High Performance Fe- and N- Doped Carbon Catalyst with Graphene Structure for Oxygen Reduction

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Proton exchange membrane fuel cells are promising candidates for a clean and efficient energy conversion in the future, the development of carbon based inexpensive non-precious metal ORR catalyst has becoming one of the most attractive topics in fuel cell field. Herein we report a Fe- and N- doped carbon catalyst Fe-PANI/C-Mela with graphene structure and the surface area up to 702 m² g⁻¹. In 0.1 M HClO₄ electrolyte, the ORR onset potential for the catalyst is high up to 0.98 V, and the half-wave potential is only 60 mV less than that of the Pt/C catalyst (Loadings: 51 µg Pt cm⁻²). The catalyst shows high stability after 10,000 cyclic voltammetry cycles. A membrane electrode assembly made with the catalyst as a cathode is tested in a H₂-air single cell, the maximum power density reached ~0.33 W cm⁻² at 0.47 V.

The oxygen reduction reaction (ORR) on the cathode is an important process in proton exchange membrane fuel cells (PEMFCs). Because the cathodic activation and reduction of oxygen are much more difficult than the anodic activation and oxidation of hydrogen, relatively, large amounts of platinum catalyst must be used on the cathode to accelerate the ORR. Due to platinum’s rarity and high cost, Pt catalyst loading is one of the most important factors hindering the commercialization of PEMFCs. Considerable attention has therefore been paid to overcome this problem by developing low-platinum and platinum-free catalysts for PEMFC cathodes1–11. Nitrogen-doped carbon has been recognized as a promising type of cathode catalyst for PEMFCs since Gong et al.12 reported the high ORR activity of nitrogen-doped carbon nanotubes in 2009. Currently, investigating doped carbon catalysts for ORR application is becoming one of the hottest topics in the fuel cell field. Many types of nitrogen-doped carbon materials, such as nitrogen-doped carbon nanotubes5,12, nitrogen-doped graphene13–15, and various metal-N₄ complexes16,17, have been investigated for their ORR activity. The Dai group12,18 found that some metal-free doped carbon nanomaterials even showed ORR activity almost comparable to platinum catalysts’ in an alkaline medium. However, there is still a long way to go before such materials have the activity and stability to make them viable replacements for platinum catalysts in practical applications, especially in acidic media.

To improve the performance of doped carbon catalysts, some researchers have investigated the addition of metal species, and significantly enhanced performance has been achieved. Recently, Wu et al.19 reported a high-performance doped carbon catalyst prepared from a polyaniline-supported microporous carbon template incorporating iron or cobalt. The catalyst showed high ORR activity (the ORR onset potential was ca. 0.93 V vs. RHE) and excellent stability for 700 h of long-term testing.

The Dodelet group reported Fe/Phen/BP catalyst19 and Fe/Phen/Z8 catalyst17, prepared by milling a mixture of carbon black BP (Black Pearl, Cabot) or the metal-organic framework material Z8, phenanthroline, and ferrous acetate, followed by pyrolyzing the mixture twice, first in argon, then in ammonia. The catalysts showed excellent performance at the cathode of PEMFCs, the best being the Fe/Phen/Z8 catalyst, with a volumetric activity of 230 A cm⁻³ at 0.8 V (IR-free). They believed that the high activity may have resulted from the high density of active sites on the catalyst, possibly caused by the high micropore surface area of the support and the fact that many of the iron cations were coordinated by pyridinic nitrogen functionalities in the interstices of the graphitic sheets within the micropores. Choi et al.20 prepared two types of FeCo/EDA-carbon catalysts, using Ketjen Black 600 (ca. 1416 m² g⁻¹) and Ketjen Black 300 (ca. 823 m² g⁻¹) as the respective carbon supports. They found that
the higher surface area may result in high active site density, and thus
in high activity. This suggestion was also supported by the work of
Liang et al.\textsuperscript{120} and Wang et al.\textsuperscript{113}.

In the present study, a high-performance doped carbon electro-
catalyst was prepared by pyrolyzing a hybrid precursor in an Ar
atmosphere. The precursor was made by impregnating melamine
with a solution of FeCl\textsubscript{3} and aniline, followed by polymerizing
the aniline and covering the melamine with it. Interestingly, the prepared
catalyst possesses a graphene structure and demonstrates a high
surface area (up to ca. 702 m\textsuperscript{2} g\textsuperscript{−1}), as well as high pyridinic-N and
graphitic-N content, high activity in an acidic medium, and high
stability.

