuel cells and metal-air batteries. Pt-based catalysts have been regarded as competitive candidates toward ORR, but the high cost, unsatisfactory durability and scarcity significantly hinder their large-scale commercialization. Alternatively, considerable attention has been paid to the metal-free or non-precious metal catalysts. [1] To date, various metal-free heteroatom-doped carbon materials have shown the competitive activity and improved durability under alkaline conditions. Their excellent activities are closely related to the doping/edge-induced electron modulation and the topological defects in carbon matrix. [2] But the ORR performance of metal-free catalysts under acidic conditions still requires further enhancement to meet the industrial demand of proton-exchange membrane fuel cell (PEMFC). On the other hand, the transition metal-nitrogen-carbon (M-N/C, M=F, Co, etc.) catalyst has emerged as another family of promising ORR catalysts that usually have higher activity than the metal-free carbon materials. [3] The enhanced ORR activities are attributed to the introduced transition metal. However, the synthesis of M-N/C catalysts involves various transition metal salts, nitrogen and carbon precursors, as well as the high-temperature pyrolysis process (700–1100 °C). Therefore, the catalysts are highly heterogeneous and have complex structures, which make the intrinsic active sites of the M-N/C catalysts under controversy. [4]

Recently, the combination of theoretical studies and experimental evidences has shed some light on it. It has been suggested that the Fe-N₅ coordination moieties are one class of highly active sites, especially in acidic electrolytes. To be specific, the ferrous low-spin Fe-N₅ site (D1) should account for, at least in part, the high activities of metal-N/C in ORR. [5, 6] By choosing suitable precursors, the D1 components may be selectively formed, and Fe-N/C catalysts with high activities in ORR can be expected. In fact, preliminary attempts have been made by employing the metal-organic frameworks (MOFs) as the precursor, because of its inherent metal-nitrogen coordination network and tunable microstructure. [6] It has been found that the ligands, cavity size and pore volume of the sacrificial MOFs had important influences on the ORR activities of the resulting M-N/C catalysts. [7] However, clarifying the formation mechanism of the Fe-N₅ as well as the rational design of the Fe-N₅ catalysts with high Fe-N₅ components and optimized structures remains a great challenge.

Similar to MOFs, porous organic polymers (POFs) are promising precursors for the preparation of high performance M-N/C catalysts. [8] Its covalent frameworks are more tolerant to harsh treatments, which may lead to a closer structural association between the POFs precursors and the carbonaceous products. [9] In addition, different from many MOFs in which the N invariably coordinate with the transition metal centers, the POFs, especially the covalent triazine framework (CTF), provide more possibilities to tune the N components and the Fe-N₅ moieties in the final M-N/C catalysts. [8, 10] Although a few CTF-based M-N/C catalysts have been reported, [11] the relationship between the CTFs precursors and the obtained ORR performance has been never reached.

To design the CTF based M-N/C catalysts with high activity, we developed a series of new sulfur-doped Fe-N/C catalysts (Fe-N/S/C) by selecting six typical aromatic nitrile building blocks with different geometries and various ratios of the nitrile group to benzene ring (N nitride/NC benzene). Non-aromatic monomers were excluded here, because our preliminary experiments revealed that aromatic rings are necessary to obtain high ORR activity in

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the Fe-N/C catalysts during heat treatment (see more discussion below). Our study on these CTF-derived catalysts shows that their ORR activities are closely correlated to the component and structure of the CTFs precursors. Importantly, the optimized sample shows high rotating disk electrode (RDE) activity comparable to the reported state-of-the-art Fe-N/C catalysts in acidic conditions and superior ORR performances to the commercial Pt/C catalysts under alkaline conditions.

Results and Discussion

FeCl₃ and S mediated synthesis of CTFs

As shown in Figure 1a, the aromatic nitriles were first polymerized to CTFs at 400 °C and then pyrolysed in Ar at 900 °C, followed by acid-leaching to remove the inorganic Fe species. Normally, molten ZnCl₂ or trifluoromethanesulfonic were used as the solvent and catalyst for the synthesis of CTFs by the cyclotrimerization of the aromatic nitriles. But they do not contribute to the formation of Fe-N/C catalysts and must be removed. To make subsequent pyrolysis process more convenient, we proposed a new mixed solvent which includes the molten FeCl₃ and sulfur. The molten FeCl₃ here not only act as strong Lewis acid to catalyze CTF polymerization, but also the Fe precursor for the final Fe-N/C catalysts. Moreover, the FeCl₃ and CTF can be uniformly mixed at the molecular level during the CTF polymerization. The decomposition of encapsulated FeCl₃ during pyrolysis will contribute to the formation of porous structures, as FeCl₃ is a good porogen that can activate carbon materials. Note that the addition of sulfur here do not hamper the CTF polymerization. According to previous studies, the addition of sulfur to the precursor mixture could relieve the disintegration of Fe-Nₓ centers and improve the ORR performance of Fe-N/C catalyst by S doping. After the pre-polymerization, the CTFs, FeCl₃ and S are already in a

