http://dx.doi.org/10.5012/bkcs.2011.32.10.3726

Effect of Cathodic Biofilm on the Performance of Air-Cathode Single Chamber Microbial Fuel Cells

Jalal Ahmed and Sunghyun Kim*

*Department of Bioscience and Biotechnology, Konkuk University, Seoul 143-701, Korea. *E-mail: Skim100@konkuk.ac.kr*
Received July 19, 2011, Accepted August 15, 2011

Biofilm formation is inevitable in a bioelectrochemical system in which microorganisms act as a sole biocatalyst. Cathodic biofilm (CBF) works as a double-edged sword in the performance of the air-cathode microbial fuel cells (MFCs). Proton and oxygen crossover through the CBF are limited by the robust structure of extracellular polymeric substances, composition of available constituents and environmental condition from which the biofilm is formed. The MFC performance in terms of power, current and coulombic efficiency is influenced by the nature and origin of CBF. Development of CBF from different ecological environment while keeping the same anode inoculums, contributes additional charge transfer resistance to the total internal resistance, with increase in coulombic efficiency at the expense of power reduction. This study demonstrates that MFC operation conditions need to be optimized on the choice of initial inoculum medium that leads to the biofilm formation on the air cathode.

Key Words : Microbial fuel cell, Cathodic biofilm, Coulombic efficiency, Internal resistance, Extracellular polymeric substance

Introduction

Microbial fuel cells are gaining more and more interest as an alternative green energy source that generates electricity, simultaneously cleaning up environmental pollutants. The depletion of fossil fuel, global warming and various dimensions of environmental pollution are the major ecological challenges in recent days. In this context, an MFC becomes a fascinating green technology because of its ability to recycle environmental wastes by utilizing organic substances contained in them using microorganisms as biocatalysts. Among different types of MFCs, single-chamber, air-cathode MFCs have the greatest potential for practical applications due to their simple design and the fact that no chemical regeneration is needed when using air.[1]

Prior to initiating the biodegradation in an MFC, a well-defined biofilm needs to be developed on the electrode surface. Biofilm growth is a multi-stage process involving initial cell attachment to a solid surface followed by surface adhesion by self-produced extracellular polymeric substances (EPS), biofilm proliferation and maturation, and finally the dispersal of cells from the biofilm.[2] Biofilm is known to accumulate biomass-derived solids that are not active biomass. In particular, EPS and inert (residual) biomass synthesis is influenced by nutrient availability.[3] For example, excess carbon and a limitation of other nutrients, such as nitrogen or potassium, might promote EPS production.[4] Carbon itself could contribute up to 90% of the biofilm biomass.[5] The consequence of EPS formation depends on the microbial community and surrounding viability of biomass composition. Characteristics and morphology of EPS govern the biofilm performance in biocatalysis and reactants/products cross-over.

A plethora of the biofilm researches are focused on the anodic biofilm because anode is the final electron acceptor[6] from the microbial metabolic system before electrons are channeled to the external circuit whose potential determines the energy gain by the bacteria. In a single chamber MFC, the growth of biofilm on the cathode is hard to avoid that forms homogenously. Its thicker pattern compared to the anode biofilm has potential effect on the performance of MFC. While increase in the biomass densities on the anode can substantially increase the MFC performance,[7] increasing biomass on the cathode has a reverse effect.[8]

Torres *et al.*[9] hypothesized that H^+ transport out of the biofilm is the main limitation for current generation. But they only considered the anode biofilm function. H^+ consumption at the cathode was not described where H^+ had to be funneled through a thick cathodic biofilm to reach the catalyst surface. A thicker CBF decreases the power production and increasingly block the proton and other cation transport to the cathode.[10] Fan *et al.* had shown that separator characteristics are very important to the design of an MFC.[1] A separator that ensures high proton transfer to the cathode and low oxygen diffusion is known to be an ideal separator. Different membrane separators such as cation exchange membranes (CEMs), anion exchange membranes (AEMs) and ultrafiltration membranes,[11] J-cloth, or glass fiber have been used in different MFCs. But the reduction in power density was resulted due to pH gradient, proton inhibition, and many other unknown factors. A few number of studies have been done over the oxygen diffusion and proton transfer phenomena through the CBF, but no in-depth research was found defining the CBF structure and its effect on the MFC performance.

