



Short communication

Improved performance of single-chamber microbial fuel cells through control of membrane deformation

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ABSTRACT

Cation (CEMs) and anion exchange membrane (AEMs) are commonly used in microbial fuel cells (MFCs) to enhance Coulombic efficiencies (CEs) by reducing the flux of oxygen through the cathode to bacteria on the anode. AEMs typically work better than CEMs, but in initial experiments we observed the opposite using a membrane electrode assembly MFC. The reason was identified to be membrane deformation, which resulted in water and gas trapped between the membrane and cathode. To correct this, stainless steel mesh was used to press the membrane flat against the cathode. With the steel mesh, AEM performance increased to $46 \pm 4 \text{ W/m}^3$ in a single cathode MFC, and $98 \pm 14 \text{ W/m}^3$ in a double-cathode MFC. These power densities were higher than those using a CEM of $32 \pm 2 \text{ W/m}^3$ (single cathode) and $63 \pm 6 \text{ W/m}^3$ (double cathode). Higher pH gradients across the membrane and salt precipitation on the cathode were responsible for the reduced performance of the CEM compared to the AEM. CEs reached over 90% for both membranes at $>2 \text{ A/m}^2$. These results demonstrate the importance of avoiding water accumulation in thin films between membranes and electrodes, and explain additional reasons for poorer performance of CEMs compared to AEMs.

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1. Introduction

Microbial fuel cells (MFCs) are devices which can generate electricity from biomass using bacteria. Future applications of MFCs include wastewater treatment, bioelectricity generation for devices in remote marine and estuarine locations, and biosensors (Logan, 2008). The main challenges for improving MFC performance are increasing the recovery of electrons from the substrate (Coulombic efficiency, CE), increasing power, and reducing material costs. The use of cation (CEMs) and anion exchange membranes (AEMs) in MFCs (Kim et al., 2007, 2009; Liang et al., 2007; Rabaey et al., 2005; Zhang et al., 2009a,b; Zuo et al., 2008) increases CE but also increases internal resistance, creates pH gradients, and reduces the power densities compared to systems that lack membranes (Kim et al., 2007; Rozendal et al., 2007). When a Nafion CEM was hot-pressed to a carbon cloth cathode, the CE increased from 9–12% to 40–50%, but power was reduced from 12.5 to 6.6 W/m^3 (Liu and Logan, 2004). This decrease in power was due to increased ohmic resistance from hot-pressing the membrane (Kim et al., 2007). Kim

et al. has shown that when a Nafion membrane is not hot-welded to the electrode, and it is kept distant from the cathode, that it does not significantly affect ohmic resistance. Recently, Zhang et al. (2009b) compared performances of different separators including glass fiber, J-cloth, and CEM. The CEM produced the lowest power density and also had the highest ohmic resistance.

The performance of MFCs with AEMs is typically better than that with CEMs (Kim et al., 2007; Zuo et al., 2008). For example, in a two-chamber MFC the power density was 610 mW/m^2 with an AEM, compared to 480 mW/m^2 with a CEM (Kim et al., 2007). One reason for the improved performance of the AEM is that pH gradients are smaller across this membrane than those obtained with a CEM. In microbial electrolysis cell tests, the pH difference between the anode and cathode solution was 6.4 with a CEM, compared to only 4.4 with an AEM (Rozendal et al., 2007). In systems lacking water between the membranes, where the ion exchange membrane was made into an electrically conductive cathode (electrically conductive paint was applied to the membrane), the AEM-based cathode still produced more power (13.1 W/m^3) than the CEM (8.3 W/m^3) (Zuo et al., 2008). The only report where the MFC performance was better with a CEM than an AEM was obtained using a tubular-shaped, membrane electrode assembly (MEA) MFC, where the membrane was sandwiched between the anode and cathode. The maximum power density with the CEM study was 5.0 W/m^3 , compared to $<2 \text{ W/m}^3$ with an AEM (Kim et al.,

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2009). With a hydrogel used between the membrane and cathode, the CEM still produced more power (6.1 W/m^3) than with the AEM (4.9 W/m^3) for reasons that were not explained (Kim et al., 2009).