Figure 1. (a) Monomers employed for catalysts synthetic and illustration of the synthetic process. Six typical aromatic nitriles with different Nitrile:Benzene were used as the building blocks for the synthesis of the Fe-N/S/C catalysts. XRD (b), Raman (c) and N2 adsorption/desorption isotherms (d) of all Fe-N/S/C catalysts; SEM and TEM of DCBP-Fe-N/S/C (e and g) and TETCB-Fe-N/S/C (f and h).
well-mixed state and can be directly pyrolysed to obtain the Fe-N/S/C catalysts. Direct carbonization of the precursor mixture only obtains low activity materials with very low yield, indicating the important role of pre-polymerization.

**Chemical structure of pristine CTFs**

To reveal the intrinsic relationship between the CTF precursors and the Fe-N/C catalysts, six typical aromatic nitriles were used as the building blocks for the cyclotrimerization (Figure 1a). These different monomers can be envisaged to tune the structure of CTFs, as different positions of the nitrile moieties and the number of benzene ring are expected to lead to different arrangements of the triazine ring in the CTF frameworks. We therefore associate the CTFs structures with the ratios of the nitrile group to benzene ring (N$_\text{hetero}$/N$_\text{benzene}$) in the building blocks. All un-pyrolyzed CTFs were purified by hydrochloric acid, acetone and tetrahydrofuran to analyze their structures. As evidenced by Fourier transform infrared spectroscopy (FTIR), the cyclotrimerization can be confirmed by the presence of triazine absorption bands at 1600‒1300 cm$^{-1}$ (Figure S1). The $^{13}$C solid-state NMR results further indicate the existence of sp$^2$ carbons from the triazine units at around 164 ppm (Figure S1). Some aliphatic C–N (−68 ppm) and C–H bonds (−24 ppm) are also detected by NMR in all samples, which should be attributed to the hydrogenation of benzenes and triazines in the presence of chlorine (decomposition of ferric chloride) and trace water. Besides, the CTFs from 1,2,4,5-tetracyanobenzene (TETCB, N$_\text{hetero}$/N$_\text{benzene}$ of 4:1) may have more complex structures than the others, because TETCB is also a precursor for the synthesis of phthalocyanine units (see more discuss in Figure S1). However, it is still a great challenge to elucidate the precise chemical structures of these CTFs.

**Relationship between CTFs and structure of catalysts**

X-ray diffraction (XRD) patterns of all the obtained Fe-N/S/C catalysts show a broad peak at 2$\theta$ = −26$^\circ$, indicating their disordered carbonaceous structures (Figure 1b). The rest of weak diffraction can be assigned to the crystalline phases of Fe$_x$S and Fe$_x$C nanoparticles, which may be encapsulated within carbon matrix and can hardly be removed by acid-leaching. Interestingly, these Fe$_x$S and Fe$_x$C peaks are weaker in the samples that were prepared by using precursors with higher N$_\text{hetero}$/N$_\text{benzene}$. These results were further supported by the Mössbauer spectra discussed later. Note that in the Raman spectra (Figure 1c), the stronger D-band intensity ($I_d$) with respect to the characteristic G-band ($I_g$) of the graphitic carbon is due to the abundant defects and edges in the Fe-N/S/C catalysts.

Morphology characterizations by SEM and TEM reveal the prominent influence of these building blocks on the macroscopic structures of the final Fe-N/S/C catalysts. As can be seen from Figure 1e and 1g, the DCBP-Fe-N/S/C sample derived from the 4,4′′-dicyanobiphenyl (DCBP, N$_\text{hetero}$/N$_\text{benzene}$ of 1:1) shows graphene-like two-dimensional structures, with abundant ripples on its surfaces. Nevertheless, bulk crystals with clear porous structures are formed preferentially, when the N$_\text{hetero}$/N$_\text{benzene}$ increases from 2:1 to 4:1 (Figure 1f, 1h and Figure S2).

