Power Generation Using Different Cation, Anion, and Ultrafiltration Membranes in Microbial Fuel Cells

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Proton exchange membranes (PEMs) are often used in microbial fuel cells (MFCs) to separate the liquid in the anode and cathode chambers while allowing protons to pass between the chambers. However, negatively or positively charged species present at high concentrations in the medium can also be used to maintain charge balance during power generation. An anion exchange membrane (AEM) produced the largest power density (up to 610 mW/m²) and Coulombic efficiency (72%) in MFCs relative to values achieved with a commonly used PEM (Nafion), a cation exchange membrane (CEM), or three different ultrafiltration (UF) membranes with molecular weight cutoffs of 0.5K, 1K, and 3K Daltons in different types of MFCs. The increased performance of the AEM was due to proton charge-transfer facilitated by phosphate anions and low internal resistance. The type of membrane affected maximum power densities in two-chamber, air-cathode cube MFCs (C-MFCs) with low internal resistance (84–91 Ω for all membranes except UF-0.5K) but not in two-chamber aqueous-cathode bottle MFCs (B-MFCs) due to their higher internal resistances (1230–1272 Ω except UF-0.5K). The UF-0.5K membrane produced very high internal resistances (6009 Ω, B-MFC; 181452, C-MFC) and was the least permeable to both oxygen (mass transfer coefficient of kO₂=0.19 × 10⁻⁴ cm/s) and acetate (kA₈=0.89 × 10⁻⁸ cm/s). Nafion was the most permeable membrane to oxygen (kO₂=1.3 × 10⁻⁴ cm/s), and the UF-3K membrane was the most permeable to acetate (kA₈=7.2 × 10⁻⁸ cm/s). Only a small percent of substrate was unaccounted for based on measured Coulombic efficiencies and estimates of biomass production and substrate losses using Nafion, CEM, and AEM membranes (4–8%), while a substantial portion of substrate was lost to unidentified processes for the UF membranes (40–89%). These results show that many types of membranes can be used in two-chambered MFCs, even membranes that transfer negatively charged species.

Introduction

Microbial fuel cells (MFCs) have been studied as bioreactors to convert various pure substrates and wastewaters into electricity (1–3). Two-chamber MFCs consist of an anode and a cathode chamber typically separated by a proton exchange membrane (PEM) such as Nafion (4). Bacteria in the anode chamber oxidize substrate and transfer electrons to the external circuit through the anode. Protons transferred to the cathode through water and the PEM combine with oxygen and electrons to form water. Although ferricyanide has been used for cathode electrolyte in some reports (5, 6), oxygen-based cathodes provide a more sustainable method of power generation (6–8).

The main function of the PEM in two-chambered MFCs is to keep the liquid contents of the reactors separate while allowing protons to pass between the chambers. While Nafion is used in most chemical fuel cells (9, 10) and many two-chambered MFCs (5, 11, 12), cation exchange membranes (CEMs) are also commonly used in MFCs (3, 13) as they are less expensive and often structurally stronger than Nafion. Both PEMs and CEMs help to reduce oxygen diffusion into the anode chamber. Liu et al. (7) demonstrated that removing the PEM in a single-chamber MFC increased oxygen diffusion into the system and reduced the Coulombic efficiency (CE) from 44–55% to 9–12%, although the power increased due to a reduction in the internal resistance. In two-chamber systems, the type of PEM affects not only oxygen transfer into the anode chamber but also substrate losses into the cathode chamber. The effect of the membrane type (PEM or CEM) on reactor performance has not been well studied in terms of oxygen and substrate fluxes in MFCs or their effects on internal resistance.

It was recently shown that cations in the MFC medium (e.g., Na⁺, K⁺, Ca²⁺, and others), typically present at 10⁵ higher concentrations than protons, are primarily responsible for the transport of positive charge across Nafion membranes (11). The transfer of these species, as opposed to protons, results in increased pHs at cathode and reduced voltages.

