Neutral hydrophilic cathode catalyst binders for microbial fuel cells[†]

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Improving oxygen reduction in microbial fuel cell (MFC) cathodes requires a better understanding of the effects of the catalyst binder chemistry and properties on performance. A series of polystyrene-bpoly(ethylene oxide) (PS-b-PEO) polymers with systematically varying hydrophilicity were designed to determine the effect of the hydrophilic character of the binder on cathode performance. Increasing the hydrophilicity of the PS-b-PEO binders enhanced the electrochemical response of the cathode and MFC power density by \sim 15%, compared to the hydrophobic PS-OH binder. Increased cathode performance was likely a result of greater water uptake by the hydrophilic binder, which would increase the accessible surface area for oxygen reduction. Based on these results and due to the high cost of PS-b-PEO, the performance of an inexpensive hydrophilic neutral polymer, poly(bisphenol A-co-epichlorohydrin) (BAEH), was examined in MFCs and compared to a hydrophilic sulfonated binder (Nafion). MFCs with BAEH-based cathodes with two different Pt loadings initially (after 2 cycles) had lower MFC performance (1360 and 630 mW m⁻² for 0.5 and 0.05 mg Pt cm⁻²) than Nafion cathodes (1980 and 1080 mW m⁻² for 0.5 and 0.05 mg Pt cm⁻²). However, after long-term operation (22 cycles, 40 days), power production of each cell was similar (\sim 1200 and 700–800 mW m⁻² for 0.5 and $0.05 \text{ mg Pt cm}^{-2}$ likely due to cathode biofouling that could not be completely reversed through physical cleaning. While binder chemistry could improve initial electrochemical cathode performance, binder materials had less impact on overall long-term MFC performance. This observation suggests that long-term operation of MFCs will require better methods to avoid cathode biofouling.

1. Introduction

Microbial fuel cells (MFCs) use electricity-generating microbes (exoelectrogens) to liberate electrons from organic compounds.

^aDepartment of Materials Science and Engineering, The Pennsylvania State University, 310 Steidle Building, University Park, PA, 16802, USA. E-mail: hickner@matse.psu.edu; Fax: +1 814-865-2917; Tel: +1 814-867-1847 MFCs represent a promising renewable energy-production technology especially when applied in wastewater treatment schemes.^{1,2} The increase in MFC power output over the years by several orders-of-magnitude is an encouraging trend.³ However, further increases in power densities are desirable to help improve the economic feasibility of MFC technologies for real-world applications.⁴ Improved MFC performance is likely to result from gains made in optimizing component properties (anode, cathode, and electrolyte) and reactor configurations. Among the MFC components, the cathode is one of the major bottlenecks to high power density⁴ and improving its performance is critical to continued development of MFCs. At the cathode, the reduction of an electrocatalyst, which in the neutral pH environment of an MFC has primarily been platinum,⁵⁻⁹ metal

Broader context

Microbial fuel cells (MFCs) are a promising renewable energy-production technology, especially in wastewater treatment applications. Among the components of MFCs, the cathode is one of the major bottlenecks for achieving high power densities, and therefore understanding the key parameters that lead to high cathode performance is critical. Using a systematic series of cathode catalyst polymer binders, this study demonstrated that increasing the hydrophilicity of neutral catalyst binders could enhance electrochemical and MFC performance. Power production in MFCs using a commercially available neutral hydrophilic polymer as a binder was not initially as large as that obtained with a more traditional (and expensive) Nafion binder. However, we found that when MFCs were operated for more than 40 days, the amount of catalyst (Pt) was more important in determining power output than the type of binder material. Our studies suggest that other types of inexpensive polymeric catalyst binders could be used to achieve similar power production in MFCs during long-term operation, and that ultimately, power production is limited by cathode biofouling. While this study was performed using Pt catalysts, our findings should be applicable to other types of catalysts for oxygen reduction in MFCs, such as Co-based compounds and activated carbon.

