



Power generation using carbon mesh cathodes with different diffusion layers in microbial fuel cells

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ABSTRACT

An inexpensive carbon material, carbon mesh, was examined to replace the more expensive carbon cloth usually used to make cathodes in air-cathode microbial fuel cells (MFCs). Three different diffusion layers were tested using carbon mesh: poly(dimethylsiloxane) (PDMS), polytetrafluoroethylene (PTFE), and Goretex cloth. Carbon mesh with a mixture of PDMS and carbon black as a diffusion layer produced a maximum power density of $1355 \pm 62 \text{ mW m}^{-2}$ (normalized to the projected cathode area), which was similar to that obtained with a carbon cloth cathode ($1390 \pm 72 \text{ mW m}^{-2}$). Carbon mesh with a PTFE diffusion layer produced only a slightly lower (6.6%) maximum power density ($1303 \pm 48 \text{ mW m}^{-2}$). The Coulombic efficiencies were a function of current density, with the highest value for the carbon mesh and PDMS (79%) larger than that for carbon cloth (63%). The cost of the carbon mesh cathode with PDMS/Carbon or PTFE (excluding catalyst and binder costs) is only 2.5% of the cost of the carbon cloth cathode. These results show that low cost carbon materials such as carbon mesh can be used as the cathode in an MFC without reducing the performance compared to more expensive carbon cloth.

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1. Introduction

A microbial fuel cell (MFC) is a promising technology for renewable energy production because it enables direct transfer of chemical energy stored in a biodegradable organic matter into bio-electricity [1]. Although great progress has been achieved in the performance of a MFC in the past ten years [2–4], one of the main challenges for commercializing scalable MFCs is the cost of the electrode materials, particularly the cathode. MFCs can be operated using different electron acceptors, such as oxygen [2], ferric iron [5], manganese [6], and other chemicals such as nitrobenzene [7]. However, oxygen is the most suitable electron acceptor for the MFC due to its relatively high oxidation potential, availability, and sustainability [8]. Therefore, single-chamber air-cathodes are likely to be used for practical MFC applications.

Air cathodes are usually made by coating a catalyst (typically Pt) held with a binder onto carbon cloth on the water-facing side of the electrode, and using several layers of polytetrafluoroethylene (PTFE) as diffusion layers on the air-side of the cathode to reduce oxygen transfer and limit water losses [2]. However, the cost of fuel cell grade carbon cloth (*ca.* \$1000 m^{-2}) could limit cost-effective applications of MFCs. Recently, efforts have been made

to replace expensive carbon cloth with less expensive materials. For example, lower cost cathodes have been made by coating ion exchange and ultrafiltration membranes with electrically conductive coatings, avoiding the need for hot pressing membranes onto carbon cloth. However, the maximum power densities produced by these approaches have been relatively low [9,10]. Another alternative is to replace the carbon cloth with a current collector like stainless steel (SS) or nickel mesh, and to build a catalyst layer (Pt with carbon black, or activated carbon) around the mesh [11–13]. This approach appears promising in scaled up MFC systems, although low cost carbon fabrics may offer a competitive alternative approach when used in conjunction with inexpensive SS mesh (large pore sizes, and therefore low metal content). Carbon mesh has a very low cost of \$10–25 m^{-2} , which can be less than that of a fine mesh SS (\$80–135 m^{-2}) that needs to have small pore sizes to hold the catalyst and binder layers [14,15]. Carbon mesh has been successfully used as an anode in an MFC [14], but not yet tested as a cathode.

In order to use carbon-based materials as cathodes (carbon cloth, carbon mesh, or carbon coated SS), additional materials called diffusion layers have to be applied to the material in order to prevent water leakage or to reduce water losses by evaporation. In one recent test a SS mesh was coated with a polypyrrole/antraquinone-2-sulfonate (PPy/AQS) film as a diffusion layer [16]. Although this diffusion layer material was simpler to prepare than more typical chemicals, such as polytetrafluoroethylene (PTFE) due to the need for only a single-step in fabrication,

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the maximum power density achieved using the PPy/AQS diffusion layer was relatively low. Polydimethylsiloxane (PDMS) mixed with carbon black is a less expensive alternative to PTFE for a diffusion layer in an MFC, and it was recently shown that this diffusion layer could achieve similar performance to a PTFE diffusion layer with a SS mesh cathode [12]. Thus, the cost and performance of the diffusion layer is another important aspect of cathode design.

