



Short communication

Mesoporous nitrogen-rich carbon materials as cathode catalysts in microbial fuel cells



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HIGHLIGHTS

- MNC was examined as an oxygen reduction catalyst for MFC cathodes.
- Maximum power of 979 mW m⁻² was only 14% less than cathodes with Pt.
- One month of operation decreased power less (7%) than the Pt cathode (11%).
- COD and CE were not affected by the use of MNC catalysts.

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ABSTRACT

The high cost of the catalyst material used for the oxygen reduction reaction in microbial fuel cell (MFC) cathodes is one of the factors limiting practical applications of this technology. Mesoporous nitrogen-rich carbon (MNC), prepared at different temperatures, was examined as an oxygen reduction catalyst, and compared in performance to Pt in MFCs and electrochemical cells. MNC calcined at 800 °C produced a maximum power density of 979 ± 131 mW m⁻² in MFCs, which was 37% higher than that produced using MNC calcined at 600 °C (715 ± 152 mW m⁻²), and only 14% lower than that obtained with Pt (1143 ± 54 mW m⁻²). The extent of COD removal and coulombic efficiencies were the same for all cathode materials. These results show that MNC could be used as an alternative to Pt in MFCs.

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1. Introduction

Microbial fuel cells (MFCs) are being developed as a technology to achieve simultaneous energy recovery and wastewater treatment [1]. Air cathode MFCs are more practical than other types of cathode configurations because they use passive transfer to provide oxygen at the cathode as an electron acceptor. Power production from MFCs can be limited by the overpotential of the oxygen reduction reaction (ORR) at the cathode. Pt is a commonly used catalyst used to reduce this overpotential, but it is very expensive

and rapidly fouls in wastewater. Several different types of catalyst have been tested for use in MFCs, including non-noble metal, metal oxides, and carbon [2,3]. Of these, carbon materials are especially promising as ORR catalysts as they are environmentally sustainable. Different types of carbon materials primarily investigated so far for ORR in MFCs are carbon nanotubes and activated carbon [4–6]. Nitrogen functionalized carbon nanotubes have been shown to have high catalytic activity for ORR [7]. The procedures to make these materials have required several synthesis steps, long preparation time, and they can possibly damage of nanotubes during functionalization. The enhanced catalytic activity is thought to be due to production of nitrogen-containing carbon materials that are pyridinic or pyrrole/pyridine, and/or quaternary types of nitrogen [8–10]. Preparation of carbon materials with good ORR properties

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therefore has required chemical pretreatments with reactive species such as HNO_3 , NH_3 , or HCN [11–13].

Recently, a new type of mesoporous carbon nitrogen-rich carbon (MNC) material has attracted a great deal of interest for ORR [14] due to cost-effectiveness, high durability, and its unique structural properties, such as high specific surface area, pore volume, tuneable pore sizes, relative inertness and resistivity towards high pressure and temperatures. More importantly, it has graphite-like and pyridine-like N atoms, and each carbon atom bonds with three nitrogen atoms. MNC can be readily produced in gram quantities, and it does not need to be further modified (like CNTs) to introduce oxygen and nitrogen functional groups. To our knowledge, there have been no reports on the activity of these MNC materials in the near neutral to slightly alkaline (near the cathode) conditions in MFCs.

In this study, we explored the performance of MNC materials as a possible cathode catalyst in MFCs. The MNC materials were synthesized by pyrolyzing polymerized ethylenediamine, and nanocasted on an SBA 15 hard template [15] at two different temperatures (600 °C and 800 °C) to examine the influence of active sites in the kinetics of the ORR reaction. MNC-loaded cathodes with different catalyst loadings were compared to the Pt-based cathode in MFCs as well as in abiotic electrochemical cells.

