Bioresource Technology 128 (2013) 14–21

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Enhanced power production of a membrane electrode assembly microbial fuel cell (MFC) using a cost effective poly [2,5-benzimidazole] (ABPBI) impregnated non-woven fabric filter

Soojung Choi [a], Jung Rae Kim [b], Jaehwan Cha [c], Yejin Kim [a], Giuliano C. Premier [b], Changwon Kim [a,*]

[a] *School of Civil and Environmental Engineering, Pusan National University, Busan 609-735, South Korea*
[b] *Sustainable Environment Research Centre (SERC), Faculty of Advanced Technology, University of Glamorgan, Pontypridd, Mid-Glamorgan CF37 1DL, United Kingdom*
[c] *Waste Energy Research Center, Korea Institute of Energy Research, Daejeon 305-343, South Korea*

HIGHLIGHTS

- ▶ The performance of a NWF was comparable to that of a PEM.
- ▶ A NWF showed stable electrical cell performance over 300 days.
- ▶ The oxygen mass transfer coefficient for the NWF was similar to that of a PEM.
- ▶ The acetate mass transfer coefficient for the NWF was lower than that of PEM.
- ▶ The MFC utilizing ABPBI can improve overall cell performance as a proton conductor.

ARTICLE INFO

Article history:
Received 29 May 2012
Received in revised form 7 October 2012
Accepted 8 October 2012
Available online 23 October 2012

Keywords:
Microbial fuel cell (MFC)
Separator
Non-woven fabric filter
ABPBI
Membrane electrode assembly (MEA)

ABSTRACT

A membrane electrode assembly (MEA) microbial fuel cell (MFC) with a non-woven paper fabic filter (NWF) was investigated as an alternative to a proton exchange membrane (PEM) separator. The MFC with a NWF generated a cell voltage of 545 mV and a maximum power density of 1027 mW/m^3, which was comparable to that obtained from MFCs with a PEM (551 mV, 609 mW/m^3). The MFC with a NWF showed stable cell performance (550 mV) over 300 days, whereas, the MFC with PEM performance decreased significantly from 551 mV to 415 mV due to biofilm formation and chemical precipitation on the membrane surface. Poly [2,5-benzimidazole] (ABPBI) was evaluated with respect to its capacity to increased proton conductivity and contact between separator and electrodes. The overall performance of the MFC with ABPBI was improved by enhancing the ion conductivity and steric contact, producing 766 mW/m^3 at optimum loading of 50 mg ABPBI/cm^2.

1. Introduction

Conventional biological wastewater treatment, despite successfully achieving removal of contaminants, is suboptimal due to high energy consumption and the need to dispose of significant quantities of activated sludge.

Microbial fuel cells (MFCs) are considered a potential technology for the production of electrical energy from biodegradable organic matter present in wastewater, by using electrochemically active bacteria (EAB) (Logan et al., 2006; Rozendal et al., 2008a). The application of MFCs in a wastewater treatment process has several advantages over existing conventional activated sludge processes, since it can harvest electrical energy directly from wastewater and treat organic pollutants (Kim et al., 2007). Furthermore, MFCs generate less excess sludge than aerobic treatment because of anaerobic catabolism in the anode half-cell (Henze et al., 2008). However, the main challenge to the utilization of MFCs is the need to reduce of material and manufacturing costs and to develop configurations that maximized power generation (Logan, 2008). High-energy facilitating anode materials such as graphite brushes (Logan et al., 2007), alternative cathode catalysts (Zhao et al., 2005; Kim et al., 2011), and separators such as J-cloth (Fan et al., 2007), have already been proposed. To create an industrially applicable MFCs system, however, these materials should have stable power production in long-term operation at minimal capital costs (Clauwaert et al., 2008).

The main components of the MFCs are the anode and cathode with a separator as an optional component (Jang et al., 2004; Ghangrekar and Shinde, 2007). If the electrodes of an MFC are

---

* Corresponding author. Tel.: +82 51 510 2416; fax: +82 51 515 5347.
E-mail address: cwkim@pusan.ac.kr (C. Kim).

0960-8524/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biortech.2012.10.013

not separated by a long distance, separators such as ion exchange membranes or filters to prevent oxygen and substrate cross-over and to reduce inhibition of anaeriobic bacteria on anode surface, by oxygen. (Logan et al., 2006). Ion exchange membranes (IEMs) such as proton exchange (PEM), cation exchange (CEM), or an anion exchange membrane (AEM) have been used in MFC studies (Kim et al., 2007b;Liu and Logan, 2004;Chen et al., 2008;Zuo et al., 2008). IEMs are expensive. Rozendal et al. (2008a) reported that the estimated capital cost of MFCs based on PEM materials currently used in laboratory systems would amount to approximately 40% of the total cost. It might be even higher for actual field-scale application because of hydrostatic pressure in large-scale reactors. The second drawback is biological and chemical fouling. Such fouling increases internal resistance, and consequently results in a decrease in MFC performance (Rozendal et al., 2006). The third drawback is a higher transfer rate of cations than protons, which can significantly inhibit electrochemical reactions on the cathode and reduce cathode cell performance. In the electrolyte of MFCs, cations typically are present at 10^5 times higher concentrations than protons. As these cations combine with sulfonated groups in Nafion and inhibit the migration of protons, pH decreases in the anode chamber and pH increases in the cathode chamber, causing a negative effect on electrochemical cell performance (Kim et al., 2007a; Rozendal et al., 2008b).

