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Polymer Separators for High-Power, High-Efficiency Microbial Fuel Cells

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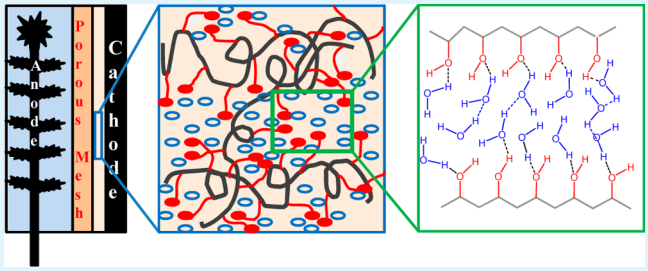
Supporting Information

ABSTRACT: Microbial fuel cells (MFCs) with hydrophilic poly(vinyl alcohol) (PVA) separators showed higher Coulombic efficiencies (94%) and power densities (1220 mW m^{-2}) than cells with porous glass fiber separators or reactors without a separator after 32 days of operation. These remarkable increases in both the coublomic efficiency and the power production of the microbial fuel cells were made possible by the separator's unique characteristics of fouling mitigation of the air cathode without a large increase in ionic resistance in the cell. This new type of polymer gel-like separator design will be useful for improving MFC reactor performance by enabling compact cell designs.



KEYWORDS: *microbial fuel cell, membrane, poly(vinyl alcohol), Coulombic efficiency, separator*

Microbial fuel cells (MFCs)[1] have received a great deal of attention as a novel process for alternative energy generation[2,3] and wastewater treatment.[4,6] Despite significant efforts focused on increasing MFC performance through reactor engineering, higher power generation and recovery of electrons from the substrate (as Coulombic efficiency; CE) must be improved for large-scale applications. Small volume (14 cm^3 reactor) single chamber, air cathode reactors have been designed to increase power generation by reducing the distance between electrodes to lower the internal resistance of the cell.[7] However, the power output of this cell design can decline as a result of oxygen transfer to bacteria on the anode.[8] Placing separators in the MFC liquid electrolyte between electrodes is necessary to overcome this adverse effect of oxygen diffusion to the anode, and to prevent short circuiting of closely spaced electrodes.

A variety of separators have been explored for use in MFCs. Ion exchange membranes (IEM) including cation exchange membranes (CEMs) such as Nafion,[5] anion exchange membranes (AEMs),[9] and bipolar membranes,[10] have been used in different types of MFCs to improve CEs by inhibiting oxygen transfer from the air cathode to the biotic anode. In most cases a decrease in power generation was observed due to pH changes that resulted from selective ion transport across the membrane.[11] An increase in internal resistance, caused by the separator's ionic impedance[12] also lowered the output power[13,14] when IEMs were used. Noncharged, size-selective separators such as porous filtration membranes[15,16] have been examined in MFCs, but these types of materials had lower CEs than IEMs due to their high oxygen and substrate permeability.[17] J-cloth (JC),[18] a macroporous filter, was a successful separator for improving power production in MFCs.[19] However, the low resulting CE and biodegradability[20] of JC are serious limitations for long-term device operation. Porous glass fiber separators exhibited higher CE and maximum power densities similar to JC, and have been shown to function well in long-term operation due to their nonbiodegradability, superior ion transport capability, and lower cost compared to IEMs.[19] Unfortunately, the poor mechanical durability of glass fiber can limit their practical application in MFCs (the fibrous material can unravel), and the lack of different form factors of glass fiber separators prevents their use in nontraditional cell geometies.[17] Additionally, the formation of thick biofilms on the cathode decreases power generation by hindering proton transfer,[21] and lowers CE because of aerobic bacterial consumption of substrate at the cathode.[20] An ideal separator should have superior hydrophilicity for high ion transport and low internal resistance, be noncharged to avoid ion selectivity and pH changes, have low oxygen transport for high CE, possess good mechanical properties for resisting deformation and shear in the reactor, and have antibiofouling properties to ensure long-term operation with stable power output.

