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# A high-performance electrocatalytic air cathode derived from aniline and iron for microbial fuel cells

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## Abstract

In this study, a high-performance electrocatalyst derived from aniline and iron is synthesized. The catalyst is prepared by pyrolyzing iron-impregnated Polyaniline in $NH_3$ atmosphere under high temperature. Pyrolyzing in $NH_3$ significantly increases the micropores, the pyridinic nitrogen on the surface of the catalyst, leading to the excellent performance for oxygen reduction. The electrocatalytic activity of this catalyst toward oxygen reduction reaction is evaluated by a rotating ring disk electrode (RRDE). This catalyst exhibits a high onset potential of about 0.92 V (vs. RHE) and the half-wave potential difference between this catalyst and the benchmark Pt/C is only about 70 mV. RRDE study also demonstrates that it is a very high selectivity catalyst for the four-electron reduction of oxygen. Applied as air cathodes in microbial fuel cells, the catalyst exhibits an excellent catalytic activity. The MFC with this catalyst achieves a maximum power density of 12.56 W/m$^3$, higher than the 9.92 W/m$^3$ of the MFC with Pt/C catalyst and the 1.34 W/m$^3$ of the MFC with bare graphite felt. These results demonstrate that this catalyst is an excellent alternative to the prohibitive Pt/C for practical applications.

**Keywords:** Microbial fuel cells; Air cathode; Power density; Catalyst; Aniline

## Introduction

A microbial fuel cell (MFC) is a bioelectrochemical system that converts chemical energy in organic matters into electrical energy by catalysis of microorganisms.[1-3] As a novel biotechnology for wastewater treatment and renewable energy production at the same time, MFC has drawn much attention in the past decade.[4-6] Great progress has been made in MFC and this technology has great potential for wastewater treatment. However, the prohibitive cost of the cathode is a pressing issue that needs to be solved. Currently, platinum cathode is the most popular catalyst used to efficiently drive oxygen reduction reaction in MFCs; however, it is estimated that this costly cathode consists up to 47% of the overall cost of an MFC system, which hinders its practical applications significantly.[7] As a consequence, there is an urgent need to explore alternatives to bring down the cost.

The development of non-precious catalyst with high catalytic activity toward oxygen reduction has recently attracted much attention not only in MFCs, but also in fuel cells.[8-11] Among these reported alternatives, carbon-nitrogen-metal catalysts synthesized by pyrolyzing precursors comprising carbon, nitrogen and transition metal (Fe, Co, Ni) are considered as the most promising candidates, because these non-precious catalysts possess excellent catalytic activity and remarkable stability for oxygen reduction reaction.[8-9, 12]

In this study, a non-precious carbon-nitrogen-metal catalyst (P-Fe) was prepared by pyrolyzing iron incorporated polyaniline in $NH_3$ atmosphere. This catalyst was comprehensively investigated by field emission scanning electron microscope (FESEM), $N_2$ physisorption, energy dispersive spectrometry (EDS), X-ray photoelectron spectroscopy (XPS) and linear sweep voltammetry (LSV).Then it is applied as an air cathode for MFCs. All the results demonstrated that this non-precious composite with high catalytic activity for oxygen reduction was an excellent alternative to the prohibitive Pt/C for practical applications in MFCs.

## Experimental

### Catalyst synthesis

The carbon-nitrogen-metal catalyst, P-Fe, was synthesized by pyrolyzing iron incorporated polyaniline in $NH_3$ atmosphere. Specifically, 3 ml of distilled aniline and 0.1 g of $Fe_2SO_4$ were dispersed in 200 ml of 0.5 M $H_2SO_4$ solution. The suspension is kept below $5^oC$ and ammonium persulfate as oxidant was slowly dripped into the suspension to initiate the polymerization of aniline. After 6 h of polymerization, the sample containing polyaniline and iron was filtered out, pre-leached by 0.5 M $H_2SO_4$ solution for 6 h, washed by deionized (DI) water thoroughly to remove unstable species, and dried in vacuum. Finally, the catalyst was pyrolyzed in $NH_3$ atomosphere at $900^oC$ for 30 min.

