

The use of nylon and glass fiber filter separators with different pore sizes in air-cathode single-chamber microbial fuel cells

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Separators are needed in microbial fuel cells (MFCs) to reduce electrode spacing and preventing electrode short circuiting. The use of nylon and glass fiber filter separators in single-chamber, air-cathode MFCs was examined for their effect on performance. Larger pore nylon mesh were used that had regular mesh weaves with pores ranging from 10 to 160 μm , while smaller pore-size nylon filters (0.2–0.45 μm) and glass fiber filters (0.7–2.0 μm) had a more random structure. The pore size of both types of nylon filters had a direct and predictable effect on power production, with power increasing from 443 ± 27 to 650 ± 7 mW m^{-2} for pore sizes of 0.2 and 0.45 μm , and from 769 ± 65 to 941 ± 47 mW m^{-2} for 10 to 160 μm . In contrast, changes in pore sizes of the glass fiber filters resulted in a relatively narrow change in power (732 ± 48 to 779 ± 43 mW m^{-2}) for pore sizes of 0.7 to 2 μm . An ideal separator should increase both power density and Coulombic efficiency (CE). However, CEs measured for the different separators were inversely correlated with power production, demonstrating that materials which reduced the oxygen diffusion into the reactor also hindered proton transport to the cathode, reducing power production through increased internal resistance. Our results highlight the need to develop separators that control oxygen transfer and facilitate proton transfer to the cathode.

1. Introduction

Microbial fuel cells (MFCs) are devices which can generate electricity from biomass using bacteria and which have drawn increasing attention as a promising technology for wastewater treatment and energy recovery.^{1–4} 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 separator is a very important component of an MFC as it allows close spacing of the electrodes, which can increase power production in an MFC but also affect CE.^{5,6} Cation exchange membranes (CEMs) such as Nafion^{7,8} and anion exchange membranes (AEM)⁹ have been used in several different types of MFCs to improve CE by inhibiting oxygen transfer. However, these ion selective membranes substantially reduce power production due to pH gradients that develop across the membrane,¹⁰ and they increase internal resistance.⁶ Ultrafiltration membranes (UF; 0.01–0.1 μm) can reduce oxygen transfer into the anode chamber, but they substantially increase internal resistance by inhibiting proton transfer.⁹ Sun *et al.*¹¹ applied microfiltration membranes (pore size of 0.22 μm) onto the water-facing side of the air cathode, and increased the maximum power density to 214 mW m^{-2} . This was about twice that obtained with a CEM (104 mW m^{-2}). Several other separator materials have been used in MFCs, including nylon, cellulose nitrate and polycarbonate filters (all 0.2 μm pore size).¹² In general,

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Broader context

Microbial fuel cells (MFCs) can be used to generate electricity from biomass using bacteria, and are therefore a promising technology for both wastewater treatment and energy production. Separators are needed between the electrodes in MFCs to allow close electrode spacing, but certain separators adversely affect MFC performance. It is shown here that the maximum power densities produced using different separators can be better understood based on the separator pore sizes and materials. Nylon separators led to a predictable increase in power density with pore sizes ranging from 0.2 to 160 μm . Glass fiber filter separators showed less of a relationship between pore size and power, although we were only able to examine a relatively small range of pore sizes (0.7 to 2.0 μm). Higher power densities were achieved large separator pores due to less obstruction of proton transport to the cathode. However, larger pores allowed more oxygen to enter the reactor, and thus more substrate was lost to bacteria using oxygen. Our results highlight that ideal separators should facilitate proton transport to the cathode but minimize current losses due to oxygen intrusion into the solution.

microfiltration membranes have worked better as separators than UF membranes due to the larger pore sizes and reduced impact on internal resistance.

