

Synthesizing Nitrogen-Doped Activated Carbon and Probing its Active Sites for Oxygen Reduction Reaction in Microbial Fuel Cells

Bo Zhang,^{†,‡} Zhenhai Wen,^{†,§} Suqin Ci,[§] Shun Mao,[§] Junhong Chen,^{*,§} and Zhen He^{*,†}

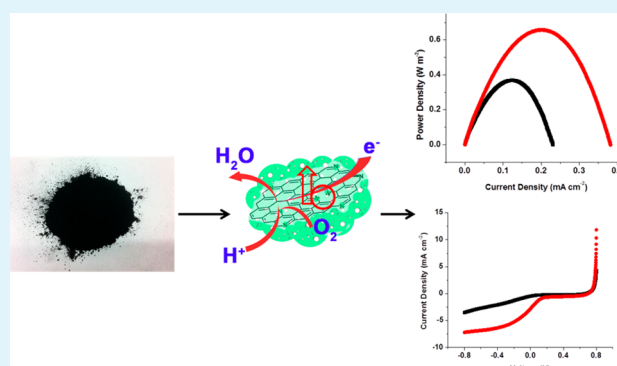
[‡]Department of Civil Engineering and Mechanics and [§]Department of Mechanical Engineering, University of Wisconsin–Milwaukee, Milwaukee, Wisconsin 53211, United States

[†]Department of Civil and Environmental Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, United States

Supporting Information

ABSTRACT: Cost-effective cathode catalysts are critical to the development of microbial fuel cell (MFC) technology. Herein, a synthesis route is presented to improve the nitrogen content and nitrogen functionality in the nitrogen-doped activated carbon (AC) as a low cost and efficient catalyst for oxygen reduction reaction (ORR). It was demonstrated that key factors for successful nitrogen doping were the proper pretreatment with acidic and alkaline solutions consecutively and the use of a solid-state nitrogen precursor. The AC pretreated with both acidic and alkaline solutions resulted in a nitrogen content of 8.65% (atom %) (in which 5.56% is pyridinic-N) on its surface, and exhibited an outstanding electrocatalytic activity for ORR in both electrochemical and MFC tests. A good agreement between pyridinic-N content and ORR activity was observed, indicating that pyridinic-N is the most active site for ORR in the nitrogen-doped AC. The pretreated nitrogen-doped AC catalysts resulted in a higher maximum power density than the untreated AC and the commercial Pt/C (10% Pt) catalysts. The exceptional performance associated with the advantages, such as simple and convenient preparation procedure, easily obtained raw materials, and low cost, makes the pretreated nitrogen-doped AC promising for the ongoing effort to scale up MFCs.

KEYWORDS: nitrogen-doping, activated carbon, oxygen reduction reaction, microbial fuel cell, bioenergy



INTRODUCTION

Microbial fuel cells (MFCs) have been intensively studied as a sustainable wastewater treatment technology in the past decade,¹ and with recovering energy from organic wastes MFCs have a potential to become an energy-neutral (even positive) treatment process.² In an MFC, the electrochemically active bacteria grown on an anode electrode oxidize organic matters in wastewater and release the electrons to the anode electrode; the released electrons then travel through an external circuit to reduce the terminal electron acceptors in the cathode. The terminal electron acceptors in the cathode play a critical role in both organic oxidation and energy recovery. Oxygen is the most commonly used terminal electron acceptor and considered to be suitable for MFC application because of its high reduction potential and readily availability.³ However, because of the high energy barrier of oxygen reduction reaction (ORR), a catalyst will be needed to facilitate the cathode reaction in an MFC. Currently, the Pt-based catalysts are the most widely applied cathode catalyst in the laboratory MFC systems, and make the capital cost of MFC reactors prohibitively high for a practical application. Therefore, exploring a low-cost and efficient alternative ORR catalyst to the Pt-based materials is of great importance to bring the MFC

technology into a practical scale. Some alternative ORR catalysts have been studied in MFCs including transition metal complexes,⁴ metal oxides,⁵ nitrogen-doped carbon nanotubes⁶ and graphenes,⁷ and microorganisms.⁸ However, the limitations associated with these alternatives, such as high manufacturing cost, complex preparing procedure, poor durability, and low performance, prevent them from being an ideal candidate for large-scale MFC applications.

There has been a trend to search for cost-effective materials for MFCs in large-scale applications with a specific focus on cheap yet efficient cathode catalysts,^{9–12} and activated carbon is of strong interest. Activated carbon (AC) is a common carbon material that can be facilely and economically produced from various carbonaceous sources such as wood, nutshells, coconut husk, peat, lignite, coal, and petroleum pitch.¹³ Recently, AC was demonstrated as an alternative cathode catalyst to Pt in several MFCs,^{13–18} in which the AC-based cathode electrodes achieved relatively higher power densities compared with the noncatalyzed cathodes; a long-term study showed that the AC

Received: February 10, 2014

Accepted: April 10, 2014

Published: April 10, 2014

cathodes exhibited much better durability than the Pt/C based cathode.¹⁹ In addition, AC has a large surface area in excess of 500 m² g⁻¹ and its low cost is very attractive compared with other nanostructured carbon materials (e.g., carbon nanotubes or graphene) or the Pt-based catalysts, thereby making AC a very promising catalyst for MFCs.