Materials and Methods

MFC Construction and Operation. Two different types of two-chambered MFCs were constructed to compare the performance of the membranes: a two-bottle, aqueous cathode MFC (B-MFC) and a two-chamber, air-cathode cube MFC (C-MFC) (Figure 1). B-MFCs were constructed using two media bottles (320 mL capacity, Corning Inc. NY) joined with a glass tube containing a 2.1 cm diameter membrane as previously described (14, 15). Anode and cathode electrodes (total electrode spacing of 12 cm) were made of plain porous carbon paper (TGPH-120 Toray carbon paper, E-Tek, Pennsylvania State University).
MFCs used for experiments.

**FIGURE 1.** (A) Two-bottle (B-MFC) and (B) and two-cube (C-MFC)

MFCs used for experiments.

2.5 cm × 4.5 cm, projected area of 22.5 cm². The cathode contained a Pt catalyst (0.35 mg/cm²; 10% Pt; E-Tek, NJ). This B-MFC has been shown to have high internal resistance (>1286 ± 1 Ω) with a Nafion membrane (12).

C-MFCs were constructed from two plastic (Plexiglas) cylindrical chambers each 2 cm long by 3 cm in diameter (liquid volume of each chamber was 14 mL) separated by the membrane. The anode was carbon cloth (non-wet-proofed, type A, E-Tek) with a projected area of 7.0 cm² of one side. The cathode electrode (30 wt % wet-proofed carbon cloth, type B, with 0.5 mg/cm² Pt) was exposed to air (16, 17). These reactors were essentially the same as those used by Liu and Logan (7), except a membrane was placed in the middle of the chamber and not hot-pressed to the cathode. This allowed oxygen to react at the air cathode, but it reduced the anode chamber volume to 14 mL. The membrane was held in place with a rubber ring on each side to prevent leakage (Figure 1B). The electrodes were placed on opposite sides at the end of two chambers (4-cm spacing).

The reactors were inoculated using anaerobic sludge (10 mL) and acetate (20 mM) in a nutrient medium containing (g/L in deionized water, pH 7): NH₄Cl (0.31), KCl (0.13), NaH₂PO₄•H₂O (2.69), Na₂HPO₄ (4.33), and a trace mineral and vitamin solution (14). The reactor then operated until the voltage started to decrease from the maximum value (270–280 mV, 1000 Ω) after ~7 days, and then it was switched to a medium lacking the sludge and operated in fed-batch mode until there was a repeatable cycle of power generation (15). This nutrient medium was used for both the anode and cathode chambers. All MFC tests were conducted over multiple fed-batch cycles, with the B-MFC tests conducted in duplicate and the C-MFCs as single reactor tests. All MFC tests were conducted in a temperature controlled room (30 °C).

**Membranes.** Nafion 117 (Dupont Co., DE) was pretreated by boiling in H₂O₂ (30% v/v) and deionized water, followed by soaking in 0.5 M H₂SO₄ and then deionized water, each for 1 h. In order to prevent membrane swelling by water when it was placed in the MFC compartment, membranes were stored in deionized water prior to use (15). CEM (CMI-7000) and AEM (AMI-7001, both from Membrane International Inc., NJ) were preconditioned by immersion in a salt solution (NaCl) to allow for membrane expansion. UF membranes (DIVFLO ultrafiltration, Amicon, Inc., MA) with three different molecular cutoff weights of 0.5K (UF-0.5K), 1K (UF-1K), and 3K (UF-3K) were stored in deionized water and gently rinsed prior to use.

**Oxygen and Acetate Mass Transfer and Diffusion Coefficients.** Oxygen mass transfer coefficients for each membrane were determined using uninoculated B-MFC reactors and nutrient medium. A dissolved oxygen (DO) probe (Foxy-21G, Ocean Optics Inc., FL) (15) was placed in the anode chamber, and the water was sparged with nitrogen gas to remove dissolved oxygen (DO). The cathode chamber was continuously aerated to maintain saturated DO conditions. The mass transfer coefficient of oxygen in the membrane, kₜₒ, was determined by monitoring the DO concentration over time and using the mass balances eq 18 (see the Supporting Information)

\[ k_{t_{0}} = - \frac{V}{A \cdot t} \ln \left( \frac{c_{t_{0}} - c_{t}}{c_{t_{0}}} \right) \]  

where \( V \) is the liquid volume in the anode chamber (320 mL), \( A \) is the membrane cross-sectional area, \( c_{t_{0}} \) is the saturated oxygen concentration in the cathode chamber, and \( c_{t} \) is the DO in the anode chamber at time \( t \). The diffusion coefficient \( D \), \( cm²/s \) for each chemical was calculated as \( D_{0} = k_{t_{0}} \), where \( L_t \) is the membrane thickness reported by the manufacturer.