Therefore, in order to overcome these problems, various size-selective separators, particularly low cost materials such as J-cloth, or ultrafiltration (UF), microfiltration membranes (MFM), and glass fibers have been tested (Kim et al., 2007b; Fan et al., 2007; Sun et al., 2009; Zhang et al., 2011). Kim et al. (2007b) found that MFCs with UF as a separator produced a relatively high power density of 462 mW/m^2, however, a high percentage of electrons lost through unidentified processes. An MFM as a separator produced a comparable power density as an MFC with a PEM (Sun et al., 2009). The use of an inexpensive J-cloth considerably improved power generation in an MFC systems (Fan et al., 2007), but the J-cloth can be biodegraded over time (Zhang et al., 2009). Zhang et al. (2009) also reported that glass fiber generated a high power density and produce low ohmic resistance due to low oxygen transfer coefficients. Sulfonated polyether ether ketone (SPEEK) and poly ethersulfone (PES) membranes which are cheaper than PEM also investgated have the potential to enhance the efficiency of MFCs (Ayyaru and Dharmalingam, 2011; Lim et al., 2012). Such separators generally showed a higher proton transfer capability and better applicability than IEMs, however, these materials should be considered in terms of sustainability and longevity before using for field applications.

The present study explored the use of a non-woven fabric filter (NWF) as a separator in MFCs to reduce capital costs. NWF is already used in water purification and wastewater treatment, and by chemical process industries. The price of NWF used in this study was as low as $4 per square meter, much lower than that of Nafion 117 at $1400 per square meter. To evaluate the performance of the NWF, power production was estimated and substrate and oxygen mass transfer coefficients and longevity were measured during long-term operation and compared with those of PEM. The NWF was supplied with an ion-specific conductor, poly [2,5-benzimidazole] (ABPBI) (Asensio et al., 2004), to improve proton conductivity and contact between NWF and cathode electrodes.

2. Methods

2.1. MFC construction

Pseudo-MEA type two-chambered MFCs Fig. S1a) were constructed to compare the performance of the PEM and NWF separators. Two-chambered MFCs comprised two plastic rectangular chambers (340 mL each), and the two chambers were the PEM or NWF. Graphite felt (GF-20-5F, Nippon Carbon Co., Japan) was used as anode (Kim et al., 2008) and connected to the cathode with a copper wire through an external resistance of 1000 Ω. The cathode was made of the same material but coated with a platinum catalyst (0.5 $mg\text{-}Pt/cm^2$). To minimize the internal resistance and space between anode and cathode, the two electrodes (36 cm^2 of project area and 0.6 cm in thickness) were installed at opposite sides of the separator, minimizing the distance between the anode and cathode to less than 2 mm. PEM (Nafion 117, DuPont, USA) and four types of NWF (1025D, 1070D, 1082D and 1443R, DuPont, USA) were tested as separators. The MFCs with PEM, 1025D, 1070D, 1082D and 1443R separators were designated as PEM, NWF1, NWF2, NWF3, and NWF4. The NWFs had similar thicknesses as PEM and the pore size of NWF was in the microfiltration membrane pore size range (0.1–10 μm). Table 1 shows the physical properties of PEM and NWF. Prior to use, the graphite felt was soaked in 100% ethanol for 30 min and in 1 M HCl for 1 h. The electrodes were washed in 1 M NaOH for 1 h and stored in distilled water before use (Chae et al., 2008). An Ag/AgCl reference electrode (MF-2052, Basi, UK) was placed in the anode chamber.

In order to estimate the performance of ABPBI as a proton transfer conductor, MEA-type single-chambered MFCs were operated (Fig. S1b). The working volume of the anode chamber was 180 mL, and the anode consisted of graphite felt with 25 cm^2 of projected area. NWF (1443R, DuPont, USA) was used as a separator. The cathode (30% wet-proofed carbon cloth, B1B30WP, E-Tek, USA, with 0.5 $mg\text{-}Pt/cm^2$), was exposed to air. ABPBI was loaded between the electrode and the separator (Fig. S1c). ABPBI was prepared by the polymerization of 3,4-diaminobezoic acid in polyphosphoric acid (Asensio et al., 2002). The electrode was impregnated with 0 mg $ABPBI/cm^2$ (Pseudo MEA type), 30, 50, and 80 mg $ABPBI/cm^2$ (MEA type).

2.2. MFC operation

Both single and two-chambered MFCs were operated in a fed-batch mode. The MFCs were inoculated using returned sludge taken from an activated sludge process (Sooyoung Domestic Wastewater Treatment Plant, South Korea), with feed solution. Before injection, the sludge was filtered through a sieve with a mesh size of 500 μm and purged with nitrogen gas for 15 min. The feed solution used in the two-chambered MFC experiment consisted of CH_3COONa (3 mM, 246 mg COD/L), while the feed solution for the single-chambered MFC contained CH_3COONa (10 mM, 820 mg COD/L) as a carbon source. A nutrient solution of KH_2PO_4, 5.8 g/L; K_2HPO_4, 10.0 g/L; NH_4Cl, 0.1 g/L and $MgSO_4{\cdot}7H_2O$, 0.01 g/L was added in both cases. In addition, 1.0 mL/L of trace metals solution was also added (Chen et al., 2008). When the cell voltage decreased below 20 mV as a result of substrate depletion, anolyte and catholyte were completely replaced with fresh medium. The cathode chamber for the two-chambered MFC was continuously aerated to supply oxygen as electron acceptor. The air flow rate was maintained at 0.5 L/min by means of a flow-meter (RMA-13-SSV, Dwyer Instruments Inc., USA).

2.3. Electrochemical monitoring and analyses

The cell voltage across the circuit with an external resistive load was measured using a digital multi-meter and a data acquisition system (Model 2700, Kiethly, USA). Electrode potentials were measured with respect to a Ag/AgCl reference electrode. The current was calculated according to Ohm's law. Polarization curves were obtained by changing the external load resistances over a series ranging from 10,000 to 10 Ω. More than three complete cycles of fed-batch operation were conducted before obtaining the polariza-

Table 1
Physical properties and cost of proton exchange membrane (PEM) and non-woven fabric filters used in this study.

