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Use of Pyrolyzed Iron Ethylenediaminetetraacetic Acid Modified Activated Carbon as Air−Cathode Catalyst in Microbial Fuel Cells

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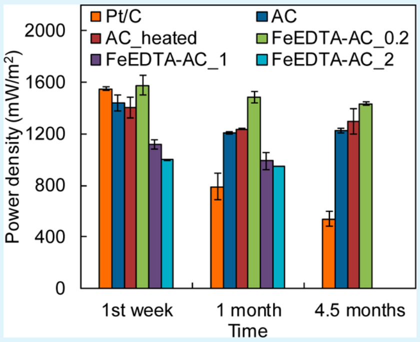
Supporting Information

ABSTRACT: Activated carbon (AC) is a cost-effective catalyst for the oxygen reduction reaction (ORR) in air-cathode microbial fuel cells (MFCs). To enhance the catalytic activity of AC cathodes, AC powders were pyrolyzed with iron ethylenediaminetetraacetic acid (FeEDTA) at a weight ratio of FeEDTA:AC = 0.2:1. MFCs with FeEDTA modified AC cathodes and a stainless steel mesh current collector produced a maximum power density of 1580 ± 80 mW/m^2, which was 10% higher than that of plain AC cathodes (1440 ± 60 mW/m^2) and comparable to Pt cathodes (1550 ± 10 mW/m^2). Further increases in the ratio of FeEDTA:AC resulted in a decrease in performance. The durability of AC-based cathodes was much better than Pt-catalyzed cathodes. After 4.5 months of operation, the maximum power density of Pt cathode MFCs was 50% lower than MFCs with the AC cathodes. Pyridinic nitrogen, quaternary nitrogen and iron species likely contributed to the increased activity of FeEDTA modified AC. These results show that pyrolyzing AC with FeEDTA is a cost-effective and durable way to increase the catalytic activity of AC.



KEYWORDS: *microbial fuel cell, oxygen reduction reaction, catalyst, activated carbon, iron ethylenediaminetetraacetic acid*

INTRODUCTION

Microbial fuel cells (MFCs) are devices that can convert chemical energy in organic matter directly to electricity using bacteria,[1] and they are a promising technology for wastewater treatment.[2] For the scale up of MFCs, the air cathode is the most useful configuration because of the inexhaustible availability, high redox potential of oxygen reduction and the avoidance of energy intensive water aeration. Catalysts are needed to reduce the overpotential for oxygen reduction, and Pt is commonly used in lab-scale reactors. However, Pt is very expensive and its performance degrades over time.[3,4] These factors limit the development of large-scale systems and widespread applications of MFCs. Other non-noble metal catalysts have been explored to replace Pt, such as transition metal macrocyclic complexes.[5] Fe and Co used in conjunction with these complexes (e.g., CoTMPP), however, resulted in catalyst costs that were just as much as Pt due to the high loadings needed for these catalysts. Thus, from an economic perspective they offer no advantages compared to Pt.[6] In addition, these Fe and Co-based cathodes have been made using expensive materials such as carbon cloth and a Nafion binder. Metal oxides[7] have also been explored as cathode catalysts, but these have relatively low performance. Therefore, whereas cathodes with these non-noble metals have previously been used in MFCs, their costs remain too high to justify their use in larger-scale MFC systems.

Activated carbon (AC) has been shown to be a more cost-effective alternative catalyst to Pt than other metal-based macrocyclic complexes for oxygen reduction in MFCs due to its low costs, when used in combination with inexpensive current collectors.[8,9] Cathodes made by pressing AC onto metal stainless steel (SS) mesh resulted in performance comparable to Pt cathodes with carbon cloth as current collector, at a much reduced overall cost.[8,10] To improve the performance of AC cathodes, Wei et al. optimized oxygen reduction kinetics by varying AC loadings. Increasing the AC loading from 7 to 43 mg/cm^2 improved power production, but further increases from 43 to 100 mg/cm^2 did not appreciably improve performance.[10] This suggested that there was a balance in the AC loading and cathode thickness. In that study, the performance of AC cathodes constructed from SS was only compared to Pt on carbon cloth, and not on SS.[10] The long-term performance of Pt on SS mesh cathodes has not been investigated, despite the economic advantages of these materials for large scale applications.[11]