2. Material and methods

2.1. Catalysts and cathodes

The mesoporous nitrogen-rich carbon materials were synthesized using SBA 15 as a hard template as previously described [15]. Briefly SBA 15 was synthesized using tetraethylorthosilicate (TEOS) as a silica source, and poly (ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) triblock copolymer (Aldrich, MW avg. 5800, EO20PO70EO20, P123) as a structure-directing agent. P123 block copolymer (4.0 g) was dissolved in water (30.0 g) with continuous stirring. Then, 120.0 g of HCl (2 M) and 9.1 g of tetraethylorthosilicate (TEOS) were added at 40 °C. After 24 h of continuous stirring, the gel composition was held at 100 °C (no stirring) for 48 h. It was then cooled to room temperature and the solid product was recovered by filtering, washing, drying, and calcining at 550 °C to decompose the triblock copolymer. Dehydrated SBA 15 (1.0 g) was treated with a mixture of 4.5 g of ethylenediamine ($\text{NH}_2\text{C}_2\text{H}_4\text{NH}_2$) and 11 g of carbon tetrachloride (CCl_4). The mixture was refluxed at 90 °C for 6 h. The obtained solid mixture (polymer silica composite) was dried and calcined at two different temperatures (600 and 800 °C) for 6 h under an inert gas atmosphere. The calcined silica carbon composite was washed with 2.5% wt of NaOH solution in an ethanol water (1:1) mixture with vigorous stirring at 90 °C for 3 h to remove the silica framework. The process was repeated two additional times. Then, the product was filtered and washed with a water ethanol mixture until the filtrate pH was 7.0, and then it was dried.

Four different carbon cloth (30% wet-proofed, type B-1B, E-TEK) cathodes (7 cm² projected area) were made by applying different catalysts on the water-facing side, and applying four polytetrafluoroethylene (PTFE) diffusion layers on the air-facing side as previously described [16]. Catalysts were applied on the water-facing side using a Nafion binder. Catalyst loading was 0.5 mg cm⁻² for Pt/C, 6.6 mg cm⁻² for MNC-800L, and 25 mg cm⁻² for MNC-600, MNC-800 cathodes.

2.2. MFC construction and operation

Single-chamber, air cathode MFCs (28 mL) were constructed as previously described [16]. Each reactor (3 cm diameter inner

chamber, 4 cm in length) contained a graphite fiber brush anode (25 mm diameter × 25 mm length, Mill-Rose, Mentor, OH). The anodes were heat treated at 450 °C for 30 min. The MFCs were inoculated with domestic wastewater from the primary clarifier of the Pennsylvania State University Wastewater Treatment Plant, and operated in fed-batch mode (duplicate reactors) at 30 °C in a constant temperature room. Sodium acetate (1.0 g L⁻¹) was used as the energy source in a nutrient solution containing Na_2HPO_4 4.58 g L⁻¹, $\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}$ 2.45 g L⁻¹, NH_4Cl 0.31 g L⁻¹, KCl 0.13 g L⁻¹ (pH 7.1; conductivity 7.01 mS cm⁻¹). The reactors were refilled when the cell voltage decreased to <10 mV ($R_{\text{ext}} = 1000 \Omega$).

2.3. Analyses and calculations

The voltage (U) across an external resistor was measured every 20 min using a data acquisition system (Model 2700, Keithley Instruments) connected to a computer. Current (I) and power ($P = IU$) were calculated as previously described [1] and normalized by the projected surface area of the cathode. Polarization and power density curves were obtained by varying the external resistance used in the circuit (3 batch cycles per resistor, multiple cycle method). Additionally, the ORR activity of the cathodes in phosphate buffer was tested in the MFC reactors, under abiotic conditions (no bioanode), in a three-electrode configuration with Pt mesh (25 × 25 mm, 100 mesh) (Sigma-Aldrich, St Louis, MO) as the counter electrode, and using an Ag/AgCl as the reference electrode (211 mV vs a standard hydrogen electrode). The steady-state electrochemical response was assessed using chronoamperometry (180 s per step) at different potentials (duplicate tests). Coulombic efficiency (CE) was calculated using the ratio of the total coulombs produced during the experiment to the theoretical amount of coulombs available from the substrate added, as previously described [1]. COD was measured using a low range (0–150 mg L⁻¹) HACH COD system (Hach Co., Loveland, CO).

3. Results and discussion

3.1. Electrochemical performance

In the first series of electrochemical tests using the three-electrode set-up, the MNC loading (6.6 mg cm⁻², denoted as MNC-800L) was initially chosen to match that of the Pt (about

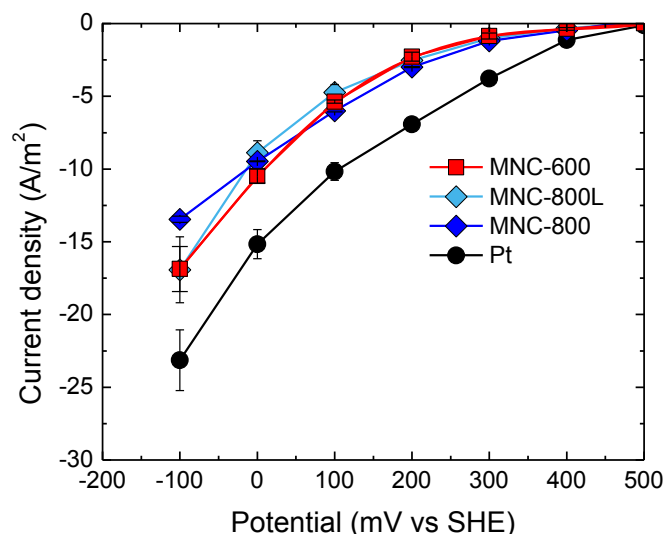


Fig. 1. Electrochemical test results on different cathodes.