However, at this moment, the low catalytic activity for ORR in AC has greatly limited its application in MFCs. It was recognized that proper modification of AC may greatly affect its catalytic performance, and among the modifying methods, nitrogen doping on some nanostructured carbon has been demonstrated to be an effective strategy to improve ORR catalytic performance.^{20,21} There have also been some attempts to improve the ORR catalytic performance of AC through nitrogen doping.^{11,15,22} These nitrogen-doped AC materials, though achieving enhanced ORR activity, still cannot satisfy the MFCs application due to multiple reasons, in which the low nitrogen content (typically below 2%) could be an important factor. In addition, the active nitrogen compounds in the doping need to be identified for further understanding of ORR catalyzed by the nitrogen-doped AC. The recent research found that three types of typically doped nitrogen, i.e. pyridinic-N, pyrrolic-N, and quaternary-N, could make different contributions to improving ORR activity: the pyridinic-N and the pyrrolic-N could reduce the thermodynamic barrier of ORR, whereas the quaternary-N could enhance the kinetic performance of ORR.²³ Nitrogen-doped carbon nanostructures indicated that increasing the contents of the pyridinic-N and the pyrrolic-N seemed to be more important because both can be beneficial to reducing the energy barrier of ORR.²⁴

Those prior findings and the strong need for cost-effective cathode catalysts for large-scale MFC development inspire us to explore a proper nitrogen doping strategy for improving AC catalysts. We hypothesize that the ORR catalytic activity of the nitrogen-doped AC would benefit from (1) increasing nitrogen content; and (2) a better understanding of nitrogen functionality. In this study, we have developed an effective and reliable method to prepare the nitrogen-doped AC with improvement in both total nitrogen-doped content and nitrogen-functionalities. We have conducted a series of experiments to examine the effects of the pretreatment on the nitrogen-doped AC, and two keys were demonstrated to be very important in fabricating an ideal nitrogen-doped AC based cathode catalyst that could outperform Pt/C catalysts for the MFC application: (1) pretreatment of AC with acidic or alkaline solutions successively before the nitrogen-doping reaction, and (2) use a solid nitrogen source, i.e., cyanamide.

■ MATERIALS AND METHODS

Synthesis of the AC Catalysts. The nitrogen-doped AC was synthesized by using commercially available activated carbon (Fisher Scientific, Bridgewater, NJ, USA), and three different types of the nitrogen-doped AC were prepared: (1) direct nitrogen-doped AC (AC_N) without any pretreatment; (2) acid pretreated nitrogen-doped AC (acidic-AC_N); and (3) acid and alkaline pretreated nitrogen-doped AC (acidic/basic-AC_N). During the synthesis of the acidic-AC_N and the acidic/basic-AC_N, the acidic pretreatment process was performed as the following: 2 g of AC powder was added into a solution containing 25 mL of H₂SO₄ (98%) and 2 g of KMnO₄ and mixed for 3 h. Afterward, the acid treated AC was washed thoroughly using DI water, and then used for nitrogen doping. To prepare the acidic/basic-AC_N, the acid pretreated AC was further treated in a 3 M KOH solution at 180 °C for 10 h; the acidic–basic pretreated AC was then

thoroughly washed with DI water and used in the following nitrogen doping.

The nitrogen precursor used in this study was cyanamide (Sigma-Aldrich, St. Louis, MO, USA). The AC samples and cyanamide were added in a 1:5 ratio (mass) and well-mixed before they were loaded into a programmable tube furnace (Lindberg, Thermo Scientific, USA). Before the doping, the tube furnace was flushed with Argon for 10 min. The temperature was increased from the room temperature to 80 °C in 10 min and maintained at 80 °C for 1 h; then the temperature was further increased to 750 °C in 4 h and maintained at 750 °C for additional 2 h. During the entire doping period, the tube was flushed with argon gas at a flow rate of 0.1 mL s⁻¹.

Characterization of the AC Catalysts. The morphology of the nitrogen-doped AC was characterized by scanning electron microscope (SEM) (Hitachi S-4800). Brunauer–Emmett–Teller (BET) test was conducted to examine the surface area and pore size distribution of the catalysts (ASAP 2020, Micromeritics, Norcross, GA, USA). During the BET test, the samples were first degassed and then used to adsorb N₂ at 76 K. The micropore area and volume was calculated by using t-plot method. XPS (5950A ESCA Spectrometer, H.P.) was employed to study the surface chemistry composition of the catalysts, and to compare the nitrogen content between different nitrogen-doped AC catalysts; the spectra were scanned from 0 to 1000 eV, and were analyzed using XPSPEAK 4.1. The chronoamperometry test was used to examine and compare the durability between the Pt/C and the acidic/basic-AC_N; the working electrode (a glassy carbon electrode) was loaded with 5 μL of catalyst ink, and then biased to -100 mV (vs Ag/AgCl reference electrode) in 100 mM PBS solution with a Pt wire as the counter electrode; before the test, the electrolyte was aerated with O₂ for 30 min and the aeration was continued at the head space throughout the experiment.

Linear sweep voltammetry (LSV) was used to examine the electrochemical performance of the AC catalysts. The catalyst ink was prepared by dissolving 5 mg of the catalyst in 0.5 mL of 0.5% Nafion solution (Sigma-Aldrich, St. Louis, MO, USA). The ink was vortexed for 5 min and then ultrasonicated for 30 min to ensure well dispersion of the catalyst. After ultrasonication, 6 μL of the ink was pipetted to the top of a glassy carbon electrode, which was dried in the air and then used in the electrochemical test. During the LSV test, the working electrode was mounted on a rotating disk electrode (RRDE-3A, BASi, West Lafayette, IN, USA). To calculate the number of electrons transferred during ORR as previously described,²⁵ the rotating speed of the electrode was varied from 100 to 3600 rpm. The counter electrode was a Pt wire (CHI115, CH Instruments, Austin, TX, USA), and the reference electrode was Ag/AgCl (Saturated KCl, 0.197 V vs standard hydrogen electrode). The potentials reported in the LSV test were the values vs Ag/AgCl reference electrode unless noted otherwise. The electrolyte used in the LSV tests was 100 mM phosphate buffer solution containing (per liter) 10.7 g of K₂HPO₄ and 5.3 g of KH₂PO₄. Before the LSV test started, the electrolyte was aerated with oxygen for 30 min, and the aeration was continued at the head space throughout the LSV test. The voltage was scanned from 0.8 to -0.8 V at a scan rate of 5 mV s⁻¹ using a potentiostat (600E, CH Instruments, Austin, TX USA).