The mass transfer coefficient and diffusion coefficients for acetate were determined in the same way (see the Supporting Information) using

\[ k_{t_{a}} = - \frac{V}{2A \cdot t} \ln \left( \frac{c_{t_{10}} - 2c_{t}}{c_{t_{10}}} \right) \]  

This equation is slightly different from eq 1 due to the depletion of acetate in the anode chamber over time.

**Analyses.** The voltage (V) across an external resistor (1000 Ω except as noted) in the MFC circuit was monitored at 30 min intervals using a multimeter (Keithley Instruments, OH) connected to a personal computer. Current (I), power (P=IV), and Coulombic efficiency (CE) were calculated as previously described (14). The power density of MFC was calculated by normalizing power to the anode projected surface area. Internal resistance, \( R_{an} \), of the reactors with different membranes (or without a membrane) was measured in duplicate using uninoculated reactors by electrochemical impedance spectroscopy (EIS) using a potentiostat (PC4/750 potentiostat, Gamry Instrument Inc., PA) with the anode as the working electrode and the cathode as the counter and reference electrode. Impedance measurements were conducted at the open circuit voltage (OCV) over a frequency range of 10⁵–0.1 Hz with sinusoidal perturbation of 10 mV amplitude (19). To obtain measurements, the two chambers were filled with a nutrient buffer media containing 50 mM phosphate (pH 7.0).

Phosphate concentrations were measured using the total phosphate method (HACH Company, Loveland, CO.) (20).
Sodium was measured using an Atomic Absorption spectrophotometer (Shimadzu, AA-6601F) equipped with a sodium lamp (VWR, Hollow Cathode Lamp, 58137-634). Acetate was measured using a gas chromatograph equipped with a FID and a DB-FFAP fused-silica capillary column with helium as a carrier gas (7).

In order to determine the fate of electrons produced by acetate degradation, a Coulombic balance was made using

\[ C_T = C_A + C_C + C_O + C_{O_2} \]  

where \( C_T \) is the total coulomb added as substrate (acetate), \( C_A \) is coulombs recovered as electricity, and \( C_C \) is the anaerobic biomass estimated from \( C_O \). \( C_O \) is coulomb loss by aerobic respiration estimated from a calculation of oxygen flux based on the measured mass transport coefficient for oxygen through the membrane, and \( C_{O_2} \) is the loss of coulombs estimated using the mass transfer coefficient for acetate flux through the membrane into the cathode chamber. \( C_T \) was calculated from the measured voltage and resistance as described above. \( C_A \) was calculated using the cellular yield of *Geobacter sulfurreducens* as previously reported (21) based on the average value taken from two different types of cocultures. \( C_O \) was calculated assuming a stoichiometric conversion of acetate with oxygen based on (22):

\[
\text{CH}_3\text{COO}^- + 1.184\text{O}_2 + 0.16\text{NH}_4^+ \rightarrow 0.16\text{C}_3\text{H}_4\text{O}_5\text{N}^- + 0.832\text{H}_2\text{O} + 0.84\text{HCO}_3^- + 0.344\text{CO}_2
\]  

\( C_O \) was derived from a mass balance equation for the anode chamber. The concentration gradient between the anode and cathode was a time-dependent variable. Therefore, an ordinary differential equation was solved to calculate the total loss of acetate over time (see the derivation in the Supporting Information) as

\[
C_A(t) = \exp(-k_A A t) \times \left( \frac{k_{O_2} \text{DO}_{\text{cathode}}}{k_{A} A} \right) \left[ \frac{M_A}{M_{O_2}} \right] \left[ 1 - \frac{1}{F e} \right] + \frac{M_A}{k_{A} A} \left( \frac{k_{O_2} \text{DO}_{\text{cathode}}}{k_{A} A} \right) \left[ \frac{M_A}{M_{O_2}} \right] \left[ 1 - \frac{1}{F e} \right]
\]  