The objective of this study is to investigate the structural

origin of CBF and its effect on the performance of MFC. We focused on physical parameters of the biofilm that hinder the power and coulombic efficiency. CBF worked as an ideal separator in a single chamber MFC with optimizing these factors because its formation was continuous by the living organisms in the living system. This function as a bio-separator plays a key role in the bioactivity of the living organism and in bioreactor performance. Power generation and waste removal could be kept constant for longer time than the present practice with a well-defined cathodic biofilm.

Experimental

Reagents and Materials. Most chemicals were of reagent grade purchased from Sigma-Aldrich and used as received without further purification. Polytetrafluoroethylene (PTFE) (DuPont) solution was used to prepare the gas diffusion layer. Non wet-proofed (type A) and 30% wet-proofed (type B) carbon clothes (BASF Fuel Cell Inc., USA) were used as anode and cathode, respectively. Free treated sludge was collected from the Jung-Nang sewage plant Seoul, Korea.

MFC Reactors. A cylindrical shape (3.0 cm ϕ × 2.1 cm L) reactor was made of Plexiglass with an internal volume of 14 mL. A catalytic layer for the oxygen reduction reaction was formed on the cathode by applying a 0.5 mg/cm^2 Pt-supported Vulcan X-72 mixed with Nafion solution (DuPont) on the solution facing side (7 cm^2 projected area). The opposite side was a diffusion layer that was prepared by applying four layers PTFE solution on one side of 30% wet-proof carbon cloth. Cathode and anode spacing was kept 2.1 cm apart.

Enrichment and Operation. MFCs were inoculated from a mixture of treated sludge and culture media. Culture media were 1 g/L acetate solution in 50 mM phosphate buffer containing 12.5 mL/L mineral and 5 mL/L vitamin solution. MFCs were operated in batch mood with a 1 kΩ external resistance. Batch change-over was done every time when voltage drops below 50 mV with same culture media. When at least five consecutive cycles exhibited parallel and stable performances in terms of voltage, the MFC was subject to the various external resistances for the construction of a polarization curve. Data were taken for three consecutive cycles for a single external resistance and average was taken for the power and voltage calculations.

Measurements and Calculations. The voltage over R_{ext} was recorded by an automatic battery cycler (WBCS300, WonAtech, Korea) as a function of time. Each electrode potential was recorded online vs the standard calomel electrode (SCE) using a multimeter (Fluke). Electrochemical impedance spectroscopy was employed to measure the internal resistance, R_{int}, at an open circuit voltage (OCV) over a frequency range of 10 kHz to 0.1 Hz with a sinusoidal perturbation of 10 mV amplitude by a potentiostat (Autolab PGSTAT 30, ECO CHEM). Total impedance was plotted on the Z_{Re}-Z_{Im} plane (Nyquist plot) to obtain R_{int}. Ohmic (R_{Ω}) and charge-transfer (R_{ct}) components that constitute R_{int} were then obtained from the impedance plot. Plot of power density vs current was constructed from the polarization curve as previously described.[12] Coulombic efficiency was calculated as described in the literature.[13] SEM images of biofilms were taken using scanning electron microscope (JEOL, Japan). Biofilms were fixed on the electrode according to the method in the literature.[14]

Results and Discussion

The cathodic biofilm works as a diffusion barrier for ions to migrate to the cathode-electrolyte interface. A large number of amphiphilic bacteria are colonized in the CBF periphery that undergo aerobic respiration, and consequently accept a portion of electrons by reducing nitrite, metal ions or perchlorate that is available on the cathode surface.[15-17] This phenomenon impedes the oxygen reduction rate, and thus reduces the cell voltage. These might be the causes of resulting higher power upon removal of CBF from the cathode.

Figure 1 represents the polarization curve which shows about 10% increase in power density when CBF was removed. But this power decreased by 5-7% (data not shown) compared to the initial biofilm developed from a sludge sample when the biofilm was allowed to grow for a long time. This level of power is 15 to 20% lower than that just after removal of CBF. This difference in power is due to the difference in the composition of the biofilm. The initial biofilm grown in sludge is known to consist of diverse organic matters that allow to form EPS with pores, flakes and channels to conduit H^+, and thus easy product diffusion is possible. However, the biofilm formed from anode respiring bacteria and a substrate medium results in a dense EPS consisted of less pores and channels channels increase the diffusion resistance and decrease the active surface area of cathodic reaction.[18]

SEM images of CBF developed in different inoculums support our explanation, in which the initially formed CBF (panel A, Fig. 2) have many pores, flakes and channels, but the CBF developed from a substrate and an anode biofilm