Electrochemical impedance spectroscopy (EIS) test was conducted using a potentiostat (Reference 600, Gamry Instruments, Warminster, PA, USA) under the same condition as the LSV test. The frequency was swept from 1 × 10⁵ to 0.1 Hz with a sinusoidal amplitude of 5 mV.

MFC Test. The MFC test was conducted in an H-shape MFC reactor, in which the anode chamber (140 mL) and the cathode chamber (140 mL) were separated by a cation exchange membrane (Membrane International, Inc., Ringwood, NJ, USA). The anode electrode was a 5 cm long carbon brush and the anode chamber was inoculated with digester effluent from South Shore Wastewater Treatment Plant (Milwaukee, WI, USA). The anolyte contained (per liter of tap water): sodium acetate, 1 g; NH₄Cl, 0.15 g; NaCl, 0.5 g; MgSO₄, 0.015 g; CaCl₂, 0.02 g; KH₂PO₄, 0.53 g; K₂HPO₄, 1.07 g; yeast extract, 0.1 g; and trace element, 1 mL.²⁶ The cathode electrode was carbon cloth coated with the prepared AC catalysts, and the catholyte was 100 mM phosphate buffer solution. The cathode

chamber was aerated with air with a flow rate of 50 mL min⁻¹. Both the anolyte and the catholyte were mixed using stirring bars.

Five different cathode catalysts were tested, including AC, AC_N, acidic-AC_N, acidic/basic-AC_N, and Pt/C (10% Pt, Fuel Cell Earth, Stoneham, MA, USA). Each catalyst was brushed onto a piece of carbon cloth using 0.5% Nafion solution (Sigma-Aldrich, St. Louis, MO, USA) as binder with a loading rate of 5 mg cm⁻². The dimension of each carbon cloth was 1 cm × 3 cm. Prior to being coated, the carbon cloth was soaked in acetone overnight and then heat-treated under 350 °C for 1 h.²⁷

The MFC performance was monitored and examined by using polarization tests and current generation across an external resistor. The polarization test was conducted by using a potentiostat (Reference 600, Gamry Instruments, Warminster, PA, USA) at a scan rate of 0.1 mV s⁻¹: the cathode electrode functioned as a working electrode, and the anode electrode acted as both the counter and reference electrodes. The polarization test was duplicated for each catalyst. Four AC-based catalysts, AC, AC_N, acidic-AC_N, and acidic/basic-AC_N, were compared for their current profile across the external resistance of 33 Ω in a batch operation. To do this, four cathodes loaded with different AC catalysts were simultaneously connected to the common anode electrode (so that the influence of different anode electrode would be minimized) in an MFC. One batch operation last for 24 h, and the anolyte and catholyte were replaced with the fresh medium after each batch.

RESULTS AND DISCUSSION

Synthesis and Characterization of the AC Catalysts.

The procedure for preparing the acidic/basic-AC_N was demonstrated in Figure 1. The synthesis starts from the

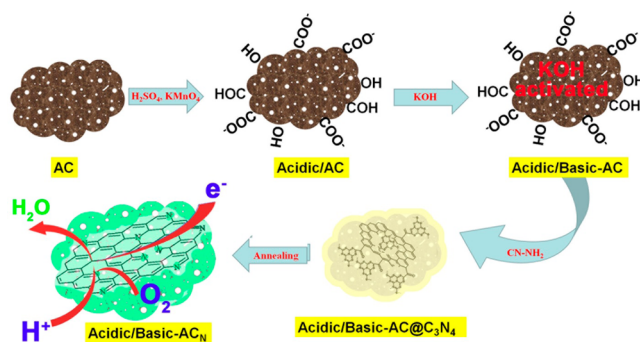


Figure 1. Schematic illustration for fabricating the acidic/basic-AC_N.

treatment of AC with strong oxidizing acid, i.e., concentrated H₂SO₄ with KMnO₄, which produces a large amount oxygen-rich group; the following KOH treatment then leads to the activation of AC;²⁸ after introducing N source (cyanamide), the oxygen-rich groups in AC would react with amine groups in

NH₂CN to form a layer of C₃N₄ polymer covered on AC; the final calcination at 750 °C leads to the acidic/basic-CA_N products through N-doping reaction between AC and the produced gas (e.g., C₂N₂⁺, C₃N₂⁺, NH₃) from decomposition of C₃N₄.²⁹

The representative SEM images of all AC samples are shown in two scales in Figure S1 (see the Supporting Information), from which one can observe that there is no significant difference in morphology among these samples, indicating that neither the acidic/basic pretreatment nor the nitrogen doping reaction obviously affect the morphology of the catalysts. This suggests that the morphology may not play a key role in impacting the performance of those AC catalysts studied here. The acidic/basic-AC_N was further characterized by taking element mapping images of carbon and nitrogen (Figure 2a–c), in which the green dots (Figure 2b) and the yellow dots (Figure 2c) are attributed to carbon and nitrogen elements, respectively. One can observe that the nitrogen elements were uniformly dispersed on the acidic/basic-AC_N sample, demonstrating the N can be uniformly doped in carbon by using the present method.

There has been an argument about the contribution of micropore area on ORR catalytic activity of activated carbon.^{13,17} In nitrogen-doped activated carbons, however, the dominant catalytic sites for ORR are thought to be the N atoms and are not the micropores per se. This was supported by the evidence obtained from the present experiments. Although the nitrogen-doped AC catalysts had smaller surface areas and micropore areas than the plain AC material (see Table S1 in the Supporting Information), their ORR catalytic performances had been improved remarkably (more details in the following sections), indicating that the surface area had little contribution to the improvement in ORR catalytic activity of the nitrogen-doped ACs. Moreover, we did not observe any noticeable change in the pore size distribution after acidic, basic or nitrogen doping treatments (see Figure S2 in the Supporting Information).