In this study, we tested carbon mesh cathodes constructed with several different diffusion layer materials, including Goretex cloth, PTFE, and PDMS. Goretex has previously been used in a different type of MFC cathode [17]. It is a good alternative to PTFE and PDMS coatings because it is a pre-manufactured material that is both waterproof and permeable to oxygen. Based on the manufacturer's data, there are more than 1.4×10^9 pores in per cm^2 of Goretex cloth. Previously, it was thought that carbon mesh could not be used as a cathode material due to its very loose weave, which could result in water leakage despite the application of a diffusion layer [14]. However, as we show here it is possible to make cathodes using this material through careful applications of the diffusion layers or by using Goretex cloth.

2. Materials and methods

2.1. Cathodes fabrication

Four different methods were used to fabricate the cathodes: carbon cloth (Type B, 30% wet proofing, BASF Fuel Cell Inc., NJ) with four PTFE diffusion layers (CC-PTFE); carbon mesh (Gaojieshi Graphite Products Co. Ltd., Fujian, China) with four PTFE diffusion layers (CM-PTFE); carbon mesh with three PDMS/carbon diffusion layers (CM-PDMS/Carbon); and carbon mesh with Goretex fabric as the diffusion layer (Rockywoods Fabrics, LLC, USA) (CM-Goretex). CC-PTFE was coated with a Pt catalyst (0.5 mg cm^{-2} , BASF) on the water-facing side, with the PTFE diffusion layers on the air-facing side to prevent water loss [2] (Fig. 1A). PTFE was applied to carbon mesh (CM-PTFE) or cloth (CC-PTFE) using the same procedure (Fig. 1B). Carbon mesh was waterproofed by immersing it in 30% PTFE solution for 45 min, air-drying the material for 30 min in a 80°C oven, and then heating it for 30 min at 370°C . CM-PDMS was made by coating a mixture of PDMS (6.25 mg cm^{-2}) on each layer and carbon black (1.56 mg cm^{-2} on each layer) to the air-facing side, and Pt catalyst (0.5 mg cm^{-2} , BASF) to the water-facing sides of the carbon mesh [11]. In order to prevent water leakage from the carbon mesh cathode, three PDMS/Carbon black diffusion layers were needed (Fig. 1C). For the CM-Goretex cathode, carbon black (1.56 mg cm^{-2}) and a Pt catalyst (0.5 mg cm^{-2}) were applied to the air-facing side and water-facing side of carbon mesh, respectively. When setting up a MFC, carbon mesh was pressed firmly to the top of Goretex cloth using two pieces of plastic meshes (Fig. 1D).

2.2. MFC reactors and operation

Single-chamber, air-cathode MFCs (4-cm long cylindrical chamber; liquid volume 28 mL) were constructed as previously described [2]. Anodes were carbon fiber brushes (25 mm diameter \times 25 mm length; fiber type PANEX 33 160 K, ZOLTEK), and all anodes were heat treated for 30 min at 450°C before use [4]. All reactors were inoculated using the effluent from an MFC operated for over 2 years. Sodium acetate (1.0 g L^{-1}) was used as an energy source in a nutrient solution containing (in 1 L deionized water): $4.0896 \text{ g Na}_2\text{HPO}_4$, $2.544 \text{ g NaH}_2\text{PO}_4$, $0.31 \text{ g NH}_4\text{Cl}$, 0.13 g KCl , and 12.5 mL of a trace metal solution and 5 mL of a vitamin solution (pH 7.0; conductivity 6.92 mS cm^{-1}) [18]. The solution was replaced when the voltage decreased to $<10 \text{ mV}$ (1000Ω fixed external resistance). All reactors