Cathode performance typically limits power production in MFCs, and thus improving the catalytic performance of the AC, without substantially increasing material costs, is very important for constructing inexpensive but larger-scale MFCs. Fe appears

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to be a logical choice for improving the performance, but previous requirements for expensive macrocyclic complexes, carbon cloth, or binders needed to be eliminated. The catalyst also needs to function effectively directly with air, avoiding the need for energy-intensive water aeration for aqueous cathodes. Aelterman et al.[12] first proposed using iron ethylenediaminetetraacetic acid (FeEDTA) without pyrolysis in graphite felt and activated cloth cathodes. However, the power densities produced were low (40.3 W/m^3) relative to those achieved with Pt-based or AC cathodes (115 W/m^3).[13] Graphite felt and activated cloth have much lower oxygen reduction reaction (ORR) catalytic activity than AC, and their system required the use of expensive carbon cloth and cathode wetting. Wang et al.[14] recently proposed the use of pyrolyzed FeEDTA, but this material was used only with carbon black, which also has less catalytic activity relative to AC, and expensive materials were used that included carbon cloth and a Nafion binder.

To create a more efficient but inexpensive ORR catalyst, we examined here the use of pyrolyzed FeEDTA[14] in combination with AC. To determine optimum conditions for FeEDTA addition, the amount of FeEDTA added was varied, and the specific surface areas of FeEDTA modified AC (FeEDTA-AC) powders were measured and evaluated in MFCs and electrochemical tests. In addition, we further examined the long-term stability of these AC cathodes modified with different ratios of FeEDTA to AC, and compared them to Pt cathodes made using the same SS mesh as current collector after 4 months of continuous operation. Long-term stability had not been previously examined in any studies using FeEDTA, and the performance of Pt/C cathodes is known to quickly degrade even after as little time as a month of operation.[3,4]

■ EXPERIMENTAL SECTION

Cathodes. AC powder (Norit SX plus, Norit Americas Inc., TX) was pretreated with FeEDTA chelate by a previously described method used only on carbon-based materials other than AC.[14] Briefly, a solution containing 20 mM $FeCl_3 \cdot 6H_2O$ and 20 mM EDTA-2Na was prepared to form a FeEDTA chelate. Then, AC powder was added into FeEDTA solution to obtain suspensions with weight ratios of ($FeCl_3$ + EDTA-2Na) to AC of 0.2:1 (FeEDTA-AC_0.2), 1:1 (FeEDTA-AC_1), and 2:1 (FeEDTA-AC_2). The dosage of FeEDTA was selected based on previous studies.[12,14] Other FeEDTA dosages were not tested as the main focus of this study was to examine the feasibility of modifying AC cathodes with FeEDTA. These suspensions were then dried with stirring at ~80 °C. The dried powders were pyrolyzed under argon gas at 800 °C (optimal temperature based on previous studies[15−17]) for 1.5 h with a heating rate of 5 °C/min to obtain FeEDTA-AC.

FeEDTA-AC cathodes were constructed on SS mesh current collectors (50 × 50, type 304, McMaster-Carr, OH) by a press method.[10] For the catalyst layer, a mixture of 43 mg/cm^2 FeEDTA-AC powder and polytetrafluoroethylene (PTFE) at a weight ratio of 9:1 was spread on one side of the SS mesh. The diffusion layer was prepared by applying two layers of a poly(dimethylsiloxane) (PDMS) solution[11] onto a textile material (Amplitude Prozorb, Contec Inc., USA), that was then placed on the air-side of the cathode.[10] The cathode and textile were then pressed together at 40 MPa for 20 min (Model 4386, Carver Inc., USA) and dried at 80 °C overnight before use.

Cathodes were also made using untreated AC and heat-treated AC (argon gas, 800 °C for 1.5 h) as controls using the same press method. Pt cathodes were made by painting a Pt catalyst layer (5 mg/cm^2 10% Pt on Vulcan XC-72 and Nafion binder) on the solution side of the cathode, and two layers of PDMS on the air-side of a SS mesh.[11]

MFC Construction and Operation. Single-chamber, cubic-shaped MFCs were constructed from 4 cm long blocks of Lexan, with an inner cylindrical chamber 3 cm in diameter.[18] The anode was a 450 °C heat-treated carbon fiber brush (2.5 cm in diameter and 2.5 cm in length) with a titanium wire core[19] that was placed horizontally in the cylindrical chamber with the edge 1 cm from the cathode.