The XPS spectra of the AC_N, the acidic-AC_N and the acidic/basic-AC_N catalysts are presented in Figure 3 and Figure S3 in the Supporting Information. According to the XPS spectra, the surface nitrogen contents of the three catalysts are: 4.2% for the AC_N, 6.0% for the acidic-AC_N, and 8.7% for the acidic/basic-AC_N (Table 1), significantly higher than those (around 2%) in two prior studies of the nitrogen-doped activated carbon¹⁵ and nitrogen-doped carbon black²² as a cathode catalyst in MFCs. The acidic pretreatment increased the nitrogen content by 45% (the AC_N vs the acidic-AC_N), and the combined acidic and basic pretreatment further improved the nitrogen content by

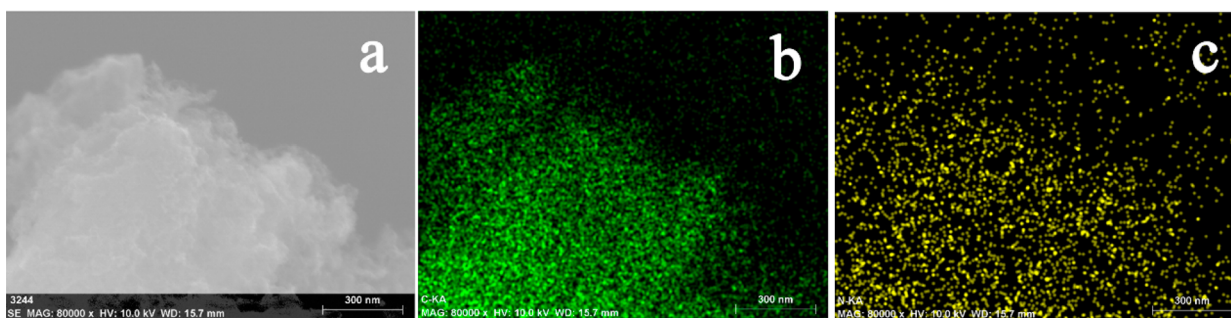


Figure 2. (a) Zero-energy loss bright-field image of the acidic/basic-AC_N, (b) the corresponding carbon element mapping, and (c) the nitrogen element mapping.

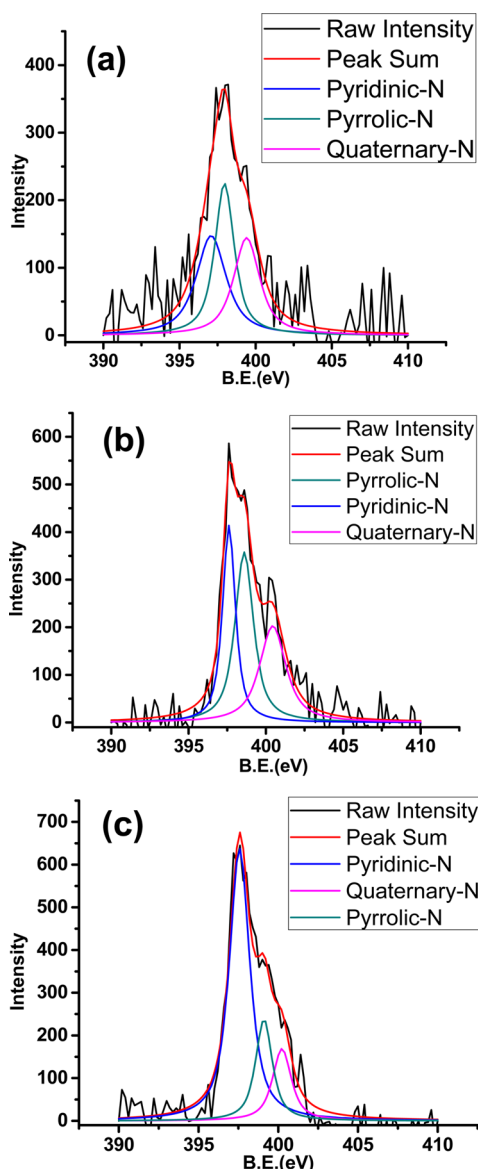


Figure 3. N 1s spectra of (a) the AC_N , (b) the acidic- AC_N , and (c) the acidic/basic- AC_N .

another 45% (the acidic- AC_N vs the acidic/basic- AC_N), which doubled the nitrogen content compared with the AC_N , indicating that pretreatment is a key factor in preparing the nitrogen-doped ACs. Although $KMnO_4$ was involved in the

pretreatment, no Mn (or Fe) was detected in the AC catalysts (see Figure S3 in the Supporting Information).

The successful nitrogen doping of AC in this study relied on two key factors: (1) proper pretreatment, and (2) the decomposition of solid precursor as a nitrogen source. The well-ordered structure of AC makes it hard for nitrogen atom to be doped into the carbon matrix; thus, it is important to introduce defects onto the surface of the carbon. The present method, through pretreatment of AC with acid and alkaline solution successively, was supposed to introduce a large amount of defects on the surface of AC. These introduced defects then became the active sites for nitrogen doping in the following steps. A solid N precursor (e.g., cyanamide) rather than conventional NH_3 gas was used in this study: upon heating (above 700 °C) the cyanamide would initially polymerize and then slowly decompose to release N-rich gases that enable the nitrogen doping reaction to proceed homogeneously on the surface of AC particles. Such a designed process could also increase the pyridinic-N and pyrrolic-N content in AC.²³

Electrochemical Performance. The results of the LSV tests of the AC, the AC_N , the acidic- AC_N , the acidic/basic- AC_N , and the Pt/C are presented in Figure 4 and Figure S4 in the

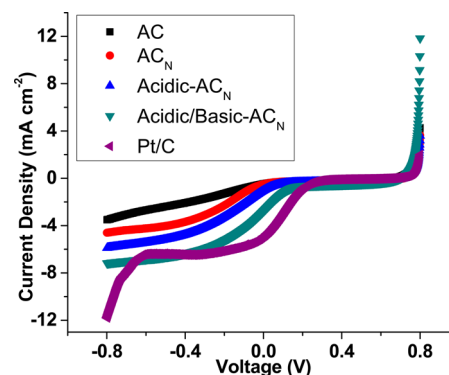


Figure 4. Linear sweep voltammetry of the AC catalysts and the Pt/C at 1600 rpm.