	PEM (PEM)	1025D (NWF1)	1070D (NWF2)	1082D (NWF3)	1443R (NWF4)
Thickness (mm)	0.19	0.13	0.18	0.25	0.13
Weight (g/m^2)	360	42	68	105	43
Water permeability (psid)	–	4.1	4.3	7.7	42.9
Pore size (μm)	–	2.01	1.78	1.81	1.21
Cost (\$/m^2)	1400	2	3	4	2

tion curve to ensure steady-state conditions. Organics concentrations were determined by a spectrophotometric method (Humas Method 1002, Humas, South Korea). The pH and conductivity were measured using a pH meter (Orion Benchtop 3-star, Thermo Fisher Scientific, USA) and a conductivity meter (Orion Benchtop 3-star, Thermo Fisher Scientific, USA), respectively. The coulombic efficiency (CE) was calculated on the basis of the current generated under steady conditions (Logan et al., 2006).

2.4. Oxygen and acetate mass transfer coefficients

The oxygen and acetate mass transfer coefficient for PEM and 1443R were determined as previously described (Kim et al., 2007b). A dissolved oxygen (DO) electrode (Orion Benchtop 3-star, Thermo Fisher Scientific, USA) was placed in the anode chamber. Prior to measurements, the anaerobic deionized water in the anode chamber was purged with nitrogen gas to remove DO. Concurrently, the cathode chamber was continuously aerated to maintain saturated DO conditions. The mass transfer coefficient K_o of oxygen in the tested PEM and 1443R, was determined by monitoring the DO concentration over time and calculated using Eq. (1).

$$K_O = \frac{D_O}{L_t} = \frac{-V}{At} \times \ln\left[\frac{(C_{1,0} - C_2)}{C_{1,0}}\right] \tag{1}$$

where V is the liquid volume of the anode chamber (340 mL), A is the PEM and 1443R the cross-sectional area. $C_{1.0}$ is the saturated DO concentration in the cathode chamber and $C_{2.0}$ is the DO concentration in the anode chamber at a time t. The contents of the anode chamber were stirred with a magnetic stir bar during the oxygen transfer experiment. The diffusion coefficient (D, cm^2/s) for each chemical was calculated as $D_o = K_oL_t$, where L_t is the separator thickness reported by the manufacturer.

In order to determine the mass transfer coefficient for acetate, acetate (180 mg COD/L) was fed into the anode chamber and distilled water was fed into the cathode chamber, and the samples were taken from the cathode chamber every 20 min. The mass transfer coefficient for acetate was determined using the following Eq. (2).

$$K_A = \frac{D_A}{L_t} = \frac{-V}{2At} \times \ln\left[\frac{(C_{1,0} - 2C_2)}{C_{1,0}}\right] \tag{2}$$

2.5. Morphological analysis

The morphologies of the biofilms and chemical deposits on the separators were observed using a scanning electron microscope (SEM) (S-4700, Hitachi, Japan). For SEM analysis, samples (1×1 cm^2) of the PEM and 1443R were taken from the reactor after completion of experiment. The samples were placed in 2.5% glutaraldehyde for 1 h, washed in 0.1 M phosphate buffer pH 7, post fixed in 2% osmium tetroxide for 1 h, and dehydrated in an ethanol series (50%, 70%, 90% and 100%) for 10 min at each step. The samples were dried at the critical point of CO_2. Before observation, the samples were coated with platinum using an ion coater (E-1010, Hitachi, Japan) (Cha et al., 2010).

3. Results and discussion

3.1. Power generation in MFCs with non-woven fabric filter

The voltage generations in MFCs with NWF were compared to those in MFCs with a conventional proton exchange membrane in fed-batch operated two-chambered MFCs. NWF4 (1443R) generated a voltage of 545 ± 22 mV which was comparable to that with PEM (Nafion 117, 551 ± 56 mV), while the voltages of NWF1, NWF2 and NWF3 were 402 ± 56, 531 ± 35 and 388 ± 21 mV, respectively. The development of anode and cathode cell potential over time with different separators is shown in Fig. 1(a) and (b). The anode potential of each reactor was initially sustained at −487 mV (vs. Ag/AgCl) until it increased to 290 mV due to substrate depletion in all MFCs (Fig. 1a). For the cathode cell potential significant differences between PEM (85 mV vs Ag/AgCl) and NWFs (NWF1-NWF4, −90 mV, 35 mV, −95 mV and 75 mV, respectively) during steady state operations (Fig. 1b) were noted. The anode electrochemical reaction was not affected by the type of the separators as it was regulated by the respiration of attached microbe, but the cathode was affected when using different separators. This result implies that proton and/or cation species transport through the separator significantly influenced cathode performance. Thus selection of membrane/separator is important to of cell performance (Zhang et al., 2010). Both pH and conductivity in the anode chamber were measured at the beginning and end of a batch cycle. When using PEM as separator, the initial pH (6.9) and conductivity (14.2 mS/cm) changed slightly to 6.8 and 14.3 mS/cm at the end of a batch cycle. Similarly, there was no observable change in pH and conductivity for a batch cycle, when using NWFs (data not shown). These findings can be explained by the high buffering capacity of buffer used.