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tetramethylphenylporphyrins,^{8–11} graphite granules,¹² activated carbon,¹³ Fe–EDTA,¹⁴ as well as a few other electrochemically active materials. The electrochemical reactions to reduce oxygen to water at the cathode involve the simultaneous impingement of electrons, protons, and oxygen on a catalytic site, but design guidelines for creating or optimizing cathodes for MFCs do not yet exist. Polymers are used to bind many of these catalysts to the electrode surface. Nafion is commonly used in hydrogen fuel cells and MFC as a catalyst binder, but it is considered to be too expensive for large-scale MFC applications. Thus, investigation of the properties of polymers used as catalyst binders is important to facilitate the design of cathodes with improved and more cost-effective performance.

In a previous study,⁵ we examined the use of sulfonated and non-sulfonated poly(sulfone) as catalyst binders for MFC cathodes as an alternative to Nafion. Cathodes with poly(sulfone) binders that had a range of sulfonate content (IEC = 0-2.54 meg g⁻¹) were fabricated and their electrochemical and MFC attributes were correlated to the physical properties of the polymers. Unsulfonated poly(sulfone), a non-ionic, hydrophobic binder, showed the highest performance in electrochemical tests even though it may have occluded electrochemically active surface area and ORR sites. The addition of sulfonate moieties to the binder polymer increased the hydrophilicity of the polymer, but increasing concentrations of negatively charged sulfonate groups lowered the electrochemical performance of the cathodes. It was hypothesized that the ionic concentration gradient at the catalyst interface caused by the presence of sulfonate groups in the binders decreased the cathode performance. These results suggested that non-ionic binders with a hydrophilic character would be useful alternatives to sulfonated polymers in MFC cathodes.

In order to study the importance of binder hydrophilicity without the addition of ions, cathodes employing poly(styrene)b-poly(ethylene oxide) diblock copolymers (PS-b-PEO) with different PEO lengths (Fig. 1) were prepared and tested as cathode catalyst binders in electrochemical cells using linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), and in MFCs. Greater PEO molecular weight segments increased the hydrophilicity of the binders as demonstrated by their water uptake since the molecular weight of poly(styrene) (hydrophobic block) was constant. While the systematic series of PS-b-PEO binders was ideal for investigating the effect of hydrophilicity of polymeric catalyst binders, the high cost of these materials would not be practical for use in MFCs. Therefore, in the second part of this study we investigated the attributes of poly(bisphenol A-co-epichlorohydrin) (BAEH) (Fig. 1), an inexpensive, commercially available, neutral hydrophilic polymer as a catalyst binder that could be deployed in large-scale MFCs. We compared the initial and long-term performance of MFCs using BAEH cathode catalyst binders to



Fig. 1 Chemical structures of neutral cathode catalyst binders.

those containing the conventional and more expensive Nafionbased binder.

2. Results and discussion

The measured current in LSV tests increased with molecular weight of the PEO segment, in the order PEO-0, PEO-25 and PEO-110 (Fig. 2), demonstrating that binder hydrophilicity was positively correlated to enhanced electrochemical performance of the cathodes. The higher hydrophilicity of the polymer binders was characterized by the increased water uptake of the films, 0 wt% (PEO-0), 10 wt% (PEO-25), and 50wt% (PEO-110) (Table 1), which confirmed that polymers with larger molecular weight PEO segments were more hydrophilic. The observed trend was further reinforced in EIS measurements (Fig. 3) where the charge transfer resistance decreased as the PEO molecular weight increased, with values of $R_{\rm ct} = 26 \Omega$ (PEO-0), 21 Ω (PEO-25) and 15 Ω (PEO-110). Increasing the hydrophilicity of the binder most likely enhanced proton flux to Pt catalyst surface by increasing the water uptake of the cathode structure.

Increased water uptake of the catalyst layer polymer binder also improved MFC performance (Fig. 4). The maximum power density of a MFC with a PEO-110 cathode was 1470 mW m⁻², whereas the MFC with PEO-25 and PEO-0 cathodes produced maximum power densities of 1410 and 1270 mW m⁻². The increase in the maximum power densities was due to improvement in cathode potentials (Fig. 4), since all the cells showed similar anode potentials as a function of current density.