### Electrode preparation

Graphite felt and glassy carbon of a rotating ring disk electrode (RRDE, disk diameter 5.61 mm, Pt ring) were used in this study. Graphite felt was used as anodes and cathodes in MFCs while RRDE was used to study the electrocatalytic activity of catalysts toward oxygen reduction in LSV. Graphite felt was pretreated by immersing successively in 1 M NaOH for 12 h and then 1 M $H_2SO_4$ for 12 h, followed by rinsing with DI water. RRDE electrode was pretreated successively in 1.0-, 0.3- and 0.05-mm aluminas slurries for 3 min at each grade, thoroughly rinsed with DI water and sonicated in Milli-Q water for 5 min.[13]

Cathodes used for MFCs were prepared by coating P-Fe or Pt/C catalysts onto the graphite felt surface using 5% Nafion solutions as the binder.[14] In brief, catalysts were firstly mixed and dispersed well in the Nafion and ethanol solution by ultrasonication. Then, the dispersion was coated onto the graphite felt followed by drying at room temperature. RRDE electrodes were also coated by P-Fe or Pt/C catalysts using the same method to characterize the electrocatalytic activity of the catalysts toward oxygen reduction. All the P-Fe coated electrodes had a loading of 1 mg/cm$^2$ and the Pt/C coated electrodes had a loading of 0.5 mg Pt/cm$^2$.

### MFC setup and operation

Single chambered air cathode MFCs with a total volume of about 100 ml were constructed as previously described.[15] Graphite felt with a diameter of 4 cm was used as anode and graphite felt with a diameter of 7 cm coated by P-Fe or Pt/C was used as cathode. Titanium wire was used to connect the anode and cathode. MFCs were inoculated using a mixed bacterial culture from another MFC in the laboratory, which was originally started up with primary clarifier overflow from the Gaobeidian Wastewater Treatment Plant in Beijing and had been running for over two years.[16] MFCs were fed a medium containing 10 mM Sodium acetate, 50 mM phosphate buffer solution ($Na_2HPO_4$, 4.09 g/l and $NaH_2PO_4$ $H_2O$, 2.93 g/l), $NH_4Cl$ (0.31 g/l), KCl (0.13 g/l), metal salt (12.5 ml/l) and vitamin (5 ml/l) solutions.[17] The feeding solution had been sparged with high purity nitrogen gas for 30 min to remove the oxygen that is harmful for the electrochemically active bacteria in MFCs. MFCs were operated in a temperature-controlled room at 30 ℃ in a fed batch mode and the feeding solutions were refreshed when the voltage dropped below 40 mV. MFCs were considered to be stable when the maximum voltage output was reproducible. All the experiments were carried out in duplicate and the average values with standard deviation were obtained.

### Analyses and calculations

The morphology of the catalyst was examined by a field emission scanning electron microscopy (FESEM) (JSM-6701F, JEOL). The chemical elements on the catalyst surface were analyzed by the X-ray photoelectron spectroscopy (XPS) (ESCALab, 220i-XL) and the energy dispersive spectrometry (EDS) (INCA X-MAX, Oxford Instruments). Specific surface area was measured by the $N_2$-physisorption method (ASAP 2010, Micromeritics).

RRDE was used to investigate the electrocatalytic activity of the P-Fe catalyst toward oxygen reduction reaction. The linear sweep voltammograms (LSV) was performed in a conventional three-electrode system at a scan rate of 5 mV/s and a rotating speed of 1,000 rpm in oxygen saturated 0.1 M $HClO_4$. A Pt foil electrode was used as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. RRDE electrodes coated by catalyst (or bare GC electrode) were used for working electrodes. Another indicator of catalytic performance for oxygen reduction was the four-electron selectivity of the catalysts, which was evaluated by the amount of hydrogen peroxide yield, calculated by the following equation:[18] $H_2O_2\%=200\times I_R/(I_R+NI_D)$, where $I_R$ is the ring current, $I_D$ is the disk current and $N$ is the ring collection efficiency (37% as provided by the manufacturer). In the experiments, the ring potential was set to 1.2 V (vs. SCE).