5 mg cm⁻² 10% Pt on Vulcan XC-72) in order to maintain a similar amount of binder. The MNC-800L had an overpotential that was ~200 mV higher than the Pt/C cathode in the typical current range of an MFC (-0.3 V up to 0.1 V) (Fig. 1). This performance of the MNC-800L was lower than that previously reported in highly alkaline media [5]. Optimization experiments (data not shown) indicated that a 4 × higher catalyst loading (25 mg cm⁻², denoted as MNC-800) produced the best performance. Further increases in the catalyst loading did not significantly improve the cathode performance, and they resulted in mechanical instability of the electrode. The use of this higher catalyst loading decreased the overpotential of the MNC-800 to ~100 mV (Fig. 1). MNC prepared at 600 °C (MNC-600) was similar to that of the MNC-800L (Fig. 1), and it also produced an overpotential of about 200 mV. The results using the MNC-800 and MNC-600 are consistent with that previously observed in alkaline media [5].

3.2. Power production

There was no appreciable difference in start-up time between the MFCs with Pt or MNC cathodes. MFCs with a Pt cathode produced maximum voltage of 0.44 V ($R_{\text{ext}} = 1000 \Omega$) after 4.1 days, and MFCs with MNC cathode produced 0.42 V after 3.9 days following inoculation (data not shown). Polarization tests based on the multiple cycle method were conducted after 5 batch cycles to obtain power density curves. MFCs with Pt cathode produced a maximum power density of $1143 \pm 54 \text{ mW m}^{-2}$, followed by MNC-800L ($979 \pm 131 \text{ mW m}^{-2}$), MNC-800 ($950 \pm 114 \text{ mW m}^{-2}$) and MNC-600 ($715 \pm 152 \text{ mW m}^{-2}$) (Fig. 2A). The MNC-800 showed better performance than MNC-600 in both MFC and

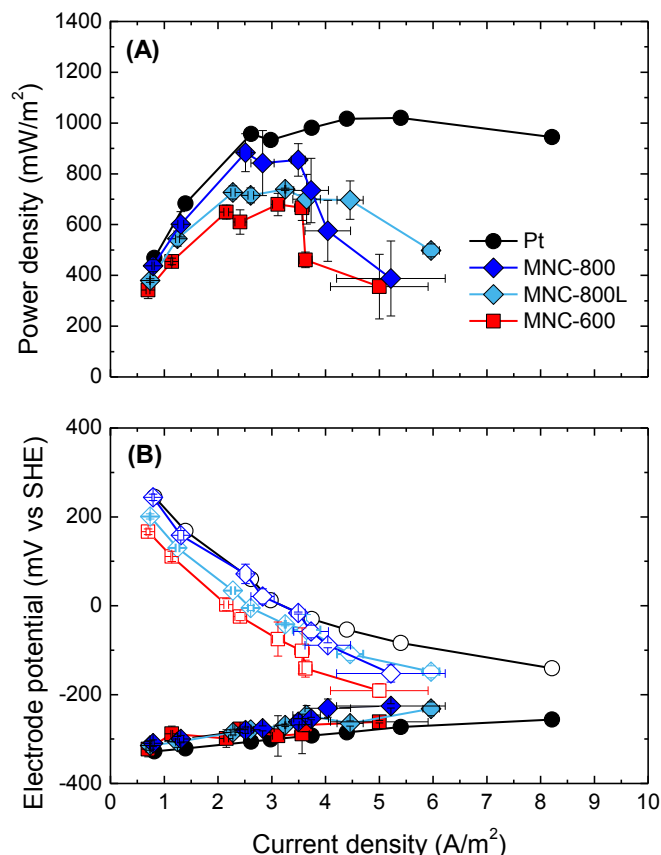


Fig. 3. (A) Power density curves and (B) electrode potentials (anode, filled symbols; cathode, open symbols) of MFC using different cathodes after 1 month of operation.

electrochemical tests, likely due to its higher surface area that resulted from the formation of larger number of micropores at the higher pyrolysis temperature [5].