One of the most successful separators reported in the MFC literature was a highly porous cloth called J-cloth (JC). JC sandwiched directly between two electrodes only slightly decreased power per surface area, but substantially improved power production on a volumetric power basis due to the high surface area of the electrodes per volume of reactor. However, the CE was low (24%, 1 k Ω resistor) with a single cloth separator.¹³ Unfortunately, the long term performance of JC material is limited because it is biodegradable, so that over time the cloth is completely degraded in the reactor.⁶

Glass fiber mats and nylon are two kinds of non-biodegradable separators, which are commonly used in lead acid batteries and nickel-metal hydride batteries. Two glass fiber mats, with 0.4 mm (GF0.4) and 1.0 mm (GF1) thicknesses, were previously compared with J-cloth and a CEM in an MFC with a 2-cm electrode spacing. Pore sizes for these materials were not provided by the manufacturer. GF1 and JC produced similar maximum power densities to each other (~ 790 mW m⁻²) and performed much better than the CEM, but CE of the GF1 was much higher than that of the JC, and the GF1 is not biodegradable.⁶ The specific characteristics of separators that affect MFC performance need to be better understood. It is likely that the pore size of the separator is an important characteristic for performance, but this feature has not previously been systematically investigated. GF1 and JC have different structures, which could be important in how these materials affect power generation. JC has large open holes in the material, while glass fibers are more uniformly dispersed in the mat of the GF1.

In order to examine the effect of pore size on MFC performance, we examined the use of large-pore nylon mesh separators that have regular pore sizes ranging from 10 to 160 μ m. We compared the performance of this mesh/weaved type of material to filters made with random and denser arrangements fibers made of nylon or glass materials (effective pore sizes ranging from 0.2 to 2.0 μ m). Our results demonstrate that the pore size characteristics of these separators have a direct impact on power production and CE in MFCs.

2. Experimental

2.1 MFC reactors

Anodes were ammonia gas treated¹⁴ carbon cloth (Type A, non-wet proofing, BASF Fuel Cell, Inc. NJ) with a 7 cm² projected area. Cathodes made of carbon cloth (Type B, 30% wet proofing, BASF Fuel Cell, Inc. NJ) were coated with a catalyst (0.5 mg cm⁻² platinum, 7 cm² projected area) on the water-facing side, and 4 polytetrafluoroethylene (PTFE) diffusion layers on the air-facing side to prevent water loss.¹⁵

Single-chamber, air-cathode, cubic-shaped MFCs were constructed as previously described with flat electrodes spaced 2 cm apart (Fig. 1), with a total liquid volume of 12 mL.^{6,8,16} The “control” MFC was operated without a separator (NS) (Fig. 1). Nylon (NY) filters with a regular weave (10 μ m, 60 μ m, 100 μ m, and 160 μ m pore diameter; Millipore Corporation, MA, USA) or a random fiber arrangement (0.2 μ m and 0.45 μ m pore diameter;

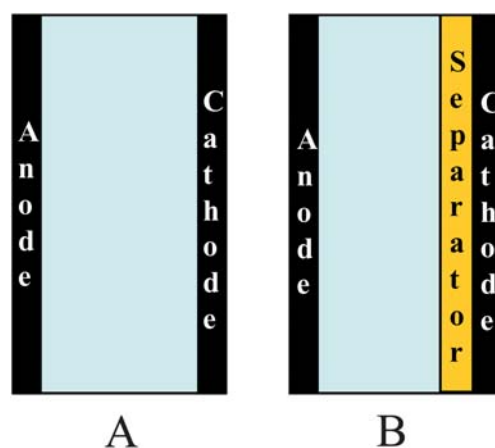


Fig. 1 Schematic of MFCs in two configurations: (A) “control” MFC without separator and (B) MFC with separator against cathode.

Millipore Corporation, MA, USA), or glass fiber filters (GFF, 0.7 μ m, 1.0 μ m, and 2.0 μ m pore diameter; Millipore Corporation, MA, USA) were placed directly against the cathode (Fig. 1). Scanning electron microscope (SEM) images ($\times 100$) of nylon and glass fiber filters are shown in Fig. 2. Characteristics of the nylon and glass fiber filters are listed in Table 1.

All anodes were enriched in MFCs lacking a separator (NS-type) using a bacterial inoculum 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⁻¹) in a phosphate buffer solution (50 mM)¹⁷ containing mineral (12.5 mL L⁻¹) and vitamin (5 mL L⁻¹) solutions.¹⁸ Following operation of these MFCs for more than 20 cycles, with all MFCs exhibiting stable and parallel performance, the different types of nylon and glass fiber separators were then added to the reactors. All MFCs were operated at room temperature (23 ± 3 °C), with a fed batch cycle time (time before the reactor medium was replaced) based on the voltage decreasing to less than 20 mV (1000 Ω fixed resistance).