In order to investigate the whole cell performances in terms of stability through repeated batch cycles, polarization and power curves were analyzed by changing the external resistance after 120 days of operation (Fig. 1c and d). The maximum power density of NWF4 was 1,027 ± 79 mW/m^3 (97.0 ± 7.5 mW/m^2) as compared to that with PEM (609 ± 41 mW/m^3, 57.5 ± 3.9 mW/m^2). The internal resistances of the NWF was estimated from the slope of the polarization curves and was lower than that of PEM (51 ± 7.5 Ω of NWF4 vs. 93 ± 2 Ω of PEM) (Table 2). Ohmic losses are related to electrode spacing, selection of separator, degree of contact between electrodes and circuit, and solution conductivity and buffering capacity (Logan, 2008). Since the electrode and wire have relatively high conductivity, ohmic losses derived from electron flow in the circuit are virtually negligible, although the interface between microbes and electrode can be a potential source of loss. In the present study, it was hypothesized that the ohmic losses would be strongly affected by cation/proton transfer from the anode to cathode chambers through the electrolyte and separator. As shown in Fig. 1c, the ohmic losses exhibited a significant difference between the five MFCs. Although NWF does not contain an ion-specific functional group, and thus does not favour specific cation (proton) transfer, it exhibited much lower ohmic losses and simultaneous higher long term stability compared to PEM. The ohmic losses of PEM, NWF1, NWF2, NWF3 and NWF4 were 73.1 ± 8.3,

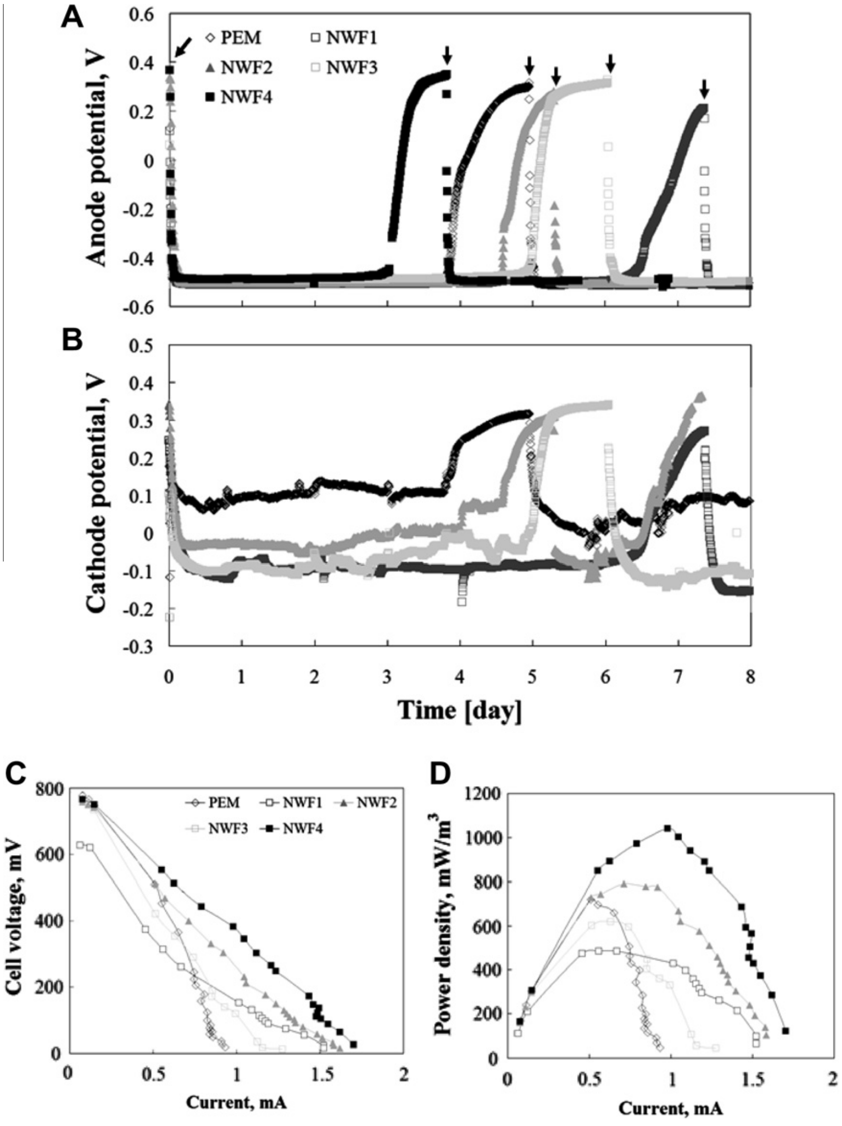

Fig. 1. Development of (A) anode and (B) cathode potentials (vs. Ag/AgCl reference electrode, 0.195 vs. NHE (normal hydrogen electrode)) over time, (C) polarization curve, and (D) power curves in MFCs with different separators. Arrow indicates acetate injection.

Table 2
Open circuit voltage (OCV), power production and internal resistance of microbial fuel cells (MFCs) by changing a series of different external resistances on the circuit from 10,000 to 10 Ω at 246 mg/L acetate.

	PEM	NWF1	NWF2	NWF3	NWF4
OCV (mV)	895 ± 13	552 ± 68	797 ± 43	793 ± 43	839 ± 30
Maximum power density (mW/m^3)	609 ± 41	432 ± 76	839 ± 69	664 ± 74	1027 ± 79
Internal resistance (Ω)	93 ± 2	43 ± 2	53 ± 6	37 ± 1	51 ± 8

60.1 ± 8.7, 59.2 ± 1.2, 72.1 ± 9.5 and 46.9 ± 6.5 Ω, respectively. High ohmic losses of PEM can be explained by higher affinity for cation species than protons. PEM has negatively charged sulfonate groups ($-SO_3^-$), which lead to a high level of proton conductivity. However, PEM has a higher affinity for K^+, NH_4^+, Ca^{2+}, and Mg^{2+} than protons (Rozendal et al., 2006). In contrast, NWFs have a larger pore size to facilitate greater overall chemical species transfer compared to PEM (1.2–2.0 μm of NWF vs. less than 0.03 μm of PEM). Therefore, they exhibited lower ohmic losses than PEM, attributed to a higher proton transfer capability (Li et al., 2011).