Cell voltages (U) across an external resistance were measured and recorded using a data acquisition system (AD8201H, Ribohua Co., Ltd). Polarization and power density curves were obtained by varying the external resistance (R) from 10 to 2,000Ω. Current ($I$) was calculated by $I = U/R$, and power density ($P$) was normalized to the MFC reactor volume, calculated as $P = U \times I$/reactor volume.

## Results and Discussion

### Physical and chemical characterization of the catalyst

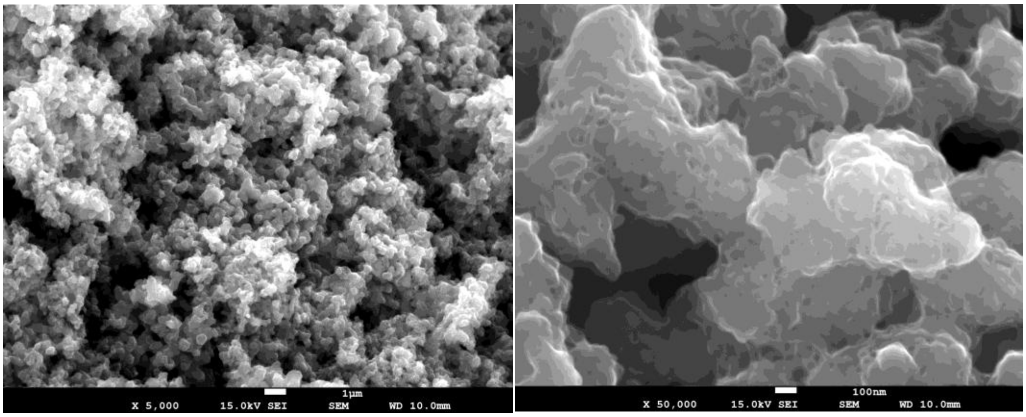

Fig. 1 FESEM images of P-Fe catalyst.

The morphology of this as-prepared catalyst is shown in Fig. 1. This representative FESEM image indicated that this catalyst exhibited a highly microporous structure. Because of the highly microporous structure, the specific surface area of this catalyst measured by the multiple point BET method was as high as 769.8 $m^2$/g and the pore volume reached 0.36 $cm^3$/g. For comparison, the catalyst without pyrolysis in $NH_3$ only had a specific surface area of 12.8 $m^2$/g and a pore volume of 0.01 $cm^3$/g. The high specific surface provided sufficient interface for the oxygen reduction reaction. In addition, previous studies indicate that micropores in carbon-nitrogen-metal catalyst are crucial for catalytic activity toward oxygen reduction because the active sites are hosted in the micropores.[19-20] EDS spectrum shown in Fig. 2 demonstrated the presence of C, N, O and Fe on the surface of this catalyst. Transition metal (Fe or Co) incorporation has been identified to enhance the oxygen reduction reaction activity in carbon-nitrogen-metal catalysts.[8] Therefore, this highly microporous catalyst incorporated with Fe was expected to be very active toward oxygen reduction.

The surface chemical composition of the catalyst was characterized by the XPS. General XPS scan of the catalyst

(Fig. 3 left) also confirmed the presence of C, N, O and Fe on the surface of this catalyst. Quantitative analysis of this spectrum based on relative sensitivity factors showed that the weight percentage of C, N, O and Fe were 89.46, 7.49, 2.87 and 0.18%, respectively. N content decreased from 17.36% before pyrolysis to 7.49% after heating in $NH_3$. The decrease of surface N content would be due to the gasification of nitrogen-containing fragments by $NH_3$ during pyrolysis. It has been demonstrated that surface nitrogen content is the most important factor for the catalytic activity in carbon-nitrogen-metal catalysts; a higher N content leads to higher density of the active sites and consequently better catalytic activity.[9, 21] Nineteen types of carbon-nitrogen-metal catalysts had been prepared on different carbon support with surface N content ranging from 0.3 to 2.5%; the catalytic activity is proportional to the surface N content in these catalysts.[21] In this study, the surface nitrogen content was much higher than those reported catalysts, so this catalyst was expected to exhibit high electrocatalytic activity for oxygen reduction.