Results
Structure characterizations. Figure 1 shows TEM images of C-
PANI, PANI/C-Mela, and Fe-PANI/C-Mela. It is clear that the C-
PANI (Figure 1a) prepared from pure polyaniline had a good
graphite-like layer structure with BET surface area ca. 392 m\textsuperscript{2} g\textsuperscript{−1}.
However, once melamine was added to the precursor, the resulting
PANI/C-Mela (Figure 1b) showed a slightly altered mixed structure,
has some different from C-PANI; its ordering seems lower than that
of C-PANI and the BET surface area of PANI/C-Mela is ca. 521 m\textsuperscript{2}
g\textsuperscript{−1}, implying that mixing melamine with the precursor affected the
structure of the final samples. It is very important that further doping
of the PANI/C-Mela system with Fe resulted in the formation of thin,
transparent graphene-like nanosheets, as shown in Figure 1 (c, d, e,
and f). The surface area of the catalyst reached 702 m\textsuperscript{2} g\textsuperscript{−1}, which is
higher than that of the graphene-based carbon nitride catalyst
reported by Yang et al.\textsuperscript{121} (542 m\textsuperscript{2} g\textsuperscript{−1}), and almost the same as that
of graphene nanosheets prepared under ultralow exfoliation
temperature (750 m\textsuperscript{2} g\textsuperscript{−1})\textsuperscript{22}. Actually, this result of high surface
area further confirms the catalyst’s graphene structure. It seems
that the Fe acted as the catalyst for the formation of graphene. It is
interesting that we hardly observe the particles of iron or iron
compound in TEM images of the Fe-PANI/C-Mela sample,
although the results of XRD and XPS revealed its existence, we
believe most iron has been removed in the process of acid leaching.

Figure 2a compares the Raman spectra of C-PANI, PANI/C-Mela,
and Fe-PANI/C-Mela. The ratios of the D band to G band integrated
intensity (I\textsubscript{D}/I\textsubscript{G}) for the three samples are 2.35, 2.39, and 1.22,
respectively. Figure 2b shows the FTIR spectra of C-PANI, PANI/
C-Mela, and Fe-PANI/C-Mela. According to the literature, the bands
at ~1243.2, ~1225.2, and ~1215.0 cm\textsuperscript{−1}, as well as the bands at
~1589.3, ~1569.9, and ~1575.7 cm\textsuperscript{−1}, can be assigned to the coordi-
nation-bonded, pyridine-type C-N bond\textsuperscript{23} and to the stretching of
the C-N bonds\textsuperscript{24}. Clearly the bands of PANI/C-Mela and Fe-PANI/
C-Mela are much stronger than those of C-PANI, implying that the
catalysts containing melamine include more certain C-N bonds.
As shown in Figure 3, the XPS results reveal the chemical state of doped N and Fe elements in Fe-PANI/C-Mela catalyst. The N1s spectrum (Figure 3a) can be deconvoluted into five peaks at 398.2, 399.1, 400.8, and 401.9 eV, which can be assigned to pyridinic N\textsuperscript{25}, N-Fe compounds\textsuperscript{16}, benzenoid amine (–NH–)\textsuperscript{26}, graphitic N\textsuperscript{17,19,25,27}, and oxidized nitrogen compounds\textsuperscript{28}, with compositions of 24.2, 10.7, 5.9, 41.9, and 17.3 at%, respectively. Our catalyst clearly has high graphitic N content (41.9 at% in total doped nitrogen) and high pyridinic N content (24.2 at%).

Figure 3b shows the Fe 2p spectrum, it can also be deconvoluted into five peaks at 710.7, 713.6, 718.7, 722.9, and 725.2 eV. The photoelectron peaks at 725.2 eV is correspond to the binding energies of 2p 1/2 of Fe(II) and Fe(III) ion\textsuperscript{29}, the peak at 722.9 eV can be assigned to the binding energies of 2p 1/2 of Fe(II) ion\textsuperscript{30}. The peak at 718.7 eV is a satellite peak for the above four peaks. Indicating the co-existing of Fe(II) and Fe(III) in the catalyst.