It is difficult to give a comparison of performances between the separators because the separators had different thicknesses, surface conditions and configuration of separator as well as the operating conditions (Li et al., 2011), nevertheless, a comparison of separator properties in terms of maximum power density and internal resistance are shown in Table 3.

3.2. Oxygen and acetate mass transfer coefficients

The oxygen flux from cathode to anode through the separator was evaluated by monitoring DO over time. As NWF4 showed higher power density and electrochemical performance than other NWF separators, the mass transport characteristics of NWF4 were investigated and compared to PEM. The DO concentration of the

Table 3
Comparison of the performance of MFCs with NWF4 (non-woven fabric filter; 1443R, DuPont, USA), proton exchange membrane (PEM) and other separators.

Separator	Maximal power density		Internal resistance (Ω)	Reference
	mW/m^3	mW/m^2		
NWF4	1027 ± 79	97.0 ± 7.5	51 ± 7.5	In this study
PEM	609 ± 41	57.5 ± 3.9	93 ± 2	In this study
MFM[a]	878 ± 41	214 ± 8	248	Sun et al. (2009)
PEM	415 ± 14	103 ± 3	672	Sun et al. (2009)
CEM[b]	–	480	1308 ± 18	Kim et al. (2007b)
AEM[c]	–	610	1239 ± 27	Kim et al. (2007b)
UF-1K[d]	–	462	1239 ± 52	Kim et al. (2007b)
J-cloth	46,000 ± 1000	786 ± 23	11.3 ± 0.3	Zhang et al. (2009)
GF1[e]	52,000 ± 2000	896 ± 49	37.6 ± 1.4	Zhang et al. (2009)
SPEEK[f]	–	670 ± 14	–	Ayyaru and Dharmalingam (2011)

[a] Microfiltration membrane.
[b] Cation exchange membrane.
[c] Anion exchange membrane.
[d] Ultrafiltration membrane.
[e] Glass fiber 1.0.
[f] Sulphonated polyether ether ketone.

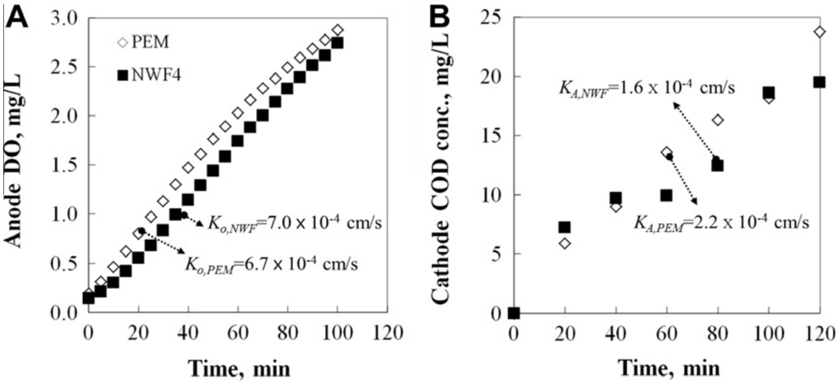

Fig. 2. (A) Oxygen and (B) acetate diffusion through a proton exchange membrane (PEM) and non-woven fabric filter (NWF4) in uninoculated MFCs.

anode chamber in the MFC with PEM increased from 0.19 to 2.87 mg/L within 100 min, while NWF4 showed an increase from 0.14 to 2.74 mg/L (Fig. 2a). The estimated oxygen mass transfer coefficient ($K_{O,PEM}$) for PEM was 6.7 × 10^{-4} cm/s ($D_{o,\ PEM} = 1.15 \times 10^{-5}$ cm^2/s) whereas the corresponding values for NWF4 were 7.0 × 10^{-4} cm/s and 0.91 × 10^{-5} cm^2/s in the MFC configuration tested.

The acetate mass transfer coefficient was also estimated based on the diffusion from anode to cathode chamber. The acetate concentration of the cathode chamber with PEM increased from 0 to 23.7 mg/L in 120 min, while it increased from 0 to 19.5 mg/L in NWF4 (Fig. 2b). The acetate mass transfer coefficient for NWF4 (1.6 × 10^{-4} cm/s) was lower than that of PEM (2.2 × 10^{-4} cm/s). The high value for the acetate mass transfer coefficient indicates that PEM resulted in a higher loss of acetate by migration into the cathode chamber, consequently decreasing cell performance by the development of biomass on the cathode catalyst. It is interesting that the PEM with cation exchanging functional groups showed a higher anion (acetate) transport capability than NWF which does not have an identified functional group for ion transport. The pore size of PEM has been reported at approximately 20–30 nm, which is two orders of magnitude smaller than that of NWFs (1.2–2.0 μm). The results imply that mass transport in MFCs, which contain high concentrations of anion and cation species in the media, may depend on various operational factors such as buffer concentration, ionic strength and substrates. The characteristics of materials such as a hydrophilic property and interaction with other ionic species, seems more important than the pore size and/or functional groups on separators to control acetate diffusion. Similar results were obtained previously by Kim et al. (2007), who showed a lower acetate mass transport coefficient in the ultrafiltration membrane (0.5 K) than Nafion 117.

