JOURNAL
OF
MICROBIOLOGY
AND
BIOTECHNOLOGY

ⓒ The Korean Society for Microbiology and Biotechnology

Power Density Enhancement of Anion-Exchange Membrane-Installed Microbial Fuel Cell Under Bicarbonate-Buffered Cathode Condition

Piao, Jingmei[1], Junyeong An[1], Phuc Thi Ha[1], Taeyoung Kim[1], Jae Kyung Jang[2], Hyunsoo Moon[3], and In Seop Chang[1]*

[1]*School of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju 500-712, Korea*
[2]*Energy and Environmental Engineering Division, National Institute of Agricultural Science, Rural Development Administration, Suwon 441-707, Korea*
[3]*School of Biological and Chemical Engineering, Yanbian University of Science and Technology, Beishan Street, Yanji, Jilin 133000, China*

We introduce a high-performance microbial fuel cell (MFC) that was operated using a 0.1 M bicarbonate buffer as the cathodic electrolyte. The MFC had a 136.42 mW/m² maximum power density under continuous feeding of 5 mM acetate as fuel. Results of the electrode potential measurements showed that the cathode potential of the bicarbonate-buffered condition was higher than the phosphate-buffered condition, although the phosphate condition had less interfacial resistance between the membrane and electrolyte. Therefore, we posit here that the increased power of the bicarbonate-buffered MFC may be caused by the higher cathode potential rather than by the interfacial membrane-electrolyte resistance.

Key words: Microbial fuel cell (MFC), anion-exchange membrane (AEM), electrochemical impedance spectrometry (EIS), electrode potential

Microbial fuel cells (MFCs) are electrochemical reactors that convert the chemical energy generated from organic materials by microorganisms into electricity [7, 10]. It has been noted that the electric power density obtained using MFCs is still low, however, which hampers their practical application for energy production processes [6]. One factor that contributes to this low power density is the internal resistance associated with both transporting ions between the anode and cathode electrodes and transporting electrons through the electrical circuit. Furthermore, the generally dominant ion-transport resistance [6] occurs in the electrolyte solution and through the ion-exchange membrane in typical MFC configurations [6]. Among MFC membranes, anion-exchange membranes (AEMs) have better performance a compared with cation-exchange membranes, as protons in the anode are consumed by OH⁻ transferred from the cathode, without further pH decreases in the anode chamber. This property of AEMs results in lowering the ion transport resistance and reducing membrane fouling and the cathode resistance caused by the precipitation of transported cations [6, 11]. However, these advantages of AEMs have a correlation with the concentration of buffering electrolytes, because AEM requires a high concentration of positively charged groups to transport negatively charged ions, which leads to the formation of an electrical double layer (in nanometer scale). In addition, the different ion transport number between the solution and membrane leads to the formation of a diffusion boundary layer (in micrometer scale) [6], suggesting that the internal resistance magnitude of MFCs with an AEM can be determined according to the buffering capacity as well as the type of buffer.

Our previous study [6] showed that the electrical double layer and diffusion boundary layer resistances of AEMs were much larger in a 10 mM phosphate buffer, compared with a 100 mM phosphate buffer. Typically, phosphate has been used as the buffer material in MFC system operations in laboratory tests [5]. However, it may not be an acceptable chemical in practical approaches because of its high cost and environmental concerns, such as its promotion of water eutrophication due to surplus phosphorus [4]. Alternatively, a (bi)carbonate buffer should be considered because of its cost advantage and high buffering capacity [4]. In this study, we investigate resistances such as the pure membrane resistance, electrical double layer resistance, and diffusion boundary layer resistance under phosphate-

*Corresponding author
Phone: +82-62-715-3278; Fax: +82-62-715-2434;
E-mail: ischang@gist.ac.kr

Table 1. Typical values of each component of interfacial resistance obtained by EIS data; the membrane and solution resistance (R_{M+S}), the resistance of the interfacial ionic charge transfer through the double layer (R_{DL}), and the resistance of the diffusion boundary layer (R_{DBL}).

Type of buffer	Conc. (mM)	pH	Internal resistance ($\Omega\ cm^2$)			
			R_{M+S}	R_{DL}	R_{DBL}	Sum
Phosphate	10	7.0	357	675	n.d.[a]	1,032
	10	7.0	408	1,146	1,554	3,108
Bicarbonate	10	8.0	433	1,274	2,038	3,745
	10	9.0	420	1,108	1,210	2,738
Phosphate	100	7.0	51	89	n.d.	140
	100	7.0	64	115	n.d.	179
Bicarbonate	100	8.0	64	127	n.d.	191
	100	9.0	64	115	n.d.	179