In concert with the morphology changes, a sudden increase of the BET surface areas from 739 m$^2$ g$^{-1}$ to more than 2000 m$^2$ g$^{-1}$ was observed when the N$_\text{hetero}$/N$_\text{benzene}$ is over 1:1 (Figure 1c and Table S1). It means the final catalyst structures partly depend on the CTF structures. The smaller N$_\text{hetero}$/N$_\text{benzene}$ of the building block can lead to less crosslinking nodes (the triazine) and more benzene rings in the CTFs, which cause higher graphitization of the final catalyst during pyrolysis (Figure 1g). All other samples display the features of type IV isotherms with hybrid micro/mesoporous structures and high BET surface areas ranging from 2123 to 2523 m$^2$ g$^{-1}$. It should be noted that the rich micropores will benefit the formation of FeN sites, while the presence of mesopores can facilitate the mass transport process during ORR.

The elemental compositions and distributions of the samples were then analyzed by X-ray photoelectron spectroscopy (XPS) and energy dispersive spectroscopy (EDS) measurement. As expected, all these catalysts contained C, O, N, S and Fe.
elements (Figure S3 and Table S2). The deconvolution results of high-resolution N 1s, S 1s and Fe 2p XPS spectra indicate that the chemical components of each sample are nearly identical (Figure S4). Taking the TETCB-Fe/N/S/C as a representative example (Figure 2a), the N 1s spectrum can be deconvoluted into four peaks that ascribed to pyridinic nitrogen (398.4 eV), graphitic nitrogen (401 eV), oxide-N (402.3 eV), and the N coordinated to Fe (399.6 eV).\(^{[21]}\) Meanwhile, the Fe 2p\(_{3/2}\) spectrum (Figure 2b) can be deconvoluted into a dominant peak at 709.7 eV and a small peak at 711.9 eV, corresponding to the N-coordinated Fe\(^{2+}\) and Fe\(^{3+}\) species, respectively.\(^{[22]}\) Note that no signal of zero-valence Fe below 709 eV can be found in the TETCB-Fe/N/S/C, suggesting the absence of the metal Fe or Fe\(_2\)C phases. This result matches the XRD pattern above and further supported by the Mössbauer spectra later. Besides, the S 2p spectrum (Figure 2c) of the TETCB-Fe/N/S/C can be deconvoluted into the thiophene–S contained 2p\(_{3/2}\) (at 163.9 eV) and the 2p\(_{1/2}\) –C–S–C–, covalent bond (at 165.1 eV), indicating the successful doping of S element into the carbon framework.\(^{[23]}\) HAADF-STEM image and corresponding EDS mapping show that the elements of C, N, S and Fe are homogeneously distributed (Figure 2d to 2h), demonstrating the introduction of Fe-N\(_x\) moieties into the s-doped N-C frameworks.

### Relationship between CTFs and ORR activity of catalysts

To probe the relationship between the CTF precursors and the catalytic performances of the obtained catalysts in ORR, the activities of all these samples were investigated by Linear Sweep Voltammetry (LSV) in O\(_2\)-saturated 0.1 M HClO\(_4\) at 1600 rpm. All background curves measured in N\(_2\)-saturated electrolytes were subtracted to eliminate capacitive currents (Figure S5). Their onset potential (\(E_\text{on}\), measured at the current density of 0.1 mA cm\(^{-2}\)) and mass-related kinetic current density (\(J_\text{on}\)) at 0.8 V are summarized in Figure 3 and Table 1. It also can find an obvious correlation between the \(N_{\text{Nitrile}}/N_{\text{Benzone}}\) of the building blocks and the ORR activity of the final catalysts. In specific, increasing the \(N_{\text{Nitrile}}/N_{\text{Benzone}}\) in the building blocks will result in higher activities, with a positively shifted of \(E_\text{on}\) and an increase of \(J_\text{on}\). For the pDCB-Fe-C/N/S, oDCB-Fe-C/N/S and mDCB-Fe-C/N/S samples with the same \(N_{\text{Nitrile}}/N_{\text{Benzone}}\), only small differences in \(E_\text{on}\) and \(J_\text{on}\) can be observed (LSV in Figure S6).