3.3. Stability of PEM and non-woven fabric filter in MFCs

It has been reported that separators in MFC have a biofouling problem during operation (Choi et al., 2011). Rozendal et al. (2006) also reported that the electrochemical cell performance of MFCs using PEM can be significantly increased after physical cleaning or replacement with a fresh PEM. Sustainability of separator function is an important factor for maintaining performance and achieving feasible field-scale application. The electrochemical performance of NWF was compared to that of PEM over 300 days of fed-batch operation. The cell potential of NWF was almost constant, even after 300 days (550 mV), while that for PEM decreased from 551 mV to 415 mV (Fig. 3a). The anode cell potential of PEM and NWF4 did not change for 300 days (Fig. 3b). The cathode cell potential of PEM significantly decreased from 85 to 27 mV after 300 days, while the cathode cell potential of NWF4 was maintained even after 300 days (75 mV vs. 74 mV). The CE for PEM also decreased from 31% to 22% after 300 days as compared to that for NWF4 which was almost the same at approximately 20%. Overall, the performance of PEM deteriorated more seriously than that of NWF4. These finding support the contention that

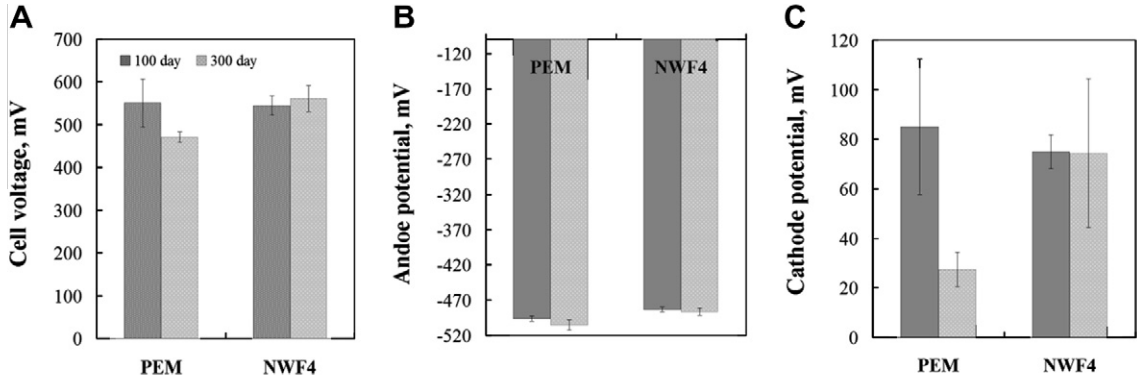

Fig. 3. Comparison of (A) cell voltage, (B) anode and (C) cathode potentials (vs. Ag/AgCl reference electrode, 0.195 vs. NHE) between PEM and NFW4 operated over 100 and over 300 days. Error bars indicate standard deviations ($n = 3$).

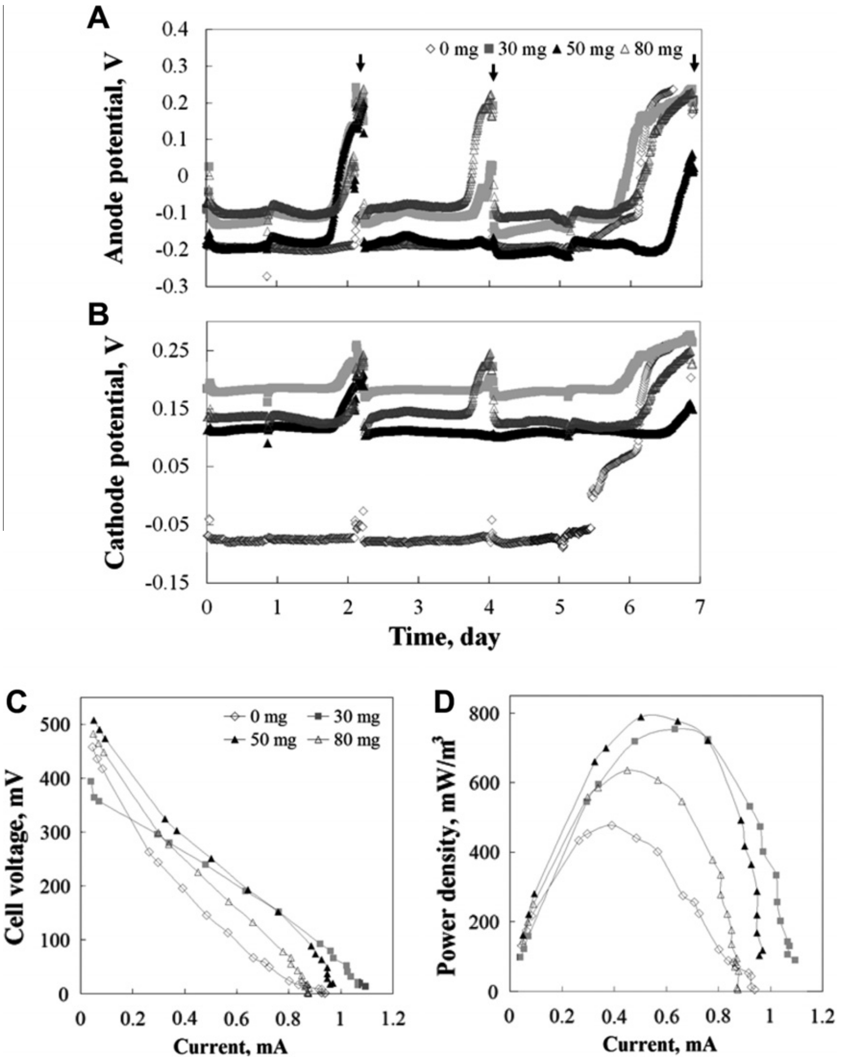

Fig. 4. Effect of ABPBI (poly [2,5-benzimidazole]) as a proton conductor on (A) anode and (B) cathode potentials potentials (vs. Ag/AgCl reference electrode, 0.195 vs. NHE) over time, (C) polarization curve, and (D) power curves in MFCs with different ABPBI loadings. Arrow indicates acetate injection.

there is a change in internal resistance over the operating period, particularly due to inhibition of proton migration for the cathode reaction by biological or chemical fouling on the PEM surface (Rozendal et al., 2006; Choi et al., 2011). It can be assumed that the overall cell performance decrease might be related to cathode potential resulting from differences in ion transport through separators.