In order to better understand the reasons for the different performance of the AEM and CEM membranes, we examined the use of these two membranes in different MFCs: single-chamber, membrane electrode assembly reactors with one or two cathode assemblies; and two-chamber reactors with the membrane separating the anode and cathode chambers. Using these systems, we identified membrane deformation, changes in solution conductivity, and additional factors that impacted power generation using AEMs and CEMs in MFCs, and showed that the use of a steel mesh avoided the need to hot-press membranes to the cathode.

2. Materials and methods

2.1. MFC reactors

Anodes were ammonia gas treated carbon brushes (Logan et al., 2007). Cathodes were made of carbon cloth (E-Tek, Type B, 30% wet proofing, BASF Fuel Cell, Inc., NJ) with 0.5 mg/cm^2 platinum (7 cm^2 projected area) and 4 polytetrafluoroethylene (PTFE) diffusion layers to prevent water loss (Cheng et al., 2006).

Single-chamber, air-cathode, cubic-shaped MFCs were constructed as previously described (Liu and Logan, 2004; Logan et al., 2007) (Fig. 1). The membrane, either a cation exchange membrane (CEM; CMI-7000) or an anion exchange membrane (AEM; AMI-7001) (Membrane International Inc., NJ), was placed against the cathode. Single-cathode MFCs (liquid volume 12 mL), with the brush anode in the middle of the chamber and the cathode on the end (2-cm long cylindrical chamber) (Fig. 1). Double-cathode MFCs had a second cathode placed on the other side of the chamber (liquid volume 9 mL). In some tests, stainless steel mesh (M; 304 SS, 30×30 openings per square inch (6.45 cm^2), woven wire diam-

eter 0.12 in. (0.31 cm), McMaster-Carr, OH) was used to press the membrane onto the cathode.

Two-chamber MFCs were used to study the effects of membrane permeability, solution conductivity, and pH. Two-chambered MFCs were constructed by placing a membrane in the middle of a 4-cm long cubic MFC, with the brush anode in one chamber, and the cathode on the far side of the second chamber (Kim et al., 2007) (Fig. 1).

All MFCs were inoculated using a bacterial suspension obtained from an MFC (originally inoculated with primary clarifier overflow) operated in fed batch mode for over one year. The reactors were fed acetate (1 g/L) in a phosphate buffer solution (50 mM) (Logan et al., 2007) containing mineral (12.5 mL/L) and vitamin (5 mL/L) solutions (Lovley and Phillips, 1988). All MFCs were operated under ambient temperature ($23 \pm 3 \text{ }^\circ\text{C}$).

2.2. Analysis

Voltage (E) across an external resistor was measured at 20 min intervals using a data acquisition system (2700, Keithley Instrument, OH) connected to a personal computer. Current ($I=E/R$), power ($P=IE$) and Coulombic efficiency (CE) were calculated as previously described (Logan et al., 2006), with the current normalized by the cathode projected surface area, and power density by the anode volume. Polarization curves were obtained by varying external resistance with 20 min intervals at each resistance.

Ohmic resistances were determined by electrochemical impedance spectroscopy (EIS) using a potentiostat (PC 4/750, Gamry Instrument Inc., PA) (He et al., 2006; Logan et al., 2007). Impedance measurements were conducted at the open circuit voltage (OCV) over a frequency range of 10,000–0.1 Hz with a sinusoidal perturbation of 10 mV amplitude. The ohmic internal resistances of reactors was determined using Nyquist plots as previously described (He et al., 2006; Logan et al., 2007). The pH and conductivity were measured using meters (SB21,