The XRD patterns shown in Figure 4 display the structures of the catalyst prepared at various conditions. Figure 4a shows the XRD patterns of Fe-PANI/C-Mela catalyst prepared at various pyrolysis temperatures. With the increase of pyrolysis temperature, the peaks of carbon at 2\(\theta\) of 21.7 and 26.3 varied obviously (short dash in Figure 4a). The intensity of the peaks at 2\(\theta\) of 26.3 gets strong with the increase of pyrolysis temperatures, indicating the changing of the structure of the carbon in catalyst. It should be point out that when the pyrolysis temperature is getting higher than 800 °C, the six characteristic diffraction peaks ((220), (311), (400), (422), (511), and (440)) of Fe\textsubscript{3}O\textsubscript{4} are emerged, and get strong with the increase of pyrolysis temperatures, implying the formation of Fe\textsubscript{3}O\textsubscript{4}. However, once the pyrolysis temperature is increased to 850 °C, five peaks at 29.8, 33.7, 43.4, 50.7 and 74.7 °C of 2\(\theta\) become clear, the peaks at 29.8, 33.7, and 43.4 °C can be assigned to the (100), (101) and (102) planes of FeS respectively; and the peaks at 43.4, 50.7 and 74.7 °C can be assigned to the (111), (200) and (220) planes of austenite (CFe\textsubscript{15.1}), indicating the co-existence of Fe\textsubscript{3}O\textsubscript{4}, FeS and austenite in the sample prepared over 850 °C. Actually, the strongest peak at 43.4 °C of 2\(\theta\), appeared in the patterns of samples prepared by pyrolyzing at 800, 850, and 900 °C, is a piled-up peak of FeS (102), Fe\textsubscript{3}O\textsubscript{4} (400) and CFe\textsubscript{15.1} (111). It is interesting that CFe\textsubscript{15.1} (200) peak at 20 of 50.7 °C gets strong at 900 °C, and is disappeared at 950 °C, whilst the piled-up peak at 43.4 °C gets weak significantly, indicating that there are no CFe\textsubscript{15.1} existed in the samples prepared over 950 °C. As we will discuss later, the sample prepared at 900 °C shows best activity, it means that maybe FeS and austenite CFe\textsubscript{15.1}, but not Fe\textsubscript{3}O\textsubscript{4}, promotes the performance of the Fe-PANI/C-Mela catalyst.

Figure 4b compared the XRD patterns of several samples pyrolyzed from various precursors, it is interesting that the sample C-Mela shows a strong and narrow diffraction peak at 2\(\theta\) of 27.6 °C, which may be assigned to the carbon materials derived from melamine, indicating its high ordered structure. And we should point out that the shift of C (002) peaks, it shifts from 25.6 of C-PANI to 24.9 of PANI/C-Mela, PANI/C-Mela, C-PANI and C-Mela prepared at pyrolysis temperature of 900 °C.
brings more nitrogen atoms in the catalyst, and the further doping of Fe.

Activity and stability towards ORR. From Figure 5a we can see that the C-Mela prepared by pyrolyzation from pure melamine shows no ORR activity and the C-PANI shows only poor activity toward the ORR. However, the addition of melamine and iron to C-PANI is greatly enhances the ORR activity. The Fe-PANI/C-Mela catalyst exhibits unexpectedly high ORR activity, with an onset potential up to 0.98 V (vs. RHE), while its half-wave potential is only 60 mV less than that of JM 40 wt.% Pt/C (51 μg Pt cm⁻²), and its limited diffusion current is comparable to that of JM Pt/C. To our knowledge, the catalyst is among the best ones of reported doped carbon catalysts for ORR in an acidic medium so far. We found that the ratio of melamine to aniline in the precursors affects the catalytic activity, the optimal ratio being 1 : 2 by weight and the optimal Fe content being ca. 5 wt.% (see Figure S1, S2 in additional information).

Figure 5b shows the effect of pyrolysis temperature on the ORR activity of Fe-PANI/C-Mela catalyst. It is clearly that the optimal temperature is 900 °C for our catalyst system, as higher or lower will yield inferior activity.