Supporting Information, and confirmed our hypothesis that nitrogen doping could increase the ORR catalytic performances of AC and that different pretreatment methods would result in the materials with different catalytic performance. According to the LSV, the AC had the lowest ORR onset potential, which is about 60 mV, whereas, as expected, the Pt/C showed the most positive ORR onset potential of +300 mV. Direct nitrogen doping (AC_N) did not obviously change the onset potential;

Table 1. XPS Results of Three Nitrogen-Doped AC Catalysts

	C/N/O	total surface N content (atom %)	surface content of different N functionalities (atom %)			no. of e^- transferred in ORR	ORR onset potential (mV)	I_{limiting} in LSV (mA cm^{-2})
			pyridinic	pyrrolic	quaternary			
AC_N	0.849/0.042/ 0.109	4.20	1.46 (35%) ^a	1.48 (35%)	1.25 (30%)	2.39	60	4.67
acidic- AC_N	0.821/0.060/ 0.119	6.00	2.30 (38%)	1.87 (31%)	1.83 (31%)	4.09	160	5.89
acidic/basic- AC_N	0.828/0.087/ 0.085	8.65	5.56 (64%)	1.36 (16%)	1.73 (20%)	3.99	180	7.18
Pt/C	n/a	n/a	n/a	n/a	n/a	3.79	300	6.42 ^b

^aThe relative percentage of each N functionality among the N content on the AC surface. ^bThis limiting current density of Pt/C was recorded at -0.6 V to avoid hydrogen production.

however, the current density of the AC_N was higher than that of AC, likely because of the increased quaternary-N content. On the other hand, noticeable positive shifts in ORR onset potential were observed in the pretreated nitrogen-doped AC: the acidic-AC_N had an onset potential of 160 mV, whereas the acidic/basic-AC_N exhibited an onset potential of 180 mV. Comparing with the AC_N, these onset potentials mark improvements of +100 mV and +120 mV, respectively, likely because of the increased pyridinic-N content resulting from the pretreatment.

The pretreated nitrogen-doped AC also showed higher current densities in LSV, which confirmed the importance of proper pretreatment. In more detail, the AC_N reached a limiting current density of 4.67 mA cm⁻², which was 33% higher than that of the raw AC (3.51 mA cm⁻²). The limiting current densities of the acidic/basic-AC_N and the acidic-AC_N were 7.18 and 5.89 mA cm⁻², respectively. The current densities of the tested catalysts generally follow a trend of AC < AC_N < acidic-AC_N < acidic/basic-AC_N. The current density of the acidic/basic-AC_N was comparable to that of the Pt/C in this study. According to the calculated number of electrons transferred during ORR (Table 1 and Figure S5 in the Supporting Information), the ORR prefers to take place in a 4e⁻ transfer pathway when using the pretreated nitrogen-doped ACs as catalysts. The raw AC had a calculated electron transfer number of 2.61, similar to that of the AC_N. A electron transfer number close to 2 indicates that the ORR was possibly proceeded in a 2e⁻ transfer pathway, which was less favorable in an MFC cathode.³⁰

Further analysis revealed that three samples, i.e., AC, AC_N, and acidic-AC_N, showed an increasing limiting current density in the LSV test rather than a steady limiting current density (see Figure S4 in the Supporting Information), suggesting that the ORR proceeded through a multistep processes with possible H₂O₂ intermediates in these electrodes. In contrast, the acidic/basic-AC_N and Pt/C catalyst exhibited a steady limiting current density, suggesting that the ORR predominantly proceeded through a one-step reaction pathway, i.e., 4e⁻, to reduce oxygen to water. In addition to the increased ORR catalytic activity, we also observed that the conductivities of the nitrogen-doped ACs decreased compared to raw AC (see Figure S6 in the Supporting Information).

We compared the stability between the Pt/C and the acidic/basic-AC_N by using chronoamperometry test. As shown in Figure S7 in the Supporting Information, after more than 7 h of reaction, the current density of the Pt/C dropped from 0.38 to 0.11 mA cm⁻², more than 73% decrease from the original value, whereas the current density of the acidic/basic-AC_N decreased from 0.33 to 0.23 mA cm⁻², which was about 30% lower than the initial current density.

The deconvoluted N 1s spectra of three nitrogen-doped AC showed distinct differences in terms of N functionalities. The relative pyridinic-N percentage increased as acid and alkaline pretreatments were employed and became dominant in acidic/basic-AC_N. Along with the increased pyridinic-N content, the catalytic activity of nitrogen doped AC increased as well. In terms of thermodynamics, the ORR onset potential shifted positively with pretreatments. The limiting current density in LSV, which was an indicator of kinetic property, also showed that the pretreated nitrogen-doped AC had higher current densities than direct doped AC. The agreements were good between the pyridinic-N content and increased ORR catalytic performance of nitrogen doped AC; however, such agreements

were not found for the pyrrolic-N or quaternary-N (Figure 5). These results suggested that the pyridinic-N might be the most