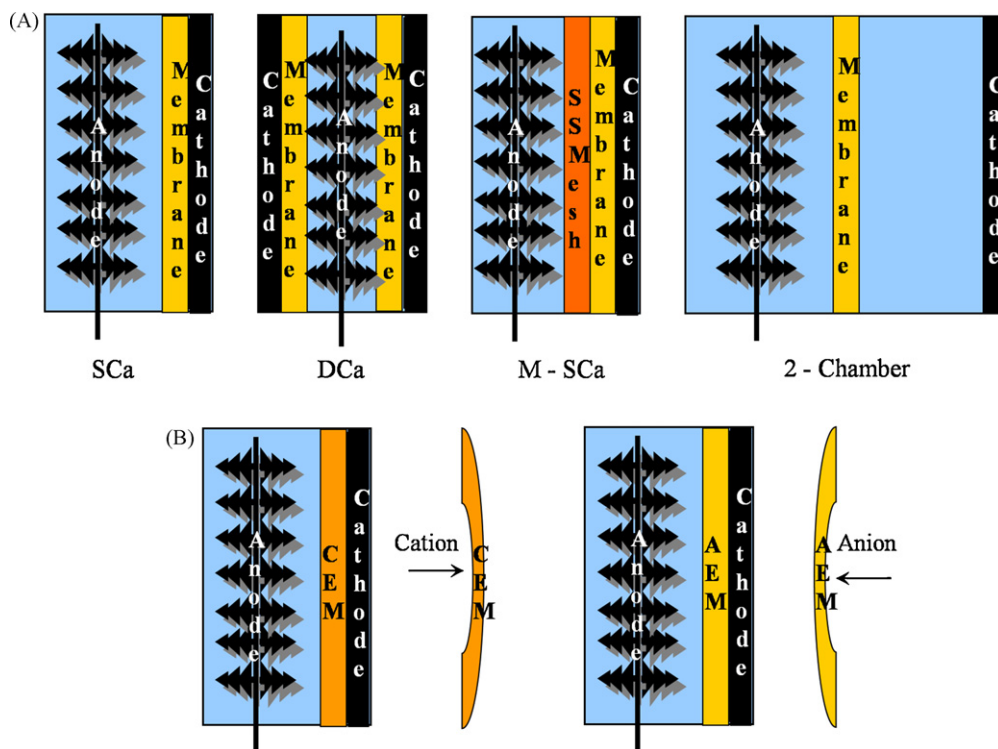


Fig. 1. (A) Schematic of MFCs in different configurations: SCa, a membrane against single cathode; DCa, membranes against double cathodes (two sides), with a brush anode in the middle; M - SCa, using stainless steel mesh; 2 - chamber, with a 2 cm spacing between the membrane and cathode. (B) Schematic showing CEM and AEM deformation.