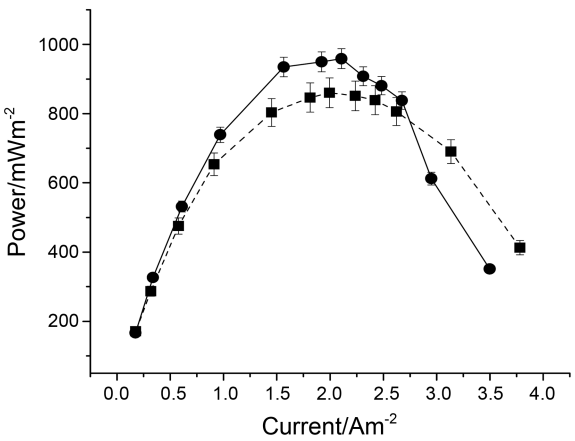

Figure 1. Variation of power density before (■) and after (●) the removal of cathodic biofilm from the electrode.

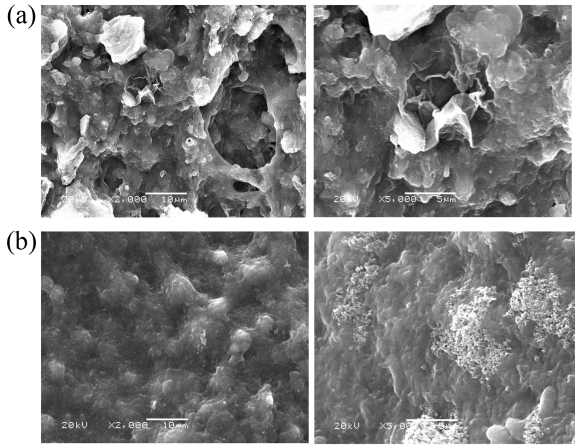

Figure 2. SEM pictures of cathodic biofilm formed from an initial sludge (a) and from the anodic biofilm and nutrient solution (b) after the removal of the initial biofilm.

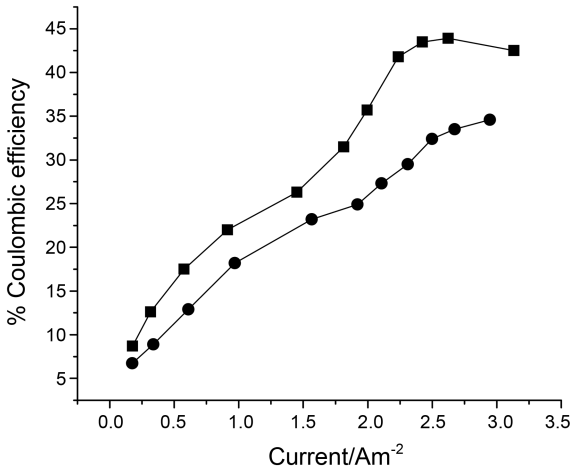

Figure 4. % Coulombic efficiencies before (■) and after (●) the removal of cathodic biofilm from the cathode.

(panel B) shows a dense biofilm structure with less channels and pores. This indicates that the constituent of a biofilm formation medium is crucial for optimal power in MFC. Potential gradient caused by the migration of ions through the CBF disappears after the removal of CBF, thus increasing current. The presence of the biofilm also decreases the effective surface area of the cathode by blocking the cathode periphery causes power reduction.

Internal resistance is the most common limiting factor to hinder to achieve high power density in MFC. From a Nyquist plot and curve fitting, it is possible to obtain individual components (Fig. 3). A Randle equivalent circuit was used to fit data. $R_{Ù}$ of 33 Ω in the presence of CBF decreased to 28 Ω after the CBF removal. This indicates that CBF works as a barrier to the proton transfer from the anode to the cathode as other conditions remain the same before and after the CBF removal. This resistive nature of CBF depends on its thickness and composition, i.e., how rigid and porous its morphological structures are. Entrapment of nonconductive solid particles and dead cells may result in higher resistance and proton migration to the cathode will slow down. The

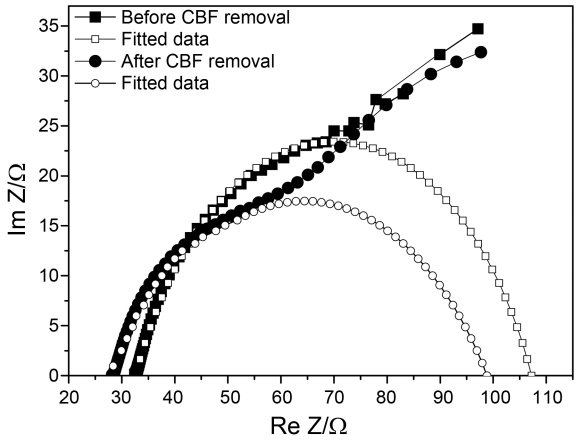

Figure 3. Nyquist plots for the variation of internal resistances before (■) and after (●) the removal of cathodic biofilm from the cathode. Open symbols are fitted data.

exact nature of CBF is not certain at the moment. R_{ct} also decreased from 74 Ω to 71 Ω, indicating the faster electron transfer at the cathode when the CBF is removed. Higher internal resistance in the presence of CBF eventually leads to a decrease in power density as shown in Figure 1.