The use of MNC catalysts in the MFCs primarily affected cathode performance (Fig. 2B). MFCs with MNC cathodes showed lower (<97 mV vs SHE) cathode potential than those from MFCs with Pt cathode. However, the anode performance of the MNC cathodes at high current density was not the same as that observed in the MFCs

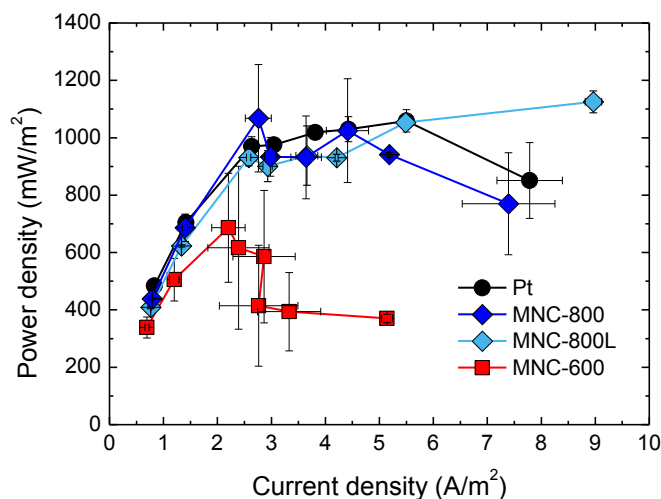


Fig. 4. Corrected power density curves following adjustment of the MNC anode potentials to match those of the Pt anodes.

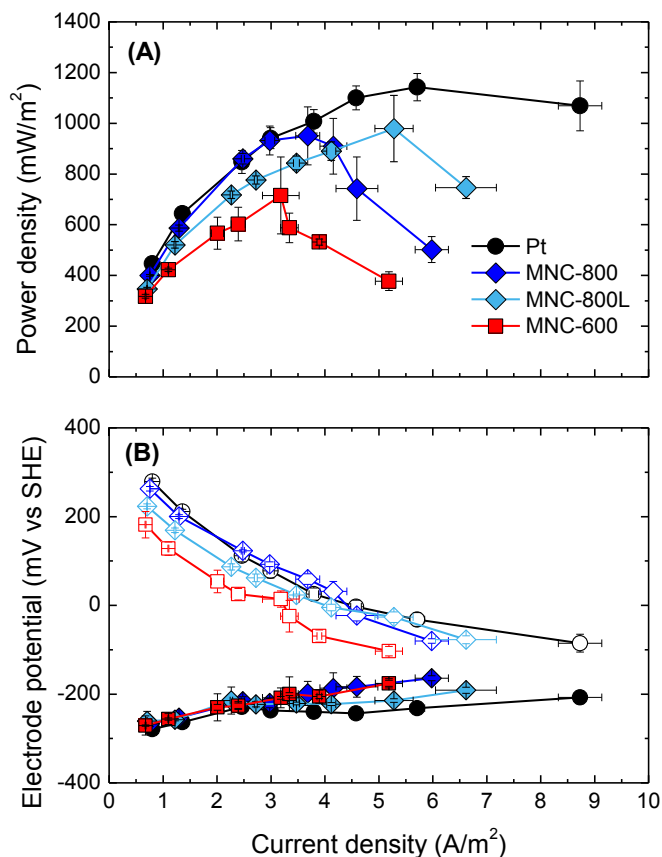


Fig. 2. (A) Power density curves and (B) electrode potentials (anode, filled symbols; cathode, open symbols) of MFC using different cathodes.