To further identify the active species in our catalysts, the poisoning experiment was performed by adding 5 mM SCN\(^-\) ions into electrolyte (Figure 4a–c). The LSV curves reveal a dramatic negative shift of half-wave potential for TETCB-Fe/C/N/S (\(N_{\text{Nitrile}}/N_{\text{Benzone}}\) of 4:1), when compared with pDCB-Fe-C/N/S (\(N_{\text{Nitrile}}/N_{\text{Benzone}}\) of 2:1). After being poisoned, the TETCB-Fe-C/N/S and pDCB-Fe-C/N/S show nearly identical LSV results, attributed to their similar BET surface areas, morphology and component characterizations. The DCBP-Fe-C/N/S (\(N_{\text{Nitrile}}/N_{\text{Benzone}}\) of 1:1) exhibits the smallest LSV change during the poisoning experiment. These results confirm that the enhanced ORR activities are attributed to the introduced Fe-N\(_x\) species, which is consistent with the Mössbauer spectra.

The Mössbauer spectra of DCBP-Fe-N/S/C catalysts can be fitted with two dominant sextets assigned to Fe\(_{1-x}\)S and Fe\(_x\)C,\(^{[22]}\) which have been suggested to be inactive in ORR (Figure 4d). The doublets (D1), corresponding to the Fe-N\(_x\) moieties in low-spin states, are believed to be the most ORR-active in acyclic media.\(^{[5a, 5b, 26]}\) However, it only accounts for 4.9% of the resonance area, in concert with its relative low \(E_\text{on}\) and \(J_\text{on}\). While the D1 resonance area increase to 9.2% for pDCB-Fe-N/S/C (Figure 4e) and 56.4% for TETCB (Figure 4f), in line with the increasing trend of \(E_\text{on}\) and \(J_\text{on}\). Note that the ORR at low potential becomes mass-transport limited.\(^{[20a]}\) Therefore, pDCB-Fe-N/S/C and TETCB-Fe-N/S/C that have highly-developed three-dimensional porous structures show larger diffusion-limited current density (\(J_\text{on}\)) than other samples.

Interestingly, we found a substantial deviation of the N/C ratio of the final catalysts (measured by XPS and elemental analysis) from the theoretical N/C ratio of the building blocks. In addition, the amount of FeN\(_x\) sites are not directly related to the N/C ratio. For example, the DCBP-Fe-N/S/C sample has the lowest theoretical N/C ratio (14.3%) but the highest measured N/C ratio, whereas it shows the worst catalytic performances (Table 1). On the other hand, the DCP-Fe-N/S/C sample derived from the non-aromatic 2,6-dicyanopyridine (DCP) has the highest theoretical N/C ratio (43%), but its measured N/C ratio (XPS/EA = 3.68/4.88) is lowest. Importantly, it show modest ORR activities (LSV in Figure S7), with the \(E_\text{on}\) of 0.87 V and \(J_\text{on}\) of 3.12 A g\(^{-1}\).

Not that it has similar XRD, Raman characterizations and high BET surface areas of 2710 m\(^2\) g\(^{-1}\) with other samples (Figure...
S8). These results indicate that the activities of these Fe-N/S/C catalysts are not only dependent on its N/C ratio but also strongly related to the CTF structures. In our case, the Fe-Nx moieties should come from the in situ transformation of the N components in the CTF frameworks, as no other nitrogen and carbon sources are introduced. According to the literatures, the activation of carbon materials to form micropores by FeCl3 start at ~280 °C.\[13\] Thermal gravimetric analysis (TGA) reveals that the DCBP-based CTF have higher thermal stability than other samples until 400 °C (Figure S9). This may favor the formation of more carbon materials with high N-component but relatively less FeN sites during pyrolysis. On the contrary, the TETCB-based CTF with more N-containing crosslinking nodes may benefit the formation of more N-doped microporous during FeCl3 activation, thus leading to more Fe-Nx moieties.

Electrochemical measurements for optimized catalyst

It should be noted that the optimized TECB-Fe-N/S/C catalyst shows an \( E_0 \) of 0.899 V and an \( E_{1/2} \) of 0.79 V under the challenging acid condition (Figure S3), which is only 40 mV lower than that of the 20% Pt/C. This value can comparable to the recent state-of-the-art non-noble metal catalysts listed in Table S3. The Tafel slope of 56 mV/dec for TECB-Fe-N/S/C is slightly lower than 63 mV/dec for the Pt/C catalyst (Figure 5a), indicating the ORR rate-determining step may be determined by migration of adsorbed oxygen intermediates.\[16\] The \( \text{H}_2\text{O}_2 \) yield measured by rotating ring-disk electrode (RRDE) test is 0.85 %.