The electronic states of surface nitrogen in this catalyst were also analyzed by the XPS. The high resolution XPS scan (Fig.3 right) for the N1s peak of the P-Fe catalyst was deconvoluted into three sets of binding energies originated from pyridinic N (398.3 eV), pyrrolic N (400.7 eV) and oxidized N (403.8 eV).[21-22] The relative intensity of the pyridinic N, pyrrolic N and oxidized N were 40.2, 47.7 and 12.1%, respectively. The previous studies have demonstrated that the catalytic sites for oxygen reduction reaction are made of pyridinic N.[9, 21, 23-24] Therefore, a higher content of pyridinic N was expected to have more active sites and ultimately, a better electrocatalytic activity.

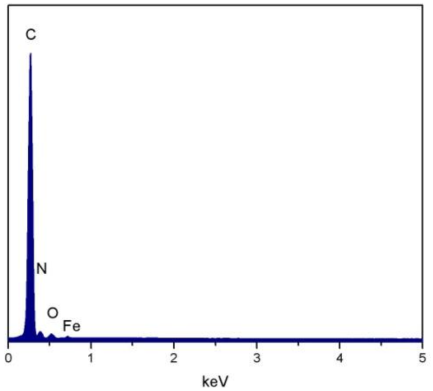

Fig. 2 EDS spectra of P-Fe catalyst.

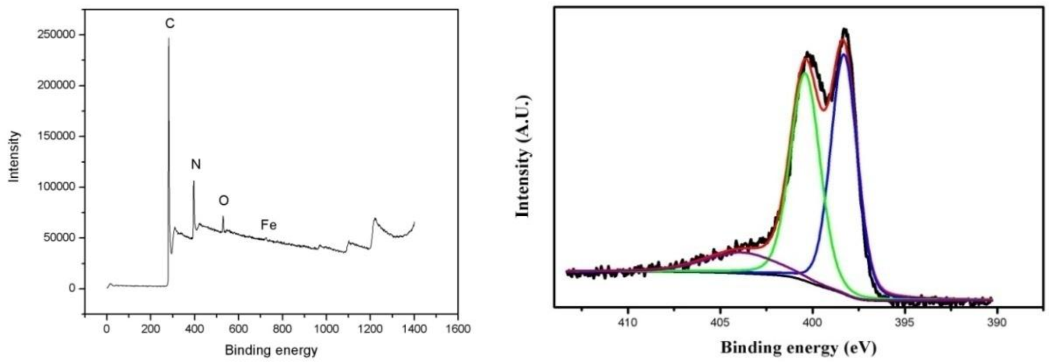

Fig. 3 General XPS scan (left) and the high resolution XPS scan (right) for the N1s core level peak of the P-Fe catalyst.

### Electrochemical characterization for oxygen reduction

In order to investigate the electrocatalytic activity of this catalyst toward oxygen reduction, LSV was conducted in a conventional three-electrode system at a scan rate of 5 mV/s and a rotating speed of 1,000 rpm in oxygen saturated 0.1 M $HClO_4$. For comparison study, bare GC electrode and the benchmark Pt/C catalyst were also investigated. As shown in Fig. 4, bare GC electrode had a quite low onset potential and disk current density, which indicated that CG was a poor electrocatalyst toward oxygen reduction. Both P-Fe and Pt/C electrodes exhibited high disk current density resulting from oxygen reduction reaction. Compared with GC electrode, P-Fe catalyst showed a much higher onset potential of about 0.92 V (vs. RHE), which was almost the same as that of Pt/C. The performance gap between P-Fe and the benchmark Pt/C, expressed as half-wave potential difference ($\triangle E_{1/2}$) in this test, was only about 70 mV. RRDE study also demonstrated that P-Fe was a very high selectivity catalyst for the four-electron reduction of oxygen. The hydrogen peroxide yield with P-Fe catalyst was less than 3% in all the potential range (Fig. 4 right).