While PEO diblock copolymer binders could be used to improve MFC performance, they are expensive relative to most commercially available polymers. Our findings here, combined with other studies, suggest that an optimal catalyst binder would be hydrophilic, water insoluble, chemically and biologically stable in water at the operating (neutral) pH conditions, and



Fig. 2 LSV of cathodes with PS-*b*-PEO diblock copolymer binders (200 mM PBS, pH 7, 30 $^{\circ}$ C).

Table 1 Water uptake of polymer binders

	Water uptake (wt%)
PEO-0	0
PEO-25	10
PEO-110	50
Nafion	30
BAEH	24



Fig. 3 EIS of cathodes with PS-*b*-PEO diblock copolymer binders at 0.2 V (*vs.* NHE) (200 mM PBS, pH 7, 30 °C).



Fig. 4 (a) Power density curves and (b) cathode and anode potentials (vs. NHE) at cycle 3 (5 days of operation; 100 mM PBS, pH 7, 0.5 g L^{-1} acetate).

inexpensive. Considering these properties, we further examined the use of BAEH (Fig. 1), an inexpensive, neutral hydrophilic polymer binder with a water uptake of 24 wt% (Table 1). Freshly made BAEH and Nafion-based cathodes with 0.5 mg cm⁻² Pt showed similar electrochemical responses in LSV (Fig. 5) and EIS (Fig. 6) tests as the LSV scans nearly overlapped each other, and EIS tests all showed that R_{ct} was approximately 15 Ω . In addition, both BAEH and Nafion showed slightly better response in LSV tests than PEO-110.

The electrochemical performance of the BAEH-based cathode from LSV and EIS tests suggested that this polymer should perform as well as Nafion in MFCs with a cathode catalyst loading of 0.5 mg cm⁻² Pt. At a low Pt loading of 0.05 mg cm⁻², significantly different electrochemical performance was observed between cathodes with BAEH and Nafion catalyst binders. The kinetic response of 0.05 mg cm⁻² Pt BAEH-based cathode in LSV tests was depressed compared to the Nafion-based cathode at the



Fig. 5 LSV of cathodes with Nafion or BAEH binders with 0.5 or 0.05 mg cm⁻² Pt (200 mM PBS, pH 7, 30 °C).



Fig. 6 EIS of cathodes with Nafion and BAEH binders at 0.2 V (*vs.* NHE) (200 mM PBS, pH 7, 30 °C), where \blacklozenge 0.5 mg Pt cm⁻² Nafion, ▲ 0.05 mg Pt cm⁻² Nafion, \diamondsuit 0.5 mg Pt cm⁻² BAEH, and △ 0.05 mg Pt cm⁻² BAEH.

same Pt loading. In addition, the R_{ct} values from EIS scans were 199 Ω for BAEH cathode and 31 Ω for Nafion (0.05 mg cm⁻² Pt). It is not clear why BAEH and Nafion-based cathodes showed significantly different electrochemical responses at lower Pt loadings. The different performance could be due to the densities of the polymer binders as Nafion is more dense (2.1 g cm⁻³) than BAEH (1.2 g cm⁻³). The resulting change in the polymer binder volume (equal polymer mass added to each cathode) could cause the BAEH to be thicker on average than Nafion and impose an additional diffusion resistance in the cathode. In addition, the wetting of the catalyst layer could have changed due to the use of different solvents and polymers in the fabrication of the catalyst layers.

BAEH and Nafion-based cathodes with different Pt loadings (0.05 or 0.5 mg cm⁻² Pt) were examined for their performance in MFCs over 150 days (60 fed-batch cycles) (Fig. 7). The voltages produced at a fixed resistance (1000 Ω) were higher for the Nafion-based cathodes than for the BAEH cathodes in the initial cycles, especially for cathodes with the lower Pt loadings. However, the voltages generated by MFCs with Nafion or BAEH cathodes became nearly identical (based on the same Pt loadings) in later cycles. These results suggest a "break in" period for these cathodes as the cathode performance equalized after repeated cycles. In one case, for the reactor with the cathode with BAEH and 0.05 mg cm⁻² Pt, the voltage increased over time, suggesting insufficient electrolyte wetting of the cathode in the



Fig. 7 Maximum voltage output for each cycle with 1000 Ω resistance over 60 cycles and 150 days.

initial cycles. This lower performance in the initial MFC cycles is in agreement with the poorer electrochemical performance of this cathode in LSV and EIS tests with new cathodes.