[a]n.d.: not detected on EIS spectra.
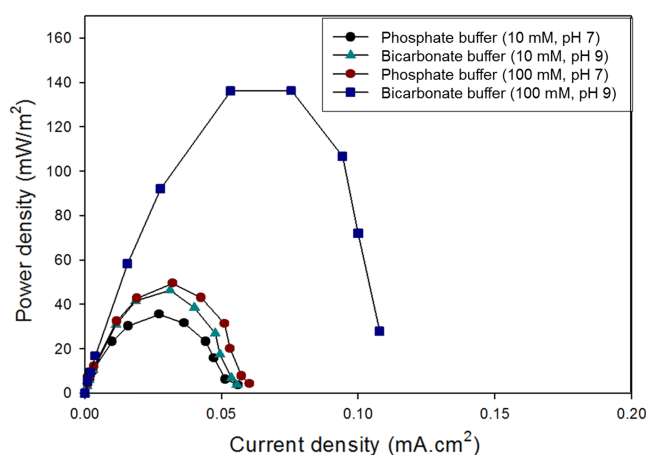Each internal resistances value was obtained from triple tests.

and bicarbonate-buffered conditions at different pH values and concentrations in order to examine the substitutability of (bi)carbonate for use in an MFC system.

Two compartments (150 ml each) in an electrodialytic cell having an AEM (AMX, Tokuyama Co., Japan) were tested under a 10 mM sodium phosphate buffer (pH 7.0) and sodium bicarbonate buffer (pH 7.0, 8.0, and 9.0) [3, 9]. First, to identify the contributions of the pure membrane, electrical double layer, and diffusion boundary layer resistances, a sinusoidal alternating current was applied to a pair of platinized titanium electrodes at a frequency range from 10^6 Hz to 10^{-2} Hz in order to measure the impedance spectra using a potentiostat/galvanostat (AutoLab, Model PGSTAT 30, The Netherlands) [9]. The voltage drop across the membrane was measured using Ag/AgCl reference electrodes that were immersed in Luggin capillaries made of glass [2, 9]. The experiment was conducted at room temperature (23°C), assuming that the diffusion boundary and AEM double layers do not vary owing to a change in temperature. MFCs were operated continuously by feeding anaerobically prepared artificial wastewater containing 5 mM acetate at a rate of 0.19 ml/min to the anode, and air-saturated buffers were fed into the cathode at a rate of 4.77 ml/min using a peristaltic pump (505S; Watson-Marlow, Falmouth, UK) [8]. Sodium phosphate buffers (pH 7.0, 10 mM and 100 mM) were used for control sets of MFCs, which were constructed as previously described [1, 8], and sodium bicarbonate buffers at pH 9.0 (10 mM and 100 mM) were used as the test sets. The MFCs were subsequently operated in a temperature-controlled room at 30°C, at an external resistance of 10 Ω. The cathode potentials of the MFCs were determined by using the Nernst equation and Henry's law to determine the theoretical reduction potential in an electrochemical cell. Here, the values of the standard half-cell reduction potential of oxygen and Henry's law constant at 25°C were cited. A multimeter (Model 2700; Keithley Instruments, Inc., Cleveland, OH, USA) connected

to a personal computer was used to measure the cathode potential of different catholyte solutions.

Table 1 summarizes the values of each resistance obtained from electrochemical impedance spectrometry (EIS) analyses. In each 10 mM electrolyte solution, all interface resistances of the bicarbonate buffer at pH 9.0 were smaller than those of buffers at pH 7.0 and 8.0. In particular, the phosphate buffer (pH 7.0) showed much smaller resistances for all interface resistances especially the diffusion boundary layer resistance, which was almost zero. In each 100 mM electrolyte solution, all buffer solutions showed almost no diffusion boundary layer resistance, whereas resistances including the membrane itself (*i.e.*, membrane resistivity) and electrolyte solution as well as the sum of all resistances displayed a significant difference in the 10 mM and 100 mM buffered conditions, regardless of type of buffer and pH.

In order to determine whether the different catholyte conditions affect the MFC performance, based on EIS results, four catholyte conditions were selected: (A) phosphate

Fig. 1. Power density curves of MFCs with anion-exchange membrane using phosphate and bicarbonate buffers.
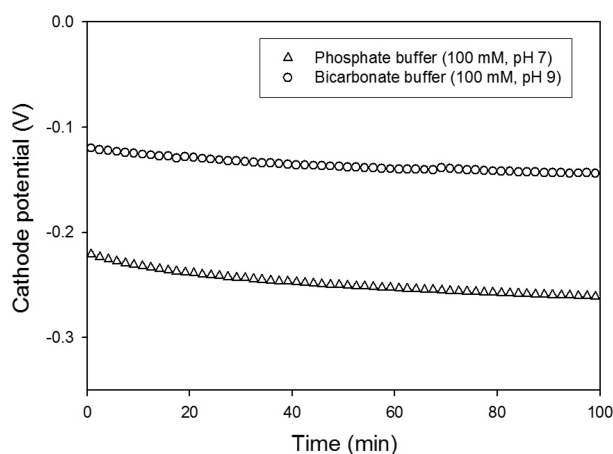
Fig. 2. Electrode potentials of the cathode solution during the MFC operation using phosphate (100 mM, pH 7.0) and bicarbonate (100 mM, pH 9.0) buffers.

Table 2. Change in DO concentration of the cathode solution during the MFC operation using sodium phosphate buffer (100 mM, pH 7) and bicarbonate buffer (100 mM, pH 9).