Reactors were inoculated with the effluent of an MFC operated for over one year. The medium (pH 7.2) contained sodium acetate (1.0 g/L) and a 50 mM phosphate buffer solution (PBS) containing Na_2HPO_4, 4.58 g/L; $NaH_2PO_4 \cdot H_2O$, 2.45 g/L; NH_4Cl, 0.31 g/L; KCl, 0.13 g/L; trace minerals (12.5 mL/L), and vitamins (5 mL/L).[20] All the reactors were operated in fed-batch mode with a 1000 Ω external resistor at 30 °C.

Analyses. Chronoamperometry tests were carried out using a potentiostat (VMP3, BioLogic, USA) in an abiotic electrochemical cell containing 50 mM PBS. The configuration of this cell was the same as that of the MFC reactor, except that the carbon brush anode was replaced by a platinum mesh. A three electrode arrangement was used as previously described.[10] To evaluate the abiotic electrochemical performance of cathodes under normal operating conditions of MFCs, the cathode potential was applied in a stepwise manner (0.4, 0.3, 0.2, 0.1, 0 V vs. SHE) to a reactor originally operated at an open circuit for 3 h. Each potential was set for 2 h to obtain steady state conditions.

In MFC tests, voltages across the external resistor were measured at 20 min intervals using a data acquisition system (2700, Keithley Instrument, Cleveland, OH). Polarization and power density curves were obtained by varying the external resistance, with one resistor used for a full fed-batch cycle (multicycle method). Tests were conducted in the first week, after 1 and 4.5 months of operation. Current and power densities were normalized to the projected surface area of the cathode (7 cm^2). All experiments were conducted in duplicate.

The specific surface areas of plain AC, heated AC, and FeEDTA-AC powders were obtained by the Brunauer−Emmett−Teller (BET) adsorption isotherm method, and the surface functional groups were determined by X-ray photoelectron spectroscopy (XPS). XPS was performed with an Axis Ultra XPS (Kratos Analytical, Manchester, U.K.). A quick survey scan was completed for each sample to identify the elements present with a high generation energy and short dwell time. High-resolution scans for quantification and chemical state information were collected afterward with a low generation energy and long dwell time.

■ RESULTS AND DISCUSSION

Electrochemical Performance of New Cathodes. Chronoamperometry tests on new cathodes under abiotic conditions showed that FeEDTA modified AC cathode with a ratio of FeEDTA to AC of 0.2:1 (FeEDTA-AC_0.2) had the highest current density in the potential range of 0.3−0 V vs. SHE (Figure 1). The electrochemical performance decreased with a further increase in the ratio of FeEDTA to AC. Heat-treated AC cathode (no FeEDTA) produced a slightly higher

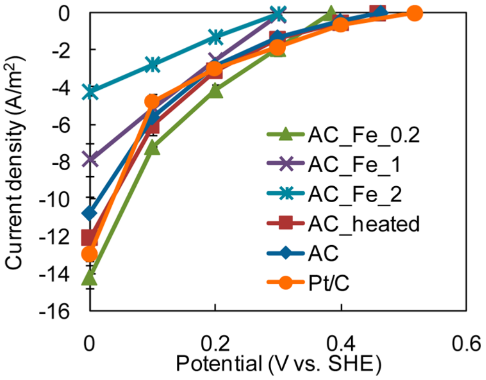

Figure 1. Current−potential curves of cathodes made with FeEDTA modified AC, AC heated under argon gas, plain AC, and Pt/C.

current density than the plain AC cathode, and the performance of the Pt cathode was similar with those of the AC and heat-treated AC cathodes.

MFC Performance and Durability. The FeEDTA-AC cathode with a FeEDTA to AC ratio of 0.2:1 (FeEDTA-AC_0.2) produced a maximum power densities of 1580 ± 80 mW/m^2 in the first week, which was 10% higher than that of the plain AC cathode (1440 ± 60 mW/m^2) and comparable to that produced using the Pt cathode (1550 ± 10 mW/m^2) (Figure 2A). The maximum power density decreased to 1120 ± 40 mW/m^2 (FeEDTA-AC_1) and 1000 ± 0 mW/m^2 (FeEDTA-AC_2) with further FeEDTA loadings. MFCs with heat-treated AC cathodes produced a power density (1410 ± 80 mW/m^2) similar to that of the plain AC cathodes. Anode potentials were essentially the same in all the MFCs, indicating the cathode potentials were the reason for the different levels of power production (Figure 2B). These cathode polarization results were consistent with the chronoamperometry results of new cathodes.