Power density curves obtained over time show the same general trends based on catalyst binder type as the voltages recorded over multiple cycles at a fixed resistance (1000 Ω) (Fig. 8). Initially (3 days of operation or 2 cycles), MFCs with Nafion cathodes performed significantly better than those with BAEH cathodes. The maximum power densities based on polarization data were 1980 mW m⁻² for Nafion versus 1360 mW m^{-2} for BAEH at the higher Pt loading (0.5 mg cm⁻²), and 1080 mW m⁻² for Nafion versus 630 mW m⁻² for BAEH at the lower Pt loading (0.05 mg cm⁻²) (Table 2). Similar anode potentials were observed for all reactors, indicating the differences in MFC performance of these reactors were due to cathode performance. The higher initial power production using cathodes with a Nafion binder compared to the cathodes with BAEH was surprising as these two cathodes had similar electrochemical performance in LSV tests. This result suggests that a dynamic test such as LSV does not fully predict steady state performance under MFC conditions, and therefore highlights that actual

MFC tests (and not just electrochemical tests) must be conducted with new types of cathodes. After 20 days (cycle 11), MFC reactors with Nafion binders showed decreased power densities compared to the second cycle, whereas MFC reactors with BAEH binders showed little degradation in performance (Fig. 8 and Table 2). The maximum power densities of cells with Nafion cathodes became similar to those of BAEH cathodes at cycle 11 (Table 2). At cycle 22, after 40 days of operation, the polarization performance of MFCs employing Nafion- and BAEH-based cathodes with the same Pt loading was nearly identical and their power output continued to be equivalent for the remainder of the cycles.

The results for the Nafion and BAEH-based cathodes showed the same trends over time as the PEO-based cathodes (all at 0.5 mg cm⁻² Pt). For example, the power densities for MFCs with PEO-0, PEO-25, PEO-110, Nafion and BAEH-based cathodes at cycle 22 (~40 days of operation) had comparable power density curves and maximum power densities (~1200 mW m⁻²) (Fig. 9). The maximum power density was also similar to results obtained with the more hydrophobic Radel binder (and Nafion binder) at later cycles in our previous study.⁵ The hydrophilic binders that absorbed water, including Nafion, BAEH, PEO-110, and PEO-25, improved the MFC performance in the initial cycles compared to the hydrophobic binder. However, the MFC performance in these two studies where 6 types of cathode

Table 2 Maximum power density (mW m^{-2}) after cycle 2 (3 days of operation), cycle 11 (20 days of operation) and cycle 22 (40 days of operation)

	Cycle 2	Cycle 11	Cycle 22
0.5 mg Pt cm ⁻² Nafion	1980	1410	1200
0.5 mg Pt cm ⁻² BAEH	1360	1310	1210
$0.5 \text{ mg} \text{ Pt} \text{ cm}^{-2} \text{ PEO-110}$	1470	1190	1200
$0.05 \text{ mg Pt cm}^{-2} \text{ Nation}$	1080	740	710
0.05 mg Pt cm ⁻² BAEH	630	730	800



Fig. 8 Power density curves and corresponding cathode and anode potentials (vs. NHE) after cycle 2 (3 days of operation), cycle 11 (20 days of operation) and cycle 22 (40 days of operation). \blacklozenge 0.5 mg Pt cm⁻² Nafion, \blacktriangle 0.05 mg Pt cm⁻² Nafion, \diamondsuit 0.5 mg Pt cm⁻² BAEH, \triangle 0.05 mg Pt cm⁻² BAEH, \triangle 0.05 mg Pt cm⁻² BAEH, \Rightarrow 0.05 mg Pt cm⁻² PEO-110.



Fig. 9 Power density curves after cycle 22 (40 days of operation).

catalyst binders were investigated all showed a trend towards similar performance after long-term operation.