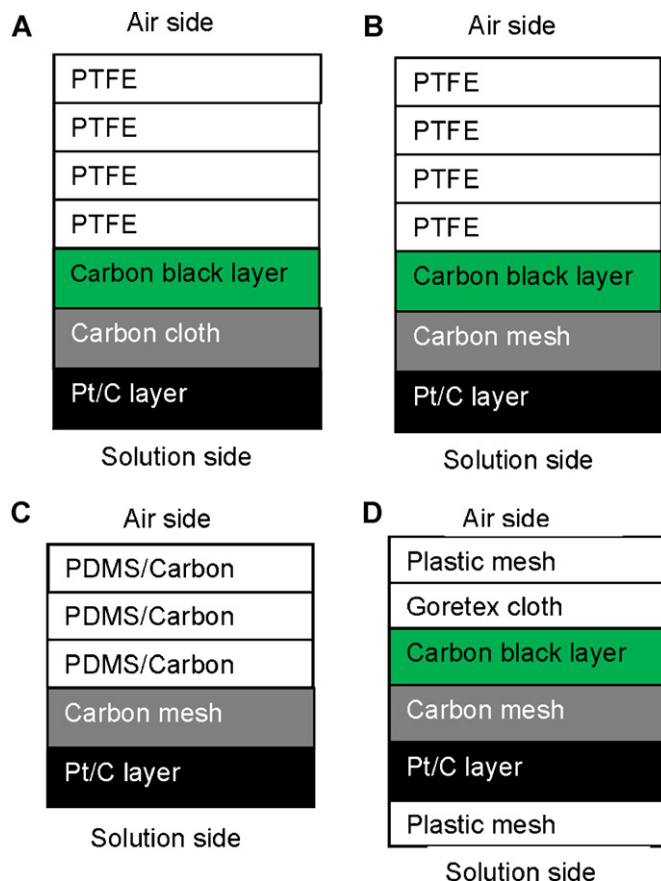


Fig. 1. The schematical fabrication procedures of the different cathodes. (A): CC-PTFE, (B) CM-PTFE, (C) CM-PDMS/Carbon, (D) CM-Goretex (CC: carbon cloth; CM: carbon mesh; PTFE: polytetrafluoroethylene; PDMS: poly(dimethylsiloxane)).

were operated with fed-batch mode at 30°C in a temperature-controlled room.

2.3. Calculations and measurements

Voltages were measured at time intervals of 20 min across an external resistor (1000Ω) using a data acquisition system (2700, Keithley Instrument, OH). Chemical oxygen demand (COD) was measured using standard methods [Method 5220, APHA et al. 1995; High range ($20\text{--}1500 \text{ mg L}^{-1}$); HACH COD system (Hach Co., Loveland, CO)]. COD removal (%) was calculated based on the initial and final COD [19]. The Coulombic efficiency (CE) was calculated as previously described with the current and power density normalized by the cathode projected surface area (7 cm^2) [8]. Maximum power densities (normalized to the projected cathode surface area) were obtained from polarization curves which were obtained using a single resistor ($1000\text{--}20 \Omega$), with 20 min intervals at each resistance over a complete fed batch cycle (multiple cycle method) by varying the resistance in decreasing order from 1000 to 20Ω in a single cycle (20 min per resistance, single cycle method) [20]. Water loss was calculated by measuring the water remaining in the reactor after a complete fed batch cycle using a graduated cylinder (100 mL).

Linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) were used to measure the electrochemical performances of the cathodes using a potentiostat (PC4/750, Gamry Instrument). Cathodes were placed in an air-cathode electrochemical cell consisting of a working electrode (cathode, 7 cm^2 projected surface area facing air on one side and

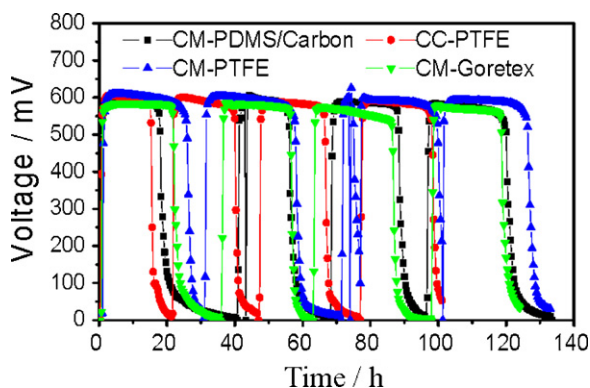


Fig. 2. Four representative voltage output curves of the different cathode (with an external resistor of 1000 Ω).

water on the other side), an Ag/AgCl reference electrode (RE-5B; BASi, West Lafayette, IN), and a Pt counter electrode [11].