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,⁷ with the current and power density normalized by the cathode projected surface area. 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).^{17,19} Impedance measurements were conducted at the open circuit voltage (OCV) over a frequency range of 10,000 to 0.1 Hz with a sinusoidal perturbation of 10 mV amplitude. The ohmic internal resistances of reactors were determined using Nyquist plots as previously described.^{17,19} A scanning electron microscope (SEM) (JSM-5400, JEOL Ltd., Tokyo, Japan) was used to inspect the surfaces of the nylon and glass fiber filters.

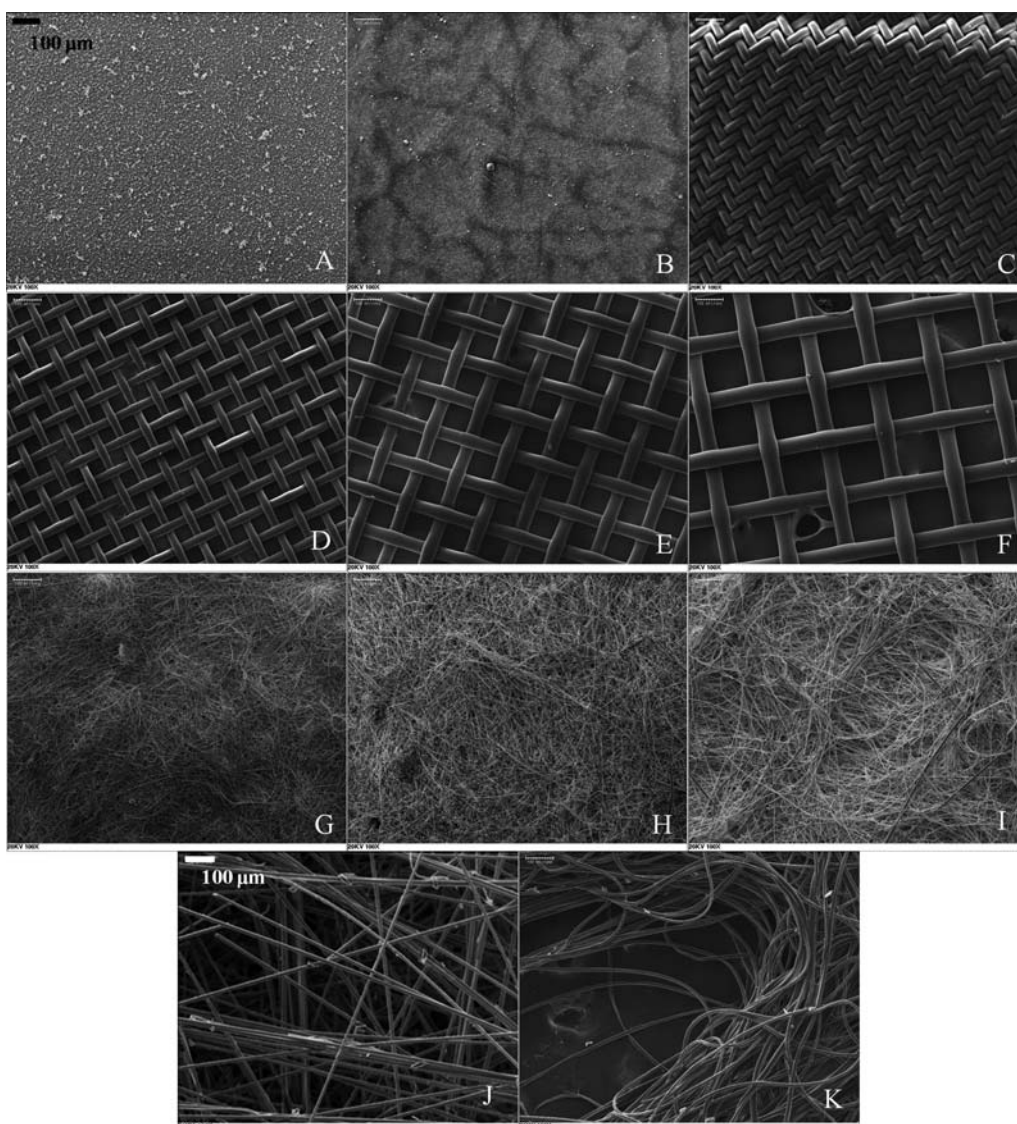


Fig. 2 SEM images of nylon (A–F) and glass fiber filters (G–I) examined in this study. Nylon filters: (A) 0.2 μm , (B) 0.45 μm , (C) 10 μm , (D) 60 μm , (E) 100 μm , (F) 160 μm ; glass fiber filters: (G) 0.7 μm , (H) 1.0 μm , (I) 2.0 μm . (J) glass fiber DC1.0 and (K) J-cloth ($\times 100$, scale bar, 100 μm) used in previous studies.