Changes in MFC performance over time were likely not due to intrinsic alteration in the cathode oxygen permeability as coulombic efficiencies of all the cathodes were similar for the entire experimental period (Fig. 10). If cathode permeability was reduced, then the oxygen penetration would have decreased and coulombic efficiencies would have increased accompanied by a decrease in power.¹⁵ The decrease in cathode performance observed here over long operation periods is consistent with that reported in previous studies.^{5,16–18} The decrease in performance is thought to be due to a result of the formation of a biofilm on the cathode surface. Thick biofilms (~ 1 to 1.5 mm) were observed on all cathodes after 8 months of operation (Fig. S1[†]). To examine the effect of biofilm formation on MFC performance, the biofilms were removed from the cathodes by rinsing with de-ionized water. Maximum power densities for MFCs with the cleaned cathodes (little visible biofilm) were compared to the performance of reactors with fresh cathodes (cycle 2) and cathodes containing biofilm (cycle 130) prior to being cleaned (Fig. S2[†]). Removal of the biofilm increased the maximum power densities of all reactors, although maximum power densities were not as high as those originally obtained for cycle 2 with fresh cathodes. These results suggest that prevention of biofilm growth by using advanced cathode catalyst binders is an important aspect for maintaining high power production in MFCs.

The properties of the catalyst binder can affect adhesion of bacteria, but after many cycles the performance of the cathodes



Fig. 10 Coulombic efficiency (%) as a function of cycle number during MFC operation (100 mM PBS, pH 7, 1000 Ω resistance, 0.5 g L⁻¹ acetate).

became similar suggesting that the properties of the cathode matrix were changed over time and that the polymers demonstrated here did not resist biofouling during long term operation. It is well known from bacterial adhesion studies of ultrafiltration membranes that surface hydrophobicity, charge, and roughness can all be factors in biofouling.¹⁹⁻²² The finding here that CE was relatively unaffected during long-term MFC performance suggests that the biofilm on the surface of the cathode did not change the oxygen permeability of the cathode, but it did affect proton transport to the cathode catalysts. Therefore, the change in power production was due to fouling of the inner cathode matrix as evidenced by an alteration of the intrinsic performance of the cathodes during MFC operation. Cathodes with different initial binder chemistries eventually all had similar performance once the outside and inner matrix of the cathodes were fouled. Since the initial performance could not be completely restored by removing the surface biofilm from the cathodes, fouling of the cathode pore space was a factor in reduced performance. Clearly, additional work will be needed to better understand the reasons for differences in power generation with different binders and the mechanisms by which the binder-catalyst structures are affected over time in MFCs. The use of anti-fouling coatings and additional examination of the cathode structure during MFC operation and fouling may help to lead to a better understanding of microbial biofilm effects on cathode performance.

3. Experimental

3.1 Polymer cathode catalyst binders

Poly(styrene)-b-poly(ethylene oxide) diblock copolymers (PS-b-PEO) were synthesized via anionic polymerization using a standard procedure modified as follows.23 Hydroxyl-terminated polystyrene (PS-OH) was synthesized via anionic polymerization of styrene and end-capped with ethylene oxide. PS-OH was then chain extended with ethylene oxide to form a PS-b-PEO diblock copolymer via anionic polymerization with potassium naphthalene as the initiator. The number of repeating units of each block and molecular weights were determined using ¹H NMR and gel permeation chromatography. The prepared series of polymers were PS_{156} -OH (M_n 16 300 g mol⁻¹, $M_w/M_n = 1.01$), PS_{156} -b- $PEO_{25} (M_n \ 17 \ 300 \ g \ mol^{-1}, M_w/M_n = 1.01)$, and PS_{156} -*b*-PEO₁₁₀ $(M_{\rm n} \ 21 \ 100 \ {\rm g} \ {\rm mol}^{-1}, \ M_{\rm w}/M_{\rm n} = 1.01)$. Subscripted numbers denote the corresponding number of repeat units of each block. PS₁₅₆-OH, PS₁₅₆-b-PEO₂₅, and PS₁₅₆-b-PEO₁₁₀ are abbreviated here as PEO-0, PEO-25, and PEO-110 (Fig. 1). The water uptake of the polymer binders was measured as previously described.^{24,25}