LSV tests were conducted over a range of -0.311 to $+0.289$ mV, at a slow scan rate of 0.1 mV s^{-1} . Impedance measurements were conducted using anodes by setting at -0.111 V (vs. Ag/AgCl; 0.084 V vs. a standard hydrogen electrode) over a frequency range of 100 kHz to 1 MHz with a sinusoidal perturbation of 10 mV. EIS spectra were fitted into an equivalent circuit as previously described using Gamry Echem Analyst software (provided by the potentiostat manufacturer) [11]. The internal resistances of reactors were determined using Nyquist plots [21]. All electrochemical measurements were performed with freshly made cathodes (prior to MFC tests). All voltages are reported vs. Ag/AgCl.

3. Results

3.1. Power generation using different cathode materials

MFCs with four different cathodes (CM-PDMS/Carbon, CC-PTFE, CM-PTFE, and CM-Goretex) were operated for more than ten cycles (1000 Ω), and demonstrated stable and repeatable performance. Representative voltage output curves are shown in Fig. 2. The maximum voltage outputs achieved from the MFCs with CM-PTFE and CC-PTFE were similar (601 ± 5 mV for CM-PTFE, 599 ± 5 mV for CC-PTFE). The maximum voltage output of MFCs with CM-PDMS/Carbon cathodes reached 594 ± 9 mV, while the maximum voltage output of the MFCs with CM-Goretex cathodes was 581 ± 5 mV.

Maximum power densities and polarization data showed that MFCs with the CC-PTFE cathodes had the highest maximum power density on average of 1390 ± 72 mW m^{-2} , although this was not significantly different than that produced using the CM-PDMS/Carbon cathode (1355 ± 62 mW m^{-2}) (Fig. 3A). The CM-PTFE cathode produced slightly less power, with a maximum power density of 1303 ± 48 mW m^{-2} . The CM-Goretex cathode produced much less power (849 ± 68 mW m^{-2}). Measurement of the electrode potentials shows that anode potentials were essentially the same for all reactors, with differences found for the cathode potentials (Fig. 3B). Thus, the differences in the maximum power densities resulted from the different cathode potentials and not the anodes.

3.2. Coulombic efficiency (CE)

The CEs of all MFCs with the different cathodes were a function of current density, with the highest CEs at the highest current densities (Fig. 4). CEs of CC-PTFE MFCs ranged from 23 to 63%, while the MFCs with the CM-PDMS/Carbon were in the range of 19 to 79%. CEs using the CM-Goretex cathodes ranged from 25 to 66%, which were similar to those with the CC-PTFE cathodes (23–63%).