3. Results and discussion

3.1 Power generation and Coulombic efficiencies of MFCs with nylon as separator

The maximum power density using nylon filter separators was significantly affected by the pore size (Fig. 3), with power densities increasing with pore size. The maximum power density of $941 \pm 47 \text{ mW m}^{-2}$ (3.0 A m^{-2}) was obtained in MFC using nylon separator with the largest pore size of 160 μm (Table 2). When the pore size was decreased for nylon filters with pore sizes of 100 μm , 60 μm , 10 μm , 0.45 μm and 0.2 μm , the maximum power densities decreased from 908 ± 24 to $443 \pm 27 \text{ mW m}^{-2}$ (Table 2). In comparison, the maximum power density for the MFC without a separator (NS) was $1013 \pm 23 \text{ mW m}^{-2}$ (3.1 A m^{-2}) (Fig. 3). Thus, the use of any separator reduced power density due to its placement next to the cathode (Fig. 3). This observation of a decrease in power generation per surface area, when electrodes

are spaced relatively far apart (from 2 cm to 4 cm), is consistent with previous findings,^{6,8} although the extent of the decrease in power output depends on the separator characteristics.

Table 1 Characteristics of nylon (NY) and glass fiber filters (GFF) provided by the manufacturer

	Pore size/ μm	Bubble point/bar	Thickness/ μm	Water flow rate/ $\text{mL min}^{-1} \text{ cm}^{-2}$	Open area (%)
NY 0.2	0.2	2.8	170	25	—
NY 0.45	0.45	2.5	170	75	—
NY 10	10	—	45	—	4
NY 60	60	—	50	—	41
NY 100	100	—	80	—	44
NY 160	160	—	100	—	53
GFF 0.7	0.7	—	380	1.4	—
GFF 1.0	1.0	—	700	2.2	—
GFF 2.0	2.0	—	380	1.3	—