The high onset potential and the high selectivity for the four-electron reduction of oxygen demonstrated that P-Fe was a highly active catalyst toward oxygen reduction. This high electrocatalytic activity would be a result of the high microporous structure, iron and the high surface nitrogen content, especially the pyridinic nitrogen. One mechanism for explaining the catalytic activity is that the catalytic sites, $FeN_4/C$ and $FeN_2/C$, are created in micropores during pyrolysis.[21, 25-26] These catalytic sites hosted in micropores could effectively lower the activation energy and facilitate oxygen reduction reaction. It has also been found that these active sites could reduce oxygen predominantly through a four-electron reduction pathway.[8, 26] In addition, it has been demonstrated that electron-accepting nitrogen atoms can impart a substantially high positive charge on adjacent carbon atoms to counterbalance the strong electronic affinity of the nitrogen atoms; this nitrogen-induced charge delocalization could change the oxygen adsorption mode from end-on adsorption to side-on adsorption, which can effectively weaken the O-O bonding and improve the oxygen reduction rate.[27] Therefore, the key requirements for producing active carbon-nitrogen-iron catalyst for oxygen reduction are iron, surface nitrogen and micropores.

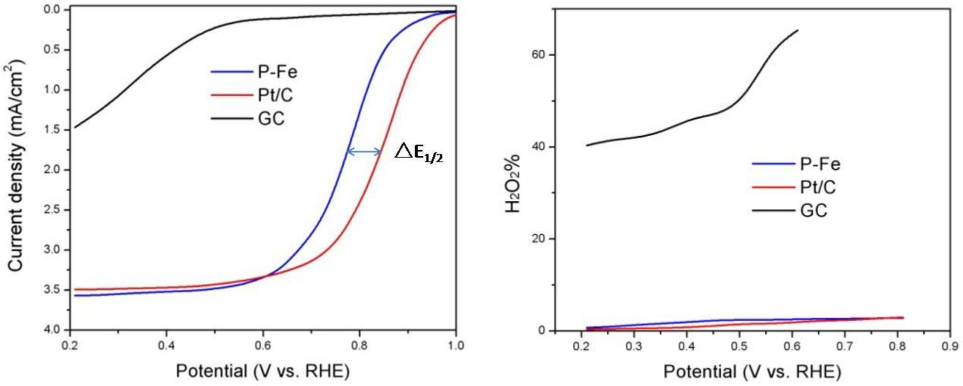

Fig. 4 Disk current (left) and $H_2O_2$ yield (right) plots during oxygen reduction reaction in oxygen saturated $HClO_4$ solution (0.1 M) (scan rate: 5 mV/s; rotating speed: 1,000 rpm).

## Cathode performance in MFCs

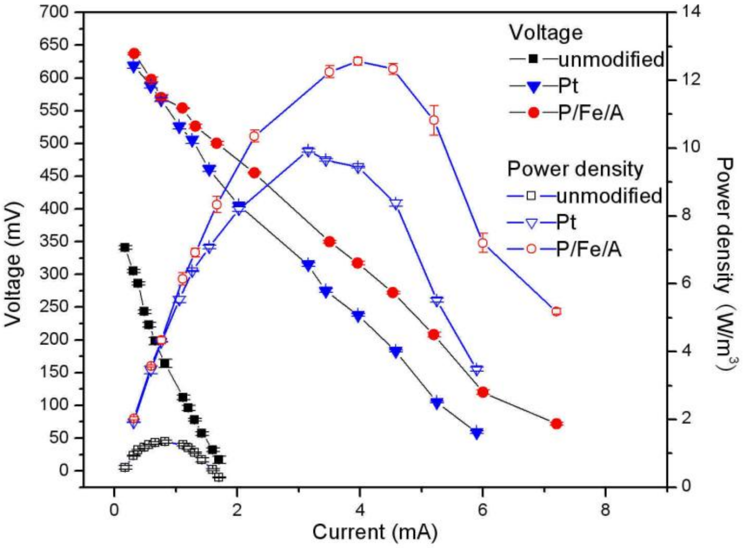

Fig. 5 Polarization (solid symbols) and power density (empty symbols) curves of MFCs with different cathodes.