Nafion solution (Nafion® 117 solution, ~5 wt% in a mixture of lower aliphatic alcohols and water) and poly(bisphenol A-*co*-epichlorohydrin) (BAEH, Aldrich, $M_w \approx 40\ 000$) (Fig. 1) were purchased from Aldrich. BAEH was dissolved in tetrahydro-furan (THF), precipitated in methanol, filtered and dried under reduced pressure at 40 °C to remove residual epichlorohydrin prior to use.

3.2 Cathode construction

All cathodes were constructed identically except for the type of polymer binder and Nafion solution was composed of an alcohol and water solvent mixture, whereas THF was used for the other polymer solutions. Round cathodes with 3 cm diameter ($A_{cathode} = 7 \text{ cm}^2$) were fabricated *via* brush application of the binder solution containing carbon-supported Pt catalyst (10% Pt on Vulcan XC-72, BASF Fuel Cell Inc.) on wet-proofed carbon cloth (type B-1B, E-TEK) with four PTFE diffusion layers as previously described.⁷ The catalyst (0.5 mg cm⁻² Pt for cathodes with PEO-0, PEO-25, PEO-110, Nafion, and BAEH binders and 0.05 mg cm⁻² Pt for cathodes with other Nafion and BAEH binders) was applied to each cathode with 33 µL cm⁻² of 5 wt% polymer solution. Cathodes were named after binders and loading of Pt, *i.e.* PEO-0, PEO-25, PEO-110, 0.5 mg cm⁻² Pt Nafion, and 0.05 mg cm⁻² Pt BAEH, 0.05 mg cm⁻² Pt Nafion, and 0.05 mg cm⁻² Pt BAEH.

3.3 Electrochemical measurements

Linear sweep voltammetry (LSV) was performed at 1 mV s⁻¹ (Gamry Instrument model PC4/750, Warminster, PA) on the cathodes at 30 °C in an atmospheric environment. The reactor (13 mL volume) was filled with 200 mM PBS (pH = 7) and equipped with 7 cm² platinum disc counter electrode and an Ag/AgCl reference electrode (RE-5B, Bioanalytical Systems Inc., ~0.2 V vs. NHE). Electrochemical impedance spectroscopy (EIS) using the same potentiostat in the same reactor configuration as for LSV was conducted at 0.2 V (vs. NHE) over a frequency range of 10⁵ to 0.004 Hz with a sinusoidal perturbation of 10 mV. The charge transfer resistance (R_{ct}) was determined by fitting the charge transfer impedance to an RC circuit. All electrochemical measurements were performed with freshly made cathodes, *i.e.* prior to MFC measurements.

3.4 MFC measurements

Single-chambered MFC reactors containing a cylindrical chamber (4 cm length and 3 cm diameter, total liquid volume 28 mL) equipped with ammonia-treated graphite brushes (25 mm diameter \times 25 mm length, 0.22 m² surface area)^{26,27} were used to examine cathode performance. Reactors were inoculated with the anode solution from another acetate-fed MFC reactor which had been running for several months with sodium acetate $(0.5 \text{ g L}^{-1} \text{ as acetate})$ in 100 mM phosphate buffer solution (PBS, 9.152 g L⁻¹ Na₂HPO₄, 4.904 g L⁻¹ NaH₂PO₄·H₂O; pH 7.0 with the addition of 0.31 g L⁻¹ NH₄Cl and 0.13 g L⁻¹ KCl). After several fed-batch cycles (using Nafion cathodes) at room temperature (23 °C), polarization and power density measurements were performed to ensure all anodes had the same performance. Then, the experimental cathodes were placed into reactors and tested for their performance. The produced voltage (E_{cell}) was monitored across a fixed resistance (1000 Ω) using a multimeter data acquisition system (2700 Keithley, USA). Electrode potentials were measured using a digital multimeter (22-813, Radioshack, USA) and Ag/AgCl reference electrode. The polarization and power density curves as a function of current density were taken after 15 min at each external resistance (75–1000 Ω). Current (I = V/R), current density (J = I/A_{cathode}), power density ($P_{\text{cat}} = IV/A_{\text{cathode}}$), and coulombic efficiency (CE) based on total input of acetate were calculated as previously described.2,28