In order to investigate biological and chemical fouling of the separators, the surface morphologies of PEM and NWF4 were observed by SEM (Fig. S2a and b). The NWF contained high density polyethylene fibers which were randomly woven on the surface, as compared to the smooth surface of PEM. After 300 days of operation, both PEM and NWF4 were covered with a biofilm and chemical precipitation. The thick biofilm on the surface may possibly inhibit the ions and proton transportation in both separators. However, in the NWF4, the randomly woven fiber formed many microscale interstitial access paths which facilitated ion transport aided by shear stresses in the bulk media, driven by diffusion and convective flow. Therefore the available porosity was maintained on the surface of NWF4 even after biofilm formation.

3.4. NWF membrane electrode assembly with ABPBI as proton conductor

In order to improve the ion conductivity and integrity of contact between NWF and electrodes, ABPBI (poly [2,5-benzimidazole]) was introduced to the membrane electrode assembly in the single-chambered MFC (Fig. S1b and c). To investigate the effect of ABPBI loading on MEA, 30–80 mg ABPBI/cm^2 was used between the electrode and NWF. In terms of cell potential, the optimal loading was 30 mg /cm^2 on the MEA, resulting in an enhanced cell voltage of 288 ± 5.0 mV as compared to 109 mV ± 2.6 mV for the control without ABPBI. Cell voltages for MFCs loaded with 50 and 80 mg ABPBI/cm^2 were 285 ± 6.8 and 222 ± 2.3 mV, respectively. The cathode cell potentials for MFCs loaded with 0, 30, 50, 80 mg ABPBI/cm^2 were −78 mV, 182 mV, 111 mV and 143 mV (vs. Ag/AgCl), respectively; while the anode potentials were relatively similar (−80 to −187 mV vs. Ag/AgCl)

Consequently, the power density for the 50 mg ABPBI/cm^2 MFC (766 ± 20 mW/m^3) was slightly higher than that for other ABPBI loadings; 30 mg ABPBI/cm^2 (736 ± 41 mW/m^3), 80 mg ABPBI/cm^2 (632 ± 21 mW/m^3), and control (413 ± 97 mW/m^3) (Fig. 4c and d). An increase in cell potential derived by applying an electrolyte medium has been reported by Kim et al. (2009). The hydrogel significantly reduced impedance and enhanced membrane-cathode contact compared to the control. In the present study, overloading with a polymer-based ion conductor (ABPBI) (over 80 mg/cm^2) might reduce performance, probably due to the extension of the ion path length to the cathode electrode. Further investigations to find a better electrolyte for MEAs in MFCs, and its optimum loading should be undertaken, with the aim of increasing the applicability of MFC technology.

4. Conclusion

An MFC utilizing NWF, especially 1443R can successfully replace costly PEM in MFCs. The MFC with 1443R generated a higher maximum power density of 1,027 mW/m^3 (vs. PEM, 609 mW/m^3). An it also showed stable cell performance over 300 days than PEM. The overall performance of an MFC was also improved by using a polymer based proton conductor, ABPBI, yielding enhanced ion conductivity and conductive contact, producing 766 mW/m^3 at an optimum loading of 50 mg ABPBI/cm^2. Many other factors such as sustainbility and mass trasfer for oxygen and acetate shoud be considered for further optimization for ABPBI.

Acknowledgements

This work was supported by the Eco-technopia 21 project of the Ministry of Environment and Mid-career Researcher Program through an NRF Grant funded by the MEST (No. 2009-0060376). This work was also financially supported by Korea Ministry of Environment (MOE) as a Human Resource Development Project for Waste to Energy. This research was partly supported by the RCUK Energy Programme, SUPERGEN Biological Fuel Cell project (EP/D047943/1) supported by Grant 68-3A75-3-150.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2012.10.013.

References

Asensio, J.A., Borros, S., Romero, P.G., 2002. Proton-conducting polymers based on benzimidazoles and sulfonated benzimidazoles.. J. Polym. Sci., Part A: Polym. Chem. 30, 3703–3710.

Asensio, J.A., Borros, S., Romero, P.G., 2004. Polymer electrolyte fuel cells based on phosphoric acid-impregnated poly (2,5-benzimidazole) membranes. J. Electrochem. Soc. 151, A304–A310.

Ayyaru, S., Dharmalingam, S., 2011. Development of MFC using sulphonated polyether ether ketone (SPEEK) membrane for electricity generation from wastewater. Biores. Technol. 102, 11167–11171.

Cha, J.H., Choi, S.J., Yu, H.N., Kim, H.S., Kim, C.W., 2010. Directly applicable microbial fuel cells in aeration tank for wastewater treatment. Bioelectrochemistry 78, 72–79.

Chae, K.J., Choi, M.J., Ajayi, F.F., Park, W.S., Chang, I.S., Kim, I.S., 2008. Mass transport through a proton exchange membrane (Nafion) in microbial fuel cells. Energy Fuels 22, 169–176.

Chen, G.W., Choi, S., Lee, T., Lee, G., Cha, J., Kim, C., 2008. Application of biocathode in microbial fuel cells: cell performance and microbial community. Appl. Microbiol. Biotechnol. 79, 379–388.

Choi, M.J., Chae, K.J., Ajayi, F.F., Kim, K.Y., Yu, H.W., Kim, C.W., Kim, I.S., 2011. Effects of biofouling on ion transport through cation exchange membranes and microbial fuel cell performance. Biores. Technol. 102, 298–303.

Clauwaert, P., Aelterman, P., Pham, T.H., Schamphelaire, L.D., Carballa, M., Rabaey, K., Verstraete, W., 2008. Minimizing losses in bio-electrochemical systems: the road to application. Appl. Microbiol. Biotechnol. 79, 901–913.