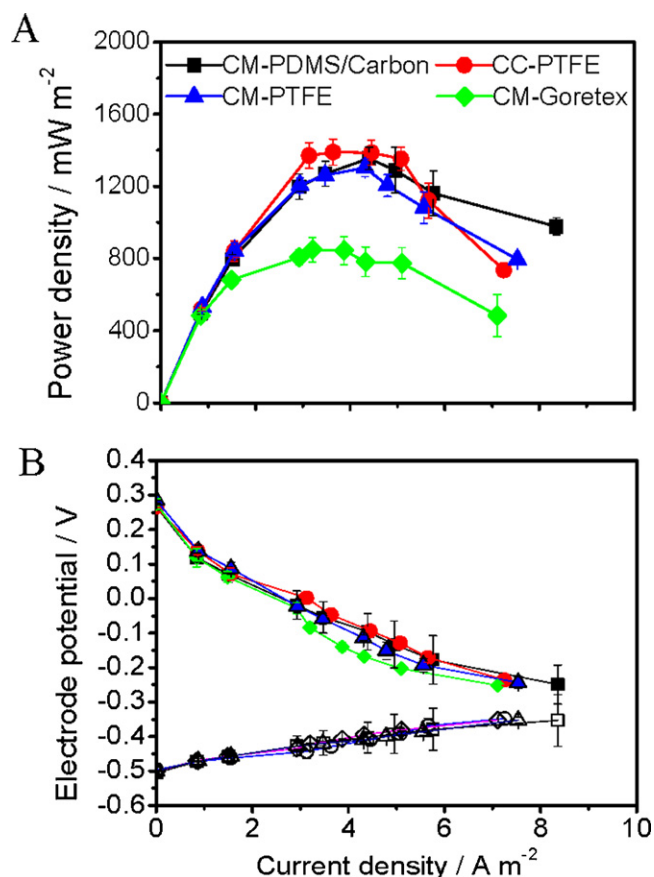


Fig. 3. (A) Power density curves, and (B) electrode potentials (cathode, filled symbols; anode, open symbols) vs. Ag/AgCl reference electrode (0.195 V vs. NHE) as a function of the different cathodes.

3.3. Water loss

Water losses of the MFCs with the different cathodes were compared based on water lost over a complete fed-batch cycle. Carbon mesh cathodes with PTFE and a mixture of PDMS and carbon as diffusion layers were relatively more effective in preventing water loss through evaporation (none of the cathodes leaked water). CM-Goretex cathodes had the largest water loss of 8.3%, compared to much lower water losses for CM-PTFE (4.2%), CC-PTFE (3.2%), and CM-PDMS/Carbon (2%).

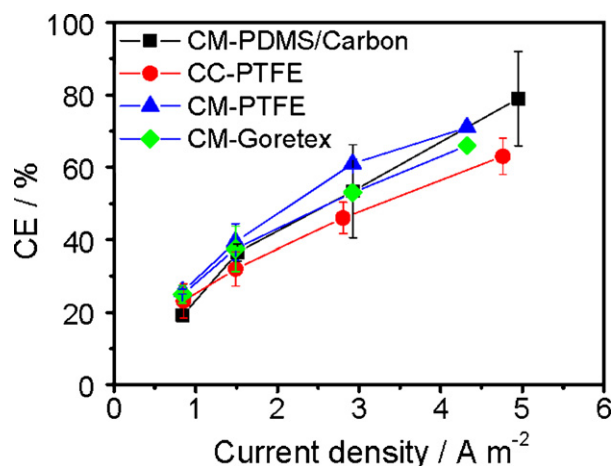


Fig. 4. Coulombic efficiencies (CEs) of MFCs using the different cathodes.

Table 1
Solution resistance (R_s), diffusion resistances (R_d), charge-transfer resistance (R_{ct}), internal resistances (R_{in}) of the different cathodes.

MFC reactor	Solution resistance (R_s) (Ω)	Diffusion resistances (R_d) (Ω)	Charge-transfer resistance (R_{ct}) (Ω)	Internal resistances (R_{in}) (Ω)
CM-PDMS/Carbon	19	18	5	42
CM-PTFE	19	18	8	45
CC-PTFE	20	13	3	36
CM-Goretex	20	33	6	59

Table 2
Cost comparison of the different cathodes.

Cathode	P_{max} ($mW m^{-2}$)	Carbon material ($\$ m^{-2}$)	Diffusion layer ($\$ m^{-2}$)	Other materials ^a ($\$ m^{-2}$)	Total cost ($\$ m^{-2}$)
CC-PTFE	1390 ± 72	1000	0.33	0.01	1000
CM-PTFE	1303 ± 48	25	0.33	0.01	25
CM-PDMS/Carbon	1355 ± 62	25	0.2	0.03	25
CM-Goretex	849 ± 68	25	39	20	84

^a Other materials contain carbon black, and plastic mesh used for the configuration of CM-Goretex. The cost of Pt catalyst and Nafion were not included because they were applied in all the cathodes with the same amount.

3.4. Electrochemical tests

Cathodes were examined using LSV to evaluate their electrochemical performance in the absence of bacteria. All four cathodes had similar current densities for applied potentials at or above -0.111 mV (Fig. 5). When the voltage was lower than -0.111 mV, current densities of CC-PTFE were slightly higher than those of the CM-PTFE electrode, which was similar to that of the CM-PDMS/Carbon electrode. CM-Goretex achieved the lowest current density compared to the other three cathodes, consistent with our expectations based on the MFC results.