4. Conclusions

Increasing the hydrophilicity of the neutral cathode catalyst binder enhanced the electrochemical performance of the cathode and increased power densities during MFC tests. Except for Nafion, which has sulfonate groups attached to the polymer backbone, neutral binders with greater water uptake increased the accessible surface area for oxygen reduction and thus increased device performance. BAEH cathodes showed similar kinetic responses compared to Nafion for oxygen reduction in LSV at high Pt loadings. BAEH-based cathodes resulted in lower MFC performance than the Nafion-based cathode during initial reactor cycles, however, the performance of cells with BAEH and Nafion-based cathodes became similar in later cycles. When MFCs were operated for more than 40 days, the performance of all reactors was nearly equivalent irrespective of the type of polymeric cathode catalyst binder used and only depended on Pt loading. Biofilm formation on the cathodes was likely a cause of the performance decrease over time and tended to induce similar performance for all cells at long reactor operation times. The CE of the cells did not increase dramatically with biofilm formation, but the power production was clearly affected by the presence of biofilm indicating that cathode matrix fouling for all polymer binders influenced the proton transport to the catalyst sites and equalized cathode performance. This study suggests that different types of polymer binders may be sufficient for long-term MFC operation, although the performance at early times may vary considerably.

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References

- B. E. Logan, *Microbial Fuel Cells*, John Wiley & Sons, Inc., Hoboken, New Jersey, 2007.
- 2 B. E. Logan, B. Hamelers, R. Rozendal, U. Schrorder, J. Keller, S. Freguia, P. Aelterman, W. Verstraete and K. Rabaey, Microbial fuel cells: methodology and technology, *Environ. Sci. Technol.*, 2006, **40**, 5181–5192.
- 3 B. E. Logan, Exoelectrogenic bacteria that power microbial fuel cells, Nat. Rev. Microbiol., 2009, 7, 375–381.
- 4 A. Rinaldi, B. Mecheri, V. Garavaglia, S. Licoccia, P. Di Nardo and E. Traversa, Engineering materials and biology to boost performance of microbial fuel cells: a critical review, *Energy Environ. Sci.*, 2008, 1, 417–429.
- 5 T. Saito, M. D. Merrill, V. J. Watson, B. E. Logan and M. A. Hickner, Investigation of ionic polymer cathode binders for microbial fuel cells, *Electrochim. Acta*, 2010, 55, 3398–3403.
- 6 F. Zhang, T. Saito, S. A. Cheng, M. A. Hickner and B. E. Logan, Microbial fuel cell cathodes with poly(dimethylsiloxane) diffusion layers constructed around stainless steel mesh current collectors, *Environ. Sci. Technol.*, 2010, 44, 1490–1495.
- 7 S. Cheng, H. Liu and B. E. Logan, Increased performance of singlechamber microbial fuel cells using an improved cathode structure, *Electrochem. Commun.*, 2006, 8, 489–494.
- 8 S. Cheng, H. Liu and B. E. Logan, Power densities using different cathode catalysts (Pt and CoTMPP) and polymer binders (Nafion and PTFE) in single chamber microbial fuel cells, *Environ. Sci. Technol.*, 2006, 40, 364–369.