Polyvinyl alcohol (PVA), a commercial polymer made from hydrolysis of poly(vinyl acetate),[22] has been studied as a membrane because of its low cost, good film-forming properties, high hydrophilicity, and good mechanical and chemical-resistant properties.[23] In this study, PVA membranes with varying porosities induced by the dissolution of a porogen (tetrabutylammonium chloride) in the PVA[24] were used as separators in MFCs. PVA membranes were prepared by

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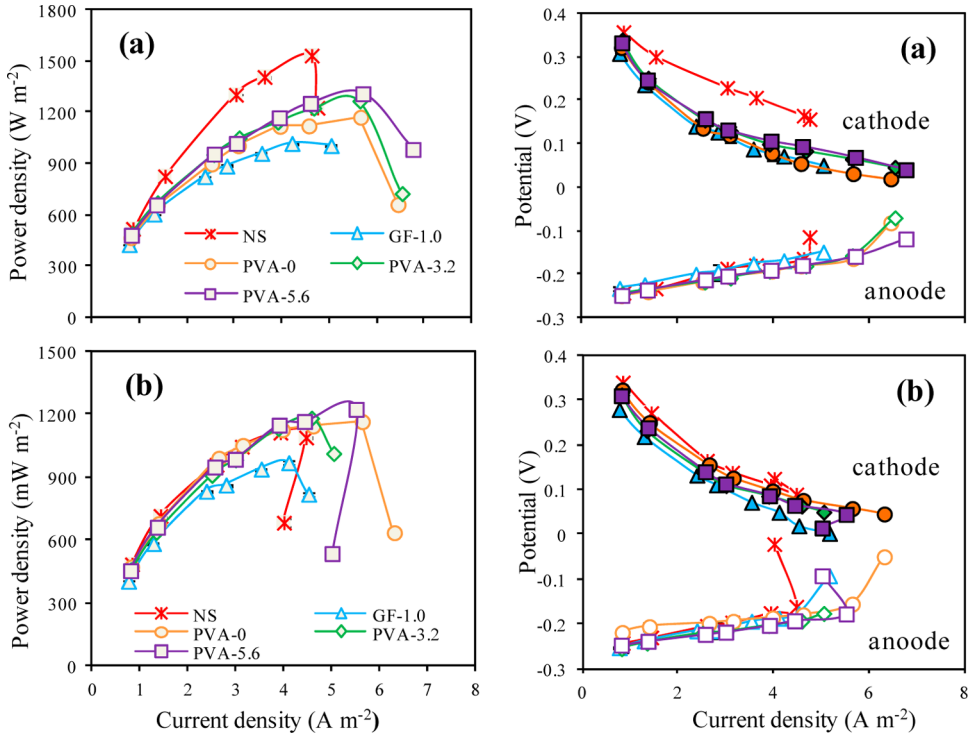

Figure 1. Power density curves (left column) and corresponding cathode and anode potentials (vs NHE) (right column) at (a) the 6th cycle and (b) the 17th cycle with different separators.

dissolving PVA powder in water at 90 °C and solution casting to form mechanically stable films (see the Supporting Information for procedures). When the membranes were placed in water (30 °C) the membranes swelled but maintained their dimensional stability. The charge-neutral structure of this separator avoids selective ion transport and formation of pH gradients in the cell[17] and its high hydrophilicity contributes to low ion transport resistance and some antifouling function at the cathode.[25] The PVA separators in this work were designed specifically to optimize the balance of CE and power production of MFCs. The MFC performance with PVA separators was benchmarked against cells without separators and previously reported glass fiber separators.

Linear sweep voltammetry (LSV) scans of the air cathodes (see Figure S1a in the Supporting Information) showed higher current densities for MFCs with no separator compared to those with separators due to an increase in internal resistance caused by the separator.[26] The solution (R_s) and charge transfer resistances (R_{ct}) of new cathodes, obtained using electrochemical impedance spectroscopy (EIS)[27] (see Figure S1b and Table S1 in the Supporting Information), with different separators were greater than those of cathodes with no separators (NS) because of the presence of the separator. This demonstrated that the separators impeded mass transfer to cathodes.[19] The R_s and R_{ct} decreased slightly with increasing porogen in the PVA separators.

During MFC operation (see Figure S2a in the Supporting Information), the maximum voltage produced (see Figure S2b in the Supporting Information) at a fixed resistance (1000 Ω) decreased slightly over many feeding cycles (with fresh medium) due to biofilm formation on the cathodes. For the initial cycles (sixth cycle), MFCs with PVA separators had higher maximum power densities (P_{max}) (Figure 1a) than those with glass fiber (GF-1.0) separators, but lower power output than NS reactors, consistent with the results of LSV and EIS tests. Among all MFCs with PVA separators, PVA-5.6 (PVA separator with 5.6 wt % porogen, see the Supporting Information) exhibited the highest P_{max}, likely due to its higher porosity than the other PVA samples (PVA-0, PVA separator without porogen; PVA-3.2, PVA separator with 3.2 wt % porogen). All MFCs had a lower P_{max} as a result of biofilm development on the cathodes after 17 cycles of operation (Figure 1b and Table S2 in the Supporting Information).