It is important that the Fe-PANI/C-Mela catalyst shows high stability. As shown in Figure 5c, its performance loss calculated from linear regression is in the range of 1.5 to 27.4% after 10,000 cycles of rotating disk electrode (RDE) testing, at 0.75 V it is ca. 27.4%, and at 0.85 V it is ca. 26.5%. Furthermore, it is found that the lower the potential is, the lower the performance loss is. There are only ca. 14% and 1.5% performance loss at 0.65 and 0.55 V, respectively.

Single cell performance. Figure 6 shows the single-cell test results when Fe-PANI/C-Mela catalyst was used as the cathode catalyst of the membrane electrode assembly (MEAs). The open cell voltage (OCV) was ~0.96 V and the maximum power density was ~0.33 W cm⁻² at 0.47 V in an H₂-air fuel cell, and it is reached the half that of the Pt/C single-cell. The current density reached ~400, ~640 and ~800 mA cm⁻² at 0.6, 0.5 and 0.4 V, respectively. This is among the best ones of reported doped carbon catalysts for single PEMFC application in an H₂-air fuel cell. It should be point out that the stability of Fe-PANI/C-Mela catalyst is still a serious problem, as shown in Figure 6(b), after a long term test of 100 hours, the performance of the single cell is degraded rapidly. The current density decreased to ~50, ~120 and ~230 mA cm⁻² at 0.6, 0.5 and 0.4 V, respectively.

Mechanism. The ORR is a multi-electron charge transfer reaction with two main possible paths: one is one step direct pathway, involving four electrons transfer to produce H₂O directly; another one is two steps indirect pathway, involving two electrons transfer to produce H₂O₂ in the first step and then the H₂O₂ get another two electrons to transform into H₂O. Generally, the two electron process is less efficient than the four electron process, and the H₂O₂ can make materials loss some ORR activity. Therefore, for the oxygen reduction at the cathode of PEM fuel cell, the catalyst, on which the oxygen can be reduced in one step four electron pathway, is the priority in the fuel cell field.

Figure 7a shows the ORR curves of Fe-PANI/C-Mela catalyst at different rotation rates from 800 to 3600 rpm. Then four current density values corresponding to the potential of 0.55, 0.60, 0.65 and 0.70 V on every ORR curve were taken. According to the Koutecky-Levich equation as below,

\[ \frac{1}{J} = \frac{1}{J_{\text{kin}}} + \frac{1}{J_{\text{diff}}} = \frac{1}{J_{\text{kin}}} + \frac{1}{B \sqrt{\omega}} \]  

\[ B = 0.62 nF_D D^{1/2} \nu^{1/6} \]  

Plot with \( J \) versus \( \omega^{-1/2} \) at each potential, we can obtain four \( J^{-1} - \omega^{-1/2} \) lines derived from these potentials points (Figure 7b). In equation (1), the current density (J) consists of a kinetic part (J_kin) and a diffusion part (J_diff), \( \omega \) is the angular velocity of the disk (\( \omega = 2\pi n \), N is the linear rotation rate), and B is a constant, its relation with electron transfer number n. Where n is the number of electrons.
transferred during the ORR, F is the Faraday constant (F = 96485 C mol⁻¹), D is the diffusion coefficient of O₂ in the 0.1 M HClO₄ electrolyte (D = 1.93 × 10⁻⁵ cm² s⁻¹), C is the bulk concentration of O₂ (C = 1.26 × 10⁻³ mol L⁻¹), n is the kinetic viscosity of the electrolyte (n = 1.009 × 10⁻² cm² s⁻¹)³⁴.

According to the Koutecky–Levich equation, the slope of the Koutecky-Levich plots is the reverse of B. Thus, combining the equation (2), we calculated the electron transfer number n from the slope of each line, being 4.08, 4.04, 4.06 and 4.37, at 0.55, 0.60, 0.65 and 0.70 V, respectively, the average value is 4.14, demonstrating that the oxygen reduction on Fe-PANI/C-Mela catalyst followed the four-electrons transfer pathway.