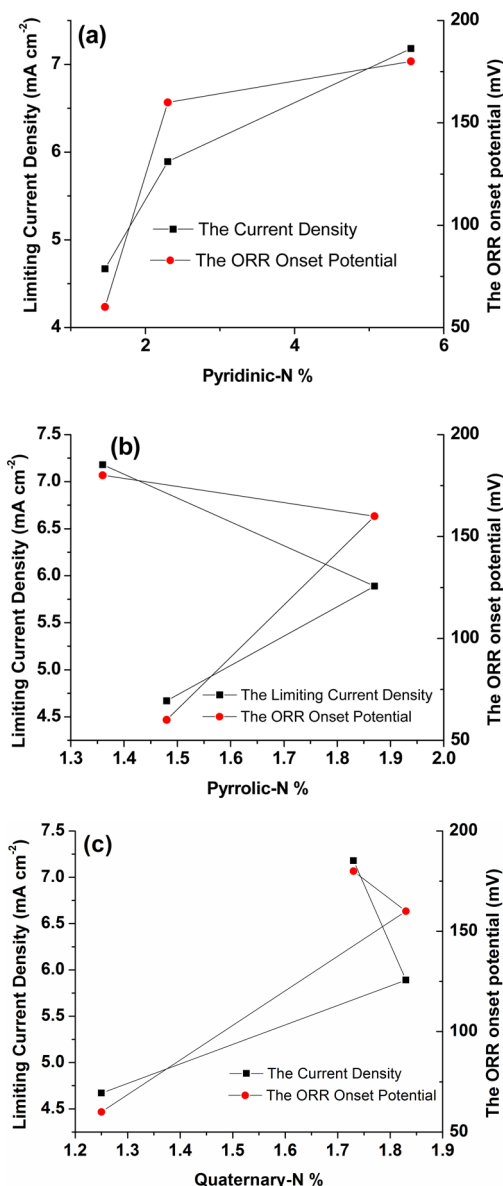


Figure 5. Correlations between different N functionalities and ORR catalytic activity: (a) pyridinic-N, (b) pyrrolic-N, and (c) quaternary-N.

active site for ORR in nitrogen-doped AC; however, the contribution of pyrrolic-N or quaternary-N should not be excluded on the basis of these results.

Electricity Generation in an MFC. The AC catalysts were examined in an MFC for power production and current generation. The maximum power densities of the MFC with different cathode catalysts obtained from polarization tests are presented in Figure 6. The acidic-AC_N and the acidic/basic-AC_N cathodes resulted in a maximum power density of 0.58 ± 0.04 W m⁻² and 0.65 ± 0.02 W m⁻² (based on the projected cathode area), respectively, 1.4 or 1.6 times higher than that of the AC_N (0.41 ± 0.00 W m⁻²). For comparison, the MFC with the Pt/C cathode reached a maximum power density of 0.45 ± 0.04 W m⁻², whereas the raw AC cathode had a maximum power density of 0.31 ± 0.08 W m⁻². The batch current profiles

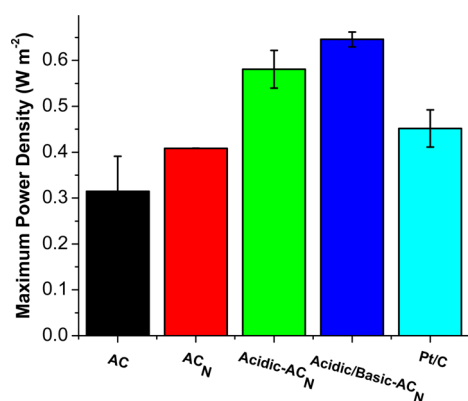


Figure 6. Maximum power densities of the MFCs with different cathode catalysts.

for the AC cathodes are compared in Figure 7; it should be noted that those batch current profiles were obtained with a

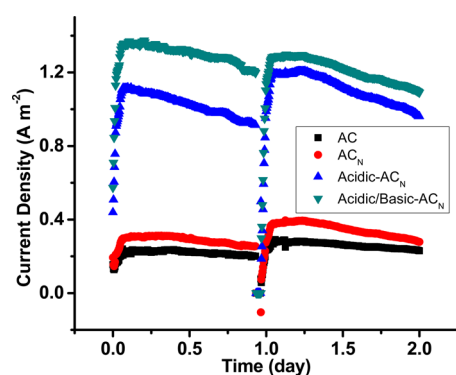


Figure 7. Profile of the current generation in the MFCs with different AC catalysts.

low external resistor that resulted in high current generation and low power output, different from the condition where the maximum power density was obtained, and the comparison of electric current focused on ORR kinetics. All three nitrogen-doped AC cathodes exhibited higher current than the nondoped AC cathode. The direct doped AC_N only showed a moderate improvement comparing to the AC; however, the pretreated nitrogen-doped AC achieved the currents roughly 4 times higher than that of the AC_N and 5 times higher than that of the raw AC.

In the MFC test, the nitrogen-doped AC with a higher pyridinic-N content showed higher power densities and current densities. More remarkably, the acidic-AC_N and acidic/basic-AC_N resulted in power densities even higher than Pt/C. Considering that the morphology and surface area were not significantly altered by pretreatment and nitrogen doping and no Mn (or other transitional metal such as Fe) was detected, the superior performances of the acidic-AC_N and the acidic/basic-AC_N should be attributed to the increased nitrogen content (especially the pyridinic-N) as a result of a proper synthesis route. This result emphasized the importance of proper pretreatment and nitrogen precursor selection in terms of improving the ORR catalytic performances of the AC for MFC cathode. The doping route employed in the current study enabled us to improve the nitrogen content and specific nitrogen moieties. Although recent studies have confirmed that the pyridinic-N and the pyrrolic-N contribute mostly to the

enhanced ORR catalytic activity of nitrogen doped nano structures,²⁴ our study suggested that the pyridinic-N is probably the most active site for ORR with the nitrogen-doped AC.

The doping method presented in this work can easily be adopted for producing a large quantity of the nitrogen-doped AC catalysts. We estimated the material cost of the nitrogen-doped AC as \$6.40 g⁻¹, of which 91.3% was attributed to cyanamide. Thus, to further reduce the catalyst cost, we must replace cyanamide with other low-cost nitrogen precursors such as melamine and urine. Even using cyanamide, the cost of the acidic/basic-AC_N was about 10% of the Pt/C powder. In addition to the cost advantages, the acidic/basic-AC_N catalyst showed better long-term stability than the Pt/C cathode, and less susceptible to sulfide.³¹ These features will make it more advantageous to use AC-based catalysts for large-scale MFC development.