Figure 4. ORR polarization curves of DCBP-Fe-N/S/C (a), pDCB-Fe-N/S/C (b) and TETCB-Fe-N/S/C (c) before and after addition of 5 mM KSCN in 0.1 M HClO4. Rotating speed: 1600 rpm; scan rate: 5 mV s\(^{-1}\).\[15\]Fe Mössbauer spectra for DCBP-Fe-C/N/S (d), pDCB-Fe-C/N/S (e) and TETCB-Fe-N/S/C (f).

Figure 5. (a) Tafel points of TECB-Fe-N/S/C and Pt-C in 0.1 M HClO4; (b) \( \text{H}_2\text{O}_2 \) yield and electron-transfer number of TECB-Fe-N/S/C; (c) LSV results of TECB-Fe-N/S/C before and after 10 000 potential cycles in 0.1 M HClO4; (d) Methanol-tolerance of TECB-Fe-N/S/C tested by chronoamperometric measurement.
to 1.1% over the potential range from 0.2 to 0.8 V (Figure 5b), which is also comparable to that of 20% Pt-C catalyst (0.26% to 1.6%). The corresponding electron transfer number (n) of ∼3.98 is consistent with the results from K-L equation (Figure S10), indicating a dominant four electron pathway. Besides, an accelerated durability test (ADT) at scan speed of 50 mV s⁻¹ between 0.6 and 1.0 V was carried out to evaluate its stability. The TEBCB-Fe-N/S/C catalyst exhibits an good stability with a less 20 mV E₁₀₂ loss even after 10000 potential cycles of the accelerated durability test (Figure 5c). Resistance to methanol test revealed that the TEBCB-Fe-N/S/C exhibited only 8% of the relative current attenuation after 5000 seconds of test, which is much lower than that of 20% Pt-C (Figure 5d). To evaluate the potential applications of the TEBCB-Fe-N/S/C catalyst in proton-exchange membrane fuel cell (PEMFC), the cathode was prepared and systematically examined in a PEMFC system (Figure S11). In agreement with the RDE test results above, the fuel cell polarization plots show a high open-circuit voltage (OCV) of 0.93 V, and the current density can reach 50 mA cm⁻² at the kinetic region of 0.8 V. The maximum power density are 278 mW cm⁻² at cell voltage of 0.430 V and current density of 650 mA cm⁻².

Under alkaline condition, the TEBCB-Fe-N/S/C catalyst shows superior RDE activity to the commercial Pt-C (20% Pt) catalysts, with an E₂ of 1.018 V (32 mV higher than that of Pt-C). In addition, the half-wave potential (E₁₂) of 0.908 V is 48 mV higher than that of Pt-C (Figure 6a). To the best of our knowledge, the TEBCB-Fe-N/S/C here shows the top ORR performance among the non-precious metal ORR catalysts under alkaline condition (Table S3). As can be seen from Figure 6b-d, the TEBCB-Fe-N/S/C also shows ideal n value (3.97–3.98), excellent stability (15 mV E₁₀₂ loss after 10000 potential cycles) and high methanol-tolerance.

Conclusions

In this work, we synthesized a series of CTF-derived Fe-N/S/C catalysts based on six typical aromatic nitriles to study the relationship between the CTF precursors, the derived catalyst structure and its ORR activities. A mixed solvent of molten FeCl₃ and element S was used for CTF polymerization, which which benefit the formation of Fe-N₃ sites and S doping during subsequent pyrolysis possess. The results indicate the high N₃/S/C before and after 10 000 potential cycles in 0.1 M KOH, and th exchange membrane fuel cell (PEMFC), the cathode was carried out on a CHI760E electrochemical measurements were carried out on a CHI760E electrochemical workstation using a typical three-electrode system. A glassy carbon rotating disk electrode (RDE) or a rotating ring-disc electrode (RRDE, Pine Research Instrumentation) coated with catalysts was used as the working electrode, a graphite rod electrode as the counter electrode and an Ag/AgCl electrode (in 3.5 M KCl solution) as the reference electrode. For the ink preparation, 5 mg catalyst was dispersed in 0.5 mL of a mixture of Nafion (5 wt%, 20 μL), isopropyl alcohol (290 μL) and distilled water (190 μL). The catalyst loading is controlled at 764 µg cm⁻². All potentials reported in this work have been converted to the RHE scale. The kinetic current density (Jk) was calculated by: Jk = Jk,J(Jk-J), Where Jk is the kinetic current density (mA