Discussion

According to the TEM Figure 1 (c, d, e, and f), the catalyst Fe-PANI/C-Mela shows a thin, transparent graphene-like nanosheets. In addition, the Raman (Figure 2a) shows that the ratios of the D band to G band integrated intensity (I_D/I_G) from 2.35 and 2.39 of C-PANI and PANI/C-Mela, to 1.22 of Fe-PANI/C-Mela, indicates that the Fe-PANI/C-Mela has fewer sp³ carbon defects and more sp² carbon, also clearly revealing the catalyst's graphene structure characteristics³⁵. Furthermore, the XPS spectra (Figure 3), FTIR spectra (Figure 2b) and XRD spectra (Figure 4) reveal the doped of N and Fe in the Fe-PANI/C-Mela catalyst. It means that we prepared a doped graphene structured material with a facile method. Why the graphene structured material can be derived from melamine and polyaniline precursors with existence of Fe? We speculate that it may be related with the planar molecular structure of melamine and linear molecular structure of polyaniline, and the Fe may be played as the catalyst for the formation of graphene structure.

Bezerra et al.³⁶ have already presented a good review of the effects of pyrolysis temperature, actually, the optimal pyrolysis temperature depends on the adapted precursors. The temperature may affect both the formation and the density of active sites on the carbon materials.

We found that the pyrolysis temperature affected the structure of doped carbon and the existing status of iron significantly, as shown in Figure 4 and mentioned above, three types of iron, Fe₃O₄, CFe₁₅.₁ and FeS are co-existed in the catalyst, and their ratio varied with the changing of pyrolysis temperature. At the optimal pyrolysis temperature of 900 °C, the ratio of austenite CFe₁₅.₁ and FeS reached highest. implying that it may be the FeS and CFe₁₅.₁ but not the Fe₃O₄, play an important role in the formation of active sites, or join in the formation of active sites.

It should point out that XPS spectra just confirm the existence of Fe(II) and Fe(III), but not zerovalent iron, it may be caused by two reasons, one is that the zerivalent iron (CFe₁₅.₁) may be dispersed in the interior of the Fe-PANI/C-Mela nanoparticle, another is that its content may be lower than the detect limitation of XPS. It is found that the sample without of iron addition in the precursor presented very poor performance (See Figure S2). Thus, we can conclude that the iron plays an important role for improving the performance of our Fe-PANI/C-Mela catalyst.

As shown in Figure 5a, the addition of melamine and iron to C-PANI is greatly enhances the ORR activity. The Fe-PANI/C-Mela...
The hybrid precursor was pyrolyzed from 700–1000°C, stirred for 24 hours below 10°C, stirred in ice bath for 30 minutes. Afterwards, oxidant ammonium peroxydisulfate (APS) and aniline) were first dispersed in 0.75 M HCl solution (120 mL) and the mixture was thoroughly washed with de-ionized water. Finally, the catalyst was obtained by pyrolyzing the leached sample in an argon atmosphere for 3.0 hours at the same temperature; we denote the catalyst as Fe-PANI/C-Mela. (when the ratio of aniline: melamine was 1:2 by weight, denote Fe-PANI/C-Mela-1/2).

For comparison, we prepared a series of doped catalysts with almost same procedures. In a typical approach, melamine (2.0 g, AR, 99.5%), aniline (4.0 mL, AR, 99.5%), and FeCl₃·6H₂O, prepared without addition of melamine and FeCl₃ and prepared by thorough washing with de-ionized water. Finally, the catalyst was obtained by pyrolyzing the leached sample in an argon atmosphere for 3.0 hours at the same temperature; we denote the catalyst as Fe-PANI/C-Mela. (when the ratio of aniline: melamine was 1:2 by weight, denote Fe-PANI/C-Mela-1/2).

Catalysts characterization. TEM images were recorded on a JEM-2100HR microscope (JEOL, Japan) operated at 200 kV. XRD was conducted on a TD-3500 powder diffractometer (Tongda, China) operated at 40 kV and 30 mA, using Cu-Kα radiation sources. Raman measurement was performed on a LabRAM Aramis Raman spectrometer (HvY, France) with a laser wavelength of 532 nm. Fourier transform infrared spectroscopy (FTIR) was recorded with a Tensor 27 (Bruke, Germany). X-ray photoelectron spectroscopy (XPS) was performed on an Axis Ultra DLD X-ray photoelectron spectrometer (Kratos, England) employing a monochromated Al-Kα X-ray source (hv = 1486.6 eV). Specific surface areas were measured by Brunauer-Emmett-Teller (BET) nitrogen adsorption-desorption on a Tristar 2020 (Micromeritics, USA) gas adsorption analyzer.
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