Fan, Y., Hu, H., Liu, H., 2007. Enhanced coulombic efficiency and power density of air-cathode microbial fuel cells with an improved cell configuration. J. Power Sources 171, 348–354.

Ghangrekar, M.M., Shinde, V.B., 2007. Performance of membrane-less microbial fuel cell treating wastewater and effect of electrode distance and area on electricity production. Biores. Technol. 98, 2879–2882.

Henze, M., Lossdrecht, M.C.M., Ekama, G.A., Brdjanovic, D., 2008. Biological Wastewater Treatment. IWA Publishing, p. 30.

Jang, J.K., Pham, T.H., Chang, I.S., Kang, K.H., Moon, H.S., Cho, K.S., Kim, B.H., 2004. Construction and operation of a novel mediator- and membrane-less microbial fuel cell. Process Biochem. 39, 1007–1012.

Kim, B.H., Changm, I.S., Gadd, G.M., 2007a. Challenges in microbial fuel cell development and operation. Appl. Microbiol. Biotechnol. 76, 485–494.

Kim, J.R., Cheng, S., Oh, S.E., Logan, B.E., 2007b. Power generation using different cation, anion, and ultrafiltration membrnaes in microbial fuel cells. Environ. Sci. Technol. 41, 1004–1009.

Kim, I.S., Chae, K.J., Choi, M.J., Verstraete, W., 2008. Microbial fuel cells: recent advances, bacterial communities and application beyond electricity generation. Environ. Eng. Res. 13, 51–65.

Kim, J.R., Premier, G.C., Hawkes, F.R., Dinsdale, R.M., Guwy, A.J., 2009. Development of a tubular microbial fuel cell (MFC) employing a membrane eletrode assembly cathode. J. Power Sources 187, 393–399.

Kim, J.R., Kim, J.-Y., Han, S.-B., Park, K.-W., Saratale, G.D., Oh, S.-E., 2011. Application of Co-naphthalocyanine(CoNPc) as alternative cathode catalyst and support structure for microbial fuel cells. Biores. Tech. 102 (1), 342–347.

Li, W.W., Sheng, G.P., Liu, X.W., Yu, H.Q., 2011. Recent advances in the separators for microbial fuel cells. Biores. Technol. 102, 244–252.

Lim, S.S., Daud, W.R.W., Jahim, J.M., Ghasemi, M., Chong, P.S., Ismail, M., 2012. Sulfonated poly (ether ether ketone)/poly (ether surfone) composite membranes as an alternative proton exchange membrane in microbial fuel cells. Int. J. Hydrogen Energy 37, 11409–11424.

Liu, H., Logan, B.E., 2004. Electricity generation using an air-cathode single chamber microbial fuel cell in the presence and absence of a proton exchange membrane. Environ. Sci. Technol. 38, 4040–4046.

Logan, B.E., Hamelers, B., Rozendal, R., Schroder, U., Keller, J., Freguia, S., Aelterman, P., Verstraete, W., Rabaey, K., 2006. Microbial fuel cells: methodology and technology. Environ. Sci. Technol. 40, 5181–5192.

Logan, B.E., Cheng, S., Watson, V., Estadt, G., 2007. Graphite fiber brush anodes for increased power production in air-cathode microbial fuel cells. Environ. Sci. Technol. 41, 3341–3346.

Logan, B.E., 2008. Microbial Fuel Cells. John Wiley & Sons, Inc., New York, pp. 53, 61.

Rozendal, R.A., Hamelers, H.V.M., Buisman, C.J.N., 2006. Effects of membrnae cation transport on pH and microbial fuel cell performance. Environ. Sci. Technol. 40, 5206–5211.

Rozendal, R.A., Hamelers, H.V.M., Rabaey, K., Keller, J., Buisman, C.J.N., 2008a. Towards practical implementation of bioelectrochemical wastewater treatment. Trends Biotechnol. 26, 450–459.

Rozendal, R.A., Sleutels, T.H.J.A., Hamelers, H.V.M., Buisman, C.J.N., 2008b. Effect of the type of ion exchange membrane on performance, ion transport, and pH in biocatalyzed electrolysis of wastewater. Water Sci. Technol. 57, 1757–1762.

Sun, J., Hu, Y., Bi, Z., Cao, Y., 2009. Improved performance of air-cathode single-chamber microbial fuel cell for wastwater treatment using microfiltration membranes and multiple sludge inoculation. J. Power Sources 187, 471–479.

Zhang, X., Cheng, S., Wang, X., Huang, X., Logan, B.E., 2009. Separator charteristics for increasing performance of microbial fuel cells. Environ. Sci. Technol. 43, 8456–8461.

Zhang, X., Cheng, S., Huang, X., Logan, B.E., 2010. The use of nylon and glass fiber filter separators with different pore size in air-cathode single-chamber microbial fuel cells. Energy Eviron. Sci. 3, 659–664.

Zhang, X., Cheng, S., Liang, P., Huang, X., Logan, B.E., 2011. Scalable air cathode microbial fuel cells using glass fiber separators, plastic mesh supporters, and graphite fiber brush anodes. Biores. Technol. 102, 372–375.

Zhao, F., Harnisch, F., Schroder, U., Scholz, F., Bogdanoff, P., Herrmann, I., 2005. Application of pyrolysed iron(II) phthalocyanine and CoTMPP based oxygen reduction catalysts as cathode materials in microbial fuel cells. Electrochem. Commun. 7, 1405–1410.

Zuo, Y., Cheng, S., Logan, B.E., 2008. Ion exchange membrane cathodes for scalable microbial fuel cells. Environ. Sci. Technol. 42, 6967–6972.