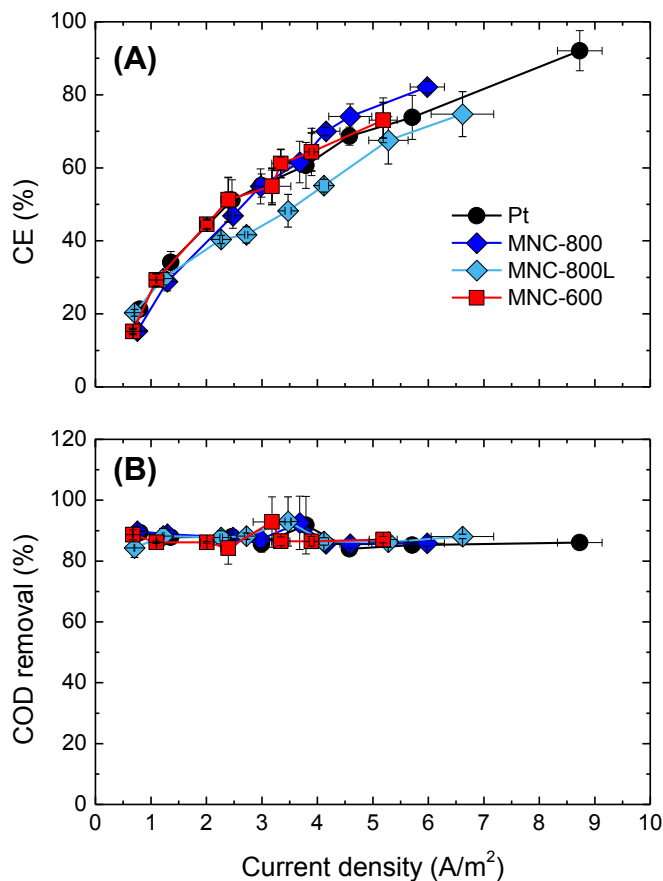


Fig. 5. (A) CEs and (B) COD removals for the MFCs with different cathodes.

with the Pt cathodes, as shown by slightly more positive anode potentials at the higher current densities. The decrease in anode performance could have been due to insufficient time for anode acclimation, which can lead to more serious anode failure known as power overshoot [17], or possibly some toxicity of the cathode materials. Polarization tests were then conducted again after another month of operation by first acclimating the reactors to a higher current density ($R_{ext} = 10 \Omega$), as this has been shown to reduce the possibility of power overshoot [17,18]. As a result of the longer period of time of continuous operation, the maximum power density of the MFCs with the Pt cathode had decreased by 11%–1021 mW m^{-2} , compared to 7% for MFCs with the MNC-800 cathode (883 mW m^{-2}). A decline in the Pt/C cathode performance is consistent with previous results that show that performance of the cathode decreases over time [19]. The anode potentials of the MFCs with the MNC, however, still seemed to be somewhat different than those in the Pt reactors at high current density (Fig. 3). The reason for this difference could not be identified.

In order to better directly compare the two cathode materials in the MFC test conditions, the polarization data were adjusted by assuming that anode potentials of MFCs with MNC cathode were same with that of MFCs with Pt cathode at each external resistance used in the test. The adjusted maximum power output from MFC with MNC-800L and MFC-800 cathodes following this adjustment were found to be comparable with the power from MFCs with Pt cathode (Fig. 4). These results suggest that better performance could have been obtained with the MNC materials if comparable performance could have been obtained with the anodes. The reasons for the slightly different anode performance will require further study.

3.3. COD removal and coulombic efficiency

The use of MNC cathode did not influence the extent of COD removal or CEs. Total COD removal ranged from $84 \pm 1\%$ to $92 \pm 2\%$ with Pt-MFCs, compared to $86 \pm 1\%$ to $93 \pm 8\%$ with MNC-MFCs (Fig. 5A). The Pt-MFCs achieved highest CE of $92 \pm 6\%$ with a $10\text{-}\Omega$ resistor, with the lowest CE = 21% at the highest resistance (Fig. 5B). The increase in the CE with current is consistent with previous results using Pt and activated carbon cathodes which show increases in CE with current [20–22]. Over a current density of $0.8\text{--}6.0 \text{ A m}^{-2}$, the CEs of MNC-600 and MNC-800 MFCs ranged from 15 to 82%, while the MFC with lower catalyst loading (MNC-800L) showed slightly lower CEs of 20–75%.

4. Conclusions

These experiments showed that MNC catalysts could be used to replace platinum in MFC cathodes. The maximum power density was $979 \pm 131 \text{ mW m}^{-2}$ with MNC-800 cathodes, which was only slightly lower than that obtained with Pt cathodes ($1143 \pm 54 \text{ mW m}^{-2}$). Both anode and cathode performance was slightly decreased using the MNC catalyst, which accounted for the slightly reduced performance. Catalyst stability is also important for MFC cathodes. After 1 month of operation the maximum power density decreased by 11% for Pt-MFCs, but less (only 7%) for the MNC-MFCs. There were no appreciable changes in CEs and COD removals over time. Thus, the MNC could be used as a more cost-effective cathode catalyst in MFCs used for power generation and wastewater treatment.

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