CONCLUSIONS

This study has demonstrated that the proper doping method is very critical to tune the N-group functionality that is of vital importance to affect the ORR catalytic activity. The as-developed acidic/basic-AC_N exhibits significantly enhanced catalytic activity for ORR in comparison with raw AC. When being used as cathode materials in an MFC, the as-developed acidic/basic-AC_N can outperform the well-known Pt/C catalysts in terms of the most important performance parameter of MFC, i.e., power density. The outstanding properties could be reasonably attributed to a high pyridine-N doping content in acidic/basic-AC_N. The acidic/basic-AC_N can be conveniently, effectively, and economically prepared at a high yield (more than 80% relative to AC), which makes it possible to mass-produce cost-effective and high-activity cathode catalysts for a practical MFC application.

ASSOCIATED CONTENT

Supporting Information

The SEM images of the AC catalysts, the pore size distribution, the whole XPS spectrum, the LSV test of different catalysts at different rotating speeds, the K-L plots of the raw AC and the nitrogen-doped AC catalysts, the EIS test of different catalysts, and the comparison of current generation between the Pt/C and the acidic/basic-AC_N during chronoamperometry test. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: jhchen@uwm.edu. Phone: 414-229-2615. Fax: 414-229-6958.

*E-mail: zhenhe@vt.edu. Phone: 540-231-1346. Fax: 540-231-7916.

Author Contributions

†Authors B.Z. and Z.W. contributed equally to this work.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This project was financially supported by an award from Research Growth Initiative (RGI) of UW–Milwaukee.