- 9 E. HaoYu, S. Cheng, K. Scott and B. Logan, Microbial fuel cell performance with non-Pt cathode catalysts, *J. Power Sources*, 2007, 171, 275–281.
- 10 F. Zhao, F. Harnisch, U. Schroder, F. Scholz, P. Bogdanoff and I. Herrmann, Application of pyrolysed iron(II) phthalocyanine and CoTMPP based oxygen reduction catalysts as cathode materials in microbial fuel cells, *Electrochem. Commun.*, 2005, 7, 1405–1410.
- 11 Y. Zuo, S. Cheng and B. E. Logan, Ion exchange membrane cathodes for scalable microbial fuel cells, *Environ. Sci. Technol.*, 2008, 42, 6967– 6972.
- 12 S. Freguia, K. Rabaey, Z. Yuan and J. Keller, Non-catalyzed cathodic oxygen reduction at graphite granules in microbial fuel cells, *Electrochim. Acta*, 2007, **53**, 598–603.
- 13 F. Zhang, S. A. Cheng, D. Pant, G. Van Bogaert and B. E. Logan, Power generation using an activated carbon and metal mesh cathode in a microbial fuel cell, *Electrochem. Commun.*, 2009, 11, 2177–2179.
- 14 P. Aelterman, M. Versichele, E. Genettello, K. Verbeken and W. Verstraete, Microbial fuel cells operated with iron-chelated air cathodes, *Electrochim. Acta*, 2009, 54, 5754–5760.
- 15 X. Y. Zhang, S. A. Cheng, X. Huang and B. E. Logan, The use of nylon and glass fiber filter separators with different pore sizes in air-cathode single-chamber microbial fuel cells, *Energy Environ. Sci.*, 2010, **3**, 659–664.
- 16 A. P. Borole, D. Aaron, C. Y. Hamilton and C. Tsouris, Understanding long-term changes in microbial fuel cell performance using electrochemical impedance spectroscopy, *Environ. Sci. Technol.*, 2010, 44, 2740–2744.
- 17 P. D. Kiely, G. Rader, J. M. Regan and B. E. Logan, Long-term cathode performance and the microbial communities that develop in microbial fuel cells fed different fermentation endproducts, *Bioresour. Technol.*, 2011, **102**, 361–366.

- 18 X. Y. Zhang, S. A. Cheng, X. Wang, X. Huang and B. E. Logan, Separator characteristics for increasing performance of microbial fuel cells, *Environ. Sci. Technol.*, 2009, 43, 8456–8461.
- 19 B. K. Li and B. E. Logan, Bacterial adhesion to glass and metal-oxide surfaces, *Colloids Surf.*, B, 2004, 36, 81–90.
- 20 M. Herzberg and M. Elimelech, Biofouling of reverse osmosis membranes: role of biofilm-enhanced osmotic pressure, J. Membr. Sci., 2007, 295, 11–20.
- 21 K. J. Howe and M. M. Clark, Fouling of microfiltration and ultrafiltration membranes by natural waters, *Environ. Sci. Technol.*, 2002, **36**, 3571–3576.
- 22 L. O. Villacorte, M. D. Kennedy, G. L. Amy and J. C. Schippers, The fate of transparent exopolymer particles (TEP) in integrated membrane systems: removal through pre-treatment processes and deposition on reverse osmosis membranes, *Water Res.*, 2009, **43**, 5039–5052.
- 23 M. A. Hillmyer and F. S. Bates, Synthesis and characterization of model polyalkane-poly(ethylene oxide) block copolymers, *Macromolecules*, 1996, **29**, 6994–7002.
- 24 H. D. Moore, T. Saito and M. A. Hickner, Morphology and transport properties of midblock-sulfonated triblock copolymers, *J. Mater. Chem.*, 2010, **20**, 6316–6321.
- 25 T. Saito, H. D. Moore and M. A. Hickner, Synthesis of midblocksulfonated triblock copolymers, *Macromolecules*, 2010, 43, 599–601.
- 26 B. Logan, S. Cheng, V. Watson and G. Estadt, Graphite fiber brush anodes for increased power production in air-cathode microbial fuel cells, *Environ. Sci. Technol.*, 2007, **41**, 3341–3346.
- 27 S. Cheng and B. E. Logan, Ammonia treatment of carbon cloth anodes to enhance power generation of microbial fuel cells, *Electrochem. Commun.*, 2007, **9**, 492–496.
- 28 S. Cheng, H. Liu and B. E. Logan, Increased power generation in a continuous flow MFC with advective flow through the porous anode and reduced electrode spacing, *Environ. Sci. Technol.*, 2006, 40, 2426–2432.