The highest P_{max} (1220 mW m^{-2}) was obtained in the MFC with the PVA-5.6 separator, which was about 10% higher than the NS reactor and 26% greater than the MFC with a GF-1.0 separator. A thicker biofilm formed on the NS cathode than on the PVA separators (see Figure S3 in the Supporting Information), resulting in higher impedance for proton transfer to the cathode, and demonstrating that PVA separators reduced bacterial growth on the cathode. The EIS results of the different separators after cycling (see Figure S1c in the Supporting Information) showed that the cathodes with PVA separators had lower R_s and R_{ct} (see Table S1 in the Supporting Information), in agreement with their higher power densities. These results are consistent with PVA separators improving power by reducing biofouling through biofilm formation or preventing biopolymer penetration into the cathode structure.

The CEs of MFCs with PVA separators were 10−15% higher than the CEs of cells with GF-1.0 and NS over a range of current densities (Figure 2). MFCs with NS showed larger increases in CE after cycling (see Table S2 in the Supporting Information) because of biofilm formation on the cathode, which increased the CE by hindering oxygen intrusion into the cell, but decreased power generation by impeding ion transport to the cathode. CEs started high and increased slightly for cells with PVA separators indicating that the PVA separators reduced oxygen permeation to the anode compared to the

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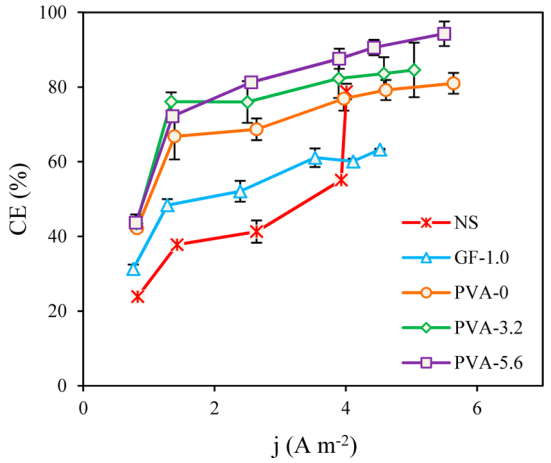

Figure 2. CE as a function of current density for MFCs with various separators.

NS case (see Table S3 in the Supporting Information). The slight increase in CE was likely due to some biofilm formation on the separator. MFCs with PVA separators showed CEs in the range of 42% to 90% (maximum current densities of 0.8 to 5.6 A m^{-2}), which were significantly higher than cells with NS over the same range of current densities (see Table S4 in the Supporting Information). PVA separators showed 10−30% higher CEs than MFCs with GF-1.0 separators.

In previous work,[19] it was shown that a trade-off existed between power generation and CE. MFCs with PVA separators uniquely showed both higher CE and higher power density compared to other common separators (Figure 3 and Table S5

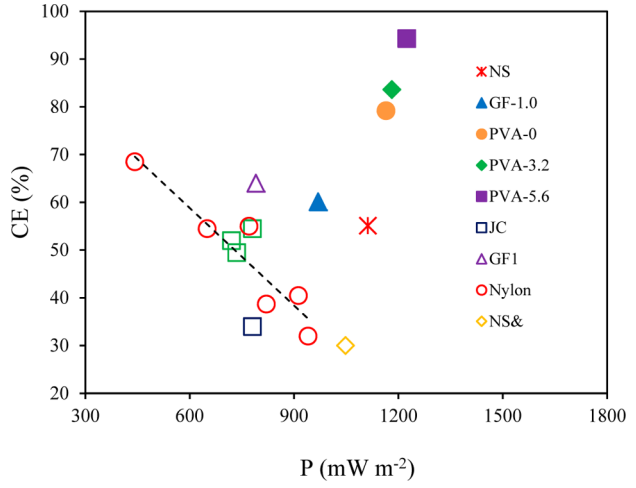

Figure 3. CE at the current density of maximum power as a function of maximum power density for different separators. Data for NS, GF-1.0, and PVA separators (filled symbols) are from this study. Data (opened symbols) for glass fiber (GF1), JC, and nylon are from Zhang et al.[19].

in the Supporting Information). PVA separators in MFCs maintained low ion transport resistance which enabled high power production. By increasing the salt content of the PVA membrane during fabrication, the power production of the cell was slightly increased. Water-swollen PVA separators also acted as a barrier to oxygen transport, which increased the CE of the cell.