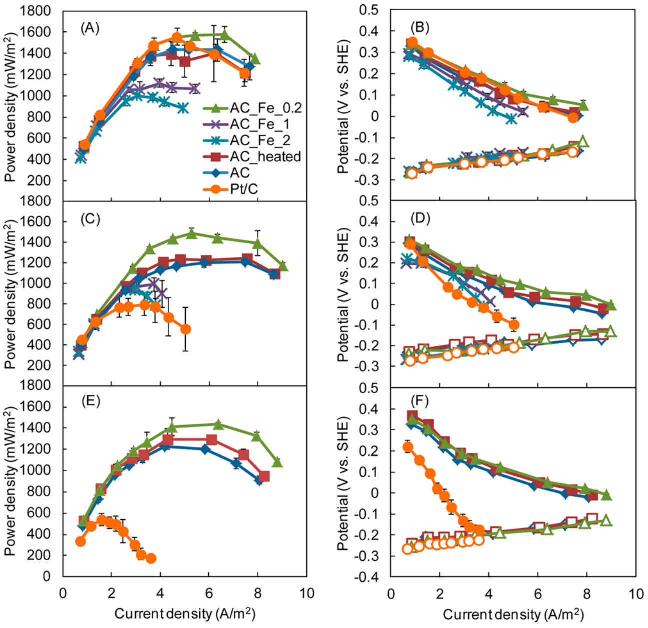

Figure 2. (A, C, E) Power densities and (B, D, F) electrode potentials (cathode, filled symbols; anode, open symbols) of MFCs with different cathodes as a function of current density. Multicycle polarization was carried out (A, B) in the first week, (C, D) after 1 month, and (E, F) after 4.5 months. Error bars are based on duplicate reactors.

These results show that the catalytic activity of AC could be enhanced by modifying it with low concentrations of pyrolyzed FeEDTA, but that high amounts of FeEDTA decreased performance. The enhanced catalytic activity of FeEDTA-AC with a ratio of FeEDTA to AC of 0.2:1 (FeEDTA-AC_0.2) likely resulted from the synergetic effects of the pyrolyzed FeEDTA and AC. As all the AC related cathodes in this study were constructed from 43 mg/cm^2 catalysts (the total mass of AC and FeEDTA was 43 mg/cm^2), it was likely that the reduced activity of the FeEDTA-AC cathodes with higher FeEDTA to AC ratios (FeEDTA-AC_1 and FeEDTA-AC_2) was due to the decrease in the active sites on AC, even though the amount of FeEDTA was increased, as further discussed below.

After 1 month of operation, the maximum power densities of the MFCs with plain AC, heated AC and FeEDTA-AC cathodes decreased by 4−16% (Figure 2C). MFCs with FeEDTA-AC cathodes at a FeEDTA to AC ratio of 0.2:1 still showed the highest power densities, with a maximum of 1490 ± 40 mW/m^2. This was 24% higher than that with the plain AC cathodes (1210 ± 10 mW/m^2). The maximum power density of the MFCs with heated AC cathodes (1240 ± 10 mW/m^2) in this period was slightly higher than that with plain AC cathodes, while power densities for the FeEDTA-AC cathodes with higher FeEDTA loadings were much lower (990 ± 70 mW/m^2 for FeEDTA-AC_1; 950 ± 0 mW/m^2 for FeEDTA-AC_2). However, the maximum power density of MFCs with the Pt cathodes decreased by 49%, to only 790 ± 100 mW/m^2. These differences in power generation mainly resulted from cathode performance as the anode potentials were similar (Figure 2D). Although plain AC, heated AC, and FeEDTA-AC (with a ratio of FeEDTA to AC of 0.2:1) cathodes could sustain a current density higher than 8.5 A/m^2, the maximum current density of Pt cathode was now lower than 4 A/m^2.