The EIS tests were used to estimate solution (R_s), diffusion (R_d), charge-transfer (R_{ct}), and internal (R_{in}) resistances of the different electrodes (Table 1). As expected, R_s were all similar for the different cathodes because the same cell configuration and solutions were used. CM-Goretex produced the highest diffusion resistance of $R_d = 33 \Omega$, while CM-PDMS/Carbon ($R_d = 18 \Omega$) and CM-PTFE ($R_d = 18 \Omega$) resistances were similar. The lowest diffusion resistance was obtained for the CC-PTFE electrode ($R_d = 13 \Omega$). Charge-transfer resistances also varied for the cathodes, with the CC-PTFE cathode having the lowest $R_{ct} = 3 \Omega$ compared to the other three cathodes. The CC-PTFE electrode had the smallest internal resistance of $R_{in} = 36 \Omega$, compared to the CM-PDMS/Carbon (42Ω) and CM-PTFE (45Ω) electrodes. CM-Goretex had the highest

$R_{in} = 59 \Omega$, consistent with its relatively poor performance in MFC tests.

4. Discussion

The power output using the CM-Goretex cathode was much lower than that obtained with the cathodes with PDMS/Carbon and PTFE diffusion layers, consistent with the poorer performance of this electrode in electrochemical tests. One reason for this lower performance could be trapped water. Although we used two pieces of plastic mesh to press carbon mesh onto the top of Goretex cloth to avoid trapped water, it is possible that some water was held in the area between the carbon mesh and Goretex cloth. This would result in a localized high pH region, which would reduce performance and could reduce oxygen transfer to the active site of catalyst [22]. The poorer intrinsic performance of the CM-Goretex cathode was shown by diffusion resistances that were 35% higher than the CM-PDMS/Carbon, and 37% higher than the CM-PTFE (Table 1).

While good performance is an essential factor for scaling up MFCs, costs of the cathodes is also important. Neglecting the costs of catalyst and binder which were used in all electrodes, the cost per m^2 of the CC-PTFE electrode based on purchase prices of the materials was \$1000, which was 40 times more than that of CM-PTFE (\$25) and CM-PDMS/Carbon (\$25) (Table 2), despite relatively similar performances of these cathodes. The total costs of the cathodes would still need to be further optimized as the Pt ($\$700 m^{-2}$) and Nafion binder ($\$1400 m^{-2}$) represent significant costs [10]. However, research has shown that these materials can be replaced with non-precious metal catalysts such as CoTMPP ($\$180 m^{-2}$) [23] or less expensive activated carbon ($\$0.37 m^{-2}$) [24], and less expensive poly (phenylsulfone) Radel binders ($\$3.5 m^{-2}$) [25]. By using these alternative materials, the total cost of MFC could be greatly reduced.

5. Conclusions

These results have shown that inexpensive carbon mesh can be used as a cathode when coated with two different diffusion layers. Carbon mesh cathodes with PDMS/Carbon produced power densities ($1355 \pm 62 mW m^{-2}$) most similar to those obtained with carbon cloth and PTFE diffusion layers ($1390 \pm 72 mW m^{-2}$). The cost of the carbon mesh cathode with PDMS/Carbon or PTFE diffusion layers is only 2.5% of the cost for the conventional carbon cloth (neglecting the cost for the catalyst and catalyst binder). Thus,

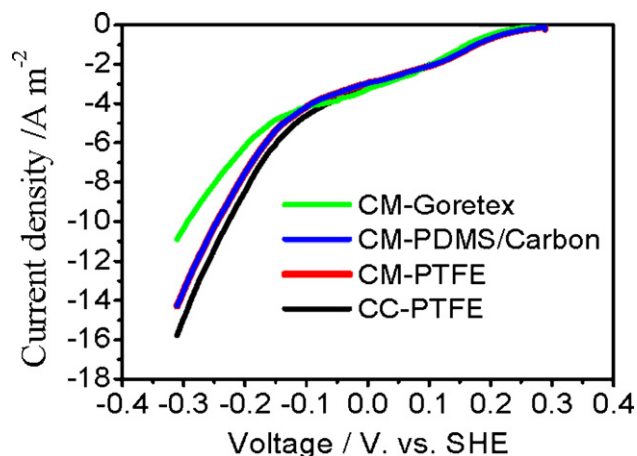


Fig. 5. LSV tests on different cathodes. (Note that the results for the CC-PTFE and CM-PTFE cathodes are almost the same, and therefore the lines are indistinguishable.)

these results have shown that carbon mesh is an efficient and cost-effective alternative to carbon cloth cathodes for MFCs.