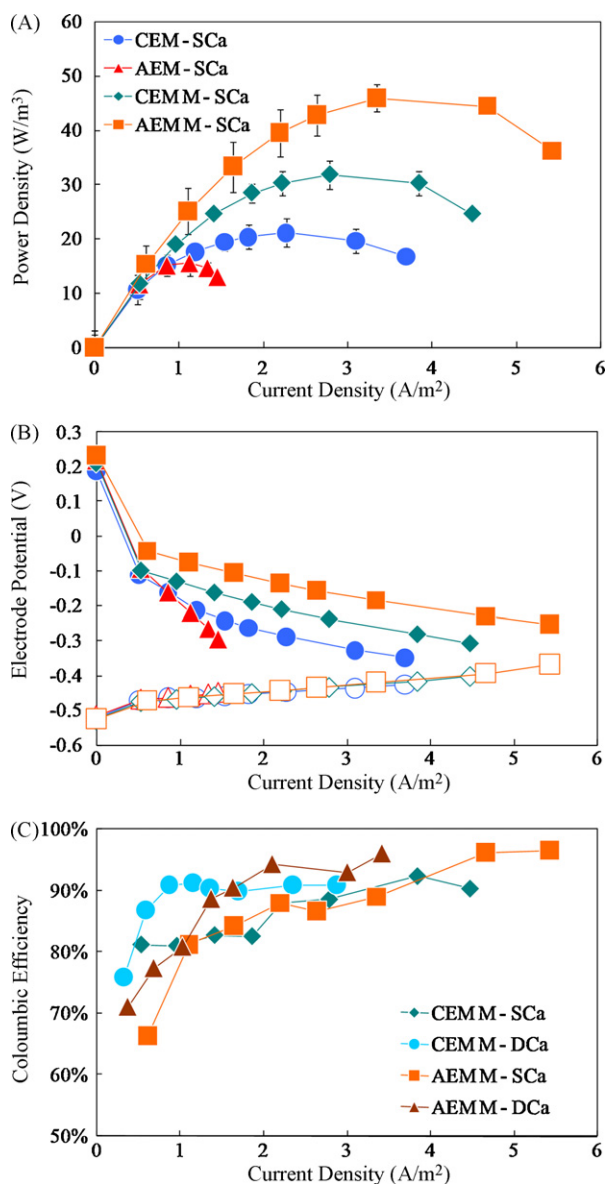


Fig. 2. (A) Power densities, (B) electrode potentials (cathode, filled symbols; anode, open symbols) vs. Ag/AgCl reference electrode (0.195 V vs. NHE) and (C) Coulombic efficiencies as a function of current density obtained by varying the external circuit resistance for MFCs with single (SCa) or double (DCa) cathodes.

VWR Scientific Products, PA; Con 6 Acorn series, OAKTON Instruments, IL).

3. Results

3.1. Power generation

In initial tests with a single cathode MFC, we found the performance with an AEM membrane ($16 \pm 2 \text{ W/m}^3$) was reduced compared to that of the CEM membrane ($21 \pm 2 \text{ W/m}^3$) (Fig. 2). Based on previous tests using two-chambered MFCs, we expected performance to be better with the AEM than the CEM. We noticed that the membranes became deformed after operation of the reactor over several cycles, with the AEM bending outwards toward the brush and the CEM bending inwards toward the cathode (Fig. 1). This deformation likely occurred as a result of membrane swelling during ion transport through the membrane. We reasoned that this deformation created a void space of water, and possibly gas (air

or CO_2), than would not be replaced or filled when the medium was replaced. The water trapped in this void space could accumulate a solution having a high pH, lowering reactor performance. Furthermore, the deformation of the AEM away from the cathode seemed to provide a larger space ($\sim 1 \text{ mm}$) than that produced with the CEM ($\sim 0.5 \text{ mm}$; after 30 cycles) in this reactor configuration, which could explain its relatively poorer performance compared to the CEM. This finding that the AEM deformed more than the CEM may explain why Kim et al. (2009) obtained better performance of the CEM than the AEM in their tests with a hydrogel between the membrane and electrode.

To test our membrane deformation hypothesis, we placed a stainless steel mesh against the membrane to keep it firmly pressed against the cathode. The mesh significantly increased the volumetric power densities of the MFC with the AEM to $46 \pm 4 \text{ W/m}^3$ (3.4 A/m^2), and it was higher than that of the CEM ($32 \pm 2 \text{ W/m}^3$) (10 days after acclimation) (Fig. 2), consistent with previous research (Kim et al., 2007; Zuo et al., 2008).

The increase in power densities resulted from a reduction in ohmic resistance due to the removal of the space between the membrane and cathode. The internal resistances of the MFCs without a mesh were $120 \pm 5 \Omega$ for the AEM, and $49.4 \pm 3.1 \Omega$ for the CEM. When the mesh was used, the ohmic resistances were reduced to $15.2 \pm 0.1 \Omega$ (AEM), and to $16.4 \pm 0.5 \Omega$ (CEM). These changes were due to the cathode as the anode potentials were not altered by membranes or mesh (Fig. 2). The open circuit potentials of anodes and cathodes were unaffected by the use of mesh or by membrane deformation (Fig. 2). We did not observe any mesh corrosion over time. Even after 80 days, the maximum power densities of these systems were unchanged, producing $45 \pm 2 \text{ W/m}^3$ (AEM) and $31 \pm 3 \text{ W/m}^3$ (CEM). In addition, the anode and cathode potentials, and CEs, were also not affected.