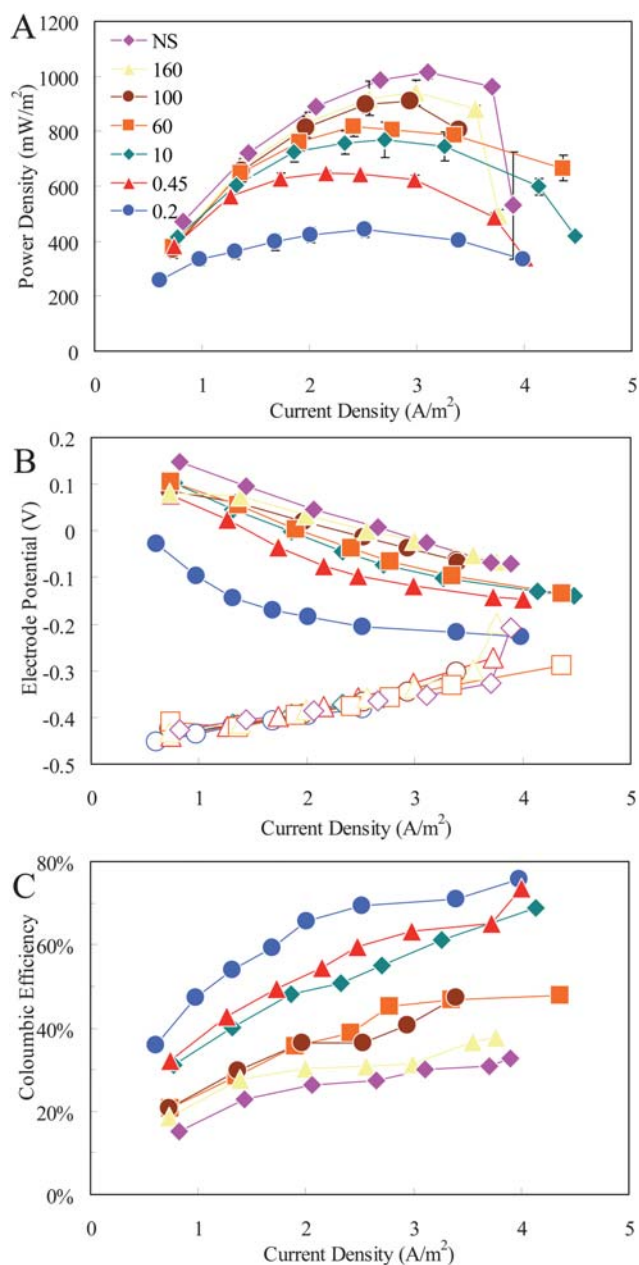


Fig. 3 (A) Power densities, (B) electrode potentials (cathode, filled symbols; anode, open symbols) vs. Ag/AgCl reference electrode (0.195 V vs. NHE) and (C) Coulombic efficiencies as a function of current density obtained by varying the external circuit resistance for MFCs with different pore sizes (from 0.2 to 160 μm) with nylon separators, and in absence of separator (NS).

Table 2 Power production and internal resistance of MFCs

Separator	Nylon						NS	Glass fiber filter		
Pore size/μm	0.2	0.45	10	60	100	160	—	0.7	1.0	2.0
Maximum power density/mW m ⁻²	443 ± 27	650 ± 7	769 ± 65	816 ± 34	908 ± 24	941 ± 47	1013 ± 23	732 ± 48	716 ± 60	779 ± 43
CE ^a	70%	63%	55%	45%	41%	31%	30%	56%	60%	55%
CE ^b	36–76%	32–74%	31–69%	21–48%	21–47%	18–38%	15–33%	36–67%	37–70%	31–66%
Internal resistance (Ω)	84.6	57.3	41.4	39.5	37.3	35.7	34.6	40.4	42.3	39.6

^a CE at the current density of maximum power density. ^b CE at the current density from 0.7 to 4.8 A m⁻².

The Coulombic efficiencies (CEs) of the nylon filters followed an opposite trend with pore size. When the nylon pore size decreased from 160 μm to 0.2 μm, the CEs increased (Fig. 3). CEs ranged from 18% to 38% in MFCs with a nylon filter with a pore size of 160 μm (maximum current densities of 0.7 to 3.8 A m⁻²). These CEs were slightly larger than those obtained with an MFC lacking a separator (CE = 15%–33%) over the same range in current densities (Table 2). The CEs were largest for the MFC using the smallest nylon filter pore size of 0.2 μm (CEs of 36%–76%) at similar current densities (Table 2).

The CEs at the current density when the maximum power density was achieved are shown in Fig. 4. When the maximum power density increased the CE decreased. The CE is related to substrate losses due to oxygen transport through cathode into the liquid anode chamber.⁶ When the pore size of the nylon filter increased, the oxygen flux increased and the CE decreased. However, proton transfer to the cathode is also reduced due to the presence of the separator, and thus the ohmic resistance decreased and the power density increased (Table 2). The nylon filters with the mesh have a very regular shape and thus produce a consistent change in either power density. Even though the nylon filters with the smaller pore sizes have a more random structure, they seem to fit into the general pattern of decreased power with pore size observed for the larger pore filters. We were not able to obtain materials with different pore sizes having the same thickness. The two properties were related here, with the material thickness increasing from 45 to 100 μm as the pore sizes increased from 10 to 160 μm, but for nylon with pore sizes of 0.2 and 0.45 μm, the thicknesses were both 170 μm. The thickness of

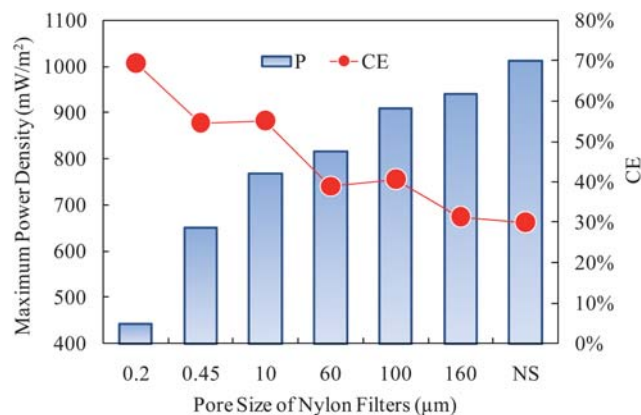


Fig. 4 Maximum power density and CE at the current density of maximum power for MFCs with different pore sizes (from 0.2 to 160 μm) for nylon separators, and in the absence of a separator (NS).

separator could also be a factor in the CEs and power densities, and this characteristic should be examined in future studies.