Experimental Section

Synthesis of CTF-based catalysts

We synthesized the Fe-N/S/C catalysts based on six typical aromatic nitriles: 4,4’-dicyanobiphenyl (DCBP), 1,4-Dicyanobenzene (pDCB), 1,3-dicyanobenzene (mDCB), 1,2,4,5-tetracyanobenzene (TCB) and 1,2,4,5-tetracyanobenzene (TETCB). In a typical experiment, the aromatic nitriles, the FeCl₃ and the sulfur (molar ratio of 3:15:30) were transferred into a glass ampule (3 × 15 cm) under Ar atmosphere in glove box. The ampule was evacuated, sealed, and heated to 400 °C for 40 h (3 °C min⁻¹ ramping). The ampule was then cooled down to room temperature and opened. The products were subsequently grounded into fine powders and subjected to a first heat treatment in Ar at 900 °C for 2 h (3 °C min⁻¹ ramping) and then leached in 0.1 M HCl at 60 °C for 8 h. Afterward, the samples were washed with deionized water, dried and subjected to a second heat treatment in Ar at 900 °C for 1 h (5 °C min⁻¹ ramping) to obtain final Fe-N/S/C catalysts.

Characterization

Samples were characterized by X-ray diffraction (Bruker D8 FOCUS, Cu-Kα radiation). Raman spectroscopy (NT-MDT with 633 nm laser excitation), ¹³C solid-state nuclear magnetic resonance spectra (BRUKER AvanceII HD 500MHz), TGA-DSC analyser (Mettler, Switzerland), X-ray photoelectron spectroscopy (Thermo Scientific, ESCALAB 250 XI), N₂ adsorption/desorption measurements (BjBulder SSA-7000), scanning electron microscope (Hitachi, S-4800), transmission electron microscopic and energy dispersive spectroscopy (JEOL, JEM-2100F).

Electrochemical measurements

The electrochemical measurements were carried out on a CHI760E electrochemical workstation using a typical three-electrode system. A glassy carbon rotating disk electrode (RDE) or a rotating ring-disc electrode (RRDE, Pine Research Instrumentation) coated with catalysts was used as the working electrode, a graphite rod electrode as the counter electrode and an Ag/AgCl electrode (in 3.5 M KCl solution) as the reference electrode. For the ink preparation, 5 mg catalyst was dispersed in 0.5 mL of a mixture of Nafion (5 wt%, 20 μL), isopropyl alcohol (290 μL) and distilled water (190 μL). The catalyst loading is controlled at 764 µg cm⁻². All potentials reported in this work have been converted to the RHE scale. The kinetic current density (Jk) was calculated by: Jk = Jk,J(Jk-J), Where Jk is the kinetic current density (mA

Figure 6. (a) ORR polarization curves of different catalysts in O₂-saturated 0.1 M KOH solution. Rotating speed: 1600 rpm; scan rate: 5 mV s⁻¹. (b) H₂Ox yield and electron-transfer number of TECB-Fe-N/S/C; (c) LSV results of TECB-Fe-N/S/C before and after 10 000 potential cycles in 0.1 M KOH; (d) Methanol-tolerance of TECB-Fe-N/S/C tested by chronoamperometric measurement.
MEAs preparation and PEM fuel cell tests

The cathode ink was made by ultrasonically mixing Fe-N/S/C catalyst, Nafion ionomer solution (5 wt%) and isopropanol/water (volume ratio of 2:1) for 1 h. The ratio mass of catalyst to Nafion is 7:3. The anode ink dispersed inks were separately made by Nafion ionomer solution (5 wt%) and isopropanol/water (volume ratio of 2:1) for 1 h. The mass ratio of catalyst to Nafion is 7:3. The anode ink was made by 60% Pt-C with the same catalyst to Nafion ratio. The well-dispersed inks were separately sprayed on the two sides of a Nafion 212 membrane (2 cm²), followed by drying in vacuum at 60 °C for 2 h. The cathode and anode loading were controlled at ~2 mg cm⁻² and ~0.4 mg cm⁻² respectively. Two pieces of carbon paper were hot-pressed onto the opposite sides of the catalyst-loaded membrane at 130 °C for 2 min under a pressure of 500 psi to obtain the final MEA. The fuel cell performance was tested by a Fuel cell test station (Green Light Company) with H₂ and O₂ at 70 °C. The polarization curves were recorded at back pressures of 1 bar and gas flow rates for H₂ and O₂ of 200 sccm and 400 sccm, respectively.

Acknowledgements

This study is supported by the National Natural Science Funds (No. 21676198) and the Program of Introducing Talents of Discipline to Universities (No. B06006).

Keywords: porous organic polymers, rational design, electrocatalysts, iron-nitrogen-carbon, oxygen reduction reaction


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