Figure 4 is the plot of coulombic efficiency (CE) as a function of current density. CEs with the cathodic biofilm are always higher than those without it. The maximum CE was about 45% with a biofilm and this value dropped to 35% when the biofilm was removed. The main reason is believed to be the oxygen cross-over to the anode from the cathode where oxygen is used as a cathodic fuel. Facultative bacteria at the anode could use oxygen as a final electron acceptor rather than transferring electrons to the anode.[19] In this regard, CBF has an ability to control oxygen mass transport to the bulk. A densely quilted CBF prevents oxygen from diffusing into the bulk, contributing high CE as observed in a J-cloth[1] or in a glass fiber separator[8] that have already been proven to be effective to the reduction of oxygen diffusion. Approximately 10% reduction in CE in our case after the CBF removal was observed. Removal of oxygen at the anode by this way needs substrates whose oxidation, however, does not contribute to the current generation. Since electrons are branched and consumed by oxygen in the absence of the CBF, consequently low coulombic efficiency and a shortened cycle time were resulted. This implies that CBF is advantageous for a better performance of MFCs. Visual inspection of the cathodes a thick biofilm of ca. 1 mm thick. After scraping off this CBF and assembling the cell with a 1 k Ω external load, about 50 mV higher voltage and a shorter cycle time were obtained than those in the presence of CBF (Fig. 5). CE further increases with the development of the CBF on the cathode even without the sludge. After running this cell for more than two months, CE reached slightly above the CE with the initial CBF, but the power decreases because this CBF is less porous and thus relatively non-conducting due to the aggregation of dead cells and non-conductive proteins. In absence of diverse organic substances that are available in sludge, CBF morphology changes

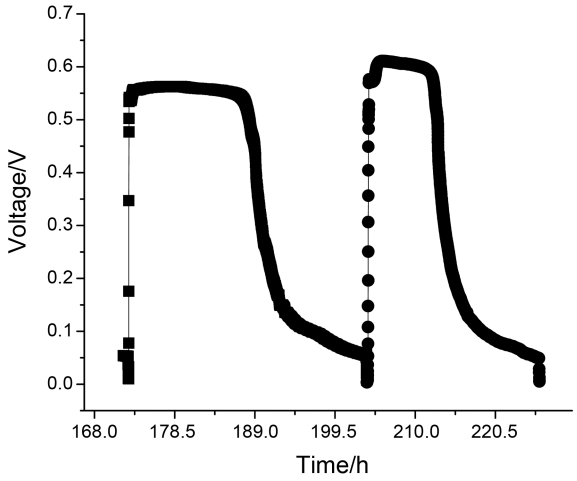

Figure 5. Cell potential variation under 1 kΩ external resistance before (■) and after (●) the removal of cathodic biofilm from the cathode.

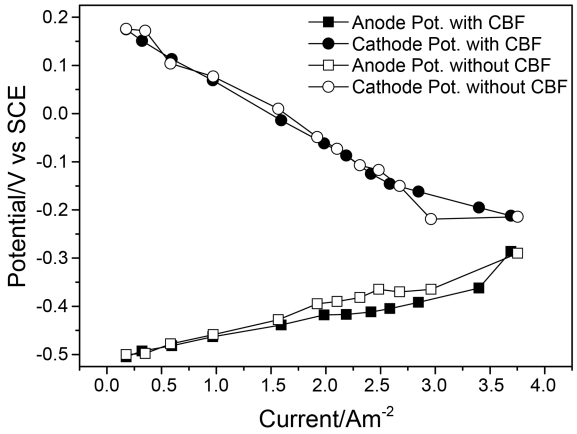

Figure 6. Cathode (●, ○) and anode (■, □) potential variations measured with SCE before (●, ■) and after (○, □) the removal of cathodic biofilm from the cathode.

and H^+ and ion migrations become more difficult through this dense CBF.