3.2 Power generation and CEs for MFCs with glass fiber filters

To further examine the effects of the pore size, three types of glass fiber filters with pore sizes of 0.7 μm , 1.0 μm and 2.0 μm were used as separators. The change in pore size had only a small effect on maximum power densities (Fig. 5), which ranged from 716 ± 60 to 779 ± 43 mW m^{-2} (Table 2). In addition, there was

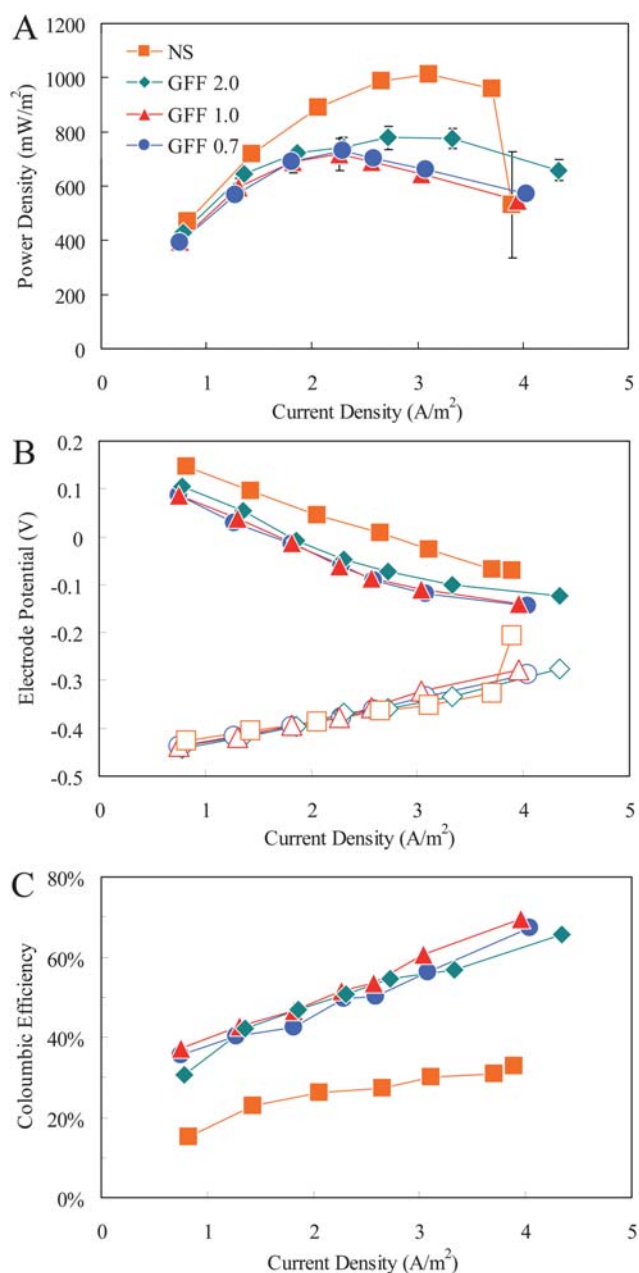


Fig. 5 (A) Power densities, (B) electrode potentials (cathode, filled symbols; anode, open symbols) vs. Ag/AgCl reference electrode (0.195 V vs. NHE) and (C) Coulombic efficiencies as a function of current density obtained by varying the external circuit resistance for MFCs with different pore sizes (0.7, 1.0 and 2.0 μm) for glass fiber filter (GFF) separators, and in the absence of a separator (NS).

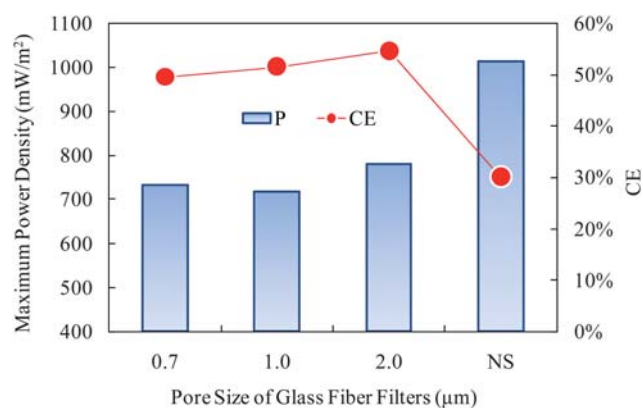


Fig. 6 Maximum power density and CE at the current density of maximum power for MFCs with different pore sizes (0.7, 1.0 and 2.0 μm) of glass fiber filters (GFF) separators, and in absence of separator (NS).