After 4.5 months, the maximum power density of the plain AC, heated AC, and FeEDTA-AC (with a ratio of FeEDTA to AC of 0.2:1) cathodes did not show appreciable changes in performance, but the Pt cathode MFCs decreased to 540 ± 60 mW/m^2 (Figure 2E, F). This maximum power density with Pt cathode MFCs was more than 50% lower than the other cathodes at the end of this study. Tests with the FeEDTA-AC cathodes with higher FeEDTA loadings (FeEDTA-AC_1 and FeEDTA-AC_2) were discontinued after the second month because of their low power production.

These results demonstrated that AC-based cathodes with SS mesh were much more durable than Pt cathodes over time. It was previously reported that the durability of Pt cathodes on carbon cloth was similar to that of AC cathodes on SS mesh.[10] Our study demonstrated that the performance of Pt cathodes degraded much faster when SS mesh was used as current collector compared to carbon cloth. As SS mesh is much looser than carbon cloth, the rapid decline in the performance of Pt cathodes on SS mesh in our study may have been due to increased biofilm growth on the solution side of cathodes due to higher rates of oxygen crossover through the more porous SS cathode. For AC-based cathodes, biofilm growth might be slower than Pt cathodes because they are much thicker (~1.2 mm for AC cathodes, ~0.5 mm for Pt cathodes). In addition, the whole AC cathode can be catalytically active, while the Pt catalyst activity is restricted to the cathode surface exposed to the water. Although the performance of AC cathodes could not be improved by simply increasing the AC loading,[10] here we provided an effective and inexpensive method that can further increase the catalytic activity of AC cathodes. The FeEDTA modified AC cathodes are promising for large-scale applications as they have shown greater stability than plain AC.

Specific Surface Areas and Functional Groups. The specific surface area of FeEDTA-AC powder with a ratio of FeEDTA to AC of 0.2:1 (FeEDTA-AC_0.2, 810 ± 5 m^2/g) was 8% lower than that of plain AC (883 ± 5 m^2/g), and the surface area decreased significantly with an increase in the ratio of FeEDTA to AC (518 ± 3 m^2/g for FeEDTA-AC_1; 267 ± 1 m^2/g for FeEDTA-AC_2) (Figure 3). This was expected as the main contributor to the surface area was the AC, and the amount of AC decreased with an increase in FeEDTA. The specific surface area of AC with heat treatment (922 ± 6 m^2/g) was slightly higher than that of plain AC, which explained its

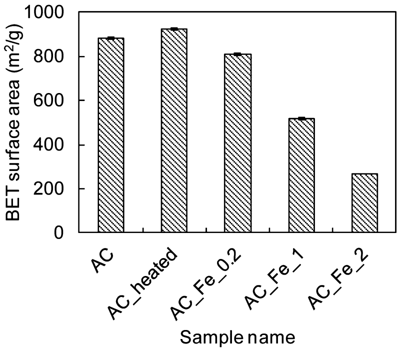

Figure 3. BET surface area of plain AC powder, AC powder heated under argon gas, and AC powder modified with different ratios of FeEDTA.

higher electrochemical performance compared to the plain AC cathodes. The maximum power densities during the first week were normalized to the BET surface area (see Figure S2 in the Supporting Information). Although the power density normalized to surface area was not increased by heat treatment, it improved with the addition of FeEDTA. This further demonstrated that modifying AC with FeEDTA could increase the catalytic activity per unit surface area. The decrease in cathode performance at higher FeEDTA loadings (FeEDTA-AC_1 and FeEDTA-AC_2) was due to their decreased surface area.

The surface composition of these materials, based on XPS analysis, showed that the plain and heated AC mainly contained C and O, and that heat treated samples had increased C (from 96.7% to 98.1%) and decreased O contents (from 3.3% to 1.9%). Pyrolyzing the AC with FeEDTA introduced N, Fe, Na and Cl heteroatoms onto the surface structure, and the relative content of these atoms increased with the amount of FeEDTA ratio (data not shown). Adding more FeEDTA decreased the atomic ratio of carbon, but it did not change the shape of its XPS spectra (Figure 4A), indicating that carbon chemical state did not exhibit appreciable changes. Most AC samples had peaks with a large background noise in the N1s spectra (Figure 4B). FeEDTA-AC sample with a ratio of FeEDTA to AC of 2:1 had the largest peaks at 398 and 401 eV. The peak at 398 eV can be attributed to pyridinic nitrogen, while the peak at 401 eV was assigned to quaternary nitrogen,[21] indicating that these two functional groups were bonded to the carbon matrix by pyrolyzing AC with FeEDTA. The AC treated with FeEDTA showed increased Fe peaks in the Fe2p spectra at 711 and 725 eV (Figure 4C). According to previous reports, Fe2p peaks at 711 eV are due to Fe (III) species coordinated to nitrogen[22] or oxygen,[23] and the peak at 725 eV would indicate the presence of iron oxide.[23]