Figure 6 represents anode and cathode potential variations with current measured with respect to SCE with and without CBF. As current increases, the cell potential, that is the difference between cathode and anode potentials, decreases. We observed a rise of cathode potential just after the removal of CBF and begin to decrease with current. The decreasing rate is higher for the cathode potential than for that of the anode, consistent with other results.[8] This indicates that the cathode potential is much affected by the presence of the CBF and the CBF functions in a manner similar to a separator. We also observed a change in the anode potential in the P_{max} region, but exact reason behind this is unrevealed yet. Notable is the effect of the solid content on the CBF formation. When inoculation process was performed in a sludge with less solid content, the cell generated nearly constant potential for more than 5 months whereas a sludge with highly solid content was used, the formed CBF was easily peeled off during the fuel cell operation and the constant voltage lasted only for a shorter period of time.

Conclusions

In this study, we have investigated the effect of the cathodic biofilm on the performance MFCs that have single chamber architecture without a separator. The CBF displayed a duel role in which it decreased the power density behaving as a barrier to the proton transfer, but increased the coulombic efficiency behaving as a barrier to the oxygen cross-over to the anode. Since CBF morphologies and structures vary depending on how they are formed, it is important to optimize MFC operation conditions on the choice of initial inoculum that leads to the biofilm formation on the air cathode when using a single chamber MFC.

Acknowledgments. This work was supported by National Research Foundation of Korea Grant funded by the Korean Government (NRF-2011-0002532).

References

1. Fan, Y. Z.; Hu, H. Q.; Liu, H. *J. Power Sources* **2007**, *171*, 348.
2. Stoodley, P.; Sauer, K.; Davies, D. G.; Costerton, J. W. *Annu. Rev. Microbiol.* **2007**, *56*, 187-209.
3. Laspidou, C. S.; Rittmann, B. E. *Water Res.* **2004**, *38*, 3349.
4. Sutherland, I. W. *Microbiol*. **2001**, *147*, 3.
5. Wingender, J.; Neu, T. R.; Flemming, H.-C. In *Mirobial Extracellular Polymeric Substances: Characterization, Structure, and Function*; Wingender, J., Neu, T. R., Flemming, H.-C., Eds.; Springer Verlag: Berlin, Germany, 1999; pp 1-19.
6. Logan, B. E.; Hamelers, B.; Rozendal, R.; Scrorder, U.; Keller, J.; Freguia, S.; Aelterman, P.; Verstraete, W.; Rabaey, K. *Environ. Sci. Technol.* **2006**, *40*, 5181.
7. Pham, H. T.; Aelterman, P.; Verstraete, W. *Trends Biotechnol.* **2009**, *27*, 168.
8. Zhang, X.; Cheng, S.; Wang, X.; Huang, X.; Logan, B. E. *Environ. Sci. Technol.* **2009**, *43*, 8456.
9. Torres, C. I.; Marcus, K. A.; Rittmann, B. E. *Biotechnol. Bioeng.* **2008**, *100*, 872.
10. Cheng, S.; Liu, H.; Logan, B. E. *Electrochem. Commun.* **2006**, *8*, 489.
11. Kim, J. R.; Cheng, S.; Oh, S. E.; Logan, B. E. *Environ. Sci. Technol.* **2007**, *41*, 1444.
12. Cheng, S.; Liu, H.; Logan, B. E. *Environ. Sci. Technol.* **2006**, *40*, 364.
13. Sharma, Y.; Li, B. *Biores. Technol.* **2010**, *101*, 1844.
14. Mclean, S. J.; Wanger, G.; Gorby, A. Y.; Wainstein, M.; Mcquaid, J.; Ishii, I. S.; Bretschger, O.; Beyenal, H.; Nealson, H. K. *Environ. Sci. Technol.* **2010**, *44*, 2721.
15. Gregory, K. B.; Lovley, D. R. *Environ. Sci. Technol.* **2005**, *39*, 8943.
16. Gregory, K. B.; Bond, D. R.; Lovley, D. R. *Environ. Mirobiol.* **2004**, *6*, 596.
17. Clauwaert, P.; Rabaey, K.; Aeltrman, P.; De Schamphelaire, L.; Pham, T. H.; Boeckx, P.; Boon, N.; Verstraete, W. *Environ. Sci. Technol.* **2007**, *41*, 3355.
18. Chung, K.; Fujiki, I.; Okabe, S. *Birores. Technol.* **2011**, *102*, 355.
19. Oh, S. E.; Kim, J. R.; Joo, J. H.; Logan, B. E. *Water Sci. Technol.* **2009**, *60*, 1311.