The remarkable combination of greater power production and higher CE obtained in this study demonstrates that hydrophilic, uncharged membranes can open new avenues to high performance MFCs. Careful design of the separator to achieve low ionic resistance, yet exclude oxygen from the anode and bacteria from the cathode, will allow more flexibility in the design of reactors that achieve high utilization of the organic substrate with high power production.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details of PVA separator fabrication, MFC constructions, and electrochemical experiments. 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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■ REFERENCES

(1) Logan, B. E.; Regan, J. M. *Trends Microbial.* **2006**, *14* (12), 512−518.
(2) Lovley, D. R. *Curr. Opin. Biotech.* **2008**, *19* (6), 564−571.
(3) Rabaey, K.; Verstraete, W. *Trends Biotechnol.* **2005**, *23* (6), 291−298.
(4) Logan, B. E. *Microbial Fuel Cells*; John Wiley & Sons: Hoboken, NJ, 2007.
(5) Logan, B. E.; Hamelers, B.; Rozendal, R.; Schröder, U.; Keller, J.; Freguia, S.; Aelterman, P.; Verstraete, W.; Rabaey, K. *Environ. Sci. Technol.* **2006**, *40*, 5181−5192.
(6) Shizas, I.; Bagley, D. M. *J. Energy Eng.−ASCE* **2004**, *130*, 45−53.
(7) Liu, H.; Logan, B. E. *Environ. Sci. Technol.* **2005**, *39*, 5488−5493.
(8) Cheng, S. A.; Liu, H.; Logan, B. E. *Environ. Sci. Technol.* **2006**, *40* (7), 2426−2432.
(9) Kim, J. R.; Cheng, S. A.; Sang-Eun, O.; Logan, B. E. *Environ. Sci. Technol.* **2007**, *41*, 1004−1009.
(10) Cao, X. X.; Huang, X.; Liang, P.; Xiao, K.; Zhou, Y. J.; Zhang, X. Y.; Logan, B. E. *Environ. Sci. Technol.* **2009**, *43*, 7148−7152.
(11) Rozendal, R. A.; Hamelers, H. V. M; Molenkamp, R. J. C.; Buisman, J. N. *Water Res.* **2007**, No. 41, 1984−1994.
(12) Harnisch, F.; Schröder, U. *ChemSusChem.* **2009**, *2*, 921−926.
(13) Kim, B. H.; Chang, I. S.; Gadd, G. M. *Appl. Microbiol. Biotechnol.* **2007**, *76*, 485−494.
(14) Rozendal, R. A.; Hamelers, H. V. M; Buisman, J. N. *Environ. Sci. Technol.* **2006**, No. 40, 5206−5211.
(15) Zuo, Y.; Cheng, S. A.; Call, D.; Logan, B. E. *Environ. Sci. Technol.* **2007**, *41*, 3347−3353.
(16) Sun, J.; Hu, Y. Y.; Bi, Z.; Cao, Y. Q. *J. Power Sources* **2009**, *187*, 471−479.
(17) Li, W. W.; Sheng, G. P.; Liu, X. W.; Yu, H. Q. *Bioresour. Technol.* **2011**, *102*, 244−252.
(18) Fan, Y. Z.; Hu, H. Q.; Liu, H. *J. Power Sources* **2007**, *171* (2), 348−354.
(19) Zhang, X. Y.; Cheng, S. A.; Huang, X.; Logan, B. E. *Energ. Environ. Sci.* **2010**, *3*, 659−664.
(20) Zhang, X. Y.; Cheng, S. A.; Wang, X.; Huang, X.; Logan, B. E. *Environ. Sci. Technol.* **2009**, *43*, 8456−8461.

(21) Cheng, S. A.; Liu, H.; Logan, B. E. *Environ. Sci. Technol.* **2006**, *40* (1), 364−369.
(22) Wang, Y. H; Hsieh, Y-L *J. Appl. Polym. Sci.* **2010**, *116*, 3249−3255.
(23) Rhim, J.-W.; Yeom, C.-K.; Kim, S.-W. *J. Appl. Polym. Sci.* **1998**, *68*, 1717−1723.
(24) Patachia, S.; Florea, C.; Friedrich, C.; Thomann, Y. *Express Polym. Lett.* **2009**, *3* (5), 320−331.
(25) Krishnan, S.; Weinman, C. J.; Ober, C. K. *J. Mater. Chem.* **2008**, *18*, 3405−3413.
(26) Watson, V. J.; Saito, T.; Hickner, M. A.; Logan, B. E. *J. Power Sources* **2011**, *196*, 3009−3014.
(27) Cheng, S. A.; Liu, H.; Logan, B. E. *Electrochem. Commun.* **2006**, *8*, 489−494.