little change in the power density despite the much different thicknesses of two of the glass fiber materials (380 and 700 μm). The CEs were also very similar at a given current density, for current densities ranging from 0.8 to 4.0 A m^{-2} (Fig. 5). The glass fiber filters reduced the cathode potential (Fig. 5), increased ohmic resistances (all in the range of 40 Ω to 42 Ω) (Table 2), and increased CEs (Fig. 5) compared to the control MFC lacking a separator. Comparing the different maximum power densities and the CEs, we can see in Fig. 6 that there was little overall impact of the pore size of these glass fiber filters on MFC performance. It may be that the variation in the pore size of the glass fiber filters (0.7 to 2.0 μm) was too limited to see a significant effect of pore size, compared with much wider range of pore sizes for the nylon materials (0.2 to 160 μm).

3.3 Relation between power density and coulombic efficiency

When both materials (nylon and glass fiber) were examined in terms of the relationship between power and CE, we found that

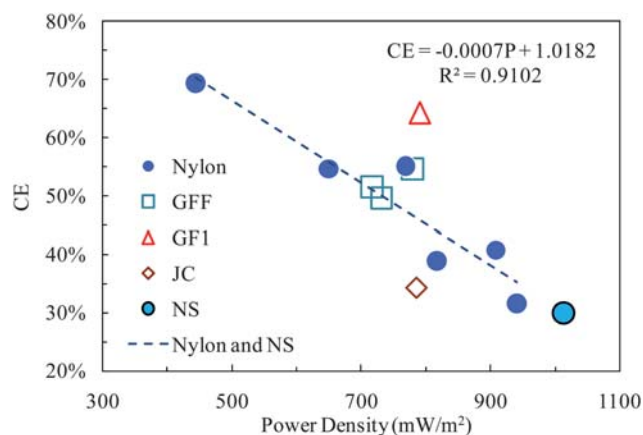


Fig. 7 CE at the current density of maximum power as a function of maximum power density for different types of filters. Data for glass fiber filters (GFF), nylon filters, and in absence of a separator (NS) are from this study. Data for glass fiber DC1.0 (GF1) and J-cloth (JC)* are from Zhang *et al.*⁶ The relationship between power density and CE was based only on filled symbols, with $p < 0.001$ for the slope of the line.

these two properties are linearly related over the range of values produced here in these MFCs (Fig. 7). Data from other studies, where the materials and construction of the separators were more variable, differ to a greater extent from this trend. For example, the GF1 material used in our previous study⁶ had a higher CE = 64% than the nylon and glass fiber separators examined here. This comparison, shown in Fig. 7, does not take into account other separator properties such as thickness of the material. In addition, the classification of the filter by a pore size is not an exact comparison as the pore sizes are not exact but rather are estimated from other measurements (such as bubble point or water flow rate). The JC material produced a much lower CE = 34% than the other materials at a comparable power density (Fig. 7). The GF1, NY10, and JC had similar power densities but much different CEs, suggesting that the proton transport properties of these different materials were similar but that the oxygen transfer properties were different.

4. Conclusions

With the pore size of nylon increasing from 0.2 μm to 160 μm , the maximum power density increased from $443 \pm 27 \text{ mW m}^{-2}$ to $908 \pm 24 \text{ mW m}^{-2}$. In contrast, the CE decreased from 36%–76% to 18%–38% (current density range of 0.7 to 4.8 A m^{-2}) with increased pore size. Glass fiber filters with pore sizes ranging from 0.7 to 2.0 μm had very similar performance. The maximum power density for an MFC lacking a separator was highest $1013 \pm 23 \text{ mW m}^{-2}$, but the CEs were lowest 15%–33%. Thus, it appears that in general there is a trade off in using separators in MFCs as CE can be increased by reducing oxygen transfer, but power will be reduced due to impeded transport of protons to the cathode. This suggests that oxygen transfer to the cathode must be carefully controlled without affecting proton transport in order to maximize power generation in MFCs with separators.

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