The pyridinic nitrogen is a type of nitrogen that can be found on the edge of a carbon plane and a carbon vacancy, and the quaternary nitrogen bonds to three carbon atoms in the plane of the carbon matrix (see Figure S1 in the Supporting Information). It is known that the pyridinic and quaternary nitrogens on the carbon matrix enhance chemisorption of O_2, and that they weaken the O−O bond.[24,25] These two functional groups increase the electron-donating ability of nitrogen-containing carbon-based catalysts.[24,25] Transition metals like Fe can stabilize the incorporation of nitrogen within the carbon matrix and facilitate the disproportionation of H_2O_2.[24,26] Therefore, it was suggested that the increased catalytic activity of the FeEDTA-AC cathodes with a FeEDTA loading of 0.2 (FeEDTA-AC_0.2) resulted from the pyridinic nitrogen, quaternary nitrogen, and iron species on the carbon matrix. AC modified with the highest loading of FeEDTA (FeEDTA-AC_2) had the highest amount of N, but it did not produce high power in MFC tests, probably because of its lower surface area than other AC samples.

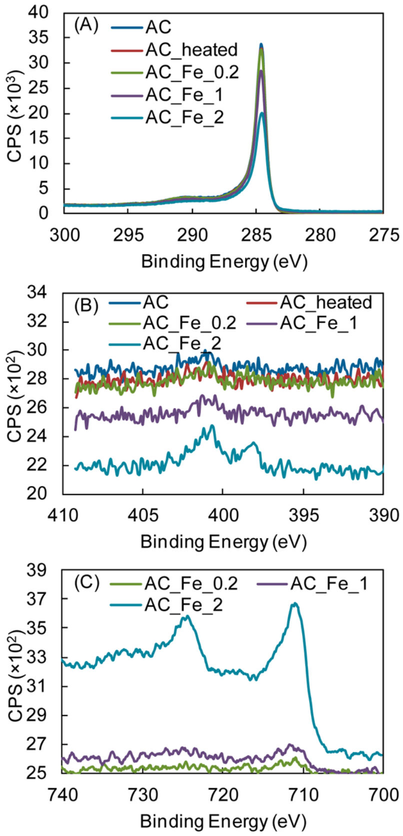

Figure 4. (A) C1s, (B) N1s, and (C) Fe2p XPS spectra of plain AC powder, AC powder heated under argon gas, and AC powder modified with different ratios of FeEDTA.

■ CONCLUSIONS

The catalytic activity of AC for ORR was enhanced by pyrolyzing it with low concentrations of iron EDTA chelate. MFCs with FeEDTA-AC_0.2 cathodes produced a maximum power density of 1580 mW/m^2, which was 10% higher than that of the plain AC cathodes (1440 mW/m^2) and comparable to that obtained with Pt cathodes (1550 mW/m^2). The durability of the AC based cathodes over time was much higher than observed for the Pt cathodes with a SS mesh current collector. The maximum power densities of MFCs with AC based cathodes decreased by 4−16% after 1 month of operation, and then did not show appreciable changes. The maximum power density of MFCs with FeEDTA-AC_0.2 cathodes (1490 mW/m^2) was 24% higher than that obtained with the plain AC cathodes (1210 mW/m^2) after 1 month. In contrast, the maximum power density of Pt cathode MFCs decreased by 49% to 790 mW/m^2 after one month, and declined further to 540 mW/m^2 after 4.5 months. The increased catalytic activity of FeEDTA-AC cathodes was attributed to pyridinic nitrogen, quaternary nitrogen, and iron species.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Example of the structure of pyridinic nitrogen and maximum power densities normalized to BET surface area. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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