P-Fe catalyst was used at the cathode to investigate its performance for power generation in MFCs. For comparison, bare graphite felt and benchmark Pt/C catalyst were also used as control in MFCs. When the MFCs became stable in power production, polarization and power density curves were obtained by varying the external resistance. The performance of the P-Fe catalyst in MFCs was in good agreement with its high electrocatalytic activity in the RRDE study. As shown in Table 1 and Fig. 5, the maximum power density of MFC with P-Fe catalyst at the cathode was about 12.56 W/m$^3$, which was significantly higher than the 1.34 W/m$^3$ produced by the MFC with bare graphite felt and also higher than the 9.92 W/m$^3$ generated by the MFC with Pt/C catalyst. In addition, the open circuit potential of the P-Fe cathode MFC was also higher than that of the MFCs with bare graphite felt and Pt/C catalyst. By calculating the slope of the polarization curves, the internal resistance of MFCs was determined; results showed that the internal resistance of the MFC using P-Fe catalyst was 83 Ω, while the internal resistances of the MFCs with bare graphite felt and Pt/C catalyst were 209 and 100 Ω, respectively.

Previous studies have shown that carbon-nitrogen-metal composites exhibit excellent performance as catalyst in the cathodes of $H_2$-$O_2$ fuel cell at 80$^o$C; the current density of these catalysts can equal that of Pt/C catalyst at a cell voltage of larger than 0.9 V.[8-9] In this study, the performance of P-Fe catalyst in mild operating temperature (30$^o$C) in MFCs was consistent with the good performance of carbon-nitrogen-metal catalysts in fuel cells, as shown by the high power density and open circuit potential.

The stability of this catalyst was tested by operating the MFCs over a period of 6 months. In the sixth month, the maximum power density of MFC using this catalyst could still reach 11.98 W/m$^3$, less than 5% decrease compared to its first month performance. The result demonstrated that P-Fe catalyst held good stability for oxygen reduction in MFCs. This was also in line with the report that carbon-nitrogen-metal catalysts displayed excellent stability in a 700-hour fuel cell test; the cell current density in the last 24 hours only dropped by 3% compared with that in the first 24 hours.[8]

It was important to note that the cost of this catalyst was substantially lower compared with Pt/C, the most popular catalyst used in MFCs. A rough estimation indicated that the cost of P-Fe produced in the laboratory was less than 1% of the Pt/C cost. A mass production of this catalyst could further bring down the catalyst cost. As mentioned above, the cost of the cathode is the largest part of the cost of an MFC system, which seriously impedes the practical applications of MFCs. Due to the extremely low cost, high catalytic activity toward oxygen reduction and excellent stability, the P-Fe catalyst could be a good alternative to Pt/C in MFCs.

Table 1 Air-cathode MFC performances with different cathodes.

| Cathodes | Open circuit potential (V) | Internal resistance (Ω) | Maximum power density (W/m$^3$) |
|---|---|---|---|
| Graphite felt | 0.43 | 209 | 1.34 |
| Pt/C | 0.70 | 100 | 9.92 |
| P-Fe | 0.72 | 83 | 12.56 |

## Conclusion

A high-performance electrocatalyst (P-Fe) derived from aniline and iron was synthesized by pyrolyzing iron-incorporated Polyaniline in $NH_3$ atmosphere at 900°C for 30 min. This catalyst had a highly microporous structure and a high pyridinic nitrogen content on the surface after pyrolyzing. The micropoers, pyridinic nitrogen and iron contributed to the excellent catalytic activity of P-Fe toward oxygen reduction. P-Fe catalyst exhibited a high onset potential of about 0.92 V (vs. RHE), which was almost the same as that of Pt/C. The half-wave potential difference between P-Fe and the benchmark Pt/C was only about 70 mV. The RRDE study demonstrated that P-Fe was a very high selectivity catalyst for the four-electron reduction of oxygen. Used as air cathodes in MFCs, the catalyst exhibited a high catalytic activity. The MFC with P-Fe as the catalyst achieved a maximum power density of 12.56 W/m$^3$, significantly higher than the 1.34 W/m$^3$ produced by the MFC with bare graphite felt and also higher than the 9.92 W/m$^3$ generated by the MFC with Pt/C catalyst. These results demonstrated that P-Fe catalyst was an excellent alternative to the cost prohibitive Pt/C for practical applications.

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