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References

- [1] K. Rabaey, W. Verstraete, Trends Biotechnol. 23 (2005) 291–298.
- [2] H. Liu, B.E. Logan, Environ. Sci. Technol. 38 (2004) 4040–4046.
- [3] Y. Fan, H. Hu, H. Liu, J. Power Sources 171 (2007) 348–354.
- [4] B.E. Logan, S. Cheng, V. Watson, G. Estadt, Environ. Sci. Technol. 41 (2007) 3341–3346.
- [5] T.A. Heijne, H.V.M. Hamelers, V.D. Wilde, R.A. Rozendal, C.J.N. Buisman, Environ. Sci. Technol. 40 (2006) 5200–5205.
- [6] A. Rhoads, H. Beyenal, Environ. Sci. Technol. 39 (2005) 4666–4671.
- [7] J. Li, G. Liu, R. Zhang, Y. Luo, C. Zhang, M. Li, Bioresource Technol. 101 (2010) 4013–4020.
- [8] B.E. Logan, P. Aelterman, B. Hamelers, R. Rozendal, U. Schröder, J. Keller, S. Freguiau, W. Verstraete, K. Rabaey, Environ. Sci. Technol. 40 (2006) 5181–5192.
- [9] Y. Zuo, S. Cheng, D. Call, B.E. Logan, Environ. Sci. Technol. 41 (2007) 3347–3353.
- [10] Y. Zuo, S. Cheng, B.E. Logan, Environ. Sci. Technol. 42 (2008) 6967–6972.
- [11] F. Zhang, M.D. Merrill, J.C. Tokash, T. Saito, S. Cheng, M.A. Hickner, B.E. Logan, J. Power Sources 196 (2011) 1097–1102.
- [12] F. Zhang, T. Saito, S. Cheng, M.A. Hickner, B.E. Logan, Environ. Sci. Technol. 44 (2010) 1490–1495.
- [13] S. You, X. Wang, J. Zhang, J. Wang, N. Ren, X. Gong, Biosens. Bioelectron. 26 (2011) 2142–2146.
- [14] X. Wang, S. Cheng, Y. Feng, M.D. Merrill, T. Saito, B.E. Logan, Environ. Sci. Technol. 43 (2009) 6870–6874.
- [15] X. Zhang, S. Cheng, P. Liang, X. Huang, B.E. Logan, Bioresource Technol. 102 (2011) 372–375.
- [16] C. Feng, Q. Wan, Z. Li, X. Yue, Y. Chen, C. Wei, Biosens. Bioelectron. 26 (2011) 3953–3957.
- [17] Z. Li, C. Feng, S. Zhou, Y. Li, Y. Wang, Process Biochem. 45 (2010) 929–934.
- [18] D.R. Lovely, E.J.P. Phillips, Appl. Environ. Microbiol. 54 (1988) 1472–1480.
- [19] S. Cheng, H. Liu, B.E. Logan, Environ. Sci. Technol. 40 (2006) 2426–2432.
- [20] J. Ditzig, H. Liu, B.E. Logan, Int. J. Hydrogen Energy 32 (2007) 2296–2304.
- [21] Z. He, N. Wagner, S.D. Minteer, L.T. Angenent, Environ. Sci. Technol. 40 (2006) 5212–5217.
- [22] S. You, J. Wang, N. Ren, X. Wang, J. Zhang, ChemSusChem 3 (2010) 334–338.
- [23] S. Cheng, H. Liu, B.E. Logan, Environ. Sci. Technol. 40 (2005) 364–369.
- [24] F. Zhang, S. Cheng, D. Pant, G.V. Bogaert, B.E. Logan, Electrochem. Commun. 11 (2009) 2177–2179.
- [25] T. Saito, M.D. Merrill, V.J. Watson, B.E. Logan, M.A. Hickner, Electrochim. Acta 55 (2010) 3398–3403.