Increasing the specific surface area of the cathodes ($156 \text{ m}^2/\text{m}^3$) with a second cathode increased power to $98 \pm 14 \text{ W/m}^3$ (AEM) and $63 \pm 6 \text{ W/m}^3$ (CEM) with stainless steel mesh. Ohmic resistances decreased to $6.2 \pm 0.2 \Omega$ (AEM) and $6.4 \pm 0.4 \Omega$ (CEM). In comparison, two-cathode MFCs lacking the mesh had internal resistances of $27 \pm 5 \Omega$ (CEM) and $52 \pm 10 \Omega$ (AEM), and produced maximum power densities of $46 \pm 1 \text{ W/m}^3$ (CEM) and $33 \pm 3 \text{ W/m}^3$ (AEM).

3.2. Effects of membranes on solution pH and conductivity

To further examine the effects of the type of membrane on performance, we conducted additional tests using two-chamber MFCs. Water permeability tests, conducted by filling the anode chamber with solution but not the cathode chamber, showed that the membrane was not hydraulically permeable as water in anode chamber could not pass through the membrane to the cathode chamber.

Membrane deformation was observed in two-chamber MFCs after 30 days of operation, with the membranes curved in the same directions noted in single-chamber MFC tests, but this time we observed a greater deformation of the CEM ($\sim 2 \text{ mm}$) than the AEM ($\sim 1 \text{ mm}$). At the end of a cycle, there was a large pH difference across the CEM, consistent with previous reports (Kim et al., 2007; Rozendal et al., 2007). The pH of the anode and cathode solutions with a CEM was 5.2 and 10.3, compared to only 6.7 and 7.4 for the AEM. Thus, the pH gradient across the AEM was only 0.7 compared to 5.1 for the CEM.

To demonstrate the effect of “trapped” water between the membrane and a cathode, we replaced the anode solution over three cycles but not the cathode solution. The cathode solution pH increased to 11.1 for the CEM but only 7.7 for the AEM. It is likely that larger changes in pH would have occurred in single-chamber MFC when the membranes deformed as the volumes of the trapped solution would be smaller.

It was also observed after 30 days of operation that salt precipitated on the cathode surface of the MFC with the CEM, but not the AEM. Salt accumulation decreases the performance of ion exchange membranes (Chae et al., 2008). In addition, the change in the solution conductivities for the CEM were much larger than those of the AEM. The solution conductivities changed from 7.7 mS/cm (anode) and 6.9 mS/cm (cathode) to 7.2 mS/cm for both chambers using an AEM. With the CEM, the anode solution conductivity decreased to 5.4 mS/cm and the cathode conductivity increased to 9.1 mS/cm. Changes in solution conductivity and salt precipitation were additional factors for reduced performance of the CEM compared to the AEM.

3.3. Coulombic efficiencies

CEs increased with current density, consistent with previous studies (Kim et al., 2007), to >90% for at >2 A/m² (Fig. 2). CEs averaged 92 ± 4% for single cathode MFCs and 94 ± 2% for double-cathode AEM MFCs, and 90 ± 2% (single cathode) and 91 ± 1% (double cathode) CEM MFCs, at >2 A/m². These CEs are significantly larger than those for MFCs lacking a membrane (9–12%) (Liu and Logan, 2004).

4. Conclusions

MFC performance was significantly enhanced using a stainless steel mesh to press the membrane against the cathode without the need to hot press the membrane to the cathode. Maximum volumetric power densities using an AEM membrane with the mesh reached 46 ± 4 W/m³ with a single cathode, and 98 ± 14 W/m³ with double cathodes, with CEs >90% for >2 A/m². The performances of the MFCs with AEMs were consistently better than those obtained with CEMs when using the stainless steel mesh, but not when the mesh was omitted. The use of a CEM resulted in high pH gradients across the membrane and larger changes in solution conductivity than observed with an AEM, and there was salt precipitation on

the cathode with the CEM. Our results demonstrate the importance of avoiding membrane deformation in MFCs, and show additional reasons for the improved performance of the AEM compared to the CEM in MFC tests due to conductivity changes and salt precipitation.

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