**Results**

**Internal Resistances in MFCs Using Different Membranes.** The relative internal resistances of the B-MFCs and C-MFCs with primarily a function of the electrode spacing as expected from previous findings (19, 23). Internal resistances for membranes in the B-MFCs ranged from 1239 to 1006, 9 1814, 84 to 98 Ω for all membranes except UF-0.5K. Both the Nafion and CEM membranes did not produce significantly larger values relative to the control (no membrane) internal resistance of 84 ± 3 Ω. These results, based on internal resistance, suggest that all membranes other than the UF-0.5K membrane were well suited for MFC use (19).

**Power Generation and CEs in B-MFCs.** Voltages generated with all membranes except the UF-0.5K membrane (maximum voltage of 100 ± 4 mV) were similar (268–298 mV) when examined in the B-MFCs (Figure 2A). The cycles of voltage generation shown in Figure 2A were all obtained after several acclimation cycles with reproducible levels of power generation. Maximum power densities, obtained from polarization and power density curves, ranged from 33 to 38 mW/m² for all membranes except the UF-0.5K membrane (Table 1). These maximum power densities values are in good agreement with those previously obtained (33–45 mW/m²) with this same B-MFC configuration and similar solution chemistry using different substrates and inocula (3, 24, 25). The power density generated is known to be limited by high internal resistance resulting from large distances between the electrodes (19, 23). Thus, the effect of the membranes on power density could not be distinguished in the B-MFCs due to the membrane not being a significantly different in the high internal resistance.

**Power Generation and CEs in C-MFCs.** The proton, cation, anion, and one UF membrane (UF-1K) were compared for maximum power density using the C-MFCs having substantially lower internal resistances. In these tests, a clear difference in power generation was observed that could be attributed to membrane performance (Figure 3A). The maximum power density was greatest for AEM (610 mW/m², 15 W/m³), followed by the Nafion (514 mW/m²), CEM (480 mW/m²), and UF-1K (462 mW/m²) membranes (Table 1; all maxima reported at the same current density of ~0.13 mA/cm²).

![Figure 2](image_url)

**Table 1.** Internal Resistances and Maximum Power Density for B-MFC and C-MFC Reactors

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Internal Resistance (Ω)</th>
<th>Maximum Power (mW/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No membrane</td>
<td>B-MFC 1230 ± 44</td>
<td>C-MFC 84 ± 3</td>
</tr>
<tr>
<td>Nafion</td>
<td>1272 ± 24</td>
<td>84 ± 4</td>
</tr>
<tr>
<td>CEM</td>
<td>1308 ± 18</td>
<td>84 ± 2</td>
</tr>
<tr>
<td>AEM</td>
<td>1239 ± 27</td>
<td>88 ± 4</td>
</tr>
<tr>
<td>UF-0.5K</td>
<td>6009 ± 58</td>
<td>1814 ± 15</td>
</tr>
<tr>
<td>UF-1K</td>
<td>1239 ± 52</td>
<td>98 ± 5</td>
</tr>
<tr>
<td>UF-3K</td>
<td>1233 ± 46</td>
<td>91 ± 6</td>
</tr>
</tbody>
</table>

*a* Not applicable. *b* Not measured.
CEs measured for the different membranes increased with current density (Figure 3B). The AEM membrane achieved the highest CEs at current densities above 0.19 mA/cm² (54% at 0.193 mA/cm² to 72% at 0.274 mA/cm²). At lower current densities (0.075–0.196 mA/cm²) the CEM membrane produced the largest CEs (41–54%). Nafion and the UF-1K membranes produced similar CEs of 41–46% and 38–49%, respectively.