Buffer condition (conc. and pH)	Time elapsed (min)				
	20	40	60	80	100
Phosphate (100 mM, 7.0)	7.30	7.74	5.83	5.32	4.97
Bicarbonate (100 mM, 9.0)	6.15	6.03	5.84	6.13	6.27

buffer (pH 7.0, 10 mM), (B) phosphate buffer (pH 7.0, 100 mM), (C) bicarbonate buffer (pH 9.0, 10 mM), and (D) bicarbonate buffer (pH 9.0, 100 mM). Fig. 1 shows the power density curves obtained from the MFC operations. In the 10 mM catholyte condition, there was not a notable difference in the maximum power density between the phosphate-buffered (c.a., 38 mW/m^2) and bicarbonate-buffered (c.a., 45 mW/m^2) conditions, whereas the maximum power density of the bicarbonate-buffered (c.a., 140 mW/m^2) condition was three times larger than the phosphate-buffered (48 mW/m^2) condition in the 100 mM catholyte. Interestingly, these power density data are not consistent with the interface resistance measurements, because the sum of all interface resistances of phosphate buffer was smaller than for bicarbonate under the 100 mM condition. In addition, the two phosphate buffer conditions (10 mM and 100 mM) showed similar power density levels. Fig. 2 presents the electrode potentials of catholyte solutions that were measured immediately following the power density measurement. The results show cathode potentials of -0.13 V and -0.24 V (*vs.* Ag/AgCl) for the 100 mM bicarbonate and phosphate buffers, respectively. As such, these results indicate that the cathode potential of the bicarbonate-buffered condition was more favorable than the phosphate-buffered condition, which could be attributed to the increased power density despite the higher interface resistances of the bicarbonate buffer. During the MFC operation, it was found out that as time goes by the DO concentration under phosphate-buffered condition was further decreased as compared with that under the bicarbonate-buffered one, despite that the initial DO concentration under phosphate buffer was 1.15 mg/l higher than under bicarbonate buffer (Table 2). This result implies that the relatively high DO concentration under the bicarbonate-buffered condition

might lead to an increase in the cathode potential, presumably due to a relatively higher oxygen solubility in bicarbonate buffer than in phosphate buffer. In addition, this result implies that control of the cathode potential for oxygen reduction may be more critical than lowering of the interface resistance in the cathode electrolyte for MFC operation.

Acknowledgments

References

1. Chang, I. S., J. K. Jang, G. C. Gil, M. Kim, H. J. Kim, B. W. Cho, and B. H. Kim. 2004. Continuous determination of biochemical oxygen demand using microbial fuel cell type. *Biosens. Bioelectron.* **19:** 607–613.
2. Choi, J. H., J. S. Park, and S. H. Moon. 2002. Direct measurement of concentration distribution within the boundary layer of an ion-exchange membrane. *J. Colloid Interface Sci.* **251:** 311–317.
3. Długołęcki, P., P. Ogonowski, S. J. Metz, M. Saakes, K. Nijmeijer, and M. Wessling. 2010. On the resistances of membrane, diffusion boundary layer and double layer in ion exchange membrane transport. *J. Membr. Sci.* **349:** 369–379.
4. Fan, Y. Z., H. Q. Hu, and H. Liu. 2007. Sustainable power generation in microbial fuel cells using bicarbonate buffer and proton transfer mechanisms. *Environ. Sci. Technol.* **41:** 8154–8158.
5. Gil, G. C., I. S. Chang, B. H. Kim, M. Kim, J. K. Jang, H. S. Park, and H. J. Kim. 2003. Operational parameters affecting the performance of a mediator-less microbial fuel. *Biosens. Bioelectron.* **18:** 327–334.
6. Ji, E., H. Moon, J. Piao, P. T. Ha, J. An, D. Kim, *et al.* 2011. Interface resistances of anion exchange membranes in microbial

fuel cells with low ionic strength. *Biosens. Bioelectron.* **26:** 3266−3271.

7. Kim, J. R., S. A. Cheng, S. E. Oh, and B. E. Logan. 2007. Power generation using different cation, anion and ultrafiltration membranes in microbial fuel cells. *Environ. Sci. Technol.* **41:** 1004−1009.

8. Lee, J. Y., N. T. Phung, I. S. Chang, B. H. Kim, and H. C. Sung. 2003. Use of acetate for enrichment of electrochemically active microorganisms and their 16S rDNA analyses. *FEMS Microbiol. Lett.* **223:** 185−191.

9. Park, J. S., J. H. Choi, J. J. Woo, and S. H. Moon. 2006. An electrical impedance spectroscopic (EIS) study on transport characteristics of ion-exchange membrane systems. *J. Colloid Interface Sci.* **300:** 655−662.

10. Pham, T. H., J. J. Jang, H. S. Moon, I. S. Chang and B. H. Kim. 2005. Improved performance of microbial fuel cell using membrane-electrode assembly. *J. Microbiol. Biotechnol.* **15:** 438−441.

11. Rozendal, R. A., H. V. M. Hamelers, R. J. Molenkamp, and C. J. N. Buisman. 2007. Performance of single chamber biocatalyzed electrolysis with different types of ion exchange membranes. *Water Res.* **41:** 1984−1994.