■ REFERENCES

- (1) Wang, H.; Ren, Z. J. A Comprehensive Review of Microbial Electrochemical Systems as a Platform Technology. *Biotechnol. Adv.* **2013**, *31* (8), 1796–1807.
- (2) He, Z. Microbial Fuel Cells: Now Let's Talk About Energy. *Environ. Sci. Technol.* **2013**, *47*, 332–333.
- (3) Logan, B. E. *Microbial Fuel Cells*, 1st ed.; Wiley-Interscience: Hoboken, NJ, 2008.
- (4) Zhao, F.; Harnisch, F.; Schroder, U.; Scholz, F.; Bogdanoff, P.; Herrmann, I. Application of Pyrolysed Iron(II) Phthalocyanine and Cotmp Based Oxygen Reduction Catalysts as Cathode Materials in Microbial Fuel Cells. *Electrochem. Commun.* **2005**, *7* (12), 1405–1410.
- (5) Zhang, L.; Liu, C.; Zhuang, L.; Li, W.; Zhou, S.; Zhang, J. Manganese Dioxide as an Alternative Cathodic Catalyst to Platinum in Microbial Fuel Cells. *Biosens. Bioelectron.* **2009**, *24* (9), 2825–2829.
- (6) Feng, L.; Yan, Y.; Chen, Y.; Wang, L. Nitrogen-Doped Carbon Nanotubes as Efficient and Durable Metal-Free Cathodic Catalysts for Oxygen Reduction in Microbial Fuel Cells. *Energy Environ. Sci.* **2011**, *4* (5), 1892–1899.
- (7) Liu, Y.; Liu, H.; Wang, C.; Hou, S.-X.; Yang, N. Sustainable Energy Recovery in Wastewater Treatment by Microbial Fuel Cells: Stable Power Generation with Nitrogen-Doped Graphene Cathode. *Environ. Sci. Technol.* **2013**, *47* (23), 13889–13895.
- (8) He, Z.; Angenent, L. T. Application of Bacterial Biocathodes in Microbial Fuel Cells. *Electroanalysis* **2006**, *18* (19–20), 2009–2015.
- (9) Xia, X.; Zhang, F.; Zhang, X.; Liang, P.; Huang, X.; Logan, B. E. Use of Pyrolyzed Iron Ethylenediaminetetraacetic Acid Modified Activated Carbon as Air-Cathode Catalyst in Microbial Fuel Cells. *ACS Appl. Mater. Interfaces* **2013**, *5* (16), 7862–7866.
- (10) Luckarift, H. R.; Sizemore, S. R.; Farrington, K. E.; Roy, J.; Lau, C.; Atanassov, P. B.; Johnson, G. R. Facile Fabrication of Scalable, Hierarchically Structured Polymer/Carbon Architectures for Bioelectrodes. *ACS Appl. Mater. Interfaces* **2012**, *4* (4), 2082–2087.
- (11) Xia, X.; Zhang, F.; Zhang, X.; Liang, P.; Huang, X.; Logan, B. E. Use of Pyrolyzed Iron Ethylenediaminetetraacetic Acid Modified Activated Carbon as Air-Cathode Catalyst in Microbial Fuel Cells. *ACS Appl. Mater. Interfaces* **2013**, *5* (16), 7862–7866.
- (12) Chen, G.; Wei, B.; Luo, Y.; Logan, B. E.; Hickner, M. A. Polymer Separators for High-Power, High-Efficiency Microbial Fuel Cells. *ACS Appl. Mater. Interfaces* **2012**, *4* (12), 6454–6457.
- (13) Watson, V. J.; Delgado, C. N.; Logan, B. E. Influence of Chemical and Physical Properties of Activated Carbon Powders on Oxygen Reduction and Microbial Fuel Cell Performance. *Environ. Sci. Technol.* **2013**, *47* (12), 6704–6710.
- (14) Zhang, F.; Cheng, S.; Pant, D.; Van Bogaert, G.; Logan, B. E. Power Generation Using an Activated Carbon and Metal Mesh Cathode in a Microbial Fuel Cell. *Electrochem. Commun.* **2009**, *11* (11), 2177–2179.
- (15) Watson, V. J.; Delgado, C. N.; Logan, B. E. Improvement of Activated Carbons as Oxygen Reduction Catalysts in Neutral Solutions by Ammonia Gas Treatment and Their Performance in Microbial Fuel Cells. *J. Power Sources* **2013**, *242*, 756–761.
- (16) Dong, H.; Yu, H.; Wang, X.; Zhou, Q.; Feng, J. A Novel Structure of Scalable Air Cathode without Nafion and Pt by Rolling Activated Carbon and Ptfе as Catalyst Layer in Microbial Fuel Cells. *Water Res.* **2012**, *46*, 5777–5787.
- (17) Dong, H.; Yu, H.; Wang, X. Catalysis Kinetics and Porous Analysis of Rolling Activated Carbon-Ptfе Air-Cathode in Microbial Fuel Cells. *Environ. Sci. Technol.* **2012**, *46* (23), 13009–13015.
- (18) Wang, X.; Gao, N.; Zhou, Q.; Dong, H.; Yu, H.; Feng, Y. Acidic and Alkaline Pretreatments of Activated Carbon and Their Effects on the Performance of Air-Cathodes in Microbial Fuel Cells. *Bioresour. Technol.* **2013**, *144*, 632–636.
- (19) Wei, B.; Tokash, J. C.; Chen, G.; Hickner, M. A.; Logan, B. E. Development and Evaluation of Carbon and Binder Loading in Low-Cost Activated Carbon Cathodes for Air-Cathode Microbial Fuel Cells. *RSC Adv.* **2012**, *2* (33), 12751–12758.
- (20) Gong, K.; Du, F.; Xia, Z.; Durstock, M.; Dai, L. Nitrogen-Doped Carbon Nanotube Arrays with High Electrocatalytic Activity for Oxygen Reduction. *Science* **2009**, *323* (5915), 760–764.
- (21) Qu, L.; Liu, Y.; Baek, J.-B.; Dai, L. Nitrogen-Doped Graphene as Efficient Metal-Free Electrocatalyst for Oxygen Reduction in Fuel Cells. *ACS Nano* **2010**, *4* (3), 1321–1326.
- (22) Shi, X.; Feng, Y.; Wang, X.; Lee, H.; Liu, J.; Qu, Y.; He, W.; Kumar, S. M. S.; Ren, N. Application of Nitrogen-Doped Carbon Powders as Low-Cost and Durable Cathodic Catalyst to Air-Cathode Microbial Fuel Cells. *Bioresour. Technol.* **2012**, *108*, 89–93.
- (23) Lai, L.; Potts, J. R.; Zhan, D.; Wang, L.; Poh, C. K.; Tang, C.; Gong, H.; Shen, Z.; Lin, J.; Ruoff, R. S. Exploration of the Active Center Structure of Nitrogen-Doped Graphene-Based Catalysts for Oxygen Reduction Reaction. *Energy Environ. Sci.* **2012**, *5* (7), 7936–7942.
- (24) Ding, W.; Wei, Z.; Chen, S.; Qi, X.; Yang, T.; Hu, J.; Wang, D.; Wan, L.-J.; Alvi, S. F.; Li, L. Space-Confinement-Induced Synthesis of Pyridinic- and Pyrrolic-Nitrogen-Doped Graphene for the Catalysis of Oxygen Reduction. *Angew. Chem., Int. Ed.* **2013**, *52* (45), 11755–11759.
- (25) Wen, Z.; Ci, S.; Zhang, F.; Feng, X.; Cui, S.; Mao, S.; Luo, S.; He, Z.; Chen, J. Nitrogen-Enriched Core-Shell Structured Fe/Fe₃C-C Nanorods as Advanced Electrocatalysts for Oxygen Reduction Reaction. *Adv. Mater.* **2012**, *24* (11), 1399–1404.
- (26) He, Z.; Wagner, N.; Minter, S. D.; Angenent, L. T. An Upflow Microbial Fuel Cell with an Interior Cathode: Assessment of the Internal Resistance by Impedance Spectroscopy. *Environ. Sci. Technol.* **2006**, *40* (17), 5212–5217.
- (27) Wang, X.; Cheng, S.; Feng, Y.; Merrill, M. D.; Saito, T.; Logan, B. E. Use of Carbon Mesh Anodes and the Effect of Different Pretreatment Methods on Power Production in Microbial Fuel Cells. *Environ. Sci. Technol.* **2009**, *43* (17), 6870–6874.
- (28) Zhu, Y.; Murali, S.; Stoller, M. D.; Ganesh, K. J.; Cai, W.; Ferreira, P. J.; Pirkle, A.; Wallace, R. M.; Cychosz, K. A.; Thommes, M.; Su, D.; Stach, E. A.; Ruoff, R. S. Carbon-Based Supercapacitors Produced by Activation of Graphene. *Science* **2011**, *332* (6037), 1537–1541.
- (29) Wen, Z.; Wang, X.; Mao, S.; Bo, Z.; Kim, H.; Cui, S.; Lu, G.; Feng, X.; Chen, J. Crumpled Nitrogen-Doped Graphene Nanosheets with Ultrahigh Pore Volume for High-Performance Supercapacitor. *Adv. Mater.* **2012**, *24* (41), 5610–5616.
- (30) Popat, S. C.; Ki, D.; Rittmann, B. E.; Torres, C. I. Importance of Oh- Transport from Cathodes in Microbial Fuel Cells. *Chemosphere* **2012**, *5* (6), 1071–1079.
- (31) Feng, Y.; Shi, X.; Wang, X.; Lee, H.; Liu, J.; Qu, Y.; He, W.; Kumar, S. M. S.; Kim, B. H.; Ren, N. Effects of Sulfide on Microbial Fuel Cells with Platinum and Nitrogen-Doped Carbon Powder Cathodes. *Biosens. Bioelectron.* **2012**, *35* (1), 413–415.