The Role of Solution Chemistry and Membranes on Performance. The improved performance of the AEM membrane in the C-MFC was due to the chemical characteristics of the membrane (–NH₃⁺ functional groups) versus those of the proton and cation membranes (–SO₃⁻ functional groups), and the chemical groups exchanged by these membranes. In order to examine system performance in terms of their effect on solution characteristics, pH, sodium, and phosphate concentrations were monitored in the anode and cathode chamber over time using the C-MFCs (Figure 4). During a batch cycle, the pH decrease in the anode chamber due to acetate oxidation and proton production, while the pH increased in the cathode chamber due to proton reduction, consistent with previous reports (11, 26). The reactions occurring at the anode and cathode were

\[
\text{anode: } \text{CH}_3\text{COO}^- + 2\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 7\text{H}^+ + 8\text{e}^- \quad (6)
\]

\[
\text{cathode: } 8\text{H}^+ + 8\text{e}^- + 2\text{O}_2 \rightarrow 4\text{H}_2\text{O} \quad (7)
\]

The pH drop in the anode chamber using a Nafion membrane was observed to be substantially lower (pH=4.9) than in tests with the AEM (pH=6.3). The increase of pH in the cathode was higher with the AEM (pH=9.8) than that found with Nafion membrane (pH=8.1) (Figure 4A,D). Anaerobic bacterial respiration of acetate (eq 6) is inhibited by low pH (27), and thus the pH may have affected bacterial respiration and hence power production. The pH increase in the cathode chamber is expected because protons are lost due to their reaction with oxygen and electrons (eq 7). Protons produced from acetate oxidation were therefore not efficiently transferred to the cathode chamber and accumulated in the anode chamber with the Nafion membrane. As shown by others (11), and also seen in Figure 4B for Na⁺, charge can be transferred through Nafion membranes by cations other than H⁺. The AEM membrane produced very little change in sodium ion concentration due to its anion exchange characteristics (Figure 4E). Thus, the performance of the MFC with a Nafion membrane was likely limited by low pH in the anode chamber rather than the charge transfer performance.

Phosphate concentrations in both chambers changed in tests using the AEM membrane due to the diffusion of phosphate anions through the membrane but not with Nafion (Figure 4C,F). As protons were produced in the anode chamber and used in the cathode chamber over time, the pH decreased in the anode chamber and increased in the cathode chamber. To maintain a charge balance phosphate ions were redistributed across the anion membrane and sodium ions diffused across the Nafion membrane. Once the cycle of power production was over due to exhaustion of the substrate, the anion and cation species redistributed to reach equilibrium of chemical concentrations. We therefore see that with the AEM, orthophosphate anion species (HPO₄²⁻ and H₂PO₄⁻) buffered the pH drop in the anode chamber while maintaining charge balance in both chambers. Because phosphate groups can transfer protons as well as help buffer pH, they increased the performance of the AEM MFC compared to that of the Nafion membrane MFC. Thus, these results show that the transport of ionic species affects voltage generation in an MFC.

Mass Transfer Coefficients. The oxygen mass transfer coefficient for Nafion of 1.3 × 10⁻⁷ cm/s was larger than those measured for the other membranes (Table 2). The CEM and AEM both had lower oxygen mass transfer coefficients, although their oxygen diffusivities were larger due to the thicker membranes. The relatively high value of kₒ means that Nafion has the potential to allow the most oxygen into the anode chamber of these membranes per unit time. While the three UF membranes had the lowest oxygen mass transfer
coefficients compared to the other membranes, two of the UF membranes (UF-1K and UF-3K) had relatively large acetate mass transfer coefficients \( (k_a = 16 \times 10^{-8} \text{ cm/s}) \) and \( (k_a = 27 \times 10^{-8} \text{ cm/s}) \), respectively. The high permeability of these membranes to acetate is consistent with their designed properties to not reject molecules smaller than their molecular weight cut offs. A high value of \( k_a \) will lead to the increased losses of substrate from the anode chamber, reducing Coulombic efficiency in proportion to the dose of substrate. The UF-0.5K membrane had the smallest acetate mass transfer coefficient \( (k_a = 0.89 \times 10^{-8} \text{ cm/s}) \), with the Nafion and AEM membranes having relatively intermediate values \( (k_a = 4.3 \times 10^{-8} \text{ cm/s}) \) and \( k_a = 5.5 \times 10^{-8} \text{ cm/s}) \), respectively. The small mass transfer coefficient of the UF-0.5K membrane is consistent with measurements showing that it has high rejection coefficients (low permeation coefficients) \((28)\).

**Coulombic Balances.** The relative importance of substrate loss by diffusion into the cathode chamber and loss through acetate consumption by aerobic respiration by bacteria in anode chamber (sustained by oxygen diffusion through the membrane) was assessed by an overall Coulombic balance (Table 3). With Nafion, CEM and the AEM membranes, a large percentage of the electrons were recovered as electricity, with CEs ranging from 67.8% to 76.9% (Table 3). Only a small fraction was lost to methanogenesis. The UF-0.5K membrane had a smaller acetate mass transfer coefficient \( (k_a = 0.89 \times 10^{-8} \text{ cm/s}) \), with the Nafion and AEM membranes having relatively intermediate values \( (k_a = 4.3 \times 10^{-8} \text{ cm/s}) \) and \( k_a = 5.5 \times 10^{-8} \text{ cm/s}) \), respectively. The small mass transfer coefficient of the UF-0.5K membrane is consistent with measurements showing that it has high rejection coefficients (low permeation coefficients) \((28)\). The maximum power density of the air-cathode C-MFC using Nafion was 514 mW/m². Nafion did not affect the internal resistance of the reactor when placed in between the electrodes (Table 1). Liu and Logan (7) found, using a similar type of reactor when Nafion was bonded (hot welded) to the cathode, the power decreased as compared with that of MFC without Nafion (262–494 mW/m²). Either this bonding process adversely affected the membrane conduction qualities, or the heat treatment reduced the permeability of the membrane where it was joined to the cathode. The similar maximum power densities of the C-MFC with a membrane, and the single-chamber MFC used by Liu et al. without a membrane, indicates that a membrane can be used without affecting power if it is not bonded to the cathode. The advantage of having a membrane is an increase CE. The CE with the single chamber was only 9–12% without a membrane, while here it was 41–47% using the Nafion membrane between the electrodes. Nafion membranes are expensive. However, by applying diffusion layers to the air-side of the cathode, the CEs of single chamber MFCs lacking a membrane can be increased to 20–32% \((16)\).
Experiments with these various membranes highlights characteristics of MFCs that make them unique in comparison to hydrogen fuel cells. MFCs are inherently limited to low proton concentrations due to near-neutral pH requirements of bacteria, but many other charged species are present that can participate in maintaining charge balance in the liquid between the membranes (11). We have shown here using the AEM that transfer of negatively charged species carrying protons (phosphate anions) will increase power due to a combination of the buffering effect of the phosphate anions, as long as the membrane does not significantly affect internal resistance. This effect of phosphate on buffering the pH was shown here using two-chamber MFCs, but the benefits of increasing solution conductivity using a phosphate buffer may also be important for single-chamber MFCs. As noted by Rozendal et al. (11), there is a possibility of highly localized pH increases at the cathode surface in single-chamber MFCs due to proton consumption. Changes in pH were seen here to be important in two-chambered systems, and it is still a reasonable expectation that localized pH changes can affect power generation. The possibility of using anion exchange-based membranes that transfer anion species that help to buffer pH, or using UF membranes that can be tailored in pore size and charge to meet the special needs of MFCs, opens a new avenue of research for MFC reactor designs for increasing CEIs and power densities.

Acknowledgments

The author thanks D. W. Jones for help with analytical measurements. This research was supported by NSF Grant BES-0401885 and USDA Grant 68-3A75-3-150.

Supporting Information Available

Calculation of diffusion coefficients of oxygen and acetate on the membrane, cell yield from Coulombic efficiency, and acetate flux from the anode chamber to the cathode chamber. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review September 14, 2006. Revised manuscript received November 20, 2006. Accepted November 27, 2006.

ES062202M